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Special Molecular Distillation Prototype to Characterization Petroleum Residue

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Due to the importance and to need in studies with heavy and extra heavy petroleum and its residues, it was designed and built up by the oil research group of LOPCA/LDPS/FEQ/UNICAMP, in partnership with the Laboratory of Valuation Processes of CENPES/PETROBRAS a pilot plant falling film molecular distillation (national prototype), where some specific operational facilities were introduced. This project resulted in a suitable system for distillation of products of high molecular weight and thermally sensitive, without degradation of them. For the assay of the properties of petroleum and petroleum products, the use of the true boiling point (TBP) distillation analysis is accepted as a common practice; 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. Even so, for higher temperatures, there is not yet a standard methodology. In this way, methodologies were established for the determination of the true boiling point for heavy fractions of petroleum above 565 °C, where it was possible to reach values up to 700 °C, representing a considerable progress in the analyses of heavy petroleum fractions. Using national falling film molecular distillation equipment, experiments were performed with atmospheric residue ETA 400 °C+, where operating temperatures were increased systematically. With results found, it was possible to extend the curve TBP until temperatures close to 700 °C.

1. Introduction

The properties of natural petroleum and petroleum products make use of the True Boiling Point (TBP) distillation analyses 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.

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However, when applied to heavy petroleum fractions, difficulties are often encountered (Yang and Wang, 1999).

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 D 2892 (American Society of Testing and Materials, 1999a) is suitable for the distillation of crude oil components boiling at temperatures lower than 400 °C. The second method, ASTM D 5236 (American Society of Testing and Materials, 1999b) performed at reduced pressures (50-0.1 mmHg) to avoid thermal cracking, permits the distillation of crude components boiling at temperatures higher than 400 °C. The maximum achievable atmospheric equivalent temperature (AET) with the method ASTM D 5236-95 is 565 °C. (Roussis and Fitzgerald, 2000).

Recently, the ability of the method to characterize heavy petroleum components with AET higher than 565 °C, the maximum achievable temperature by conventional distillation, has been exploited. Batistella et al. (2005) developed a methodology and a correlation (Equation 1) to extend TBP through molecular distillation process using a glass falling film molecular distillation equipment.

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

where: AET = Atmospheric Equivalent Temperature, °C

T_{DM} = Operating Temperature of the Molecular Distillation Equipment (°C).

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. According to Batistella et al. (2005), the extension of TBP curve, from DESTMOL correlation, reached values next to 700°C, 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. 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 (Maciel Filho et al, 2001). 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 (Batistella et al., 2000).

The new molecular distillation equipment (prototype) is robust equipment due to the high technology used in its construction. The process must be conducted according to good operating conditions and the design of the equipment is determinant for efficient operation. It was designed and built by the petroleum research group of both Laboratories mentioned LOPCA and LDPS. It is a falling film molecular distiller pilot plant and the main features of this distiller are:

- heating of the operation lines to prevent oil and products to deposit at them;
- different levels of heating in the evaporator to establish better control of distillation;

- development of automated control system to ensure facility and speed in operation;
- feed flow rate strictly constant and controlled;
- heating of the operation lines with high thermal control;
- heating of evaporator divided by sector with an efficient system of measurement and control;
- condenser cooling system with controlled temperature;
- adjustable film generator rotation according to the process;
- high-vacuum system designed for the most extreme conditions of process;
- automatic control of the exit mass in order to guarantee mass balance closure and automatic true boiling point points.

The objective of this work is to evaluate this Brazilian Falling Film Molecular Distillation Equipment extending the TBP curve, through Equation 1, until temperatures close to 700 °C.

2. Experimental

The experiments were conduced with petroleum residue from the bottom of atmospheric tower (atmospheric residue) ETA 400 ºC+ (fantasy name) from Brazilian Petroleum Company (PETROBRAS).

The apparatus used was Brazilian laboratory-scale molecular distillation equipment designed by Separation Process Development Laboratory (LDPS/UNICAMP). The system is a falling film evaporator, shown in Figure 1, capable of varying flow rates from 0.3 to 5 L/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 with an electric system. It is also attached to an internal condenser for cooling with water. The evaporation and condensation surface areas are 0.11 and 0.10 m^2, respectively. The feed vessel is heated with electrical system. The discharge systems consist of two separated points, 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.

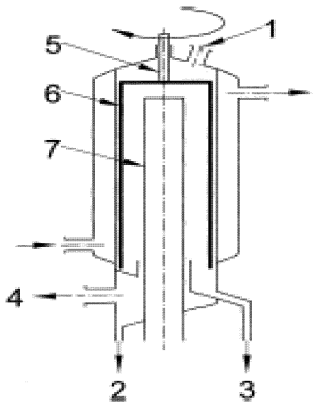

Figure 1. Scheme of a falling film molecular evaporator. 1 - feed, 2 - distillate, 3 – residue, 4 – vacuum source, 5 – wiper frame, 6 – wiper, 7 – condenser.

A constantly rotating gear pump feeds the sample on a rotating distribution plate from a heatable 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. Distillate and residue streams are each one collected in separated recipients (Sbaite et al, 2006).

The experiments were conduced at constant pressure (10^{-6} bar), with evaporation temperature ranging from 170 to 320 ºC, and feed flow rate was kept constant – 15 % (750 mL/h). The feed temperature used was 110 ºC, the temperature of the condenser about 80 ºC and the evaporator agitation was 150 rpm. All these variables were carefully monitored by the controllers present in the falling film molecular unit. Each experiment produced one distilled and one residue cut. According to Maciel Filho et al. (2001), 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.

In order to extend TBP, operational temperatures of molecular distillation equipment were converted in atmospheric equivalent temperature through Equation 1 and they compose the TBP curve obtained by ASTM.

3. Results

In Table 1 are shown the experimental data obtained for petroleum residue ETA 400 ºC+ through molecular distillation and the converted evaporator temperature values using Equation 1.

Table 1. Experimental data for residue petroleum ETA 400 ºC+

Run	Molecular distillation temperature (ºC)	Cumulative percentage of distillate (%Dcum)	AET (ºC)
1	170	50.77	510
2	220	63.65	545
3	270	71.35	595
4	320	76.81	662

Figure 2 shows the TBP curve of the residue ETA 400 °C +, including data obtained by molecular distillation equipment and the extension of TBP by DESTMOL correlation. Information about conventional methods, ASTM D 2892 and ASTM D 5236, was provided by CENPES / PETROBRAS/Brazil.

It can be seen in Figure 2 that the first point in the extension is out of the TBP curve. It occurs because the DESTMOL correlation is used for temperatures above 540 ºC (Batistella et al., 2005).

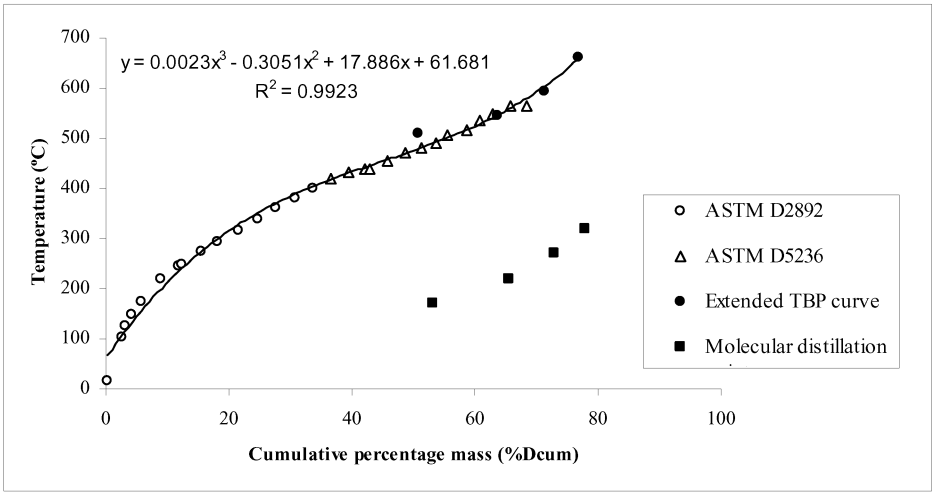

Figure 2. Extension of the True Boiling Point curve for residue ETA 400 ºC+ through molecular distillation methodology.

Using national molecular distillation equipment, it was possible to extend TBP curve reaching approximately 700 ºC+, presenting continuity and good agreement with the ASTM curves. 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 cumulative percentage of distillate for residue ETA 400 ºC+ reached values next to 77%. The increase in distilled percentage was approximately 43% from the atmospheric residue studied. This result is of great interest because a large quantity of distilled can be recovered without thermal degradation of the material, preserving the physical properties of the compounds. This is due to use of high vacuum (10^{-6} bar) and low temperature and operational time.

4. Conclusions

Brazilian falling film molecular distillation prototype is a potential equipment to work with heavy and extra heavy petroleum. It presented high operational stability, ease to control its variables and speed to carry out the experiments. These are consequences of the automated system implemented on the equipment.

Molecular Distillation process made possible the extension of TBP curve with very good precision using DESTMOL 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 petroleum, what it can contribute in the definition of better routes of processing increasing the commercial value of petroleum residues.

References

American Society of Testing and Materials, 1999a, ASTM D 2892: Distillation of Crude Petroleum (15-Theoretical Plate Column). Annual Handbook of ASTM Standards 05.01.

American Society of Testing and Materials, 1999b, ASTM D 5236: Distillation of Heavy Hydrocarbon Mixtures (Vacuum Potstill Method). Annual Handbook of ASTM Standards 05.01.

Batistella C.B., Sbaite P., Wolf Maciel M.R., Maciel Filho R., Winter A., Gomes A., Medina L., Kunert R., 2005, Heavy petroleum Fractions Characterization: A New Approach Through Molecular Distillation. 2nd Mercosul Congress on Chemical Engineering & 4th Mercosul Congress on Process Systems Engineering, Costa Verde, RJ, Brazil.

Batistella C.B., Wolf Maciel M.R., Maciel Filho R., 2000, Rigorous Modeling and Simulation of Molecular Distillations: Development of a Simulator under Conditions Non Ideality of the Vapour Phase. Computers & Chemical Engineering 24, 1309-1315.

Maciel Filho R., Wolf Maciel M.R. and Batistella C. B, 2001, FRAMOL Project, UNICAMP/CENPES/PETROBRAS/FINEP, 2001.

Roussis S. G. and Fitzgerald W. P., 2000, Gas Chromatographic Simulated Distillation-Mass Spectrometry for the Determination of the Boiling Point Distributions of Crude Oils. Anal. Chem. 72, 1400-1409.

Sbaite P., Batistella C.B., Winter A., Vasconselos C.J.G., Wolf Maciel, M.R., Maciel Filho R., Gomes A., Medina L., Kunert R., 2006, Evaluation of Atmospheric and Vacuum Residues Using Molecular Distillation and Optimization. Petroleum Science and Technology 24(3-4), 275-283.

Yang G. and Wang R.A., 1999, The Supercritical Fluid Extractive Fractionation and the Characterization of Heavy Oils and Petroleum Residua. Journal of Petroleum Science and Engineering 22, 47-52.