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Simulated Distillation of Fractions of Petroleum Distillates by Molecular Distillation

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In this work, residues of oils Zeta and Eta have been distilled in falling film molecular distillation equipment. Special feature of molecular distillation is the fact that the process can be performed at pressures lower than 0.01 mmHg absolute. This means that the evaporation can be carried out at temperatures considerably lower than with any other method, even vacuum distillation. This produces a much milder distillation, so that fractions can be distilled without reaching the range of decomposition temperature. Starting from cuts made by molecular distillation simulated distillation was carried out with the distillation stream, for these samples in each range of temperature obtained from molecular distiller. In this work, the residue is distillate first in molecular distillation and after this product is analyze in distillation simulated. The objective is the extension of the TBP curve (True Boiling Point) and acquisition of little distillation curves obtained for each temperature in the molecular distiller through distillation simulated. The simulated distillation is a chromatographic analysis that should be capable of providing, as the final result, a distillation curve similar to the curve generated by the conventional method TBP. It was obtained a good result when compared the curve TBP extended by molecular distillation versus simulated distillation. In this methodology, the work is making with better residue, because of molecular distillation. The results are very goods when compares with others works that not use the molecular distillation first. The curves of simulated distillation completely coincide with the curve TBP extended to the two oil under study. The molecular distillation is an innovative and high technology, so this work has a great contribution to research into heavy oil.

1. Introduction

In this work used the molecular distillation process was used which is presented as potential technique to obtain the percentage by weight in relation to the temperature of the distillate fractions. After separation by molecular distillation, the samples were submitted to the second analysis, the simulated distillation.

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The molecular distillation is used to extend the curve TBP. The oil is evaluated in terms of curve TBP, which may allow research fields of production, establish operational strategies and optimization of processes (MACIEL FILHO, 2006).
The operation is a distillation unit (physical process of separation), which uses the principle of differences in boiling points of substances in a mixture to separate them. The distillation is: taking the curve TBP (True Boiling Point) of oil and obtaining cuts.

2 Metodology

In the petroleum industry, distillation is the process of separation more used. The knowledge on the distribution of boiling points of components and raw oil products from the refining of oil is essential to control this process and ensure the quality of it. The first distillation procedures, standardized by the American Society for Testing and Materials (ASTM), dating from 1926 (FERREIRA, 2005). However, in the sixties, the concept of simulated distillation (SD, or SIMDIS) was introduced, which now provides much reliable information to the oil industry in a shorter time.
The simulated distillation has the basic principle fact that the components of the sample flow the chromatographic column in ascending order of points of elution (Abbott, 1983; DURAND, 1998). Dorbon et. al. (1991), conducted a comparative study on the use of some types of stationary phases in the analysis of simulated distillation. According to the authors, the main differences arise when the samples analyzed showed a high level of aromatic compounds
The technology used in this process is based on gas chromatography, initially proposed the use of columns filled. With the advent of the SD, based on chromatographic methods, the methods of distillation came to be known as conventional methods of distillation physics, as a way to differentiate between the processes.
The chromatographic analysis of simulated distillation should be able to provide, as a final result, a distillation curve similar to the curve generated by the conventional method TBP.
Comparing the two techniques mentioned above, there is a relationship of advantage and disadvantage in the use of simulated distillation in the conventional method TBP. Among the advantages of this method, can be cited: The sample can be obtained in a less time; the values of TBP (True Boiling Point) results are much higher; small amounts of samples are needed for the low cost tests; high level of automation involved in the process and greater reproducibility of data due to limited intervention by the operator.
Among the disadvantages, it has been: it has not possible to obtain samples of distillate analyses.
The SIMDIS is a technique of separation where the mobile phase consists of an inert carrier gas, while the stationary phase can be composed of a liquid or solid. Through this method, gas or substances volatile can be separated according to the differential phases.
The High-Temperature Simulated Distillation, SD, can not be regarded as a curve TBP, it is useful in qualitative estimate of income from derivatives and the comparison between oil and can replace the TBP in specific cases where detailed knowledge is required of the income of distillates oil. The simulated distillation (SD) is a method of separation and not as molecular distillation. In these methods cited, no other generation of cuts is impossible, therefore, the characterization of new chains, such as distillate and residue that are generated in the process of molecular distillation. The molecular distillation is an experimental technique of separation. In molecular distillation the raw

material is the residue of a vacuum. So hitting the high temperatures is needed for the extension of the curve TBP.
In conventional simulated distillation, SIMDIS, The raw material is used as the residue of atmospheric 400 º C for the extension of the curve TBP. In this work, even using the SIMDIS, our raw material is the fraction of distillate 400 ºC + extra that comes as a product of molecular distillation.
Advantage of this procedure: it will be used to free distilled fraction of complex compounds such as asphaltenes and resins that would clog the column of the technique of chromatography SIMDIS.

2.1 Falling Film Distillator

A special feature of molecular distillation is the fact that the process can be performed under the pressure of 0.01 mmHg absolute. This means that the evaporation can be done at temperatures considerably lower than with any other method of vacuum distillation. Moreover, the film (between 0.05 and 2 mm depending on the viscosity of the material under study) makes possible a very short time of residence on the surface of heated evaporator, that is, less than a minute. This distillation produces a very soft, so that fractions can be distilled without reaching the range of temperature of decomposition.

3 Results and Conclusion

The SD shows a typical behavior with respect to conventional TBP. The simulated curve is close to the start curve TBP in mass%, but moves closer to the curve TBP% in volume at the end of distillation. Therefore, the SD can not be regarded as a curve TBP, but is useful for qualitative estimation of the income derived and the comparison between oil and can replace the TBP in the specific cases where not required precise knowledge of the income of the petroleum distillates.
The possibility of using the SD directly discarded this, because if the oil is introduced directly into the column, they clog the roads, impossibility the study. Than, it is necessary first to remove the heavy components such sample to then enter in the column chromatogram, in DS. Therefore it is essential to the separation by molecular distillation, as this project is working with waste oil, oil that will not be distilled by PETROBRAS.
After being obtained from the cuts in distillate molecular distiller for 05 temperatures studied, was the simulated distillation (SD) for each of these samples. The principle of the method is to isolate the fraction, and with data from the SD you can build another curve, but this small curve to match the curve TBP in the range of temperature where it obtained the cut.
In Tables 1 and 2 you can view the Table SD with the values of the simulated x Distillation temperature for each cut in both waste oil studied. There was the last cut for the SD, both for the residue of oil Eta, as for the Zeta, for these are somewhat viscous. Table 1 lacks some temperatures for the end of the simulated distillation; the tests were not carried out due to low viscosity of the sample.
With these results we can build the graphs that follow, TBP curve extended by molecular distillation, via DESTMOL, coupled to the simulated distillation of each cut of the distillate of molecular distillation.
Then, having the figure, 1, illustrating the SD to the last cut of the distillate residue Zeta + 400 º C, together with the curve of the residue TBP Zeta 400 º C +. Note that for

Figure 1 reflects the curve of the residue TBP Zeta 400 º C + coupled with the SD's cutting 400-676 º C +. The curves should coincide in the range of temperature where the experiment was done in this case the points tally at 400-676 ° C.
The residue of oil Eta 400 º C +, built up more 01 charts with the same line of reasoning. Figure 2 illustrates the behavior of SD's cutting (oil) 400 to 609 º C +. In the two waste oil studied, it is observed that the curve of the simulated distillation curve coincides exactly with the TBP of each oil. The SD curve is very important because it assesses the quality to TBP extend the curve that was performed at work. The results are very good and show the efficiency of the method and equipment for molecular distillation.
The technique of molecular distillation is relatively new and has excellent results for the oil studied so far. The use of SIMDIS in this work, combined with the technique of molecular distillation, is a breakthrough in the extension of the curve TBP. This is an important contribution to the work so far developed, fully accepted and already in use by PETROBRAS.

2. Illustrations And Tables

Table 1: Simulated distillation oil Zeta 400 º C +.

DS	400-435ºC	400-476ºC	400-581ºC	400-676ºC
1,0	295,4	318,0	302,8	334,2
3,0	315,8	351,6	328,8	376,2
5,0	328,0	371,8	346,8	391,4
7,0	338,0	384,0	361,6	398,8
9,0	347,0	391,0	374,0	404,6
20,0	383,4	410,2	402,2	428,4
40,0	409,0	432,8	427,0	470,6
60,0	428,2	453,4	451,2	524,6
80,0	456,4	482,2	500,8	595,2
91,0	609,6	510,8	677,2	735,2
92,0	649,8	516,0	712,0	750,0
93,0	684,4	522,8	750,0	-
94,0	724,2	533,0	-	-
95,0	750,0	556,0	-	-
96,0	-	620,2	-	-
97,0	-	750,0	-	-

Table 2: Simulated distillation oil Eta 400 º C +

DS	400-481ºC	400-481ºC	400-481ºC	400-481ºC
1,0	363,9	366,5	373,2	380,3
3,0	371,4	373,6	381,8	390,9
5,0	375,3	377,8	386,9	397,4
7,0	378,4	381,0	390,8	402,7
9,0	381,1	383,7	394,0	407,2
20,0	391,2	394,0	406,7	427,0
30,0	397,6	400,6	415,6	442,8
40,0	403,2	406,5	423,3	460,2
50,0	408,5	412,2	430,1	479,6
60,0	414,0	418,1	437,2	499,7
70,0	420,1	424,6	444,4	520,5
90,0	438,9	445,8	465,6	568,9
100,0	562,0	613,1	515,6	622,9

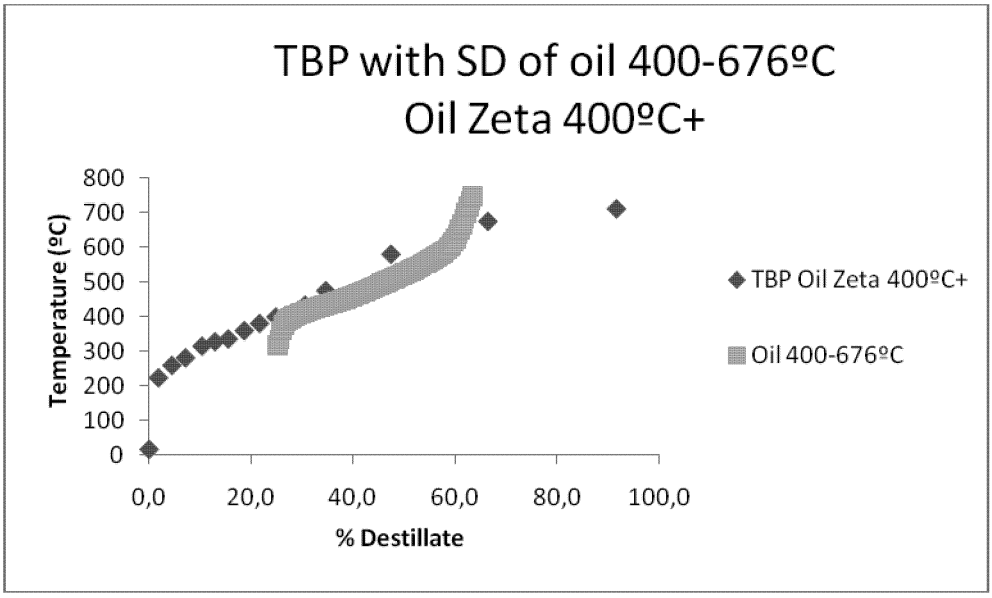

Figure 1: True Boiling Point with SD of oil Zeta 400ºC+

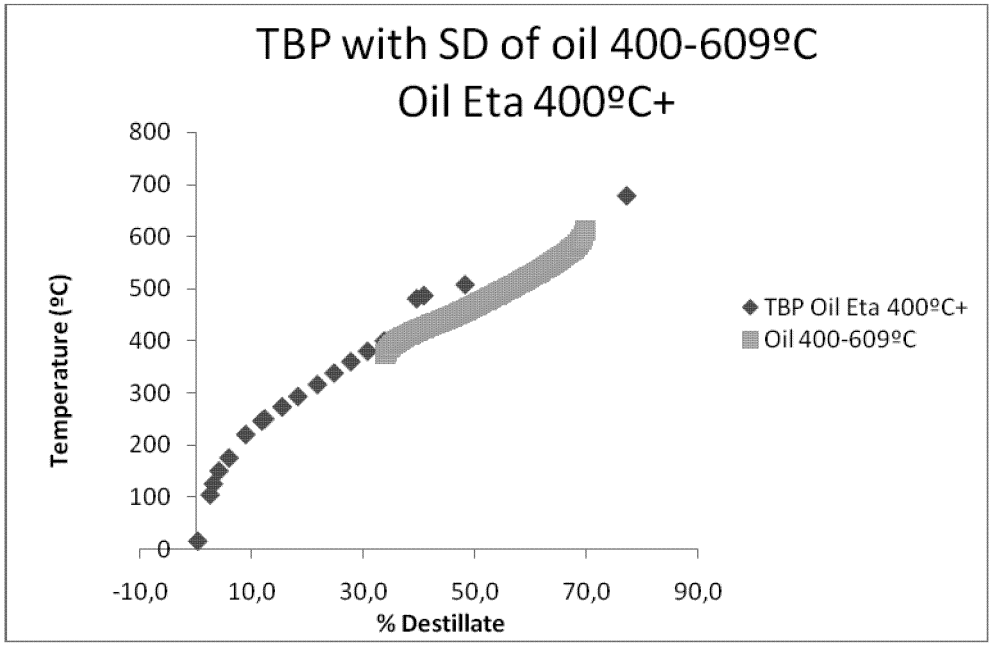

Figure 2: True Boiling Point with SD of oil Eta 400ºC+

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