

**CONSEQUENCES OF PROPERTY ERRORS ON THE DESIGN OF
DISTILLATION COLUMNS**

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Abstract

In modern design simulators the initial input for the estimation of the phase behaviour of mixtures is a series of characteristic parameters of the pure species, such as the normal boiling point, T_b , the critical temperature, T_c and the critical pressure, P_c . For many components encountered in practice these parameters are not available from experiment and therefore they must be estimated.

The study of the propagation of errors in these estimated parameters through to the final design of an item of process plant – a distillation column separating binary and ternary mixtures - is the purpose of the present work. The likely magnitude of uncertainties in the input T_b , T_c and P_c is generated by the application of several popular and accepted methods.

Considerable uncertainties in the predicted designs are demonstrated. There would be great benefit from the development and employment in modern simulators of more sophisticated methods ensuring better description of molecular structures and intermolecular interactions.

Keywords: Critical properties, Method of calculation, Normal boiling point, Plant Design, Vapour - Liquid Equilibria.

1. Introduction.

Uncertainty analysis in the simulation of chemical processes and plants has been the subject of many publications and these have included studies of the effects of uncertainties in the thermophysical properties of particular process streams upon the design of plants [1]. The analysis of the effect of the thermodynamic data on estimated process performance has suggested techniques for the assessment of uncertainties [2-6]. Work has focused more recently on areas such as process synthesis under uncertain conditions [7], process design [8], etc.

However, the practical design process starts from a different point. For modern design simulators the initial input for the estimation of the properties of mixtures is a series of characteristic parameters of the pure species to be encountered in the plant, such as the normal boiling point, T_b , the critical temperature, T_c and the critical pressure, P_c . For many components encountered in practice these parameters are not available from experiment and therefore they must be estimated. The study of the propagation of errors in these estimated parameters through to the final design of an item of process plant is the purpose of the present work. We have chosen as the item of plant a distillation column and we examine binary and ternary mixtures. The likely magnitude of uncertainties in the input T_b , T_c and P_c is generated by the application of several popular and accepted methods.

2. Methodology.

We have decided to study the separation of binary and ternary mixtures of high molecular mass hydrocarbons because it is generally considered that the properties of the hydrocarbons are the easiest to predict and because the errors involved with different estimation methods are higher for higher molecular masses. For the purposes of our

analysis we have chosen to study mixtures of *n*-tetradecane, *n*-eicosylbenzene and *n*-pentacosylcyclopentane. Each molecule selected is a representative member of a major homologous series. While the particular hydrocarbons do not have direct relevance to industrial separations, crude oil fractions with average boiling temperatures similar to those of these pure components are typically separated in refineries.

We have chosen to employ the methods for estimation of T_c and P_c , proposed by Joback [9], Twu [10] and Ambrose [9], and the correlations for T_b suggested by the first two authors. All these methods are widely recommended in handbooks and are among the choices provided by commercial simulators. They can be classified as first order group contribution methods and reflect only the influence of the particular groups into which a chemical structure is divided. Refinements proposed by Stein and Brown [11] for improving the prediction of T_b by the Joback method, and the correlations of Somayajulu [12] building upon the methods of Ambrose for critical properties, were also used. However, results with the method of Somayajulu for the particular compounds we study coincide with those of the Ambrose method and are not presented here.

It is worth emphasising that the current simulation software usually provides only first order group contribution methods. Recently, many authors have suggested second order methods. The latter can be of varying levels of sophistication and include some intermolecular interactions [13, 14]. As an example of second order methods we have included in the study the new correlations for estimation of the respective characteristic parameters of hydrocarbons which we have recently reported [15, 16]. They are derived from pre-designed databases, and straightforward combinations of contributions (atom counts, topological indices and descriptors from simulated molecular mechanics). Hereunder, these methods will be referred to as “CWS”.

Normal boiling temperatures have a dual contribution to the uncertainties of the design because they are employed both in the estimation of critical temperatures and as a separate quantity (e.g., in the estimation of acentric factors). Consequently, the present study has been organised to address separately the uncertainties introduced solely by methods for the estimation of T_c and P_c , and the uncertainties resulting jointly from both the methods for critical properties and the methods for estimation of T_b .

The parameters of the three sample hydrocarbons estimated by the different methods are summarised in Table 1. It includes also “best estimates” of the required values. These were obtained by extrapolation, with asymptotic behaviour correlations [17, 18] of recommended experimental data for the lower members of the respective homologous series [15]. The table illustrates the two main influences being studied and the possible uncertainties in the estimated parameters. An author’s name, followed by “1” (scheme 1) denotes that only errors in T_c and P_c are involved. If the name is followed by “2” (scheme 2) the combined influence of uncertainties in T_b , T_c and P_c is included.

In our study, we follow a typical methodology for the design of a distillation column to perform a prescribed task. We have overall, studied a large variety of different combinations of methods and design cases. However, in what follows, only two of all cases, simulated with HYSYS [10], are presented. These illustrate the Fenske-Underwood-Gilliland short-cut approach to the design of a distillation column for the separation of the binary system, and the rigorous design of a distillation column for the separation of the ternary system. In all cases studied the feed to the column was chosen to be 100 kmol h^{-1} equimolar mixture at temperature of $T = 658 \text{ K}$. The latter corresponds to the temperature at which usually the vacuum distillation of the heavy ends of petroleum fractions takes place.

For each of the two schemes, we seek to design a distillation column to achieve a specified separation of the binary or ternary mixture. We adopt a single thermodynamic model, a given design method and we prescribe a fixed feed composition, temperature and pressure. We then first design the column using a commercial simulator and the best estimates of T_c and P_c of the pure components. Subsequently, we redesign the column using, in turn, each of the sets of values of parameters listed in Table 1. This procedure leads to a range of designs of the column that arise solely from the uncertainties in the characteristic parameters of the fluids. It follows that the particular design considered, while reasonable, is in some sense arbitrary.

2.1. *The two component system.*

We examine in this case the separation of *n*-eicosylbenzene and *n*-tetracontane. We prescribe that a distillation column should be designed for the following conditions: Pressure of the input stream (P) - 10 kPa; Condenser pressure - 9.6 kPa, Reboiler pressure - 10.4 kPa; Maximum concentration of the heavy key component in the distillate – less than 0.01 mole fraction; Maximum concentration of the light key component in the bottom product – less than 0.001 mole fraction.

We compare the designs by two different means. Firstly, we examine the actual number of theoretical stages obtained at a certain value of the external reflux ratio. Secondly, we examine the reflux ratio for a fixed number of theoretical stages. For the first case, we set the external reflux ratio to 1.2 times the minimum reflux ratio, determined by the process simulator, and then the actual number of theoretical stages required to achieve the specified purity is calculated. For the second case, the number of theoretical stages is fixed to the number of stages determined with the best estimated data; the external

reflux ratio, required to achieve the specified purity, is then calculated for each other design.

2.2. *The three component system.*

We examine in this case the separation of *n*-eicosylbenzene, *n*-pentacosylcyclopentane and *n*-tetracontane in a particular distillation column. We prescribe that it should be designed to operate under the following conditions: Number of stages of the column – 40; The input stream is a mixture of the three components, with mole fractions 0.33, 0.34 and 0.33, respectively, fed into the column at $P = 12$ kPa; Maximum concentration of the light key component in the bottom product – less than 0.03 mole fraction; Maximum concentration of the heavy key component in overhead vapour product - less than 0.05 mole fractions; Condenser pressure - 10.7 kPa; Reboiler pressure - 12.2 kPa. The aim of the separation is the production of a side stream containing not less than 0.92 mole fractions of *n*-pentacosylcyclopentane.

3. Results and discussion.

It may be seen from Table 1 that in the scheme 1 case, all first order methods for T_c predict considerably higher critical temperatures, whereas the predicted critical pressures may be higher (Ambrose, Twu) or lower (Joback). The over-prediction of T_c by the Joback method and especially - of P_c by the Ambrose method is outstanding, but could easily pass unnoticed in an automated design. The uncertainties in the determination of T_b (scheme 2) generally influence the predicted values negatively. The Stein and Brown corrections limit the errors in the estimation of T_c , but the absolute deviations remain significant. The second order methods (CWS) in all cases match closely the best estimates.

In order to appreciate the sensitivity of the process design to its various components, it is necessary to examine results at the intermediate stage and consider explicitly the phase behaviour of the mixture and its modelling. In all cases studied, the thermodynamic model applied is the Soave-Redlich-Kwong cubic equation of state (SRK CEOS) with the binary interaction parameters set to zero. The variation of predicted behaviour therefore arises solely from the predicted characteristic parameters that enter the model.

3.1. Two-component system.

Figure 1 and Figure 2 represent the P - x phase envelopes of the n -eicosylbenzene + n -tetracontane system, obtained applying scheme 1 and scheme 2, respectively.

Except for the data predicted with Joback's method, the uncertainties in the determination of the critical properties do not seem to influence dramatically the phase behaviour of the studied system (Figure 1). Their effect is more pronounced in the liquid phase branch of the envelopes than in the vapour branch. The detrimental negative influence of large errors in T_b on the phase behaviour is clearly illustrated in the case of the Ambrose method (Figure 2). The data estimated by Twu's method largely over-predict the broadness of the phase envelope mainly because of the incorrect prediction of the distribution of the components in the liquid phase.

Whether the different distribution of the components between the two equilibrium phases has an important impact on the predicted performance of the specific process unit is seen in the design case studies. The number of the theoretical stages needed to achieve the prescribed separation is shown for scheme 1 in Figure 3 and in Figure 4 for scheme 2. The figures also show the reflux ratios (Figure 3a and Figure 4a, respectively) needed to achieve the required purity of the two components at the fixed number of theoretical stages determined with the best estimates of the parameters of the two compounds.

In both cases studied, the differences between the predictions made with the best estimates and the CWS method are negligible, which is not surprising following the almost identical phase envelopes produced by both methods. Obviously, the differences in the prediction of the component distribution between the equilibrium phases play a most important role in the design, which is demonstrated especially by the calculated value of the reflux ratio required to achieve the prescribed purity. Since the influence of T_b is more pronounced and the differences among the liquid phase predictions are larger the most dramatic discrepancies are observed for scheme 2. For example, the reflux ratio that is calculated with the best estimate is 1.39. The reflux ratio required by the method of Twu is 0.99, and the one required by the Ambrose method with the Stein and Brown correction for the T_b is less than 0.3. In the extreme cases of the predictions by the method of Joback, and the Ambrose method using the uncorrected Joback method for T_b , the Fenske-Underwood-Gilliland short - cut design procedure failed to converge.

3.2. Three-component system

Figures 5 and 6 show the triangular composition diagrams of the *n*-eicosylbenzene + *n*-pentacosylcyclopentane + *n*-tetracontane system at $T = 658$ K and $P = 12$ kPa. We have chosen to present the vapour-liquid equilibrium regions calculated with the data for *n*-pentacosylcyclopentane and *n*-eicosylbenzene calculated from the best estimate and just two of the methods studied – CWS (Figure 5) and Joback's method (Figure 6), applying both schemes *only to* the data of the intermediate component *n*-pentacosylcyclopentane. Although only the properties of the intermediate component are varied, the effect on the phase behaviour predictions can be dramatic, especially when the influence both of T_b and the critical properties are taken into consideration.

To estimate the influence of the *n*-pentacosylcyclopentane property errors on the design of the distillation column, we look first at the possibility to achieve the prescribed purity of *n*-eicosylbenzene in the overhead product, and of *n*-pentacosylcyclopentane in the intermediate product with the particular column. The design with the properties obtained from the best estimated parameters shows that both conditions can be met, and that the intermediate product with the required purity (not less than 0.92 molar fractions *n*-pentacosylcyclopentane) can be withdrawn from the 15th stage of the column (Figure 7). Only the data of CWS yield the same conclusion. The conclusion for data generated with the Ambrose method with respect to the production of the prescribed composition of the intermediate product from the 15th stage is ambiguous. The method of Joback, even with the correction for the T_b of Stein and Brown, predicts totally different compositions both for the overhead and the intermediate streams.

Secondly (Figure 7 a), we determine the tray (counted from top to the bottom) from which the intermediate component should be withdrawn in order to achieve a purity of not less than 0.92 mole fractions *n*-pentacosylcyclopentane. It may be seen that only the

CWS method predicts correctly the number of that tray (15th) to be the same as for the best estimates. Joback's method with the Stein and Brown T_b correction suggests, at the extreme, tray 22.

If the data predictions for all three components are varied, the results obtained naturally demonstrate even more pronounced discrepancies. The Ambrose method with the Stein/Brown correction highly over-predicts the purity of the components - 0.9826 mole fractions of the *n*-eicosylbenzene in the overhead product, and 0.9624 of *n*-pentacosylcyclopentane, withdrawn from the 15th stage. If the data of Joback is applied, the design algorithm for the column simply fails to converge.

4. Conclusions.

The correct estimate of the input characteristic properties plays an important role in plant design. We have demonstrated that even small uncertainties, produced using the current first order group contribution methods provided by simulation software as standard facilities, can dramatically mislead the designer. On the other hand, even small uncertainties in the prediction of the composition of a particular product (i.e., of the order of less than one mass per cent) can be significant if the required purity cannot be achieved, the product is of high value, or is produced in large quantities.

The above conclusion becomes even stronger if account is taken of the fact that additional errors (e. g., with the choice of the models and the quality of equilibrium data) are involved in the practical design procedure. Second order methods including intermolecular interactions in the description of molecular structure provide precise estimates of the input parameters studied and therefore more realistic designs; they should be incorporated in simulation programmes at the earliest opportunity.

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Table 1: Properties of n-tetracontane, n-pentacosylcyclopentane and n-eicosylbenzene, estimated by different methods

Method, combination	T _b , K	T _c , K	P _c , atm
n-tetracontane, C₄₀H₈₂, density (d₄²⁰) = 0.8190^a			
Best estimate ^a	790.8 ^a	874.0 ^a	4.48 ^a
CWS, 1	790.8 ^a	871.6	4.24
CWS, 2	793.4 (CWS ^b)	873.3	4.24
Joback, 1	790.8 ^a	1058.4	3.86
Joback, 2	1114.6 (Joback ^b)	1373.9	3.86
Joback, 2 St/Br	839.6 (Stein/Brown ^b)	1123.7	3.86
Ambrose, 1	790.8 ^a	907.7	6.31
Ambrose, 2	1114.6 (Joback ^b)	1279.4	6.31
Ambrose, 2 St/Br	839.6 (Stein/Brown ^b)	963.8	6.31
Twu, 1	790.8 ^a	897.1	5.40
Twu, 2	801.3 (Twu ^b)	891.0	4.32
n-pentacosylcyclopentane, C₃₀H₆₀, density (d₄²⁰) = 0.8328^a			
Best estimate ^a	729.3 ^a	847.8 ^a	6.23 ^a
CWS, 1	729.3 ^a	847.3	6.02
CWS, 2	732.2 (CWS ^b)	851.6	6.02
Joback, 1	729.3 ^a	894.4	6.43
Joback, 2	901.8 (Joback ^b)	1106.0	6.43
Joback, 2 St/Br	727.2 (Stein/Brown ^b)	891.8	6.43
Ambrose, 1	729.3 ^a	871.0	8.62
Ambrose, 2	901.8 (Joback ^b)	1077.0	8.62
Ambrose, 2 St/Br	727.2 (Stein/Brown ^b) ^c	868.5	8.62
n-eicosylbenzene, C₂₆H₄₆, density (d₄²⁰) = 0.8548^a			
Best estimate ^a	693.2 ^a	834.4 ^a	9.05 ^a
CWS, 1	693.2 ^a	832.4	8.74
CWS, 2	695.5 (CWS ^b)	834.1	8.74
Joback, 1	693.2 ^a	851.7	8.63
Joback, 2	821.0 (Joback ^b)	1008.7	8.63
Joback, 2 St/Br	689.4 (Stein/Brown ^b)	847.0	8.63
Ambrose, 1	693.2 ^a	848.6	10.58
Ambrose, 2	821.0 (Joback ^b)	1005.1	10.58
Ambrose, 2 St/Br	689.4 (Stein/Brown ^b) ^c	844.0	10.58
Twu, 1	693.2 ^a	846.49	9.83
Twu, 2	670.76 (Twu ^b)	834.01	10.58

^a – Estimated by extrapolation from the available experimental data for the lower members of the homologous series with an asymptotic behavior correlation. Considered closest to the real value of the parameter.

^b – The name in brackets denotes the method used for the estimation of the normal boiling temperature.

Figure captions

Figure 1. P - x phase envelopes of the n -eicosylbenzene + n -tetracontane mixture at $T = 658$ K, scheme 1. — best estimate; ○ CSW, 1; ■ Joback, 1; ◇ Twu, 1; ▲ Ambrose, 1.

Figure 2. P - x phase envelopes of the n -eicosylbenzene + n -tetracontane mixture at $T = 658$ K, scheme 2. — best estimate; ○ CSW, 2; ■ Joback, 2; ◇ Twu, 2; ▲ Ambrose, 2.

Figure 3. Number of theoretical stages required to separate the two-component system, scheme 1.

Figure 3a. Reflux ratio, needed to achieve the required purity, scheme 1.

Figure 4. Number of theoretical stages required to separate the two-component system, scheme 2.

Figure 4a. Reflux ratio, needed to achieve the required purity, scheme 2.

Figure 5. Vapour-liquid equilibrium of the n -eicosylbenzene + n -pentacosylcyclopentane + n -tetracontane system at $T = 658$ K and $P = 12$ kPa. Properties of n -pentacosylcyclopentane estimated with the CSW method. — best estimate; -●- CWS, 1 - - CWS, 2

Figure 6. Vapour-liquid equilibrium of the n -eicosylbenzene + n -pentacosylcyclopentane + n -tetracontane system at $T = 658$ K and $P = 12$ kPa. Properties of n -pentacosylcyclopentane estimated with the Joback's method. — best estimate; -●- Joback, 1, — ● — Joback, 2, - - Joback (Stein/Brown)

Figure 7. Purity of n -eicosylbenzene (mole fractions) and n -pentacosylcyclopentane (mole fractions). ■ - purity of n -eicosylbenzene

Figure 7a. The tray from which n -pentacosylcyclopentane must be withdrawn to achieve a purity not lower than 0.92.

List of symbols

P pressure [kPa]

P_c critical pressure [kPa]

T temperature [K]

T_b normal boiling point [K]

T_c critical temperature [K]

x_i mole fraction of the i -th component, liquid phase

y_i mole fraction of the i -th component, vapour phase