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Extension of the TBP curve of petroleum using the correlation DESTMOL

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Abstract

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 petroleum characterization and design and operation of refinery units. So, 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. Through petroleum distillation curve (TBP), it is possible to evaluate the yields of the products that will be obtained in the refineries, as well as to establish operational strategies and process optimizations, as the cracking process. The TBP curve is very important for the oil industry and is used to understand the behavior of oil before distillation. For when the oil is subjected to a distillation tower on an industrial scale is already known about the percentage of distillate obtained working at a specific temperature. In the oil refining industry as the distillations follow: Atmospheric Distillation (distillation up to 673 K - ASTM D 2892) and vacuum distillation (distillation to 838K - ASTM D 5236). This work creates the possibility of extending the temperature range of distillation of oil to 973K. The goal of this work is extend the TBP by DESTMOL, the extension of the TBP curve oil reaching approximately 973 K exceeding the curves generated so far that reach only 838 K. The DESTMOL correlation applies pretty good showing continuity and asymptotic profile of the TBP curve. The results help to meet the waste oil and can thus use the waste for more noble ends. As the result of DESTMOL, we can better define the strategiesand operating conditions for oil processing, achieving better economic results in the use of heavy oil, due to its better characterization.

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1. Introduction

True Boiling Point (TBP) distillation is one of the most common experimental techniques for determination of petroleum properties. The methods for performing TBP distillation experiments are described by ASTM D2892 and by ASTM D5236. However, these methods are established for petroleum fractions that reach temperatures up to 838 K.

In this work, three petroleum residues were distilled in a falling film molecular distillation prototype and the data were used to obtain the extension of the TBP curve above temperatures of 838 K. It was possible to extend the TBP curve of these petroleum up to temperatures close to 973K with consistency and continuity in comparison to the standard curve.

The TBP distillation data were the most commonly available information regarding the volatile behavior of hydrocarbon mixtures. Specific cut fractions (part of the TBP range), used in the generation of petroleum products directly influence pricing of crude oils [1]. The other major use of these data is in deciding refinery processes needed to refine a given crude oil. TBP distillation can also be used as a method to isolate a specified fraction from a crude oil for testing [2].

Two conventional physical distillation procedures, specified by the American Society for Testing and Materials (ASTM), are needed for the determination of the boiling range distributions of crude oils. The first method, ASTM D2892 (American Society of Testing and Materials, 1999a) is suitable for the distillation of crude oil components boiling at temperatures lower than 673 K. The second method, ASTM D 5236(American Society of Testing and Materials, 1999b) performed at reduced pressures (0.1 Pa) to avoid thermal cracking, permits the distillation of crude components boiling at temperatures higher than 673 K. The maximum achievable atmospheric equivalent temperature (AET) with the method ASTM D 5236-95 is 838 K. Curve-fitting mathematical techniques are used to combine the data obtained by the two methods into a single continuous distillation curve [3].

Recently, the ability of the method to characterize heavy petroleum components with AET higher than 838 K, the maximum achievable temperature by conventional distillation, has been exploited. A correlation New DESTMOL has been developed (Equation 1) to extend TBP curve through molecular distillation process [4].

$$AET = -1x10^{-5}T_{MD}^{3} + 0.008xT_{MD}^{2} - 0.581xT_{MD} + 427 \quad (1)$$

where: AET = Atmospheric Equivalent Temperature,
T_{MD} = Operating Temperature of the Molecular Distillation Equipment.

The DESTMOL correlation, as it was called, allows conversion of the operating temperature of molecular distillation in equivalent atmospheric temperatures that are used in the conventional TBP curves. The extension of TBP curve from DESTMOL correlation reached values next to 973 K, with continuity and substantial coincidence with the curve obtained from ASTM points.

The molecular distillation process is an efficient method for separation, purification and concentration of natural products, usually composed of complex and thermally sensitive molecules [4].

Furthermore, this process has advantages over other techniques that use solvents as the separating agent, avoiding problems with toxicity. Molecular distillation has also been used for heavy petroleum characterization, demonstrating the potential of this separation process in other applications [5]. It is characterized by a short exposure of the distilled liquid to elevated temperatures, high vacuum in the distillation space and a small distance between the evaporator and the condenser [6].

The molecular distillation process must be conducted according to operating conditions and the design of the equipment is crucial for efficient operation with petroleum residues. Therefore, it was designed and built up by the petroleum research group of the Separation Process Development Laboratory (LDPS) and of the Laboratory of Optimization, Design and Advanced Control (LOPCA) at UNICAMP/Brazil, in partnership with the Laboratory of Valuation of CENPES / PETROBRAS, a falling film molecular distillation pilot plant suitable to work with heavy petroleum fractions. Operational facilities were introduced, such as: heating of several pipes to prevent solidification of the product; evaporator with tree points of heating to establish better control of distillation; automated control system to ensure easiness, speed and stability in operation. Within this context, the objective of this work is to extend the TBP curve of three petroleum residues.

Nomenclature

AET	tmospheric Equivalent Temperature
TBP	True boiling point

2. Experimental

The experiments were performed with three petroleum residues from Brazilian Petroleum Company (PETROBRAS). These samples came from the bottom of atmospheric tower (atmospheric residue) and their assumed fantasy names such as Eta Teta and Gama.

The apparatus used was Brazilian laboratory-scale molecular distillation equipment designed by the research group mentioned in the previous item. The system is a falling film evaporator, shown in Figure 1, capable of varying flow rates from 0.3 to 5 Kg/h. It is equipped with a short path evaporator, a wiper basket assembly, a cold trap, a feed vessel, a discharge system and a vacuum pump set. The short path evaporator is heated in tree separated points with an electric system. It is also attached to an internal condenser cooled with water. The evaporation and condensation surface areas are 0.11 and 0.10 m2, respectively. The feed vessel is heated with electrical system. The discharge systems consist of two separated pipes, one for the distillate, the other one for the residue. The vacuum pumps set consist of a dual rotary vane pump and an air cooled oil diffusion pump.

The molecular distillation process occurs in steady-state, thus the continuously fed and two product flows are continuously generated: distillate cuts and residue of molecular distillation. As soon as all temperatures (feed temperature, evaporator temperature, condenser temperature and product temperatures) and the vacuum pressure are reached, the wiper system is started. Then, the rotating gear pump feeds the sample from a heat feed container. Centrifugal gravity forces distribute the material into the inner surface of the evaporator in the form of a very thin film, with a thickness which will depend on the mixture viscosity and feeding flow rate. Volatile components vaporize from the film and condense on the cooler inner condenser. Distillate cuts and residues from molecular distillation are collected separately in

reservoir cylinders assembled in two carousels. The vacuum pressure (0.1 Pa) in the distiller is set by a rotary vane pump and a diffusion pump. The residence time depends on the molecular distillation conditions, especially on the evaporator temperature. It ranges between 5 and 8 min. In this work, a collecting time of 15 min was used.

A constantly rotating gear pump feeds the sample on a rotating distribution plate from a feed vessel. The centrifugal force distributes the material on the inner surface of the evaporator, and the gravity makes it to flow downward; the wiper basket 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. Distillate and residue streams are each one collected in separated recipients [7].

The evaporator temperature is the significant variable in the process and it is used in DESTMOL correlation. Therefore, the experiments were performed in the molecular distillation prototype changing this temperature. For the Eta, the evaporator temperature was ranged from 413 to 593 K, for the Teta, the range was from 403 to 593 K, and, for the Gama, the range was from 423 to 608 K.

All these variables were carefully monitored by the controllers present in the falling film molecular prototype. Each run produced one distilled and one residue cut and they were weighted. The evaporator temperatures were converted in atmospheric equivalent temperature through Equation 1.

In order to extend TBP curve, these converted data and the distillate weight percentage of each experimental run were plotted above the TBP curve obtained by standard methods.

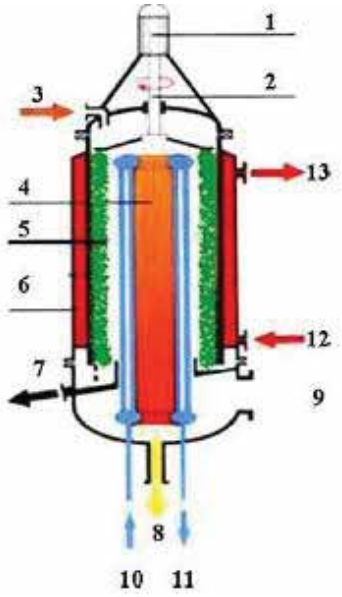

Fig. 1. Configuration of falling film molecular distillatory 1 and 2, engine and agitation blades; 3, feeding; 4, condenser; 5, falling film; 6, evaporator; 7, residue output; 8, distillate output; 9, vacuum system; 10 and 11, cooling fluid; 12 and 13, thermal fluid [8].

3. Results

In Figures 2, 3 and 4 are shown the extended TBP curves of petroleum Eta, Teta and Gama. Data for extension were determined from the evaporator temperature (converted in AET by the DESTMOL

correlation) and from the distillate weight percentage obtained in each experimental run of molecular distillation process. These data were associated with standards data to construct the extended TBP curves of these petroleums. Information about conventional methods, ASTM D2892 and ASTM D 5236, were provided by CENPES.

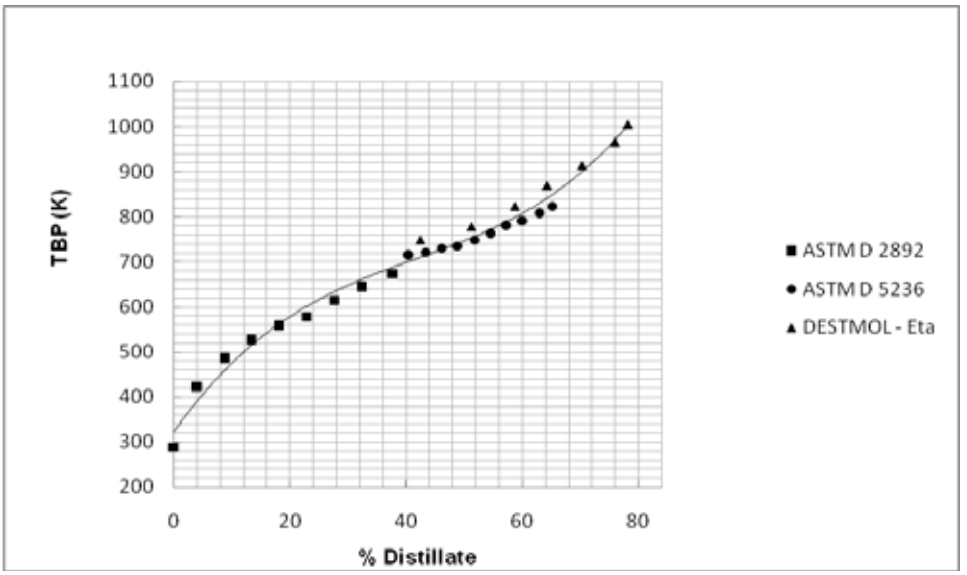

Fig. 2. Extended True Boiling Point curve of the petroleum Eta

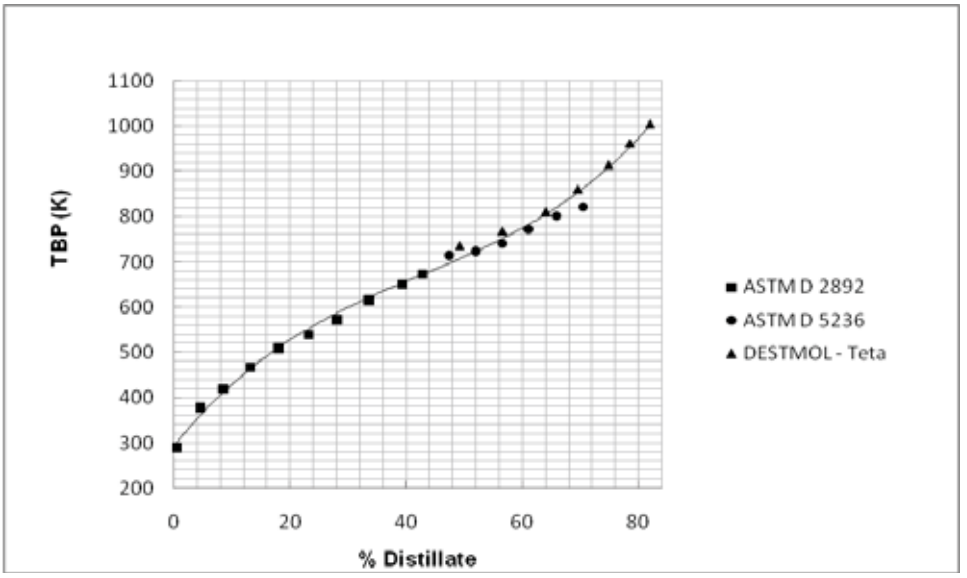

Fig. 3. Extended True Boiling Point curve of the petroleum Teta.

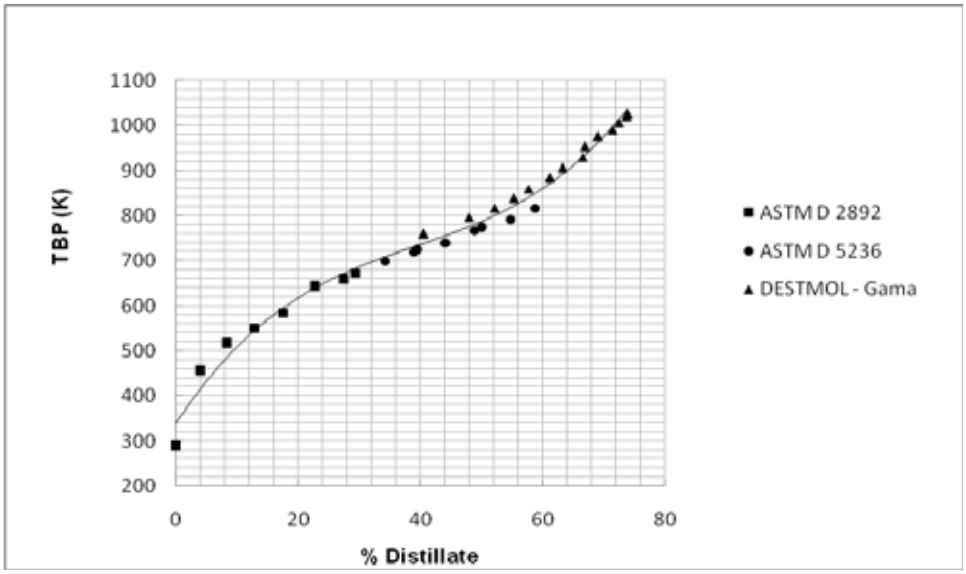

Fig. 4. Extended True Boiling Point curve of the petroleum Gama

Using the molecular distillation prototype, it was possible to extend the TBP curve reaching approximately temperatures of 973 K for each petroleum studied. Furthermore, it can be seen in Figures 2 3 and 4 that the extended data presents continuity and good agreement with the ASTM curves. There was an increase in the distillate weight percentage for petroleum Eta, Teta and Gama of 11%, 14 % and 10%, respectively, using the molecular distiller equipment. This is a gain in distillate since the maximum values achieved by standard methods were lower.

4. Conclusions

The falling film molecular distillation prototype was suitable to work with heavy petroleum residues without thermal degradation of the materials, i.e., with the physical properties of the compounds preserved.

The DESTMOL correlation was appropriated to covert the molecular distillation evaporator temperatures to atmospheric equivalent temperatures, so, extending TBP curves of three petroleum. It was possible to extend the TBP curves up to temperatures close to 973 K with continuity and good agreement with the ASTM at lower temperatures curves for these three petroleums.

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.

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