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NEW METHODOLOGY OF DETERMINATION OF BOILING POINT AT VERY LOW PRESSURE: PETROLEUM CASE

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Abstract
Molecular distillation is a specific separation process which occurs at reduced pressure, exposing, hence, the material at reduced temperatures. This technique involves, basically, two stages: evaporation and condensation, in which vapor molecules escape from the evaporator in direction to the condenser, where condensation occurs. It is necessary that these generated molecules find a free path between the evaporator and the condenser, and then it is necessary that the condenser be separated from the evaporator by a smaller distance than the mean free path of the evaporating molecules. Since heavy petroleum residues can be easily cracked by thermal heating, the process mentioned above allowed the development of a new methodology for characterization of these types of residues. Usually, the evaluation of the TBP (True Boiling Point) curve of crude oils has been carried out through ASTM D 2892 and D 5236 methods; these methods are so important because at the same time that the TBP Curve is defined, petroleum fractions are obtained, but values of final temperatures are limited to 565 ^{o}C. For higher temperatures, a well established method which makes possible to get both objectives, to extend the TBP Curve and to get heavier fractions does not exist, although this is a very important issue to be studied. So, the innovative technique shown here presents large potential for the determination of boiling point of heavy oils using low pressure system. Its potential can be verified in works which uses molecular distiller[1-3]. The aim of this work is to apply this new methodology for the determination of the TBP of petroleum above 565 °C, getting and characterizing extra-heavy fractions at the same time. Experiments using Falling Film Molecular Distiller were carried out using two residues of Brazilian petroleum, where operating temperatures were increased systematically. According to the results, it was obtained an improvement of percentage of distillate (above 10%) and it was possible to reach values up to 720 °C, representing a considerable progress in the analyses of heavy petroleum fractions. Distillate and residue streams obtained were characterized through gas chromatography distillation (SIMDIS), specific gravity and vapor pressure osmometry. It is important to mention that the results of this work are concerned with Boiling Point, True Boiling Point, development of a robust correlation and with experimental data.

Keywords: True Boiling Point, Heavy oil, Petroleum

1. Introduction

Residues of petroleum distillation are referred as the bottom products of two types of distillation towers of the refining processes. The term atmospheric residue describes the material at the bottom of the atmospheric distillation tower which has an atmospheric equivalent temperature (AET) above 380^{o}C. Molecular Distillation (MD) is a separation process, which uses high condenser, two important parts of the distiller. It is a process in which vapor molecules escape from the evaporator in direction to the condenser under high vacuum, and , so, with operation at reduced temperatures, low exposition of the material at the operating temperature and a small distance between the evaporator and the condenser, where condensation occurs[2-4]. Moreover, under these conditions, e.g., short residence time and low temperature, distillation of heat sensitive materials occurs without or with only a

negligible thermal decomposition. Furthermore, the product flow rates are technologically viable[3,5]. Since heavy petroleum fractions have high molecular weight and are easily cracked, the process conditions above mentioned allow applying this technique in petroleum characterization[6].

On the other hand, the shrinking supplies in conventional light crude oils are, and will be, increasingly forcing the petroleum industry towards upgrading heavier crude oils and residues. The properties of natural petroleum and petroleum products make use of the True Boiling Point (TBP) distillation analysis and it has been proved to be very useful for design and operation of refinery units. The TBP distillation analysis has contributed to the petroleum science and technology, to the classification of petroleum, to the development of petroleum property correlations and it has been used worldwide. However, when applied to heavy petroleum fractions, difficulties are often encountered[7]. 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^{o}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. On the other hand, large amounts of crudes processed in oil refineries are set aside as distillation residue. At present, these residues are of relatively poor commercial value. More detailed structural characterizations are necessary before to improve process routes to upgrade these materials, to lead them to have added values[8]. Brazilian petroleum is becoming heavier, making more difficult the refining process. A new alternative to obtain heavier petroleum residues was developed[7].

So, the objective of this work is to use the Molecular Distillation process to obtain Boiling Point (BP) at Very Low Pressure and, finally, with these data, extend the TBP curve (above 565°C) through DESTMOL Equation in order to use it for characterizing residue of heavy petroleum. This is of great importance for the optimization of refining processes and environmental issues.

2. Experimental Procedure Using Falling Film Molecular Distiller

The Falling Film Molecular Distiller (FFMD) was used. Figure 1 shows the scheme of a FFMD. The basic design of the FFMD 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. It, also, has a feed device with gear pump, rotating carousels that hold discharge sample collectors for distillate and residue streams (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.

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 downward; 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.

In this work, each distillation experiment was conducted at a constant pressure (10^{-3} mbar). Each step produced one distillate cut and one residue cut. Several kinds of Brazilian residues were analyzed and here, only two cases of study are represented to illustrate the extension of the TBP curve. In this case, a 420^{o}C+ Brazilian residue (called here Delta –fantasy name) was used and five distillate and residue fractions were produced through MD, namely 80^{o}C, 140^{o}C, 200^{o}C, 260^{o}C and 340^{o}C (T_{DM}). Also a 400^{o}C+ Brazilian residue (called here Eta –fantasy name) was used and five distillate and residue fractions were produced through MD, namely 105^{o}C, 123^{o}C, 166^{o}C, 282^{o}C and 330^{o}C (T_{DM}). The MD temperatures (evaporator temperatures called T_{DM}) ranged from 80^{o}C to 340^{o}C and 105^{o}C to 330^{o}C for Delta 420^{o}C+ and Eta 400^{o}C+, respectively (equivalent approximately to 377^{o}C to 718^{o}C (Delta) and 481 to 678^{o}C (Eta) atmospheric equivalent temperature (AET)): these converted values of TDM to atmospheric equivalent temperatures (AET) are obtained through DESTMOL correlation. The feed flow rate was 500 ml/h. All these variables were carefully monitored by the controllers present in the equipment. The final temperature is a limitation of the equipment.

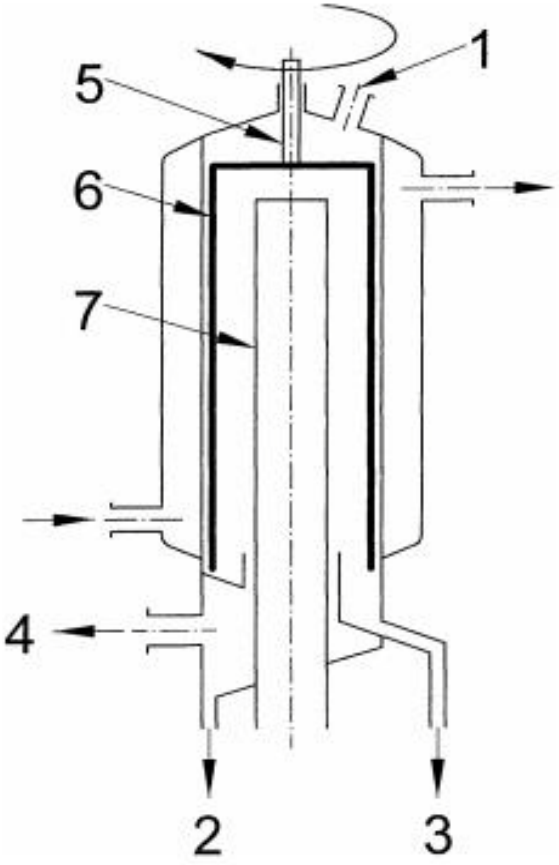


Figure 1. Scheme of a FFMD: 1 – feed; 2 – distillate stream; 3 – residue stream; 4 – vacuum source; 5 – wiper frame; 6 – evaporator; 7 – internal condenser.

3. Extending the TBP Curve

A new correlation for AET calculation was developed[9]. It is robust, of easy use and applied to heavy oil (fractions obtained up to 565^{o}C). The methodology used was based on two procedures, data training and Simulated Distillation, which allow converting the data from Molecular Distillation process to AET. Furthermore, it allows extending the True Boiling Point (TBP) curve. This methodology originates the DESTMOL Equation, which is used for extending the TBP Curve, but it requires the boiling point at very low pressure, goal of this paper.

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 by ASTM.

4. Results and Discussion

4.1. Falling Film Molecular Distillation

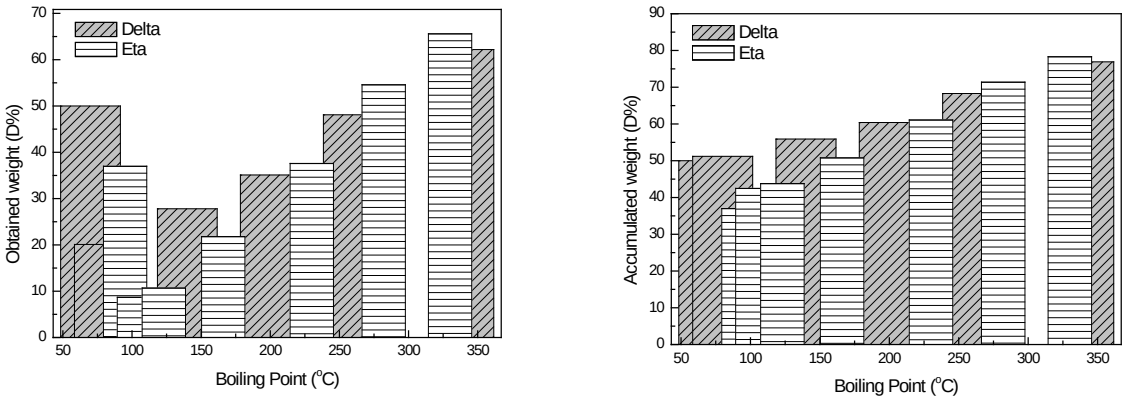
FFMD was performed at pressure of 0.001 mmHg and feed flow rate at 500 g/h. Residues of petroleum considered were Delta 420^{o}C+ and Eta 400^{o}C+ and the operating temperature was between 80 to 340°C and 105 to 330^{o}C, respectively. Table 1 shows the results of Delta residue carried out in these conditions, obtaining weight fractions (%) and Boiling Point, in °C. In Table 1, it can be verified that at 70°C there are a lot of compounds with boiling points under 70°C, and there is a percentage of 62.2 compounds with boiling points above 340°C, both at 10^{-3} mmHg. Table 2 shows the results of Eta residue and it can be verified that at 95°C there are a lot of compounds with boiling points under 95°C, and there is a percentage of 65.6 compounds with boiling points above 340°C, both at 10^{-3} mmHg. Furthermore, it can be seen that the use of Molecular Distillation also enabled to obtain better improvement of the crude oil (gain of about 17% in distillate – see "accumulated weight, %" in Tables 1 and 2). Figure 2 shows these results.

Table 1. Boiling Point obtained by Molecular Distillation and obtained and accumulated weight (%) for Delta residue

Boiling Point, ^oC	*Obtained weight, %*	*Accumulated weight, %*
70	*50.1*	*50.1*
80	*20.1*	*51.2*
140	*27.8*	*55.9*
200	*35.1*	*60.4*
260	*48.1*	*68.3*
340	*62.2*	*76.9*

Table 2. Boiling Point obtained by Molecular Distillation and obtained and accumulated weight (%) for Eta residue

Boiling Point, ^oC	*Obtained weight, %*	*Accumulated weight, %*
95	37.0	37.0
105	8.7	42.5
123	10.7	43.8
166	21.8	50.8
282	54.6	71.4
330	65.6	78.3



(a) **(b)**

Figure 2. Delta and Eta (a) obtained weight and (b) accumulated weight in several fractions by Molecular Distillation

4.2. Characterization of distillates obtained through Molecular Distillation

Based on the results of the characterization performed for the distillate fractions obtained by molecular distillation, it is possible to verify the potential application of the correlation DESTMOL to conversion of T_{DM} to TBP. The results shown in Table 3 (specific gravity and molecular weight) indicate that the fractions of distillate obtained above 500ºC (TBP) are heavier than those obtained by conventional refining (heavy petroleum fractions).

Table 3. Molecular weight and density of distillates obtained through Molecular Distillation for Delta 420°C and Eta 400°C residues

	T_{DM} (°C)	TBP (°C)	Molecular weight (g/mol)	Specific gravity (20/4°C)
Delta 420°C	200	545	456	0.951
Delta 420°C	340	718	672	0.963
Eta 400°C	166	508	290	0.950
Eta 400°C	330	678	538	0.956

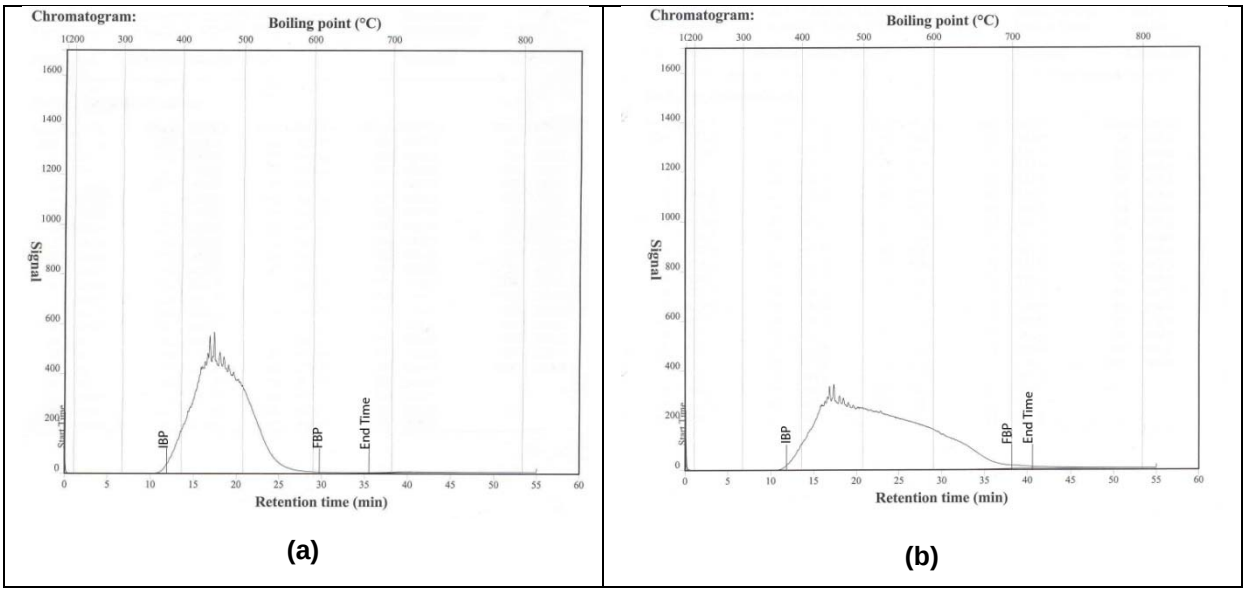


Figure 3. Chromatograms obtained through Simulated Distillation (SIMDIS): (a) Distillate obtained through MD at 200°C (545°C using DESTMOL correlation) and (b) Distillate obtained through MD at 340°C (718°C using DESTMOL correlation).

Table 4. Results of Initial Boiling Point (IBP), Final Boiling Point (FBP) and estimate of the Carbon Chains of distillates obtained through Molecular Distillation by Simulated Distillation (SIMDIS)

	T_{DM} (°C)	IBP (°C)	FBP (°C)	Estimate of the Carbon Chains
Delta 420ºC+	200	375.0	610	C20 – C58
Delta 420ºC+	340	375.5	700	C20 – C90
Eta 400ºC+	166	369.0	515	C20 - C36
Eta 400ºC+	282	375.5	623	C20 –C62

The distillate obtained were also characterized by Simulated Distillation (SIMDIS) for both cases (Delta and Eta), and the results of the chromatograms of the Delta are shown in Figure 3 as an example (the same type of chromatograms were also obtained for the Eta) for evaluating the Initial Boiling Point (IBP) and Final Boiling Point (FBP) and an estimate of the carbon chains present in each fraction of distillate, as shown in Table 4, which is necessary for the characterization of these new products obtained by MD to define a future application of these products. These results show that both the use of MD and the correlation DESTMOL enable better use of oil, which is of great economic interest, regardless the type of oil used, since the oil Delta has an ^{o}API 19.7 and Eta has ^{o}API 18.2.

5. Conclusions

Regarding to the results obtained, it is possible to obtain Boiling Point at very low pressure using Molecular Distillation. These data are necessary for obtaining extended TBP curve through Molecular Distillation, and, so bring important information on petroleum and its characteristics, with very good precision using the DESTMOL correlation. This is useful to define better strategies and operating conditions for the petroleum processing, valuing economically heavy petroleum, as for example, in lighter components and asphalt. 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 availability of heavy petroleum today encountered.

Acknowledgments

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