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Research Paper

Comparison of The Experimental TBP Curve with Results of Empirical Correlations And Commercial Simulators

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ABSTRACT : *The evaluation of oil is fundamental to understand the physical chemical behavior of the fractions and the valorization of the oils. Among the methods used for it, the yield information in certain temperature ranges is obtained from the true boiling point (TBP), performed on bench scale according to ASTM D 2892. In this article, the experimental data from the TBP of Light oils are compared to the curve estimated from empirical correlations and to commercial simulator. The correlation used has the temperature range and density related constants as input variables, and presented a greater deviation compared to the experimental TBP curve. The data of the experimental TBP curve, and oil properties such as viscosity at different temperatures and density were inputs for the HYSYS simulation, with the result showed a smaller deviation from the experimental one. The comparison of the experimental and alternative methodologies show the importance of the development of faster and less deviation techniques to determine the TPB curve and for the evaluation of the oils.*

Keywords: *Crude Oil, Distillation, Properties petroleum, Simulation, True boiling Point Curve.*

I. INTRODUCTION

Oil is commonly referred to as crude oil, and consists of a mixture of hydrocarbons and other constituents such as sulfur, nitrogen and oxygen compounds, with physical properties such as viscosity, density and volatility varying widely depending on the proportions of the blend. [1] The price of a barrel of oil is highly dependent on its quality, evaluated by density, API grade or sulfur content. [2] Data from the US Energy Information Administration (EIA) present the price estimates between August and December 2016, for a petroleum with a content of sulfur compounds smaller than 15 ppm and another with a content higher than 500 ppm, the price difference is approximately 27% higher for the first. The average accepted content of sulfur compounds for light oils with API grade from 31 to 32 is 1,45 ppm. The main consequences in the process arising from the cited variations are such as the impact in the yield of each fraction produced in the separation processes [1]. This consequence has an impact not only on the price of the barrel, during the exploration stage, but also on the operating conditions of the refinery units. For this reason to characterize oil effectively is a primordial stage. The quality and value of a crude depends significantly on its true boiling curve (TBP), which correlates the boiling point versus the percentage of volume or distilled mass. [3] According to Fahim et al. (2012), the TBP curve is obtained by batch in an atmospheric distillation according to ASTM D 2892. This analysis allows collecting the sample at different boiling point intervals, which cuts can be submitted to various complementary physical and chemical analysis for the crude oil evaluation [3]. For the construction of the TBP curve with a boiling point higher than 400 °C, it is necessary to distillate the residue generated from the previous method at lower pressures in accordance with ASTM D 5832.

These physical methods require more than one liter of sample, reaching up to 70 L depending on the objective of the analysis, and its complete experimental procedure lasts two or more days of uninterrupted operation while is subject to variables such as the operator training, the type of sample used and operating conditions.[4] After determining the percent yields of the oil as a function of the boiling point, a mathematical treatment is required to generate a TBP curve. The experimental determination of TBP curves is expensive and time-consuming, so it is currently impractical to use them as a tool for the daily monitoring of distillation units. [2] This requires the development of calculation methods, requiring a minimum of experimental data, but with sufficient precision for the daily monitoring of operations. It is very important for the oil industry to develop faster, more efficient and more accurate methods for determining the TBP curve. The objective of this work is to compare the results obtained by an experimental methodology, the use of commercial software and the application of empirical correlations

II. METHODS

2.1experimental method

Standard ASTM D-2892 standardizes the method of obtaining the true boiling curve using a distillation column at atmospheric pressure. The defined experimental conditions are boiling final temperature of 400ºC, reflux ratio (L/D) of 2:1, developed in a column with 15 to 18 theoretical plates, maintained the operating pressure of 0,674 kPa to 0,27 kPa, with volume of 1 L to 30 L and operating in batch. The feed is supplied in the bottom balloon, which shall be maintained under magnetic stirring and minimum heating power of 0,12 W/mL. The outer surface of the column shall contain an insulation blanket, in order to minimize heat losses to the environment. The condenser located at the top shall be capable to condense the C_4 fractions and for this purpose the temperature of the cooling fluid should be -20ºC. The method used in this work to obtain the experimental TBP curve was performed under conditions established in ASTM D 2892 .The properties of lightweight distillate Arab oil are: API grade density, density ($d^{20}{}_4$) and dynamic viscosity (μ). Data are presented in the Table 1.

Table 1 – Crude oil proprieties

°API	32
d_4^{20}	0,8611
$\mu\ (cP)$ at $20\,^{o}C$	5,191
$\mu\ (cP)$ at $60\,^{o}C$	3,273

The fractions collected at the top of the distillation column were separated and their variables of interest are determined, which are the initial and final boiling temperatures of each fraction, the volumetric and mass accumulated percentage of each fraction and a density at 20ºC.

2.2. Empirical Correlations

The first work to develop empirical correlations to obtain the TBP curve started in 1920 and used ASTM curves ASTM D 86, simulated distillation curve (ASTM D 2887) and flash vaporization as the input variable. However, no correlation was proposed to estimate the entire range of petroleum distillation, particularly heavy compounds. proposed a correlation based on the probability distribution model for the heptane and heavier fraction fractions in crude oil and reservoir fluids. [4] The correlation proposed by [4] is presented in equation (1):

$$\frac{T-T_o}{T_o}=\left[\frac{A}{B}\ln\left(\frac{1}{1-x}\right)\right]^{1/B} \quad (1)$$

In the equation (1), there is no end point of distillation, even where 100% of the fraction is vaporized, ie $(x=1)$, which means that the final boiling point is infinite. Theoretically, every light product has a limited final boiling temperature, in which a small amount of fraction is obtained. A, B, and T_o are parameters determined by regression of available distillation data.

From equation (1), developed an empirical correlation to estimate the TBP curve from the viscosity. For this, they use the correlation proposed by[4], in which the regression analysis and B value of the light fractions is higher than that those for the heavier fractions and is usually greater than 1.5. It was considered B=1,5, and used temperature normalization as a variable U, as well as used a continuous complex mixture to represent the other parameters. [2] Thus, we obtained the correlation proposed in equation (2):

$$x_D[A,B,D]=\frac{B^2 e^{-\frac{BU^B}{A}U^{-1}+B}}{A} \quad (2)$$

Equation (2) was evaluated for 224 petroleum samples with density d_4^{15} between 0,7883 and 0,9024,, divided into four groups I $(0,7883 - 0,8886)$, II $(0,8095 - 0,8970)$, III $(0,8685 - 0,9047)$ and IV $(0,8581 - 0,9024)$.. For group I, in which the oil in question is found, the determined constants were: $A = 14,8859$ and $B = 0,908937$.

2.3. simulators

Hysys (version 8.2), developed by Honeywell, is the process simulation program used in this work. It is a simulator of the sequential-modular type, which means that the program calculates the unit operations individually, feeding the next unit operations with the data of the process streams, in an established sequence. Experimental data and oil properties were included in Hysys, in Oil Manager setup, referring to the data presented in Table 1 and the experimental TBP curve (Temperature versus accumulated mass%). With this information, the program uses empirical correlations and extrapolation methods to estimate a new TBP curve with boiling point ranges covering the entire range of petroleum distillation (atmospheric and vacuum). For the calculation of the simulated curve, the program uses the extrapolation method. For the curve extension up to 100% of vaporized mass, there are three options of calculations: least squares, Lagrange or exponential. For the article it was used the exponential method.

III. Results

In the experimental methodology, the determined variables are initial and final boiling temperature of each fraction, the accumulated mass and volumetric percentage and the density $\left(d_4^{20}\right)$ at 20ºC. This information is tabulated according to the initial temperature of the fraction and is shown in Table 2.

Table 2 - Distillation data to determine the TBP of Light Arab oil.

Temperature $(°C)$	% accumulated ma	% accumulated volume	d_4^{20}
15	1,1	1,6	-
61	3,9	5,2	-
87	6,1	8,1	0,6807
110	9,1	11,6	0,7138
127	11,4	14,4	0,7288
159	16,9	20,7	0,7571
191	22,4	26,8	0,7806
208	25,2	30,0	0,7895
226	28,5	33,5	0,7956
252	33,2	38,5	0,8106
291	40,4	46,0	0,8370
311	44,3	49,9	0,8505
330	47,8	53,4	0,8647
363	53,0	58,4	0,8844
384	56,2	61,5	0,8933
421	61,8	66,8	0,9127

The empirical correlation shown in equation (1) was used with the constants determined by [2], $A = 14,8859$ and $B = 0,908937$. However, it was not possible to calculate the cumulative mass % for the beginning of the TBP curve. Considering these values in equation (1), the calculated TBP curve is presented in Table 3. The results obtained in the Hysys, inserted the data of Tables 1 and 2 are presented in Table 3.

Table 3 - TBP curve calculated by empirical correlation and in Hysys.

Temperature $(°C)$	% accumated mass (correlation)	% accumated mass (Hysys)
-171,1	-	0,0
4,3	-	1,0
29,4	-	2,0
54,0	3,5	3,5
73,8	7,0	5,0
97,2	10,5	7,5
115,8	14,0	10,0
132,7	17,4	12,5
146,8	20,9	15,0
161,2	24,3	17,5

175,6	27,8	20,0
204,8	31,2	25,0
232,1	34,7	30,0
259,1	38,1	35,0
286,2	41,6	40,0
311,7	45,0	45,0
339,9	48,5	50,0
371,5	51,9	55,0
404,1	55,3	60,0
436,8	58,8	65,0
470,4	62,2	70,0
506,5	65,7	75,0
546,3	69,1	80,0
592,2	72,5	85,0
648,5	76,0	90,0
683,8	79,4	92,5
727,2	82,8	95,0
760,7	86,3	96,5
803,0	89,7	98,0
842,1	93,1	99,0
896,4	96,6	100,0

The results of Tables 2 and 3 are presented in Figure 1 which shows the boiling point versus percentage of mass accumulated.

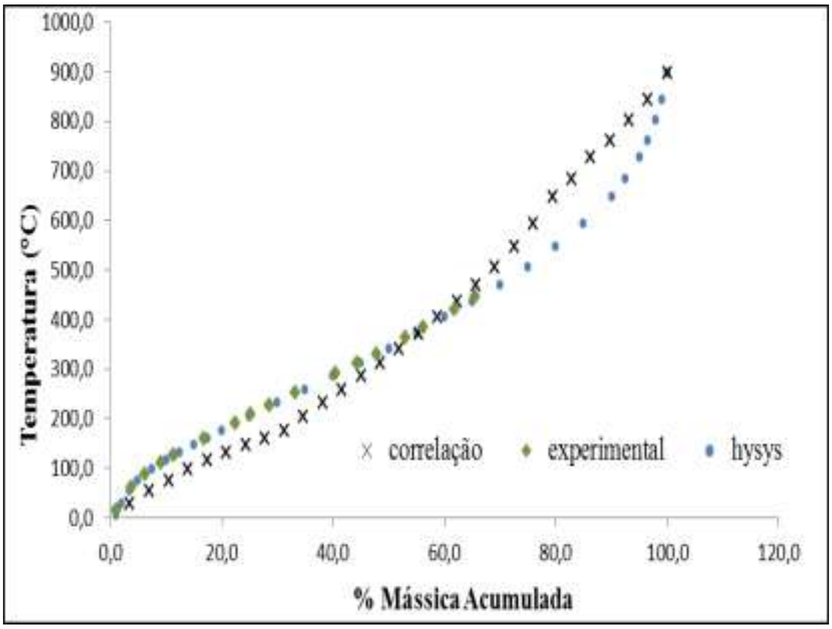

Figure 1 - Graph of the experimental TBP curves, calculated by empirical correlation and in Hysys.

Alternative to experimental methodologies make it possible to estimate the extent of the TBP curve above 400 ° C, exceeding the information by ASTM D 2892. To obtain these data experimentally, ASTM recommends distillations at atmospheric pressures (ASTM D 5236) or the use of simulated distillation (ASTM D 2887). As can be seen in Figure 1, the estimation of the extent of the curve presents relevant discrepancy. Data from the literature, such as that of [8], show that the profile of the light petroleum distillation curve is not approximated by a straight line, as proposed in the TBP curve estimated by empirical correlations,

By evaluating only the data that comprise the experimental distillation range, it is concluded that the HYSYS estimate has a smaller deviation when compared to the experimental result. This result is expected since the input parameters in the software include the data of the TBP curve, and the software uses the extrapolation of the data as a tool. The estimation of the TBP, corresponding to atmospheric pressure, by empirical correlations has approximation considered only in a narrow temperature range between 350 ºC and 450 ºC, interval corresponding to fraction C_7.

IV. Conclusion

The true boiling curve defines the oil characteristic to be processed in a refinery, from the definition of the temperatures at which the yield of each fraction is obtained and allows meeting the desired profile of the production of the products, considering the demand and quality of the oil derivatives. Given the relevance of this information, the delay and complexity of experimentally obtaining these results for oil evaluation and monitoring of a distillation unit, emphasizes the importance of developing faster and more efficient experimental methodologies. As well as, the improvement of methodologies that allow an estimation of the TBP curve with less deviation from the experimental one.

It is recommended to extend the comparisons made in this work to other oils with a wide range of API grade density, to identify which are best represented by already proposed methods and in which temperature range greater deviations are obtained in order to evaluate which alternative method (Simulator or correlation) is more appropriate and propose adjustments, if necessary. For future work, in addition to evaluating other oils with different characteristics, it is also important to compare with other proposed correlations for curve interconversion, such as the ASTM D 2887 or ASTM D 86 curves.

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