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Characterizing a Brazilian Petroleum Residue by Molecular Distillation Process

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Abstract

The increasing evolution of the quality of petroleum derivatives and the increase of heavy petroleum leads to the need of a better characterization and utilization of this oil. The properties of natural petroleum and petroleum products make use of the True Boiling Point (TBP) distillation analyses and this is very useful for petroleum characterization, for design and operation of refinery units, for the classification of petroleum, for the development of petroleum property correlations and it has been used worldwide. Two conventional methods specified by the American Society for Testing and Material (ASTM) are necessary for determination of the boiling point of crude oil distribution. The first method, ASTM D2892, is satisfactory for the distillation below 400ºC. The second method, ASTM D5236, is used at reduced pressures (50-0,1 mmHg). The maximum atmospheric equivalent temperature reached with ASTM D5236 method, can be 565ºC. In this work, the TBP curve was extended above 700ºC. The molecular distillation process is a potential technique for fractionating products of high molecular weight and it was used in this work for extending the TBP curve.

Keywords: petroleum, True Boiling Point curve, molecular distillation

1. Introduction

Since the petroleum source is progressively decreasing, the demand for upgrading heavy fractions is increasing and so, this is an important matter of study. Brazilian petroleum is becoming heavier, making the refining process each time more difficult and expensive. On the other hand, the demand for lighter products is increasing. To achieve this demand, the refineries tend to convert part of their residues in light fractions.

Oils are evaluated in function of the distillation curve TBP (True Boiling Point), which is one of the most important reference properties of petroleum. From the oil distillation curve, generated in function of the temperature, it is possible to calculate the products that can be obtained in the refinery, supplying, so, important information on the operating aspect of the oil before be processed.

Two conventional methods specified by the American Society for Testing and Material (ASTM) can reach temperatures up to 565ºC and, so, when applied to heavy petroleum fractions, difficulties are often encountered. For higher temperatures, a well established method does not exist, although this is a very important achievement, in order to improve the crude oil processing.

The molecular distillation or short path distillation is a separation process usually used in processes that demand high purity and quality. This technique does not use solvents and operates at very low pressures so that it allows to use low temperatures preventing thermal degradation of the material, being suitable to purify thermal sensitive products. Nowadays, this process favors the separation, concentration and purification mainly of natural products and products with high molecular weight (Erciyes et al., 1987).

Molecular distillation involves, basically, two stages: evaporation and condensation, in which vapor molecules escape from the evaporator in direction to the condenser, where condensation occurs. Then, it is necessary that the vapor molecules generated find a free path between the evaporator and the condenser. This is possible because the low operating pressure and the small distance between the condenser and the evaporator which is of the order of the mean free path of evaporating molecules (Batistella and Maciel, 1998, Batistella et al., 2000, Moraes et al., 2004). The operating pressures are in the order of 0.0001 to 0.001 mmHg.

In this process, the evaporation rate is governed only by the evaporated molecules that escape from the surface of the liquid and reaches the condenser easily. Since, practically, there is no return of the evaporated molecules to the liquid phase, vapor liquid equilibrium is not established, so, the molecular distillation is a non equilibrium process (Hickman, 1943, Perry and Chilton, 1980).

In this work, it was developed a methodology for generating, from molecular distillation process, the liquid volume percentage in relation to temperature, to build up the distillation curve, using one of the streams (distilled) of the process. In Batistella (1999), Burrows (1960) and Boduszynski and Altgelt (1994), it can be verified the robustness of this method since it enables operation at low temperatures, short residence times, being ideal for working with high molecular weight and thermally sensitive compounds (Batistella and Maciel, 1998). In the petroleum case, it avoids thermal cracking, allowing, thus, the development of a methodology for determination of the real TBP curve. It is necessary, however, establish a relationship between the operating conditions of the molecular distiller and the TBP curve.

In Batistella et al. (2005), data of temperature and percentage of distilled from molecular distiller, obtained experimentally, were used in the TBP curve extension, and a new correlation (FRAMOL correlation) was presented (Equation 1).

$$TBP = 456.4 + 0.1677 \times T_{DM} + 1.64.10^{-4} \times T_{DM}{}^{2} + 4.13.10^{-6} \times T_{DM}{}^{3} \quad (1)$$

where: TBP = True Boiling Point (°C);

T_{DM} = Operating temperature of the Molecular Distiller (°C).

This correlation allows conversion of the operating temperature of molecular distiller to equivalent atmospheric temperatures, which are, indeed, used in the conventional TBP curves. According to the authors, the extension of TBP curve, from FRAMOL correlation, reached values next to 700°C, with continuity with the curve obtained from ASTM points.

Several heavy petroleum fractions were used in order to get enough information to be able to obtain the correlation with wider applicability and precision. It is important that the correlation has continuity in relation to the TBP curve obtained from ASTM. This equation was developed from 05 different types of petroleum. Then, this correlation allows to determine the AET (atmospheric equivalent temperature) of any petroleum in the range of 540°C up to next to 700°C.

In Batistella et al. (2005), it is presented the same procedure for extending the TBP curve, however, in that case, the petroleum studied was Gamma (fantasy name) and in this paper the heavy petroleum is Beta 540ºC+ (fantasy name). The new generalized correlation named FRAMOL was used for extending the TBP curve.

2. Materials and Methods

The falling film molecular distiller (UIC-Gmbh KDL 5 unit) was used (Figure 1). The basic design of the falling film molecular distiller unit is the Short Path Distillation unit: a vertical, double jacketed cylinder (evaporator) with a cooled and centered internal condenser and a rotating roller wiper basket with an external drive, shown in Figure 1. It, also, has a feed device with gear pump, rotating carousels that hold discharge sample collectors for distilled and residue streams (each carousel consists of 06 collectors which can be positioned and moved by the operator without interrupting the distillation process), a set of vacuum pumps with an in-line low temperature cold trap and 04 heating units.

Figure 1: Molecular distillation apparatus (UIC-Gmbh KDL 5 unit)

The distiller feed is the residue Beta 540ºC+. The samples were obtained from the Brazilian Petroleum Company (PETROBRAS).

The experimental molecular distillation was conducted at constant pressure (10^{-3} mbar) and the variables were carefully monitored by the controllers present in the unit (UIC-GmbH KDL 5 unit). Each experiment produced one distilled and one residue cut. It is important to emphasize that it is used a much lower temperature in the molecular distiller than in the conventional distillation to promote the separation of the molecules in both cuts, i.e., both product streams (Maciel et al., 2006).

The evaporator temperature ranges 230-340ºC and the feed flow rate ranges 350-650mL/h. At 230ºC, the petroleum Beta 540ºC+ starts to form two streams: distilled and residue. At lower temperatures, the distilled stream is not formed. The highest temperature (340ºC) is the equipment limitation.

3. Results and Discussion

The converted values of molecular distillation temperatures to atmospheric equivalent temperature (AET) are obtained through ASTM D1160 correlation and through FRAMOL correlation. The ASTM D1160 correlation is shown in Maciel et al. (2006), and it is going to be used here just to evaluate its potentiality in extending the

TBP curve, since it was not developed to be used in this range. The experimental data obtained for petroleum Beta (460ºC+) through molecular distillation and the converted evaporator temperature values using both correlation are shown in Table 1.

Table 1: Experimental data for petroleum Beta 540ºC+

Feed Flow Rate (mL/h)	Evaporator Temperature (ºC)	AET (ºC) (ASTM D1160)	AET (ºC) (FRAMOL Correlation)	% mass of Distilled	% mass of Residue
500	230	584	554	1.29	98.71
394	246	605	569	3.15	96.85
606	246	605	569	3.06	96.94
500	285	653	613	14.00	86.00
350	285	653	613	19.03	80.97
500	285	653	613	15.17	84.83
650	285	653	613	12.60	87.40
500	285	653	613	16.31	83.69
394	324	700	668	29.51	70.49
606	324	700	668	28.50	71.50
500	340	718	695	32.35	67.65

In Table 1, it can be seen that increasing the evaporator temperature the distillate percentage increases, independent of the feed flow rate. The highest distillate percentage(32.35%) occurs at the highest evaporator temperature (340ºC).

Moreover, it can be seen that AET values using both correlations present some differences. Since ASTM D1160 is not correlated from molecular distillation data, this is expected. We just have used this correlation to carry out some comparison. Indeed, the right procedure is to use FRAMOL correlation.

The distillation curve was determined from the evaporator temperature and the percentage of distillate obtained experimentally (Table 1). This is a new procedure to build-up this curve. The relationship between the operating conditions from molecular distillation and the data obtained from the atmospheric column (given by CENPES/PETROBRAS) generates the extension of the TBP curve, which was analyzed in this work.

The extension of distillation curve was determined from experimental results of evaporator temperature and percentage of distillate (Table 1). This is a new procedure to extend this curve. The relationship between the operating conditions from molecular distillation and the data obtained from CENPES/PETROBRAS generates the extension of the TBP curve, which was analyzed in this work.

Figures 2 and 3 shows the extension of the TBP curve of petroleum Beta 540ºC+ through the molecular distillation methodology using ASTM D1160 and FRAMOL correlation respectively.

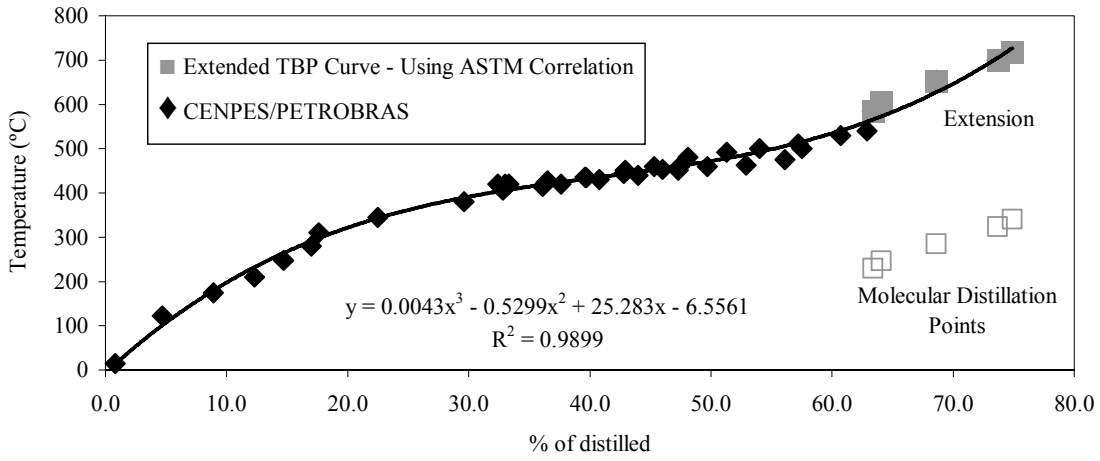

Figure 2: Extension of the true boiling point curve for petroleum Beta 540ºC+ through molecular distillation considering ASTM D1160 correlation.

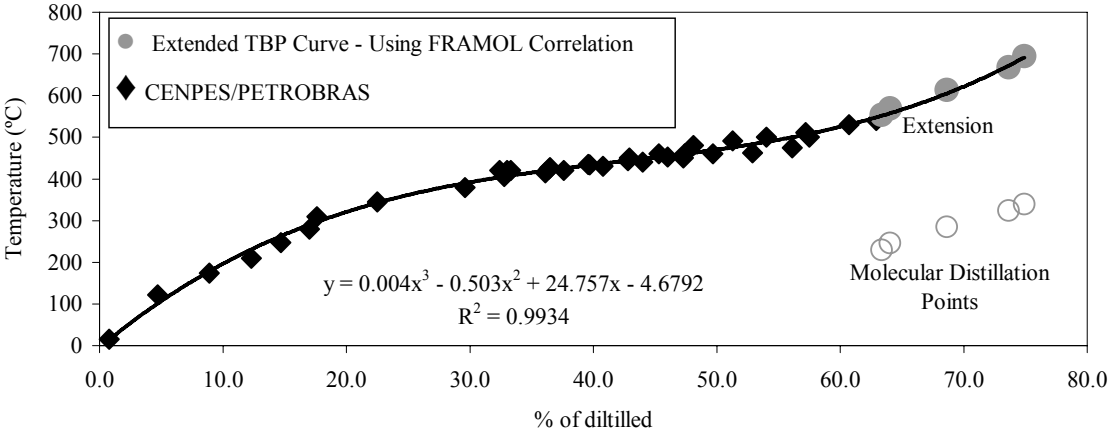

Figure 3: Extension of the true boiling point curve for Beta 540ºC+ petroleum through molecular distillation considering FRAMOL correlation.

In Figure 2 the extended TBP curve is in good agreement with the existing one, even using the ASTM D1160 correlation, which is not the most appropriated to be used, because this correlation was developed to conventional vacuum distillation. In Figure

3 the TBP curve was extended using FRAMOL correlation, that was develop for molecular distillation process. The extension of the curve reached approximately 700ºC+ and present continuity and good agreement with the ASTM curve. The extended curve coincides with the conventional ASTM. This is an important issue for petroleum upgrade process development, since there is no discontinuity for the whole range.

The accumulated percentage of distilled for residue Beta 540ºC+ arrived values next to 76%. The increase in distilled percentage is approximately 19%. This result is of great interest because a large quantity of distilled can be recovered without thermal material degradation, that preserves the physical properties of the compounds for using high vacuum (10-3 mmHg) and low temperature and operational time.

Figure 4 shows the TBP curves and its extensions obtained with the FRAMOL and ASTM correlations for 100% of distillate.

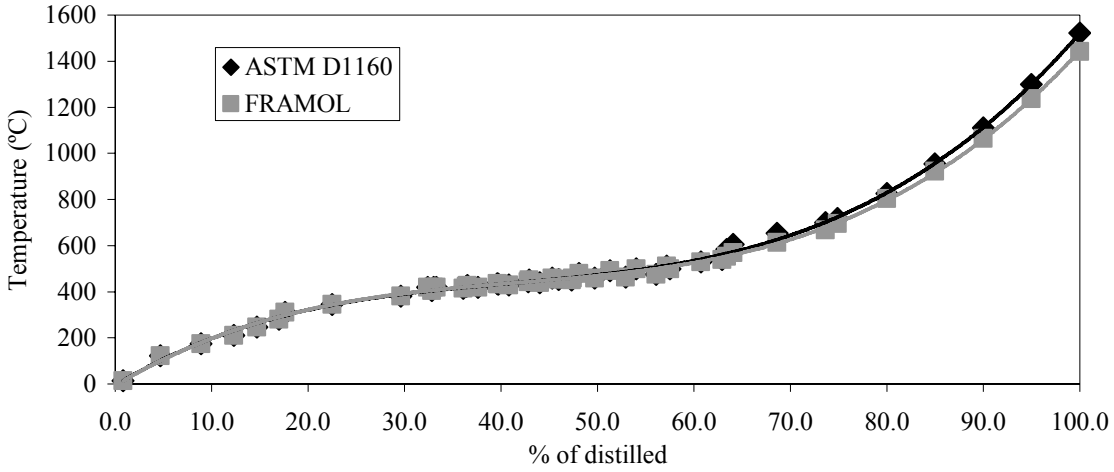

Figure 4: True Boiling Point Curves from ASTM and FRAMOL correlations and extensions to 100% of distillate for Beta 540ºC+ petroleum.

In Figure 4 it is possible to verify that the tendency of the FRAMOL and ASTM curves is to have an asymptotic, as it was expected. In Batistella et al 2005, it was possible to realize that, for Alfa petroleum, ASTM D1160 correlation can not be used in the extension until values next to 100% of distilled. Furthermore, the curves also do not present continuity to the results found with FRAMOL correlation, inclusive turning downwards, indicating a reduction of the distilled percentage when approaching to 100% of distilled, what it is not acceptable. For that, the FRAMOL correlation is the appropriated to be used for heavy petroleum residues. For petroleum Beta 540ºC+, the conventional correlation worked well.

4. Conclusions

For petroleum Beta 540ºC+ the FRAMOL correlation shows an extension with continuity and asymptotic, included for an extension until values next a 100% of distilled, showing that the molecular distillation process is a good alternative for extend the TBP curve.

Molecular Distillation process made possible the extension of TBP curve with very good precision using the FRAMOL correlation and this is very important to define better strategies and operating conditions for heavy petroleum processing, leading to upgrade these fractions.

Yet, the TBP curves was extended until values next to 700°C, increasing considerably the characterization of heavy petroleums, what it can contribute in the definition of better routes of processing increasing the commercial value of petroleum residues.

The developments achieved in this work are very important since no standard methodology is available for calculating the TBP extended curve, considering the large amount of heavy petroleum today encountered.

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