UNCERTAINTY ANALYSIS APPLIED TO THE CALCULATION OF THE BUBBLE POINT TEMPERATURE OF MIXTURES

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Abstract: The article presents the calculation of the bubble point of a mixture of n-butane, iso-butane, n-pentane and isopentane from the bottom of a distillation tower. This work aims to calculate the bubble point of a mixture using the Monte Carlo (MC) method. The calculation was performed under uncertainty in the Antoine parameters, which were obtained in the literature and optimized using Excel's Solver genetic algorithm and Stochastic simulation through MC method. In this way, the result is not a point temperature, but a range of probable values for the temperature of the bubble. This method proved to be promising and means more accurate process calculations, generating energy savings in industrial units.

Keywords: Uncertainty analysis, Monte Carlo method, process calculation, phase equilibria.

ANÁLISE DE INCERTEZAS APLICADA AO CÁLCULO DA TEMPERATURA DE BOLHA DE MISTURAS

Resumo: O artigo apresenta o cálculo do ponto de bolha de uma mistura de n-butano, iso-butano, n-pentano e iso-pentano proveniente do fundo de uma torre de destilação. Com isso, esse trabalho objetivou calcular o ponto de bolha de uma mistura usando método de Monte carlo (MC). O cálculo foi realizado sob incerteza nos parâmetros de Antoine, que foram obtidos na literatura e otimizados utilizando o algoritmo genético do solver, no Excel e simulação estocástica através do método MC. Dessa forma o resultado não é uma temperatura pontual, mas uma faixa de valores prováveis para temperatura de bolha. Esse método se mostrou promissor e significa cálculos de processos mais precisos, gerando economia de energia nas unidades industriais.

Palavras-chave: Análise de incertezas, método de monte Carlo, Cálculo de processos, equilíbrio de fases.

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1. INTRODUCTION

A common mistake made in process calculations is to treat problems punctually and not as a range, without considering the uncertainties associated with parameter measurements. Engineers must therefore know the importance of reliability in the property data of pure substances and mixtures and understand how small uncertainties in this information can significantly affect the technical and economic performance of an industrial plant. [1]

Uncertainties can be introduced mainly in two ways, the first is associated with the method used and depends, for example, on the thermodynamic model used, or on the numerical method used to make the calculation convergence. The second error propagates in the result of errors present in the input data. Thus, the better the quality of the data provided and the accuracy of the prediction methods, the better the estimate of the desired property will be. [2,3]

Data uncertainties are of a random and systemic nature; knowing them and evaluating them is of paramount importance; thus, the quantification of uncertainties, in general, consists basically of three steps: representing the uncertainties in the input parameters of the system; propagation of uncertainty throughout the process, and estimate the stochastic effect on production. The output is usually a deterministic result with a mean error to indicate uncertainty ranges. A density function is desirable to describe uncertainty statistics. [4,5]

Stochastic methods have been proposed to estimate and minimize these uncertainties. A widely used method is the Monte Carlo (MC) method. In this method, random numbers are basically generated and a series of probability calculations have been performed that estimate the chance of a future event happening. Thus, several simulations are performed to calculate the hit or miss probabilities. The generation of random numbers must follow a probability density function. And respect a certain range. [6]

Thus, with the help of computation and the use of these techniques, uncertainties can be measured and their propagation calculated along with chemical processes. Literature is already being developed for this type of simulation, and the authors already use stochastic methods to quantify and measure the propagation of uncertainties along with real chemical processes. [6]

A typical example of the application of methods that use random numbers is the calculation of the bubble point of a mixture with the pressure at the bottom of a distillation tower constant.

Therefore, this work aims to calculate the bubble point of a mixture using the MC method and Excel's Solver genetic algorithm to optimize the parameters and find the optimal interval for the bubble point temperature at a constant pressure.

2. METHODOLOGY

The case studied in this work is based on an example from Seader et al. (2011) [7] where the bottom product of a distillation tower nC4-rich has the composition given in table 1 and a constant pressure equal to 100psia (689 kPa), and the objective is to estimate the bubble point temperature of the mixture.

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Table 1. Mixture composition

Component	kmol/h	zi=xi
i-butane	8.6	0.031852
n-butane	215.8	0.799259
i-pentane	28.1	0.104074
n-pentane	17.5	0.064815

For the calculation of the temperature of the bubble, it is considered that $z_i = x_i$, and that the condition that.

$$\sum K_i x_i = 1 \quad (1).$$

With that, just choose how the K_i will be calculated. If ideally, using Raoult's law, or with non-idealities through modified Raoult or using the Phi-Phi (equations of state for both phases) or Gamma-Phi (G^e model for the liquid phase and EOS in phase) formulations steam).

The methodology consisted of using Microsoft Excel and its tools, such as the solver, achieving target and visual basic for applications (VBA) to perform the calculation of the bubble temperature of a mixture of hydrocarbons, as can be seen in images 1 to 3 (VBA code and solver setup). The method used to calculate Ki was Raoult's law, as described in equation 2.

$$K_i = \frac{P^{sat}}{P} \quad (2)$$

Where P^{sat} can be calculated using Antoine's equation.

$$\log_{10} P(bar) = A - \frac{B}{T(K) + C} \quad (3)$$

An iterative method was used to determine the temperature range of the mixture bubble. An uncertainty of 2% on the value of Antoine's constants available in the literature was then applied. 200 random numbers are then generated according to the MC method.

Image 1. VBA code for Random numbers

```
'i-butane
    Application.Run "ATPVBAEN.XLAM!Random", ActiveSheet.Range("$G$18:$G$217"), _
       1, 200, 2, , iba, iba * x
       Application.Run "ATPVBAEN.XLAM!Random", ActiveSheet.Range("$h$18:$h$217"), _
       1, 200, 2, , ibb, ibb * x
       Application.Run "ATPVBAEN.XLAM!Random", ActiveSheet.Range("$i$18:$i$217"), _
       1, 200, 2, , ibc, ibc * x
'n-butane
    Application.Run "ATPVBAEN.XLAM!Random", ActiveSheet.Range("$m$18:$m$217"), _
       1, 200, 2, , nba, nba * y
       Application.Run "ATPVBAEN.XLAM!Random", ActiveSheet.Range("$n$18:$n$217"), _
       1, 200, 2, , nbb, nbb * y
       Application.Run "ATPVBAEN.XLAM!Random", ActiveSheet.Range("$o$18:$o$217"), _
       1, 200, 2, , nbc, nbc * y
'i-pentane
    Application.Run "ATPVBAEN.XLAM!Random", ActiveSheet.Range("$s$18:$s$217"), _
       1, 200, 2, , ipa, ipa * z
       Application.Run "ATPVBAEN.XLAM!Random", ActiveSheet.Range("$t$18:$t$217"), _
       1, 200, 2, , ipb, ipb * z
       Application.Run "ATPVBAEN.XLAM!Random", ActiveSheet.Range("$u$18:$u$217"), _
       1, 200, 2, , ipc, ipc * z
'n-pentane
    Application.Run "ATPVBAEN.XLAM!Random", ActiveSheet.Range("$y$18:$y$217"), _
       1, 200, 2, , npa, npa * k
       Application.Run "ATPVBAEN.XLAM!Random", ActiveSheet.Range("$z$18:$z$217"), _
       1, 200, 2, , npb, npb * k
       Application.Run "ATPVBAEN.XLAM!Random", ActiveSheet.Range("$aa$18:$aa$217"), _
       1, 200, 2, , npc, npc * k
```

Once the constants were generated, the bubble temperature was calculated for each of the 200 MC simulations. Through the boxplot plot, the outliers were removed and a bubble temperature range was found.

Image 2. VBA code for boil point temperature

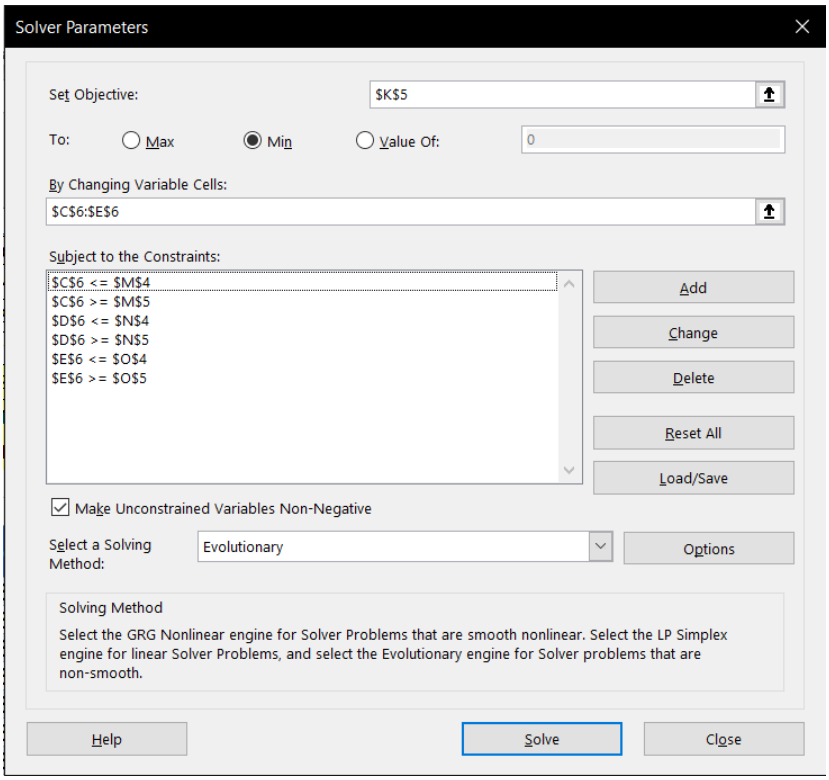
```
Dim i As Integer

Worksheets("T ponto de bolha").Activate
For i = 0 To 200
 Cells(18 + i, 31).GoalSeek Goal:=1, ChangingCell:=Cells(18 + i, 10)
 Next i
End Sub
```

Experimental vapor pressure data for each component was exported from Aspen Plus, and these values were compared with those obtained using the Antoine equation for that temperature range. The least squares method was applied in Solver to minimize the uncertainty between the calculated value and the experimental value. Thus, new parameters were defined, optimized for the previously estimated temperature range.

The solver tool, from excel, was used to optimize the parameters, using the method of least squares, minimizing the objective function through the genetic algorithm, and the restrictions of the parameters a, b and c of Antoine in Solver were the maximum and minimum values obtained in generation of random numbers from the MC simulation for each parameter.

Image 3. Solver for optimization of Antoine parameters



Using an uncertainty obtained via the solver, a new MC simulation was performed, and a new probability interval for the bubble temperature was found.

3. RESULTS AND DISCUSSION

Using Raoult's law for resolution, the following answer is found through iterative calculation methods.

Table 2. Traditional boil point temperature

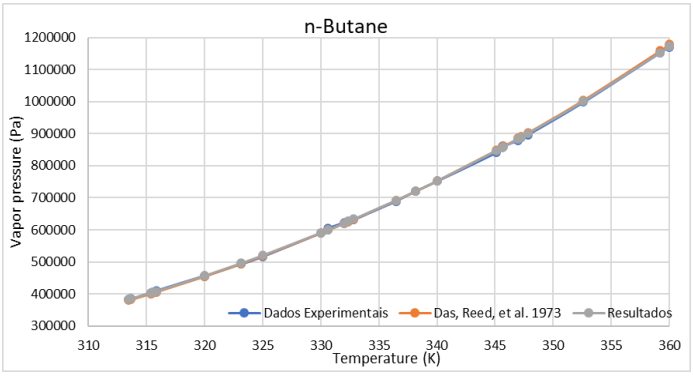
Component	kmol/h	zi=xi	T (°C)	P^{sat}	Ki (Raoult)
i-butane	8.6	0.031852	67.5161	1021.9079	**1.4832**
n-butane	215.8	0.799259	67.5161	754.6924	**1.0953**
i-pentane	28.1	0.104074	67.5161	346.3621	**0.5027**
n-pentane	17.5	0.064815	67.5161	265.3221	**0.3851**
sum	*270*	*1*			*0.9999*

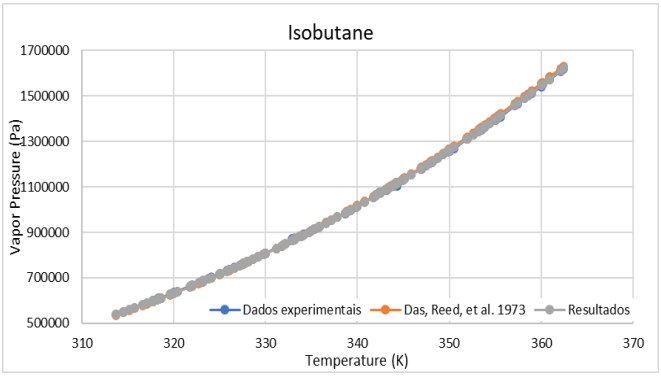
The values of the parameters optimized by Solver were identified in table 3, and we can see a good reduction in the uncertainty between the experimental and immediate vapor pressure in the temperature range between 313.32 K and 362.50 K (which is the initial temperature range obtained by MC simulation and used for optimization).

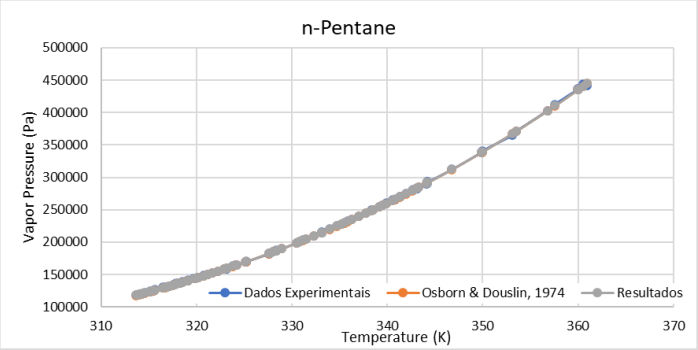
Table 3. Antoine parameters

Component	Reference	Temperature Range	A	B	C	Uncertainty
n-butane	Das, Reed, et al., 1973	272.66 - 425.	4.3558	1175.5810	-2.0710	0.348%
	Calculated	313.32-362.50	4.3260	1165.6803	-2.0585	0.238%
Isobutane	Das, Reed, et al., 1973	261.31 - 408.12	4.3281	1132.1080	0.9180	0.318%
	Calculated	313.32-362.50	4.3012	1123.1978	0.9259	0.139%
n-pentane	Osborn and Douslin, 1974	268.8 - 341.37	3.9892	1070.6170	-40.4540	0.278%
	Calculated	313.32-362.50	3.9839	1068.8359	-40.4485	0.234%
Isopentane	Stull, 1947	300.9 - 453.5	3.9718	1,021.86400	-43.23100	2.757%
	Calculated	313.32-362.50	3.8816	996.81510	-43.85299	0.369%

Figure 1. graphical comparation between experimental, literature and calculated parameters for a) n-butane, b) isobutane, c) n-pentane, d) isopentane.







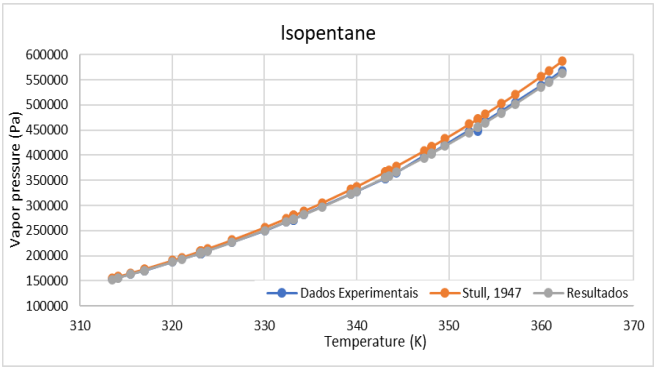


Table 4. Results

Input Data Uncertainty				Output results uncertainty	Average	Standard deviation
nC4	iC4	nC5	iC5			
2%				16.57%	66.10°C	10.95°C
-				15.31%	65.94°C	10.09°C
-				14.87%	65.94°C	9.81°C
0.24%	0.14%	0.23%	0,37%	1.56%	66.85°C	1.05°C

In table 4 we can see the uncertainty in each of the calculation steps. In the first MC simulation, the input uncertainty was 2%, which resulted in a 16.57% impact on the output temperature. When optimized, the input uncertainty was between 0.14 and 0.37% and the output uncertainty was only 1.56%. In this way, it can be accurately said that the average bubble temperature of the mixture at a pressure of 100psia (689 kPa) is actually 66.85°C, which may vary 1.56% more or less, a difference of 0.67°C compared to the traditional calculation method (67.52°C). Despite the small numerical difference, in industrial processes with large flows, this difference can mean millions in energy savings.

Figure 2. Initial and final temperature range.

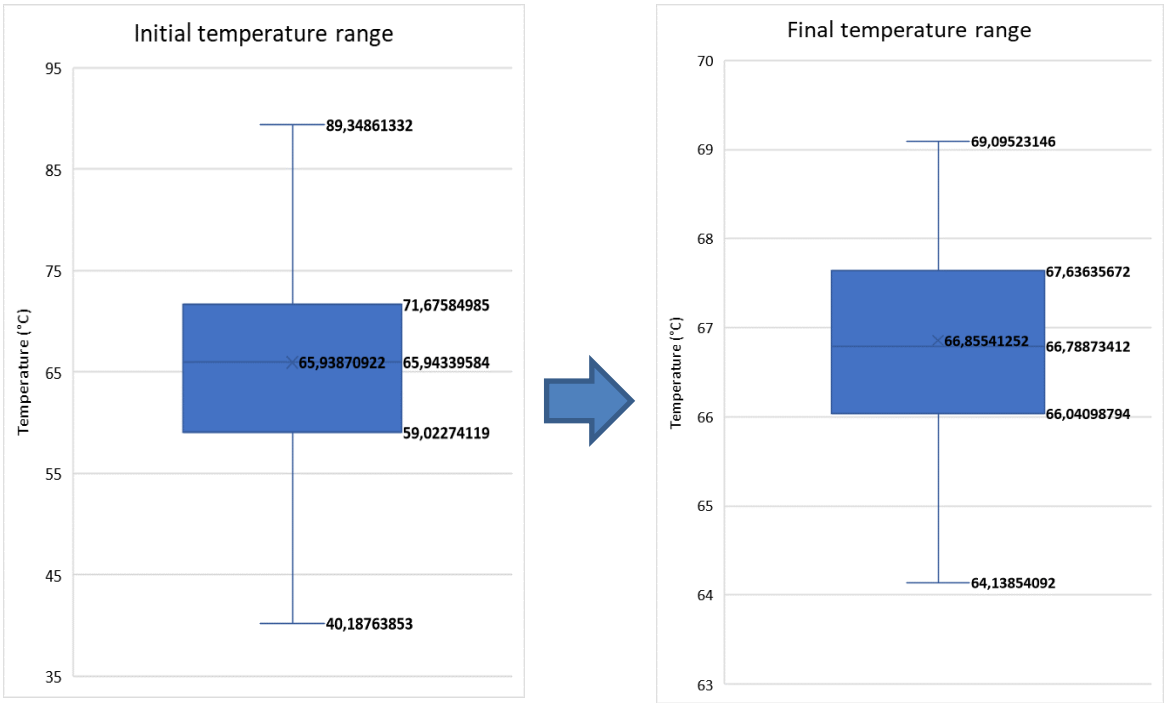


Figure 3. Initial Boil Point temperature PDF.

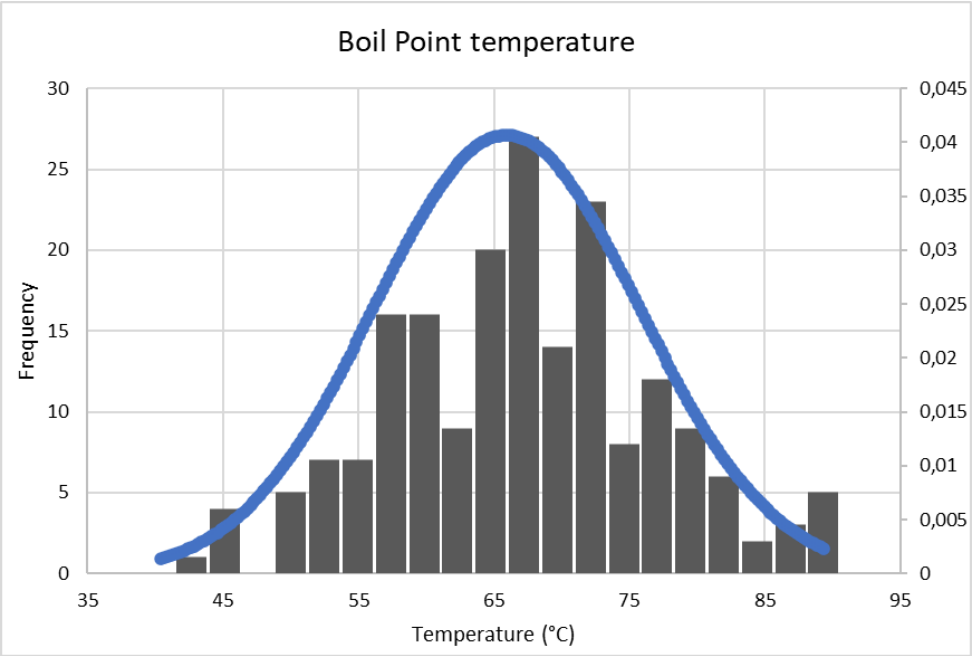
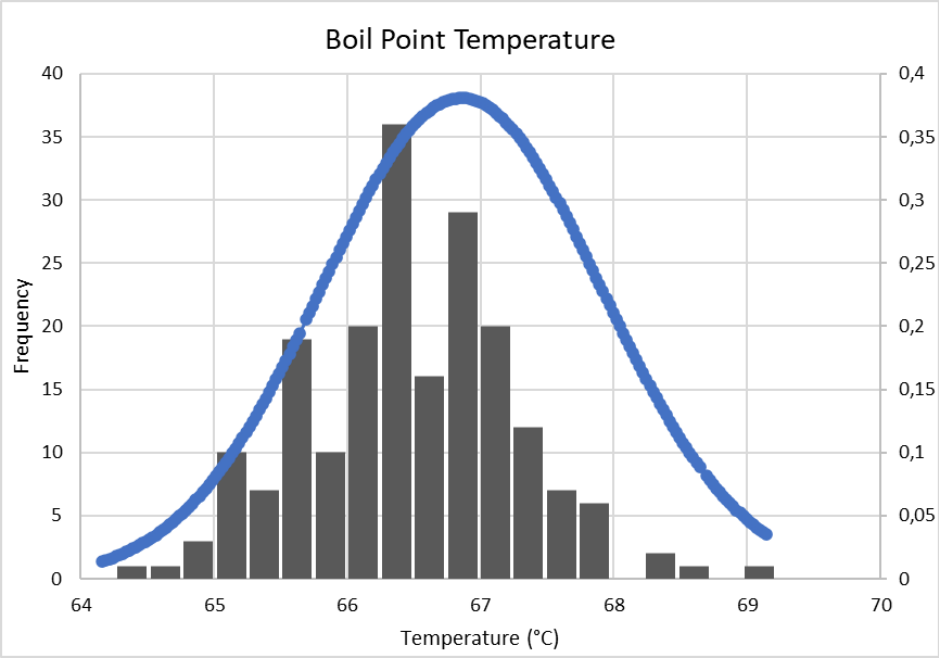


Figure 4. Final Boil Point temperature PDF



4. CONCLUSION

Uncertainties are intrinsic to any process, so the approach to real physical problems must be seen as a range of probable values and not as a punctual result. The Monte Carlo (MC) method is a widely used stochastic method for calculating uncertainties. In this work, the method was applied to a routine problem in the calculation of chemical processes, the calculation of the bubble temperature. And

through this method, it was possible to obtain a range of probable results with less associated uncertainty and new parameters for the Antoine equation for the components under study.

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