Effects of Uncertainties in Thermodynamic Data and Models on Process Calculations†

Wallace B. Whiting*

Department of Chemical Engineering, West Virginia University, P.O. Box 6102,
Morgantown, West Virginia 26506-6102

Thermodynamic models and experimental data exhibit systematic and random errors. The severity of their errors depends on their use, such as for process calculations in a process simulator. Similarly, the value of better thermodynamic models and/or data should be measured with reference to such use. Strategies for quantification of such thermodynamics-induced process uncertainties via Monte Carlo simulation, regression analysis, and analogies to optimization are described, with simple examples. Such approaches can be used for safety-factor/risk analysis, guidelines for process simulator use, experimental design, and model comparisons.

Introduction

When one designs a process, it is convenient and sometimes necessary to assume that inputs to the simulation, be they design parameters or physical properties, are known accurately and precisely. However, such assumptions can be misleading, especially when they are made implicitly and when the risk of their use is not considered.

It is common in chemical process design to consult experts who choose the best physical property models and computer programs for the design engineer. Although these choices may be the best ones and the programs may be state-of-the-art, the uncertainty in the physical properties calculated is often not communicated to the design engineer. The accuracy, precision, and range of applicability of models are often overestimated by the users of the models. In fact, Mathias and Klotz (1994), in the first of their “Laws of Industrial Thermodynamics”, point out that “process engineers will use models outside recommended ranges”. Even terminology reinforces these misconceptions. To the physical properties expert, a “rigorous” model is one with a certain level of thermodynamic and other consistency and one that can be used over a range of conditions. It is not meant to imply a high degree of accuracy. To many process engineers, however, “rigorous” means “correct”.

This lack of communication of uncertainty information occurs not only between model developers and process engineers but also between experimentalists and model developers. Full uncertainty analyses are rare in experimental papers, as are comparisons of model error and experimental error in articles on model development.

The problem then is to consider the entire system of data generation, model development/choice, and process simulation (Figure 1). One goal is to develop optimal process designs, and this requires accurate process simulation, accurate thermodynamic models, and accurate experimental data. The random and systematic error inherent in experimental data affect the final design. So, too, the errors in any thermodynamic model degrade that design. What we need is a strategy for communicating the uncertainties so that their effects on the final design are understood and used in assessing the quality of the design.

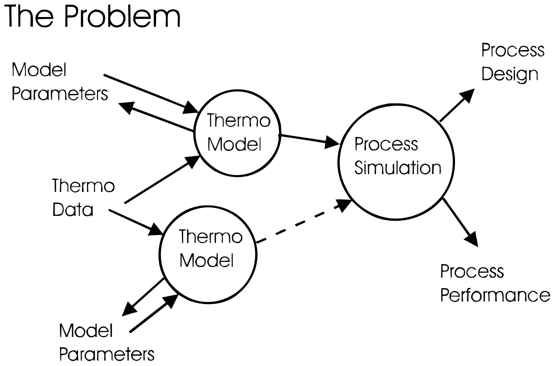

Figure 1. Connections between data generation, model development/choice, and process simulation.

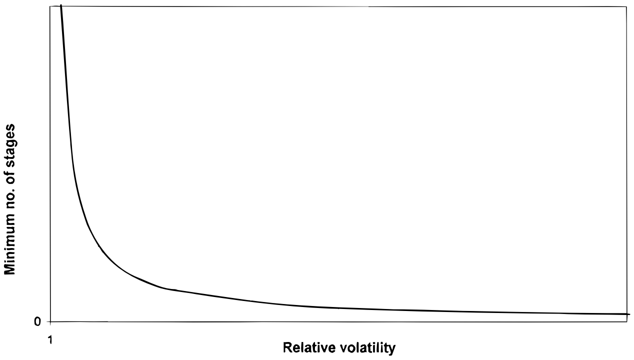

Figure 2. Sensitivity of minimum stages required in a column.

Identification of the Problem

The problem of uncertainty in process design is illustrated with the traditional relationship between the minimum number of stages required in a distillation column and the relative volatility of the key components, shown in schematic form in Figure 2. If there is uncertainty concerning the value of the relative volatility, there is certainly uncertainty concerning the number of stages for the column. Even this simple sketch shows the value of considering effects of uncertainties in thermodynamic data on design. Of course, there are many other inputs to the determination of the actual number of stages required.

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* Present address: Chemical & Metallurgical Engineering Department, University of Nevada, Reno, NV 89557-0136.

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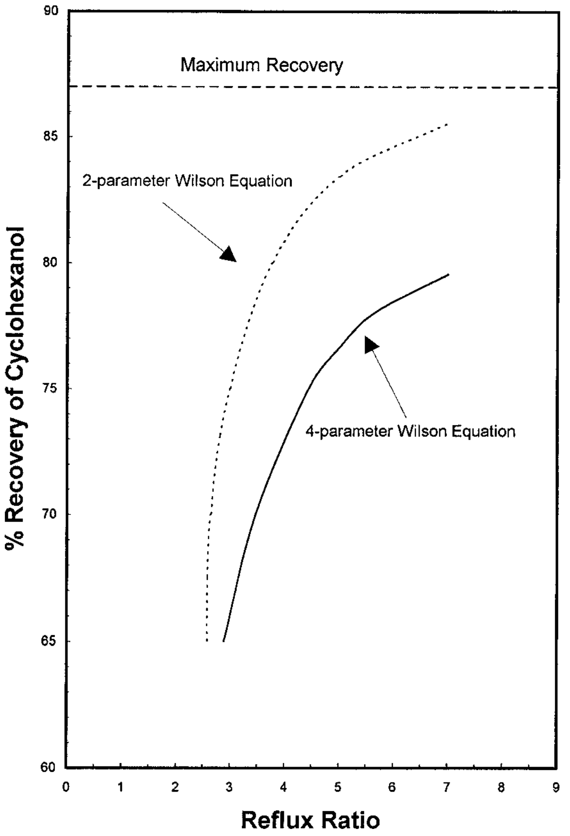

Figure 3. Effect of selection of VLE correlation and heat of mixing on recovery by distillation of cyclohexanol from phenol: 40 actual trays, feed at 12. Redrawn with permission from Murthy and Zudkevitch (Effect of Heat of Mixing and Vapor-Liquid Equilibrium on Design, Performance and Economics of Distillation. *Inst. Chem. Eng. Symp. Ser.* **1979**, No. 56, 1.1/51–1.1/78). Copyright 1979 Institution of Chemical Engineers.

Tray efficiencies are calculated from inexact hydrodynamic models that use experimentally determined physical properties. At some point in the design process, a guesstimate of the uncertainties *is* made, in the form of a "safety factor". It is the rational quantification of these safety factors or their replacement that is needed.

Model Choice Uncertainty

Much work on identifying the problem of physical property errors and process uncertainties was done by Zudkevitch and others in the 1970s (Murthy and Zudkevitch, 1979; Zudkevitch 1980). Figure 3 shows one of their case studies. Two different liquid-state activity-coefficient models were used to calculate the recovery of cyclohexanol from phenol in a given distillation column. For a given reflux ratio, the recovery differs substantially for the two sets of calculations. The predicted maximum recovery for one model was approximately 81%, while that for the other was 87%. Neither model is correct in any strict sense, so the uncertainty is high and unacceptable. Of greater concern is that the level of uncertainty would have gone unnoticed if the case study had not been done. Both models give reasonable regression fits to the vapor–liquid equilibrium data. Similar case studies have been done by Nelson et al. (1983) and others.

Even seemingly simple systems can show significant uncertainties. Figure 4 is reproduced from an article by Hsu (1987) in which the propylene/propane separation was studied. Relative volatilities calculated from Raoult's law and from the Soave–Redlich–Kwong (SRK) equation are compared to experimental data, and the deviation is dramatic. Hsu describes the effects on the design of a column to perform this separation. Again, if one used only a single equation of state for the system, one would get no estimate of the uncertainty of the resulting design.

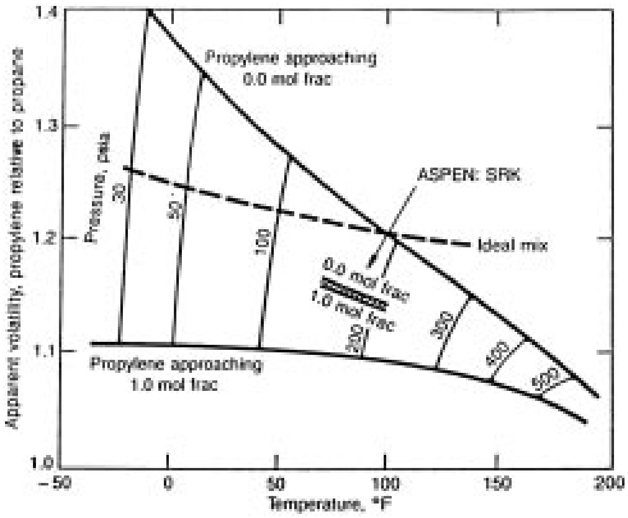

Figure 4. Apparent relative volatility of propylene to propane deviates from ideal mixing. Reprinted with permission from Hsu (Beware! propylene-propane split. *Hydrocarbon Process.* **1987**, *66* (4), 43–44). Copyright 1987 Gulf Publishing Co.

Many other examples can be given, and many process engineers have related their stories to the author. In the typical situation, they inadvertently change their thermodynamic package option and are surprised (sometimes disturbed) by the significant effect on calculated results. Although they do get help in choosing the model from the physical property experts (including warnings not to go outside a specified temperature, pressure, or composition range), the important question is not simply "Which model is best?" but rather "How good is the best model?".

Model Parameter Uncertainty

Hernandez et al. (1984) looked at the uncertainty of the calculated relative volatility in an ethylene/ethane superfractionator. Figure 5 shows their results of a case study in which two different equations of state were used in the calculation, and then the experimental values were compared. Again, there is the expected deviation among these three sets of values. However, the fourth curve in Figure 5 shows that the choice of binary interaction parameters for the SRK equation is more significant than is the choice of SRK over the BWR equation. This leads to the concept of evaluating design uncertainties by studying the effect of varying model parameters as well as varying models.

Macchietto et al. (1986) used this same case to study the sensitivity of the ethylene purity in the distillate to changes in the various binary-interaction parameters. Figure 6 shows their results for the ethane/ethylene binary-interaction parameter. Although the "linear approximation" line can be determined quite simply from a linear sensitivity approach from a base set of parameters, the authors show that the actual sensitivity was nonlinear and much more significant. They established the importance of considering simulations across the expected range of model parameters. However, the appropriate range to use in the uncertainty analysis must somehow be determined.

The minimum information necessary for a linear sensitivity analysis is the set of derivatives of key output variables (e.g., reflux ratio) with respect to key input variables (e.g., binary-interaction parameters). In the absence of analytical derivatives, this multidimensional

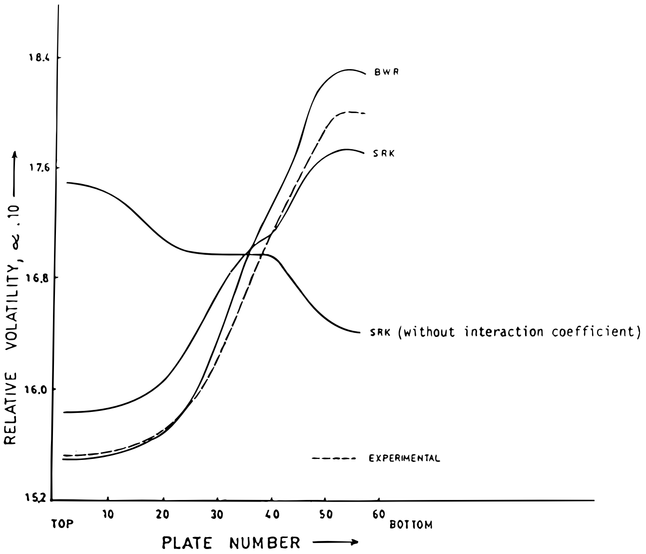

Figure 5. Relative volatility profiles for the ethylene/ethane system. Reprinted with permission from Hernandez et al. (The Prediction of Properties and Its Influence on the Design and Modeling of Superfractionators. *Proceedings, Second International Conference on Foundations of Computer-Aided Process Design*, Snowmass, CO, June 1983; CACHE Publications: Ann Arbor, MI, 1984; pp 709–740).

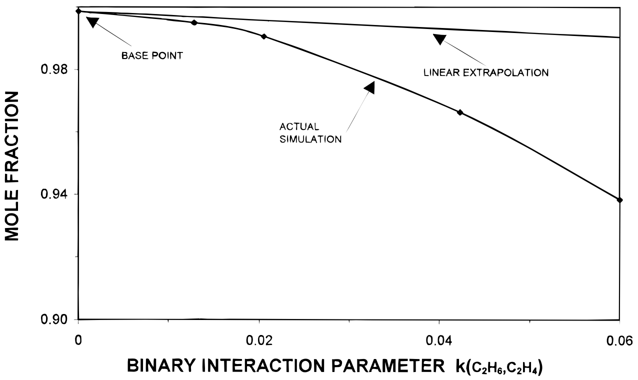

Figure 6. Distillation example: ethylene purity in distillate vs k_{23}. Redrawn from Macchietto et al. (Exact Determination of Process Sensitivity to Physical Properties. *Fluid Phase Equilib.* **1986**, *29*, 59), with kind permission of Elsevier Science-NL, Amsterdam, The Netherlands.

linear approximation would require one additional simulation of the process, very near the final design, for each input variable. However, one expects (and Macchietto shows) that the sensitivities are nonlinear. In addition, the real question is not how sensitive the design is to small changes in the input data but rather how sensitive the design is to the *actual* uncertainty of the input data. A derivative of the output variable with respect to the input variable is not that helpful unless (1) it is normalized in some meaningful way, and (2) it is a reasonable estimate over the entire expected range of the variable.

Experimental Data Uncertainty

All model parameters, pure-component and binary, ultimately are determined from some form of experimental data. Zeck (1991) showed that these data may be sparse or contradictory, even for common binary systems. As an example, Zeck showed (Figure 7) the range of data (and correlations) available for the system chlorobenzene + ethylbenzene and noted that the differences in data from different sources are “an unacceptable order of magnitude for a test system for the calibration of distillation columns.”

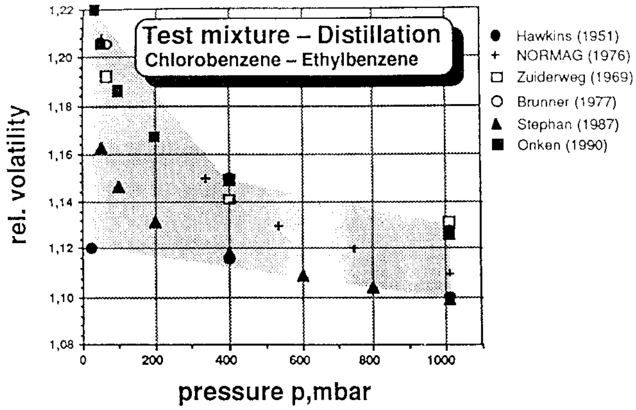

Figure 7. Literature data, data banks, measurements, correlations, parameters. Reprinted from Zeck (Thermodynamics in Process Development in the Chemical Industry--Importance, Benefits, Current State and Future Development. *Fluid Phase Equilib.* **1991**, *70*, 125–140), with kind permission of Elsevier Science-NL, Amsterdam, The Netherlands.

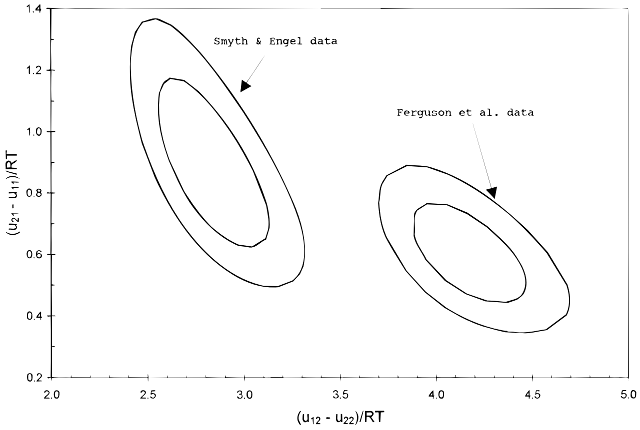

Figure 8. Confidence regions (90% and 99%) of Wilson parameters for ethanol–heptane. Data are from Smyth and Engel (Molecular orientation and the partial vapor pressures of binary mixtures. II. Systems containing alcohol. *J. Am. Chem. Soc.* **1929**, *51*, 2660–2670) and from Ferguson, Freed, and Morris (The system: ethyl alcohol–heptane at 30°. *J. Phys. Chem.* **1933**, *37*, 87–91).

Figure 8 shows an example of the uncertainty in model parameters that can arise from random and systematic errors in experimental data. Two sets of data for the system ethanol–heptane are considered. Both sets seem reasonable, and each individually exhibits the characteristic confidence regions for the Wilson binary interaction parameters. Both the 90% and the 99% confidence regions are shown, based on a traditional maximum-likelihood regression. To study the uncertainty of a design to uncertainties in these model parameters, one might use the indicated range of values. However, the two 99% confidence regions (one for each set of data) do not overlap. Thus, if the proper regression procedure were used, one might infer with a high degree of confidence that the Wilson equation does not fit this system, a conclusion not reached from evaluation of one data set by itself. Alternatively, one might pool the data or use a much larger parameter space that would include both sets of individual confidence regions. If sufficient uncertainty information on the measured variables is available, one could decide to use only the more precise data set. However, the lack of overlap shown in Figure 8 suggests either a systematic error in one (or both) of the data sets or a systematic error in the Wilson model.

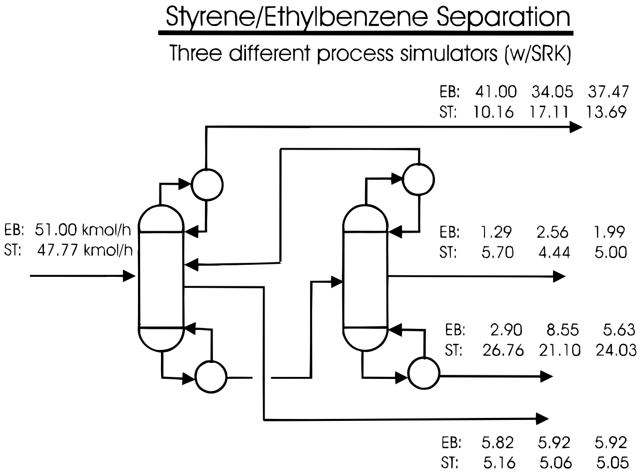

Figure 9. Styrene/ethylbenzene separation with three different process simulators. Redrawn from Sadeq et al. (Anomalous Results from Process Simulators. AIChE Annual Meeting, Miami Beach, November 1995; paper 30d).

Although an estimate of the error in the reported experimental data is required by some journals, the basis of the estimate is often not specified. Is it meant to include only errors in precision (random errors), or are accuracy (systematic errors) estimates included? Are the reported values estimated standard deviations or average absolute deviations? Was the American National Standards Institute (1985) or another standard error analysis procedure used? If "rouge" data were eliminated, on what basis was this done? These are all questions that need to be addressed.

Process Simulator Uncertainty

Beyond the choice of model, the regression of model parameters, and the evaluation of experimental data, the process simulator can introduce uncertainty. Differences in algorithms or tolerances can affect designs, but even when one attempts the same problem on different process simulators, differences arise. Sadeq et al. (1995) studied the classic styrene + ethylbenzene separation with three different popular process simulators. In each case, the model chosen was the standard SRK equation. However, as shown in Figure 9, the results for the product flow rates and purities are quite different. The ethylbenzene flow rate from the bottom of the second tower, for example, was calculated to be 2.90, 8.55, and 5.63 kmol/h from the three different simulators. Sadeq et al. attribute some, but not all, of the differences to the pure-component database in the three simulators.

Some organizations standardize on one process simulator, but engineers who have used two or more simulators have reported similar, distressing differences in simulation outputs. From heat exchangers to compressors, from reactors to distillation columns, cases have been reported to the author where (as far as the process design engineer knew) precisely the same simulation was being done, but different results were being obtained. Although these differences have sometimes been resolved (with some difficulty) as occurring from convergence tolerance differences, from nuances in the way thermodynamic models are used to calculate properties, and from programming errors, they do point to an uncertainty problem that can be easily overlooked. In fact, it is not clear how these uncertainties can even be recognized if one uses only a single process simulator.

Monte Carlo Approach

In an attempt to address the concerns that output uncertainties are nonlinear, that they should be related to the uncertainties of the inputs, and that the procedure should lend itself to risk analysis, various authors have applied the Monte Carlo technique to design uncertainties. For example, Uddin and Bell (1988), Badar et al. (1993), and others have applied Monte Carlo to the uncertainty in heat exchanger design to uncertainties in design variables, measured process variables, and calculated physical properties. We (Reed and Whiting, 1993; Whiting et al., 1993) have studied the effect of thermodynamic model parameters on process design and predicted performance for several cases.

In a Monte Carlo simulation, process simulations are repeated with variations in input variables (such as thermodynamic model parameters or raw material costs). The output variables from the set of simulations show a distribution from which uncertainty analyses can be performed. The values for the input variables are drawn from distributions based on the uncertainty. For example, our best estimate for the binary parameter k_{ij} may be 0.02, but we may find that there is a 2.5% chance that it is actually above 0.03 and a similar chance that it is below 0.01. If we assume a Gaussian distribution, the mean would be 0.02 and the standard deviation would be 0.005. Other distributions may be used, and frequently a log-normal or a triangular distribution is the choice. Joint probability distributions for the uncertain input parameters can be used, for example, with a co-variance matrix. Especially with highly correlated parameters, such as those of liquid-state activity-coefficient models, such a treatment is essential. Fortunately, the final cumulative frequency distribution is reasonably insensitive to the form of the distribution; however, it is sensitive to the mean and standard deviation.

Our philosophy is to treat the process simulator as an experimentalist treats laboratory equipment. Experiments are, in general, time consuming and costly. Therefore, to obtain the maximum useful information from the fewest experiments, the experimentalist uses a statistical design to choose the conditions at which to run the experiment. Similarly, we use experimental design to choose a set of model parameter values for which to run the simulation. In a typical multicomponent simulation, there are many such parameters to vary. Thus (as in the experiment), we would not merely vary one parameter at a time. Rather, we would look throughout the feasible region of parameter space with a relatively small number of experiments. And, as with the true experimental matrix, we should perform more experiments in regions of the parameter space that are more important vis-à-vis the final application of the data. Thus, we sample from the probability distributions of the parameters (corresponding to their uncertainties), and we use a stratified sampling technique (e.g., Latin Hypercube Sampling) to choose our "experimental" matrix of conditions. The details are given elsewhere (Whiting et al., 1993).

Figure 10 (from Reed and Whiting, 1993) shows the results of such a set of simulations for the separation of benzene and toluene. In this case, there are seven uncertain input parameters, each with associated uncertainties from standard sources. In this illustrative example, the uncertainties distributions are assumed independent, which can overestimate the output uncertainty. (A treatment of this example with such correlation included is given elsewhere [Reed, 1992].) For fixed product purities and $R/R_{\min}$, the uncertainty in the number of theoretical stages

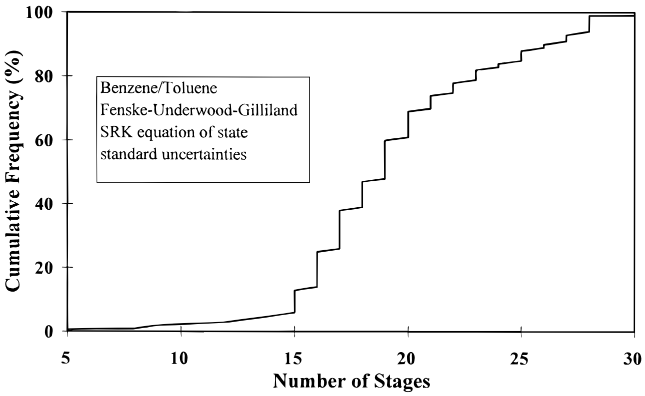

Figure 10. Uncertainty in theoretical stages.

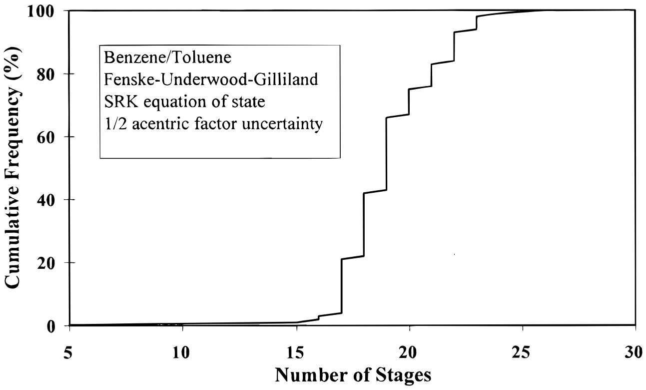

Figure 11. Uncertainty in theoretical stages with reduced model-parameter uncertainty.

required is significant. Such a figure reminds the process engineer that there is approximately 50% chance that the base design (i.e., the *only* design that is available if only one simulation is run) is adequate. Of course, some safety factor is always applied. Figure 10 provides a rational alternative to traditional safety factors because it shows the quantitative risk reduction achieved by any given increase in the number of stages.

An alternative to substantial overdesign is to improve the quality or quantity of experimental data and, thereby, the quality of the model parameter values. If there are two data sets of unequal uncertainty, choosing the better data set could improve the quality of the parameter values. Additional data may improve the accuracy of the model parameters, but they more likely will improve their precision. In Figure 11, Reed and Whiting show the quantitative effect of increased parameter precision on design uncertainty. With the original parameter precision (Figure 10), 25 stages (40% overdesign) are required to attain 80% design confidence. Yet, with the improved parameter precision (Figure 11), only 21 stages (17% overdesign) are required. The value of additional experimentation can thus be quantified. It is the savings achieved by reducing the extent of overdesign, for a given risk benchmark. There are, of course, other factors (operating and capital costs, process flexibility, etc.) that can be included in the simulation.

Sensitivity/Regression Approach

Although, as noted previously, a simple linear, differential sensitivity approach is not very useful, the results of a Monte Carlo study provide data over the entire expected range of the input variables (e.g., model parameters). Such data can be regressed with multilinear or multinonlinear approaches both to rank the model parameters and to provide simple sensitivity data.

Table 1. Sensitivity Coefficients (Benzene/Toluene Example)

	no. of stages		reflux ratio	
	SRC	PCC	SRC	PCC
Tc (benzene)	0.094	0.160	0.059	0.102
Pc (benzene)	−0.067	−0.119	−0.013	−0.023
ω (benzene)	0.529	0.685	0.493	0.664
Tc (toluene)	−0.141	−0.245	−0.119	−0.211
Pc (toluene)	0.001	0.002	−0.013	−0.023
ω (toluene)	−0.614	−0.732	−0.665	−0.762
k_{ij}	0.005	0.009	0.005	0.009

For example, the data generated in the set of Monte Carlo simulation runs can be regressed to obtain standardized regression coefficients (the SRC_i in the regression eq 1), or partial correlation coefficients (PCC_i in eq 2) can be obtained by performing two separate regressions (one with all input variables and one with the subject input variable ignored).

$$\frac{y - \bar{y}}{\sigma_y} = \sum_{i=1}^{m} \mathrm{SRC}_i \frac{x_i - \bar{x}_i}{\sigma_{x_i}} \tag{1}$$

$$\mathrm{PCC}_i^2 = \frac{\sum_{j=1}^{n} (y_j - y_j^{\text{regress model without } x_i})^2 - \sum_{j=1}^{n} (y_j - y_j^{\text{full regress model}})^2}{\sum_{j=1}^{n} (y_j - y_j^{\text{regress model without } x_i})^2} \tag{2}$$

where y is an output variable, the x_i are input variables, σ is the standard deviation, m is the number of input variables, and n is the number of Monte Carlo simulation runs made.

Both of these coefficients range from −1 to +1, and larger magnitudes indicate greater sensitivity of the output variable (y) to changes (on a normalized basis) in the input variable (x).

While there are other alternatives (nonlinear regression coefficients, simple correlation coefficients, rank regression coefficients, etc.), all of these techniques provide more useful information because the data from the Monte Carlo simulation runs are from the actual probability distributions of the input (model) parameters. The data cover the entire model-parameter range of interest, and they are more concentrated in the more likely ranges. The sensitivities calculated, therefore, are standardized and can be compared directly, even though the standard deviations of the model parameters can be quite varied.

For example, Table 1 shows sensitivity coefficients for the benzene/toluene problem mentioned earlier. These results show that the precision of the acentric factor has the greatest impact on the uncertainty in the number of stages. Although the precise meaning of the coefficients in Table 1 is beyond the scope of this article, these values do show that, if the true value of the acentric factor is one standard deviation above the mean value reported, the number of stages required will be affected more greatly than it would if any of the other model input parameters were varied by one standard deviation. Such deviations are all equally likely; thus, the coefficients provide a tool both for risk assessment of and for rank ordering the impact of experimental errors on the simulation result. Such a ranking of input variable sensitivities was used to decide which input variable to investigate for the improved-precision study shown in Figure 11. Identification of the

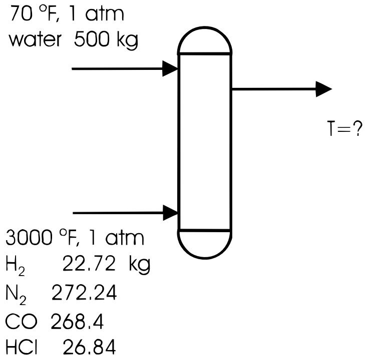

Figure 12. Flow diagram for gas cooling example.

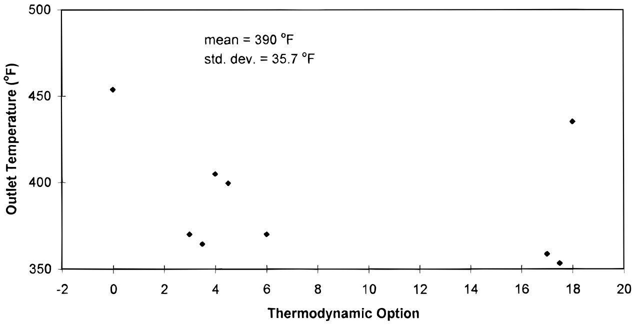

Figure 13. Outlet temperature sensitivity to model choice for gas cooling example. The abscissa variable is an arbitrary numbering for thermodynamic options from two different process simulators.

most important variable for further experimental study is made via the sensitivity analysis. The value (in reduced risk or reduced overdesign) of the additional experimental work then is estimated by comparing the Monte Carlo simulations for two different standard deviations of the input variable.

Optimization-Analog Approach

On current chemical process simulators, various (numerous) options are given for calculation of physical properties. The number of possible combinations of models for K-factors, enthalpies, densities, etc., is huge. In this environment, the process engineer chooses a set of models, often with the guidance of the physical-properties expert. Additional guidance is sometimes provided in the documentation for the process simulator. Even in a simple problem such as that shown in Figure 12 (Klein, 1993), however, unexpected differences occur for different similar property-model choices. In this process, a hot gas stream is cooled by the addition of a water spray. The outlet is all vapor, and no reactions occur. Yet Figure 13 shows a significant variation in calculated outlet temperature. The results shown are for the standard equation-of-state options for two different process simulators.

The difference between running the simulation with only one of these options and running the simulation with several options is dramatic. The process engineer, having been offered only one option, would have a great deal of confidence in the result. However, if the process engineer investigated several different (yet similar) property options, the inherent uncertainty in the calculated outlet temperature would be clear. The difference between the results from two models is not itself an estimate of the uncertainty. However, if both models are believed to be of equal quality for calculating the property of interest, the difference between them is an estimate of the lower bound of the uncertainty of the models.

In this simple example, the most important property is the enthalpy of vaporization of water, and the models used predict widely varying values of this property. This property is known experimentally to great accuracy, but it is very poorly predicted by equation of state models. We have used this example at several large chemical companies, and the physical properties experts were surprised by the variation in predicted outlet temperature. However, through this approach of trying several model options, the problem was revealed, which guided the proper analysis of the cause of the model uncertainty. Another possible source of uncertainty could be the heat-capacity correlations used in the calculation. For each calculation, the same standard correlations were used; thus, the effect of this uncertainty is not revealed in the analysis.

One approach to this problem is to consider the choice of physical-property model to be analogous to any optimization problem. There are no "exact" models, but some models are better than others. As in the traditional search techniques in optimization or other numerical methods, we begin at an initial point and try to improve the answer by increasing the order of the method. In other words, we use better techniques that involve fewer assumptions or less truncation error. As one moves closer to the optimum, a traditional way to estimate the error in the answer is to compare the best answer to the second-best answer. If the procedure is rapidly converging, this estimate is reasonable.

In the choice of property model, one can also consider several models of increasing expected accuracy. The difference between the results of a process simulation with the expected "best" model and the results obtained with the expected "second-best" model can be used to obtain a crude estimate of the uncertainty of the result. On the other hand, if there are several equally good models, one can run the process simulation with each (as in Figure 13) to estimate the uncertainty. This, too, is a technique that we have used in optimization studies.

Conclusions

The accuracy and precision of physical property data and models have significant impacts on the results of process calculations. Without the quantification of these impacts, the process design engineer cannot rationally assess the risk of process failure, the appropriate extent of overdesign or, indeed, the value of high-quality physical property data and models. Monte Carlo simulations and probabilistic sensitivity analyses can provide uncertainty information for specific models, when the uncertainty of the underlying experimental data are available. Comparisons of the results of process simulations using different models (and even different process simulators) can provide further uncertainty information to the process design engineer. In each case, the connection between errors in experimental data, property models, and process calculations must be recognized.

To obtain the uncertainty information needed will require a coordination of efforts. Clear, rational, and consistent statements of estimated uncertainties are needed in experimental papers. Critical evaluations of experimental data must include estimated uncertainties. When model parameters are regressed from data, the uncertainties in the parameter values (including correlations between parameters) must be given. Estimates of uncertainties in values calculated from the model should also be presented. Finally, process simulators should include estimates of the uncertainty of their results, based on the uncertainties in the models used for physical properties.

Literature Cited

ANSI/ASME. *Measurement Uncertainty*; PTC 19.1-1985; American Society of Mechanical Engineers: New York, 1985.

Badar, M. A.; Zubair, S. M.; Sheikh, A. K. Uncertainty Analysis of Heat-Exchanger Thermal Designs Using the Monte Carlo Simulation Technique. *Energy* **1993**, *18*, 859−866.

Hernandez, M. R.; Gani, R.; Romagnoli, J. A.; Brignole, E. A. The Prediction of Properties and Its Influence on the Design and Modeling of Superfractionators. *Proceedings, Second International Conference on Foundations of Computer-Aided Process Design*, Snowmass, CO, June 1983; CACHE Publications: Ann Arbor, MI, 1984; pp 709−740.

Hsu, S.-L. Beware! propylene-propane split. *Hydrocarbon Process.* **1987**, *66* (4), 43−44.

Klein, D. J. Personal communication, Pittsburgh, PA, 1993.

Macchietto, S.; Maduabeuke, G.; Szczepanski, R. Exact Determination of Process Sensitivity to Physical Properties. *Fluid Phase Equilib.* **1986**, *29*, 59−67.

Mathias, P. M.; Klotz, H. C. Take a Closer Look at Thermodynamic Property Models. *Chem. Eng. Prog.* **1994**, *90* (6), 67−75.

Murthy, A. K. S.; Zudkevitch, D. Effect of Heat of Mixing and Vapor-Liquid Equilibrium on Design, Performance and Economics of Distillation. *Inst. Chem. Eng. Symp. Ser.* **1979**, No. 56, 1.1/51−1.1/78.

Nelson, A. R.; Olson, J. H.; Sandler, S. I. Sensitivity of Distillation Process Design and Operation to VLE Data. *Ind. Eng. Chem. Process Des. Dev.* **1983**, *22*, 547−552.

Reed, M. E. Probabilistic Analysis of the Effect of Error in Thermodynamic Parameters on the Computer Simulated Design and Cost Estimation of Distillation Columns. M.S. Ch.E. Thesis, Department of Chemical Engineering, West Virginia University, Morgantown, WV, 1992.

Reed, M. E.; Whiting, W. B. Sensitivity and Uncertainty of Process Designs to Thermodynamic Model Parameters: A Monte Carlo Approach. *Chem. Eng. Commun.* **1993**, *124*, 39−48.

Sadeq, J.; Duarte, H. A.; Serth, R. W. Anomalous Results from Process Simulators. AIChE Annual Meeting, Miami Beach, November 1995; paper 30d.

Uddin, A. K. M. M.; Bell, K. J. Effect of Uncertainties on the Performance of a Feed-Effluent Heat Exchanger System. *Heat Transfer Eng.* **1988**, *9* (4), 63−72.

Whiting, W. B.; Tong, T.-M.; Reed, M. E. Effect of Uncertainties in Thermodynamic Data and Model Parameters on Calculated Process Performance. *Ind. Eng. Chem. Res.* **1993**, *32*, 1367−1371.

Zeck, S. Thermodynamics in Process Development in the Chemical Industry-Importance, Benefits, Current State and Future Development. *Fluid Phase Equilib.* **1991**, *70*, 125−140.

Zudkevitch, D. Forensic Thermodynamics: Erroneous Decisions on Thermodynamic Data Can Cause Plant Failures. *ERCE Publ. Ser.* **1980**, No. 11, 885−905.

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