

Comparison of the Distillation Curve Obtained Experimentally with the Curve Extrapolated by a Commercial Simulator

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Abstract—True Boiling Point distillation (TBP) is one of the most common experimental techniques for the determination of petroleum properties. This curve provides information about the performance of petroleum in terms of its cuts. The experiment is performed in a few days. Techniques are used to determine the properties faster with a software that calculates the distillation curve when a little information about crude oil is known. In order to evaluate the accuracy of distillation curve prediction, eight points of the TBP curve and specific gravity curve (348 K and 523 K) were inserted into the HYSYS Oil Manager, and the extended curve was evaluated up to 748 K. The methods were able to predict the curve with the accuracy of 0.6%-9.2% error (Software X ASTM), 0.2%-5.1% error (Software X Spaltrohr).

Keywords—Distillation curve, petroleum distillation, simulation, true boiling point curve.

I. INTRODUCTION

THE methods for performing TBP distillation experiments are described by ASTM D2892 and ASTM D5236 [1]-[5]. The standard method defines the TBP curve (temperature versus perceptual accumulated volume) and petroleum fractions with settled boiling ranges which are used for the crude oil test. Its full experience reaches two or more days of operation if uninterrupted. Variables such as operator qualification, the type of sample used, and operating conditions are important in the result [6].

The experimental determination of the whole TBP curves is slow and impractical to use for daily monitoring of crude distillation unit (CDU) operations [7]. It is very important to monitor the characteristics of the crude oil. The combustion process depends on the quality of products produced in the distillation column. The combustion process provides maximum energy; it reduces the amounts of pollutants released by them; it enables the greatest efficiency; it arranges the closest compatibility between the fuel and the system which consumes it, reducing damage to the hardware [8].

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Thus, it is important to develop faster techniques to estimate the TBP curve accurately. In this context, different methods capable of reproducing the TBP curve have been proposed in the last years.

The oldest method to estimate the TBP curve was developed by Riazi and it is used for estimation of the boiling points of C7+ fractions [9]. Another correlation is proposed by Argirov et al. using the viscosity and results in the decrease of the average relative deviation from 5.95% to 3.74% as input parameters [5]. The new techniques for characterization of petroleum are infrared spectroscopy, molecular distillation, and recent methods such as nuclear magnetic resonance or gel permeation chromatography [3], [8]-[10].

The purpose of this work is to evaluate the capabilities of two techniques in order to determine the distillation curve with a few experimental points. In this context, a very important tool is the application of software that helps forecasting the properties of the fractions. The key of a simulation model is to properly describe the phase equilibrium involved and consequently a consistent thermodynamic model based on accurate experimental information [9].

II. METHODOLOGY

The methodology conventional is ASTM D 2892 for the TBP curve. The first method, ASTM D2892, is suitable for the distillation of crude oil components boiling at temperatures lower than 673 K. The second method, ASTM D5236, is performed at reduced pressures (0.1 Pa) to avoid thermal cracking and it permits the distillation of crude components boiling at temperatures higher than 673 K [1]-[5]. According to this standard, a light oil (density 856.0 kg/m³ and density API grade 32) was distilled in a column of trays (feed: 20L) The result is TBP curve with initial boiling temperature of 348 K and final boiling temperature of 623 K.

The main column used in this work is different from the specifications of the standard, but it is a high efficiency column Spaltrohr, model HMS-500, with bottom feed of 0.5 L, condenser, withdrawal by the top, semi-automatic (Fig. 1).

The vacuum system is controlled by a vacuum pump. The heating system consists of two mantles, one in the bottom flask and the other that surrounds the distillation column. The temperatures of the mantle, the temperature of the feed load and the top product, and the pressure of the system are measured. The conditions as pressure and temperature in which 18 cuts were produced are shown in Table I.

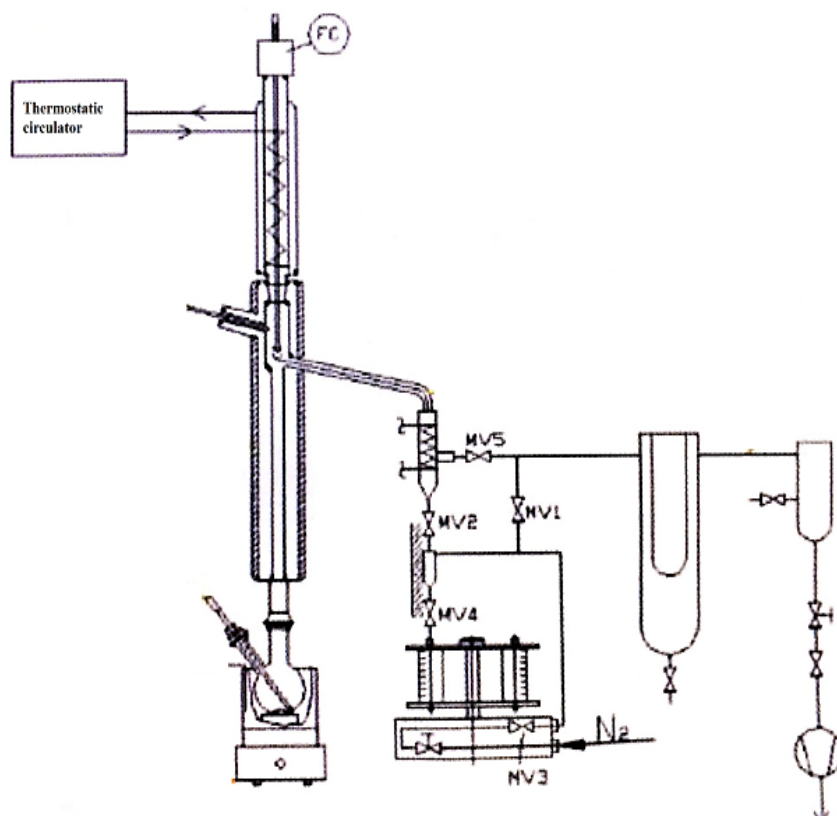


Fig. 1 Schematic of the distillation unit HMS-500

TABLE I
OPERATIONAL PARAMETERS TO DISTILLATION TO OBTAIN THE DISTILLATION CURVE

Cuts	Range temperature (K)	Operation pressure (Pa)
1 to 5	348 to 448	101,325.02
6 to 10	473 to 573	9,999.18
11 to 14	598 to 673	266.64
15 to 18	698 to 823	40.00

The physical properties determined for the oil and all the cuts were mass and density (according to ASTM D 4052 in an Anton Paar densimeter model DMA 4500 M). The volumetric fraction of each cut and the accumulated one are calculated. The obtained results should be compared to the standard methodology, and the cuts are verified by gas chromatography to evaluate the quality of the cuts.

The distillation results on the Spaltr column were inserted into the HYSYS commercial software (version 8.8). The equation of state Peng-Robinson was selected as the thermodynamic model to be applied. The eight first points of the distillation curve (the interval between 348 K and 523 K) and the respective density curve versus accumulated volumetric percentage were inserted in the Oil Manager. For the standard data, the trend analysis with least squares regression was applied, and a new curve is estimated with higher boiling temperatures than the one obtained experimentally.

III. RESULTS

Table II shows the results of the distillation according to standard ASTM D 2892 and ASTM D 5236.

TABLE II
DISTILLATION DATA ACCORDING TO ASTM D 2892 AND ASTM D 5236

Temperature (K)	Percentage accumulated in volume	Specific gravity
348	6.73	0.6624
373	10.28	0.6983
398	14.62	0.7270
423	19.44	0.7514
448	24.50	0.7713
473	29.29	0.7857
498	33.73	0.7979
523	42.21	0.8371
548	46.34	0.8428
573	50.38	0.8517
598	54.47	0.8701
623	58.64	0.8859
648	62.80	0.8959
673	66.82	0.9050
698	70.61	0.9180
723	74.18	0.9266
748	77.55	0.9414
773	80.64	0.9479
798	83.65	0.9550

Table III shows the results of the distillation in the Spaltr column for the average of five distillations of the same oil

under the same conditions and the average of the results obtained in the software for all distillations.

TABLE III
DISTILLATION DATA EXPERIMENTAL AND ESTIMATED

Temperature (K)	Percentage accumulated in average volume (experimental)	Specific gravity average (experimental)	Percentage accumulated in average volume (estimated)
348	6.50	0.6502	6.83
373	10.74	0.6970	10.62
398	15.16	0.7224	15.20
423	20.06	0.7459	19.81
448	25.46	0.7657	25.35
473	29.36	0.7852	29.48
498	34.06	0.7941	34.13
523	38.66	0.8080	38.33
548	43.44	0.8268	43.20
573	48.04	0.8408	47.32
598	51.14	0.8589	51.30
623	56.02	0.8693	55.96
648	60.30	0.8833	59.26
673	64.34	0.8923	63.98
698	65.74	0.8971	67.36
723	68.98	0.9053	71.58
748	72.60	0.9173	76.11

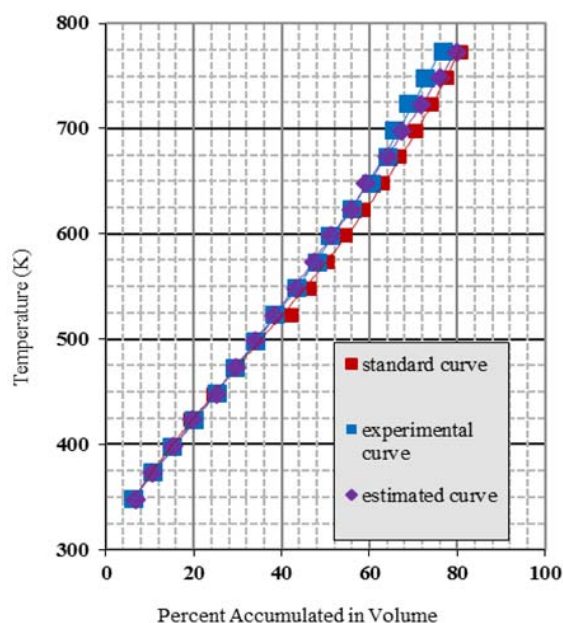


Fig. 2 Distillation curve

Fig. 2 shows the graphical representation of the temperature versus the percentage accumulated in volume of the results referring to the standard curve (red) obtained according to the norms, the experimental blue curve of the distillation carried out in the Spaltrohr column, and the curve calculated in the software (purple).

The curves shown in Fig. 2 were interpolated by a third degree polynomial and the respective models of the standard curves in (1) with the respective determination coefficient:

$$y = 6 \times 10^{-4} x^3 - 5.86 \times 10^{-2} x^2 + 6.7859 x + 307.93 \quad (1)$$

$$R^2 = 0.9993$$

The model of the estimated curve is (2):

$$y = 2 \times 10^{-6} x^3 + 8.2191 \times 10^{-3} x^2 + 5.0512 x + 316.73 \quad (2)$$

$$R^2 = 0.9997$$

The model of the experimental curve is (E):

$$y = 4 \times 10^{-4} x^3 - 0.0296 x^2 + 5.9913 x + 311.14 \quad (3)$$

$$R^2 = 0.9991$$

The models were represented by third-degree polynomials according to the Ockham principle in which any phenomena should assume only the premises strictly necessary to explain the same and eliminate others that would not make any difference in the prediction of the hypothesis. Other important point is the determination coefficient, above 0.9991 and limit of 0.9997, considered satisfactory since $R^2 \rightarrow 1$.

The error and variance of the standard and experimental (see Table IV), standard and estimated (see Table V) and experimental and estimated (see Table VI) results are shown.

The distillation results were compared according to the conditions of ASTM D 2892 and ASTM D 5236, the error is 0.2% and 8.4% in the Spaltrohr distillation column. The advantages of this equipment are the required amount of sample (0.35 L) and the time required (two days) to obtain 18 cuts with temperature range between 348 K and 773 K.

TABLE IV
ERROR AND VARIANCE, EXPERIMENTAL X STANDARD

Temperature (K)	Error (%)	Variance
348	3.4	0.05
373	-4.5	0.21
398	-3.7	0.29
423	-3.2	0.38
448	-3.9	0.92
473	-0.2	0.00
498	-1.0	0.11
523	84	12.57
548	6.3	8.41
573	4.7	5.50
598	6.1	11.10
623	4.5	6.88
648	4.0	6.25
673	3.7	6.14
698	6.9	23.74
723	7.0	26.99
748	6.4	24.46

The distillation results on the Spaltrohr column were inserted into HYSYS in the Oil Manager. We tested how many points of the distillation curve and density curve need to be provided to obtain the extrapolation of the curve, as well as the most appropriate method, among least squares, probability and exponential options. The most suitable method of calculation was the least squares as a function of the final

temperature of the estimated boiling point, above 900 K. The number of points inserted was decisive because the deviation of the last points of the estimated curve is smaller. It was found that eight points (348 K, 373 K, 398 K, 423 K, 448 K, 473 K, and 498 K) were sufficient to estimate the error curve between 0.2% and 5.1% as shown in Table IV.

TABLE V
ERROR AND VARIANCE, ESTIMATED X STANDARD

Temperature (K)	Error (%)	Variance
348	-1.5	0.01
373	-3.3	0.11
398	-4.0	0.33
423	-1.9	0.14
448	-3.5	0.73
473	-0.6	0.04
498	-1.2	0.16
523	9.2	15.02
548	6.8	9.86
573	6.1	9.38
598	5.8	10.08
623	4.6	7.18
648	5.6	12.52
673	4.3	8.07
698	4.6	10.57
723	3.5	6.72
748	1.8	2.06

TABLE VI
ERROR AND VARIANCE, ESTIMATED X EXPERIMENTAL

Temperature (K)	Error (%)	Variance
348	-5.1	0.11
373	1.2	0.02
398	-0.3	0.00
423	1.3	0.06
448	0.4	0.01
473	-0.4	0.02
498	-0.2	0.01
523	0.9	0.11
548	0.6	0.06
573	1.5	0.52
598	-0.3	0.02
623	0.1	0.00
648	1.7	1.08
673	0.6	0.13
698	-2.5	2.63
723	-3.8	6.77
748	-4.8	12.33

To estimate distillation curve, empirical correlations are also applied to calculate physical properties such as density, viscosity, molar mass, and others. Thus, the estimated distillation curve has smaller errors when compared to experimental distillation curve, especially at the end of the curve because, for higher temperatures, there may be cracking of the oil.

According to Fig. 3, it is found that cuts at temperatures below 500 K have a positive deviation of up to 10%, after 500 K the results have a negative deviation of up to 10%, and after

700 K the experimental deviation is higher than the estimated. When comparing the distillation curves obtained in the Spaltrohr column and the estimated curve in HYSYS, as shown in Fig. 3 and Table IV, the software's potential to estimate the TBP curve is verified. This allows predicting the results and verifying the experimental conditions in order to obtain correct cuts in the specified range.

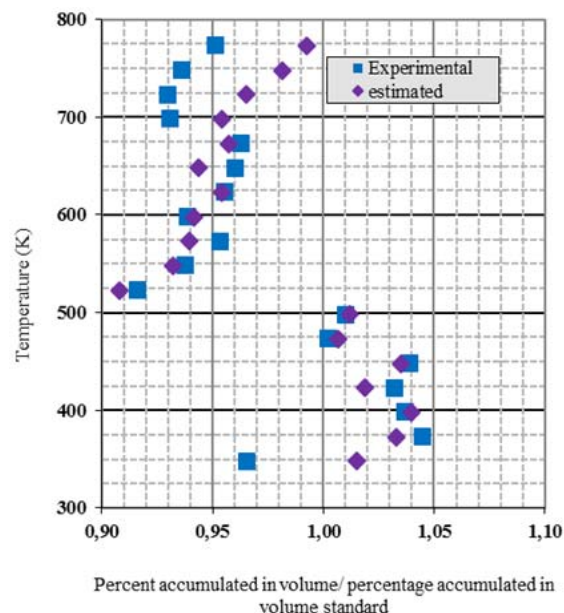


Fig. 3 The distribution of the % Accumulated in volume / % accumulated in volume standard versus temperature

IV. CONCLUSION

The TBP curve is very important to characterize the petroleum. However, this method is performed in two or more days. If the initial points of the TBP curve are known, it can be extrapolated with mathematical methods and empirical correlation. The software Aspen HYSYS has the module Oil Manager in which the curve can be extrapolated. The TBP curve of a light petroleum can be extrapolated from eight points. The mathematical method of extrapolation by least squares is appropriate because the adjustment is more accurate. The error was 0.2% and 5.1%.

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REFERENCES

- [1] American Society of Testing and Materials, 1999b. ASTM D 5236: Distillation of Heavy Hydrocarbon Mixtures (Vacuum Potstill Method). (Annual Handbook of ASTM Standards, 2002).
- [2] American Society of Testing and Materials. ASTM D 4052: Standard Test Method for Density, Relative Density, and API Gravity of Liquids by Digital Density Meter. (Annual Handbook of ASTM Standards, 2015).
- [3] M.S. Lopes, R. Maciel Filho, M.R. Maciel, L.C. Medina: Extension of the TBP curve of petroleum using the correlation DESTMOL. *Procedia Engineering*, Vol. 42 (2012), p. 726.

- [4] M.L.S.P. Marques: Microdestilação Caracterização de petróleo– alternativa para avaliação de petróleos. Rio de Janeiro, Federal University of Rio de Janeiro, BR, (2011).
- [5] G. Argirov, S. Ivanov, G. Cholakov: Estimation of crude oil TBP from crude viscosity. *Fuel*, Vol. 97 (2012), p. 358.
- [6] M. Khanmohammadi, A.B. Garmarudi, M. de La Guardia: Characterization of petroleum based products by infrared spectroscopy and chemometrics. *Trends in Analytical Chemistry*, Vol. 35, (2012).
- [7] J.J. Espada, S. Fernández, L. Velasco, B. Coto: Evaluation of different methodologies to determine the n-paraffin distribution of petroleum fractions. *Fuel*, Vol. 109 (2013), p. 470.
- [8] J.M.V. Patrinos, R.V. Román, E.M. Corona, J.A.I. Méndez, E. Q. Pérez: Computer aided molecular design for undefined petroleum fractions. *Fluid Phase Equilibria*, Vol.: 390 (2015), p. 14.
- [9] L.Z. Liñan, N.M.N. Lima, M.R.W. Maciel, R. Maciel Filho, L.C. Medina, M. Embiruçu: Correlation for predicting the molecular weight of Brazilian petroleum residues and cuts: An application for the simulation of a molecular distillation process. *Journal of Petroleum Science and Engineering*, Vol. 78 (2011), p. 78.
- [10] American Society of Testing and Materials, ASTM D 2892: Distillation of Crude Petroleum (15-Theoretical Plate Column). (Annual Handbook of ASTM Standards, 2015).

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