A True Boiling Point Curve Through Molecular Distillation Using FRAMOL Correlation

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Petroleum is evaluated mainly in terms of its True Boiling Point (TBP) curve, what makes possible to investigate the yields of the products that will be obtained in the refineries, as well as to establish operational strategies and process optimization. However, for heavy petroleum fractions, some difficulties appear for determination of TBP of these petroleum fractions.
The determination of TBP is well established for petroleum fractions that reach the TBP up to 565°C through ASTM. For higher temperatures, there is not yet available a standard methodology. In this way, data were obtained and a methodology was established for the determination of the true boiling point curve for heavy petroleum fractions above 565°C, where it was possible to reach values up to 700°C, representing a considerable progress in the analyses of these fractions. Through falling film molecular distillation apparatus, experiments were carried out using heavy fractions of petroleum, where operating temperatures were increased systematically. Molecular Distillation is a separation process that does not require the use of solvents and operates at low pressures (high vacuum), it allows using low temperatures, short exposure of the material at the operating temperature and a small distance between the evaporator and the condenser. The FRAMOL correlation, developed previously by this research group, was used and it has shown to be applied for the new petroleum studied here proving its robustness.

1. Introduction

Since the petroleum production is progressively decreasing, the demand for upgraded heavy fractions is increasing and so, this is an important matter of study.
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. However, when applied to heavy petroleum fractions, difficulties are often encountered. Usually, the evaluation of the TBP curve of heavy petroleum fractions has been

carried out through ASTM D2892 and D5236 methods, but values are limited to temperatures below 565°C. 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 process (Wolf Maciel and Maciel Filho, 2001, 2004) introduces a potential technique for attainment of liquid volume percentage in relation to temperature for the distilled fractions. In Batistella (1999), 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, avoids thermal cracking, allowing, thus, the development of a methodology for determination the real TBP curve. The molecular distillation technique has being reported. It is necessary, however, establish a relationship between the operating conditions of the molecular distiller and the TBP curve (Burrows, 1960 and Boduszynski and Altgelt, 1994).

In Batistella et al. (2005), data of temperature and percentage of distillate from molecular distiller, obtained experimentally, were used in the TBP curve extension, and a new 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).

The FRAMOL correlation, as it was called, allows conversion of the operating temperature of molecular distiller in equivalent atmospheric temperatures, that are 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 and substantial coincidence with the curve obtained from ASTM points.

Several heavy petroleum fractions were used in order to get enough information to be able to obtain an expression 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 of any petroleum in the range of 540°C up to next to 700°C. This equation will be used for calculating the TBP curve of petroleum Beta (fantasy name).

2. Materials And Methods

The falling film molecular distiller (UIC-Gmbh KDL 5 unit) was used. 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 distillate and residue (each carousel consists of 6 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 4 heating units.

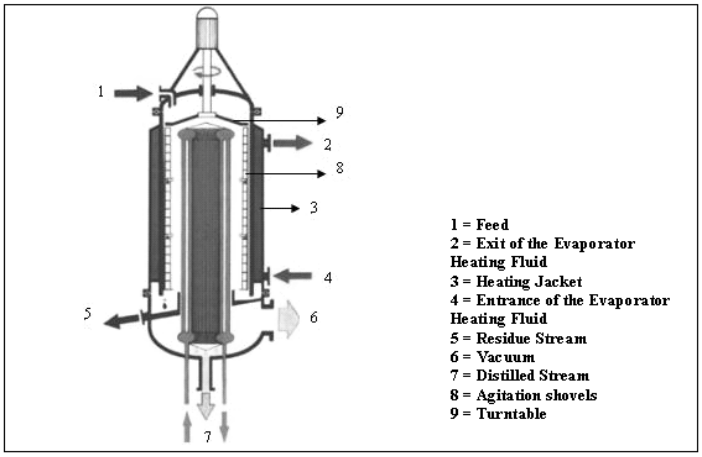

Figure 1: Internal Vision of Filling Film Molecular Distiller

A constantly rotating gear pump feeds the sample on a rotating distribution plate from a heated feed container. The centrifugal force distributes the material on the inner surface of the evaporator and the gravity makes it to flow downstream; the roller wiper system constantly redistributes it as a very thin film on the evaporator internal surface. The volatile components of the feed material vaporize from this thin film and condense on the cooled inner condenser. The most volatile of these vapors condenses on the cold trap and it is collected. Distillate and residue are each one collected in reservoir cylinders assembled in the two carousels.

It is important to know some technical information about the unit: the size is approximately 2×2×1 m, the feed flow rate capacity is 0.3 to 1.7 mL/h, the evaporator area is 0.048 m^2, the evaporator diameter is 10 cm, the height of the evaporator is 23 cm, the evaporator temperature ranged from 70 to 350^oC, the condenser area is 0.065 m^2, the condenser temperature ranged from -20 to 120^oC, the feed temperature ranged from 40 to 200^oC, the exit residue temperature ranged from 50 to 300^oC. The distance between the wall of the evaporator and the condenser is of the order of 5 to 2cm, in whose space exists vacuum of the order of 10^{-3} to 10^{-4} mmHg.

3. Results And Discussion

The experiments of molecular distillation with petroleum Beta (460ºC+) was carried out at constant pressure (10^{-3} mmHg) and produce distillate and residue cuts. 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 distillate and residue cuts (Maciel et al. 2006).

The evaporator temperature ranges 170-340ºC. At 170ºC the Beta petroleum starts to form two streams: distillate and residue. At lower temperatures, the distillate stream is not formed. The highest temperature (340ºC) is the equipment limitation.

The converted values of molecular distillation temperatures to atmospheric equivalent temperature (AET) are obtained through ASTM D 1160 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

Feed Flow Rate (mL/h)	Evaporator Temperature (ºC)	AET (ºC) (ASTM D1160)	AET (ºC) (FRAMOL Correlation)	% mass of Distillate	% mass of Residue
394	315	689	655	57.8	42.20
606	195	538	526	18.22	81.78
606	315	689	655	55.34	44.66
394	195	538	526	20.24	79.76
500	170	505	510	11.94	88.06
500	340	718	695	60.93	39.07
350	255	604	578	41.51	58.49
650	255	604	578	37.86	62.14
500	255	604	578	39.66	60.34
500	255	604	578	38.45	61.55
500	255	604	578	41.58	58.42

In a first analysis of Table 1, it can be seen that the highest percentage of distillate occurs at the highest evaporator temperature. 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.

Figure 2 shows the extension of the TBP curve of petroleum Beta through the molecular distillation methodology using ASTM D1160 correlation. The extended TBP curve is in good agreement with the existing one, even using this correlation, which is not the most appropriated to be used, because this correlation was developed to conventional vacuum distillation.

Figure 3 shows the extension of the TBP curve of petroleum Beta through the molecular distillation methodology using FRAMOL correlation. 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.

Table 2 shows that the use of molecular distillation also enabled to obtain better improvement of the crude oil (gain of about 27% in distillate).

Table 2 - Improvement (upgrade) obtained through Molecular Distillation in percentage of distillate accumulated.

Petroleum	Percentage of Distillate Accumulated
Beta	27

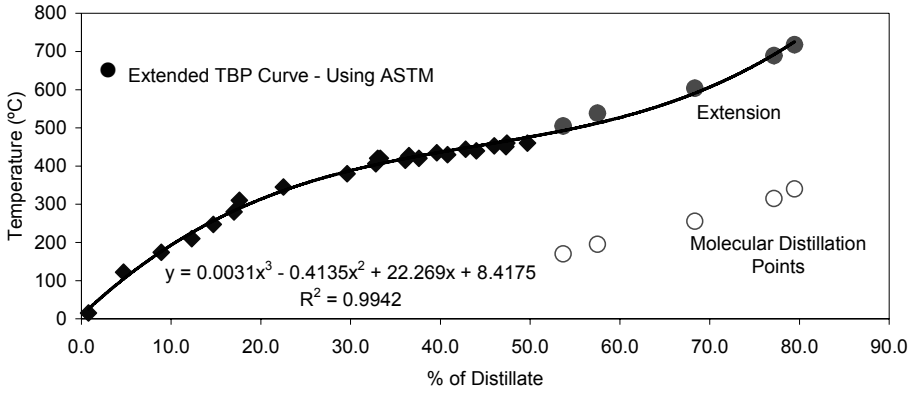

Figure 2: Extension of the true boiling point curve for petroleum Beta 460+ºC through molecular distillation considering ASTM D1160 correlation.

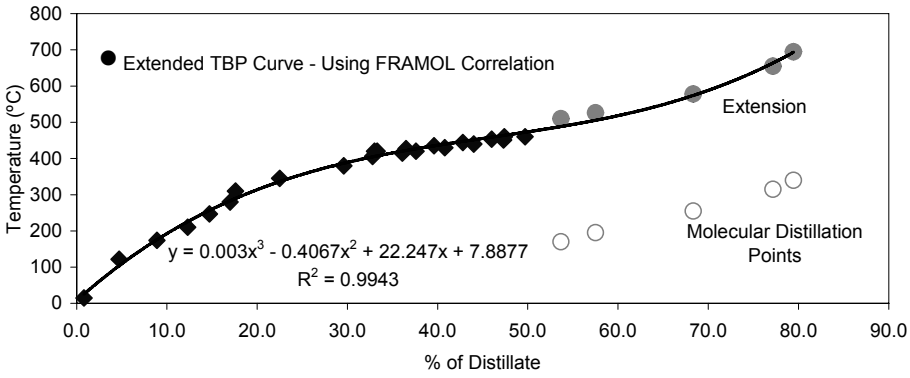

Figure 3: Extension of the true boiling point curve for Beta 460+ºC petroleum through molecular distillation considering FRAMOL correlation.

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

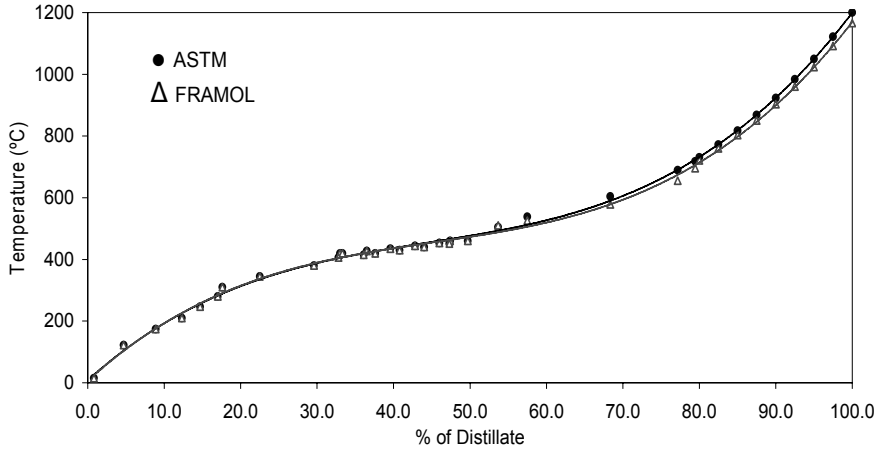

Figure 4: True Boiling Point Curves from ASTM and FRAMOL correlations and extensions to 100% of distillate.

4. Conclusions

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. 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.

5. References

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