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SimDis-HT Analysis of Crude Oils as a Tool to Define Operating Conditions for Primary Treatment Processes

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The main objective of this article is to determine the true boiling point (TBP) curve of 08 crude oils (Campinas, Guaratinguetá, Leme, Pacaembu, Poá, Registro, Sales, and Sertãozinho – fantasy names – names of cities in the Sao Paulo State, Brazil) by high temperature gas chromatography, using the high temperature simulated distillation (SimDis-HT) analysis (ASTM D7169). Knowing the initial boiling point (IBP), it is possible to determine the loss of volatile components during the process. Accordingly, the distillation ranges showed different classes of oils, with Registro being the lightest, with 98.8 % recovery, followed by Sertãozinho (93.2 %) > Leme (90.6 %) > Guaratinguetá (89.7 %) > Poá (86.8 %) > Sales (84.1 %) > Pacaembu (74.8 %) > Campinas (57.1 %). Although Registro is considered the lightest oil (highest recovery), the oil that demonstrated the lowest IBP was Sertãozinho. Furthermore, Leme, Pacaembu, and Sertãozinho oils had their IBP around 40 ºC, and Guaratinguetá at 50 °C. Thus, these oils presented losses of light fractions at low temperatures (25 – 30 °C is the maximum temperature to avoid losses), limiting their processing in open and heated systems. Registro started to lose volatiles at 65 °C, and Campinas, Sales, and Poá at 75 to 80 °C. Therefore, these oils can be processed at higher temperatures (maximum of 60 °C), without suffering mischaracterization in open and heated systems. The distillation profile should not change after processing the oils, which means this analysis can provide important data to define the operating conditions of different types of processes (mainly in the primary treatment processes). Consequently, the SimDis-HT analysis can be considered as an efficient tool to find initial process parameters and to provide information for possible scale-up of processes with high temperatures and opened vessels.

1. Introduction

To commercialize oil, the oil industry performs a series of oil characterizations. Before its commercialization, the main concern is the verification and control of its processes. Then, one of the physicochemical characteristics that stands out is the definition of the TBP curve, for the correct specification of hydrocarbon mixtures. The TBP curve, usually obtained in distillation columns, shows the ability of a particular oil to provide different proportions of products (e.g., gasoline, diesel, naphtha, kerosene, among others), depending on the length of its hydrocarbon molecules. When extracting crude oils, they carry undesirable components, most of which are already removed on platforms. In refineries, they are removed before the distillation units through primary treatments. However, on smaller scales, processing oils before determining their TBP curve may become impractical. Therefore, alternative techniques are needed to provide the same information in a faster and more accurate way.
At the analytical level and on an industrial scale, complete characterization of oils is essential before their processing in refining stages. The contaminants cause incrustations and corrosion in the pipes, having losses and stops in the pre-refining systems, besides increasing transport and storage costs (ESTEVES, 2016).
Generally, after conventional distillation processes, it is possible to evaluate the profile of compounds present in the oil, which is based on TBP curve. With the SimDis-HT technique, it is possible to obtain this information even before processing it.

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In the vacuum distillation, for example, it is possible to evaluate whether more light components are possible to be extracted beyond atmospheric distillation. Then, recovering light components as much as possible avoids the loss of volatiles. Therefore, if the processes are not carried out together, the oil industry can have an economic loss, since light fractions are important for derivation. However, even before processing them, it is possible to obtain the complete distillation profile using the SimDis-HT technique. For this reason, this technique has important relevance for the oil industry. Knowing the raw material, without even processing it, is an economic gain for the oil industry. In addition, it is important to note that there are several other characteristics to be determined for crude oil. The ASTM D4057 (2019) standard lists some analyzes (Table 1) that can be performed on crude oil samples for characterization. Moreover, there are also some other forms of oil classification: type of hydrocarbons in the mixture (paraffinic, naphthenic, and aromatic); and specific mass (°API) of oil, created by the American Petroleum Institute (API): light (°API ≥ 31), medium (°API = 22 – 31), heavy (°API = 10 – 22), and extra-heavy (°API < 10) (ANP, 2019).

Table 1: Some of oil characterization analyzes (ASTM D4057, 2019)

Analysis	ASTM
Acid Number – Potentiometric Titration	D664 (2018)
Asphaltenes Content	D6560 (2017)
Boiling Point Distribution – SimDis-HT	D7169 (2020)
Carbon Residue	D4530 (2020)
Density, Relative Density, and API Gravity	D1298 (2017), D287 (2012), D5002 (2019), and D6822 (2017)
Metals (Nickel, Vanadium, Iron, and Sodium)	D5863, Method B (2016)
Organic Chloride Content	D4929 (2019)
Pour Point	D97 (2017) and D5853 (2017)
Salts	D3230 (2019) and D6470 (2020)
Sediments	D473 (2017) and D4807 (2020)
S & W	D4007 (2016)
Sulfur	D2622 (2016) and D4294 (2016)
Trace Nitrogen	D4629 (2012) and D5762 (2018)
Vapor Pressure	D323 (2020), D5191 (2020), and D6377 (2020)
Viscosity	D445 (2019)
Water Content	D4006 (2016), D4377 (2011), and D4928 (2018)

Boiling point distribution is listed as one of the most important oil characterization analyzes, through SimDis-HT. ASTM D7169 (2020) is a specific standard for crude oils. Other works have used ASTM D7169 to characterize oils, bitumen, and other products from petrochemical industry: Gholami et al. (2021), Styani et al. (2020), Ramírez et al. (2017), among others. Besides that, other authors use ASTM D2887, which also determines the boiling range distribution, but for petroleum products (Lima et al., 2012).
Therefore, the objective of this work was to determine the distribution range of the boiling points of samples of crude oils by ASTM D7169, through SimDis-HT technique.

2. Methodology

This procedure follows the guidelines of ASTM D7169 (2020). The amount of waste (or sample recovery) is determined using an external standard. This test method extends the applicability of simulated distillation with samples that do not elute completely in the chromatographic system (ASTM D7169, 2020).
The SimDis-HT analyzes were performed without prior treatment (dehydration, desalting, and sediments removal) of these crude oils, in order to determine the class of oils. Depending on the water, salt, and sediments contents present in the sample, the analysis may not be very representative. However, the aim is to quickly and efficiently check the distillation curve of each oil. Then, it allows the definition of preliminary operating conditions of primary treatment processes. In cases of open vessel processes, it is essential to know what temperature to work at, so as not to exceed the temperature that begins to lose volatiles.
The analyzes were performed with a gas chromatograph, from Agilent Technologies (model 7890A), with Flame Ionization Detector (FID). It is equipped with analytical module (Analytical Controls SimDis-HT-750), using nitrogen (as carrier gas), and nitrogen, hydrogen, and synthetic air for the detector.
Thus, the 08 crude oils had their boiling ranges characterized by the SimDis-HT technique (up to 720 ºC, which corresponds to the elution temperature of n-C_{100}).

2.1 Blank Sample

To compensate the baseline, carbon disulfide (CS_2) is used as blank sample. The blank run has two purposes: to clean and condition the column, and to serve as a baseline for the treatment of data from the calibration standard, reference sample, and samples (ASTM D7169, 2020). Therefore, it is important to inject the blank sample at least in duplicate.

2.2 Calibration Standard Mixture

A standard mixture, used as a retention time calibration mixture, should be prepared to calibrate the boiling points, developing a curve of a retention time versus boiling point (ASTM D7169, 2020). Boiling points are calibrated with a mixture of light (C_5-C_{28}) and heavy (C_{30}-C_{120}) n-paraffin standards, diluted in CS_2. The mixture prepared in the vial can be reused until the solution is finished, since it is a qualitative standard. The ASTM D7169 (2020) standard requires that the standard mixture should always be injected into each sample sequence. The calibrator's function is to create a correlation or calibration between the retention times and the boiling point. As the calibration is done with saturated and linear hydrocarbons, this correlation only applies to crude oil and oil fractions, whose composition is mostly hydrocarbons. The calibration of the boiling points is done by correlating the number of carbons, boiling point, and standard retention time for each carbon (Table 2). It is important to note that the values of the retention times may change according to the column used. In addition, if the column has been used for a while, it may also suffer a drag from the retention times. Boiling points must be obtained using a normal paraffin calibration curve versus retention time to convert the retention times of the model compounds to a corresponding temperature (ASTM D6352, 2019).

Table 2: Linear hydrocarbons and their respective boiling points and usual retention time in the SimDis analysis (ASTM D6352, 2019)

Carbon Number	Boiling Point (°C)	Retention time (min)	Carbon Number	Boiling Point (°C)	Retention time (min)
5	36		32	466	14.79
6	69		36	496	16.88
7	98		40	522	18.74
8	126		46	556	21.26
9	151		50	575	22.77
10	174	0.25	52	584	23.47
11	196		56	600	24.82
12	216	0.58	60	615	26.08
13	235		66	635	27.81
14	254	1.61	70	647	28.88
15	271	2.40	76	664	30.39
16	287	3.27	80	675	31.31
17	302	4.18	86	691	32.64
18	316	5.07	90	700	34.25
20	344	6.78	96	712	
24	391	9.84	100	720	
28	431	12.48			

2.3 Reference Sample

A reference sample (Reference Lube Oil) should be used, diluted in CS_2. The purpose of the reference oil is to evaluate the quality of the correlation of the boiling points. This oil is a material that has its known boiling points ranges. Also, a reference sample create a response factor for the quantification of the samples. The software calculates the initial and final boiling temperature for the oil, following ASTM parameters. After validating the correlation verified with the reference oil, the crude oil samples are analyzed.

2.4 Crude Oil Samples

The 08 crude oil samples were homogenized and weighted around 0.01 g in vials. 1 mL of CS_2 was added into each vial. All vials were identified, and the masses used in their preparation were noted for later use in the equipment.

3. Results and Discussion

The distillation ranges determined by SimDis-HT (Table 3) show different classes of oils.

Table 3: SimDis-HT analyzes results of the 08 oil samples

Campinas		Guaratinguetá		Leme		Pacaembu		Poá		Registro		Sales		Sertãozinho	
(%wt)	(°C)	(%wt)	(°C)	(%wt)	(°C)	(%wt)	(°C)	(%wt)	(°C)	(%wt)	(°C)	(%wt)	(°C)	(%wt)	(°C)
IBP	79.0	IBP	48.2	IBP	38.3	IBP	42.0	IBP	75.9	IBP	64.9	IBP	76.9	IBP	37.2
10.0	283.8	10.0	191.8	10.0	196.4	10.0	179.2	10.0	222.4	10.0	202.7	10.0	228.2	10.0	175.2
20.0	378.6	20.0	259.3	20.0	265.8	20.0	249.1	20.0	295.7	20.0	270.5	20.0	305.3	20.0	247.3
30.0	452.9	30.0	314.0	30.0	322.3	30.0	311.4	30.0	350.2	30.0	326.8	30.0	372.1	30.0	308.0
40.0	538.1	40.0	370.8	40.0	383.7	40.0	380.0	40.0	403.6	40.0	382.7	40.0	433.1	40.0	368.6
50.0	643.3	50.0	423.7	50.0	438.7	50.0	445.4	50.0	449.3	50.0	432.8	50.0	484.9	50.0	425.7
57.1	719.6*	60.0	472.5	60.0	495.8	60.0	523.3	60.0	503.8	60.0	477.3	60.0	551.0	60.0	479.0
		70.0	538.6	70.0	568.1	70.0	640.2	70.0	573.6	70.0	534.0	70.0	623.6	70.0	544.1
		80.0	623.1	80.0	648.4	74.8	719.5*	80.0	655.0	80.0	598.9	80.0	683.2	80.0	621.3
		89.7	719.6*	89.6	719.6*			86.8	719.6*	90.0	658.4	84.1	719.6*	90.0	679.5
										98.8	718.5*			93.2	719.6*

%wt: Mass recovered: “percentage of the sample eluted” (ASTM D7169, 2020);
(°C): Boiling point temperature;
IBP: Initial Boiling Point: “the temperature corresponding to an accumulated 0.5 % of the total area of the eluted sample after correcting for the percent of sample recovery” (ASTM D7169, 2020);
*Final Boiling Point (FBP): Final distillation range determinable according to ASTM D7169 guidelines, which is “the temperature, for fully eluting samples (recovery = 100 %), at which 99.5 % of the sample is eluted” (ASTM D7169, 2020).

Registro has the highest recovery with 98.8 % at 718.5 °C, followed by Sertãozinho with 93.2 %, Guaratinguetá (89.7 %), Leme (89.6 %), Poá (86.8 %), Sales (84.1 %), Pacaembu (74.8 %), and Campinas (57.1 %). Moreover, Leme, Pacaembu, and Sertãozinho oils had their IBP around 40 ºC, and the Guaratinguetá at 50 °C. Thus, these oils presented losses of light fractions at low temperatures (25 – 30 °C is the maximum temperature to avoid losses), limiting their processing in open and heated systems. Registro started to lose volatiles at 65 °C, and Campinas, Sales, and Poá at 75 to 80 °C. Therefore, these oils can be processed at higher temperatures (maximum of 60 °C), without suffering mischaracterization in open and heated systems. To have a better visualization of the distillation curve, the data in Table 3 were transformed into graph in Figure 1, demonstrating the recovery in temperatures of the highest and lowest recovery oils.

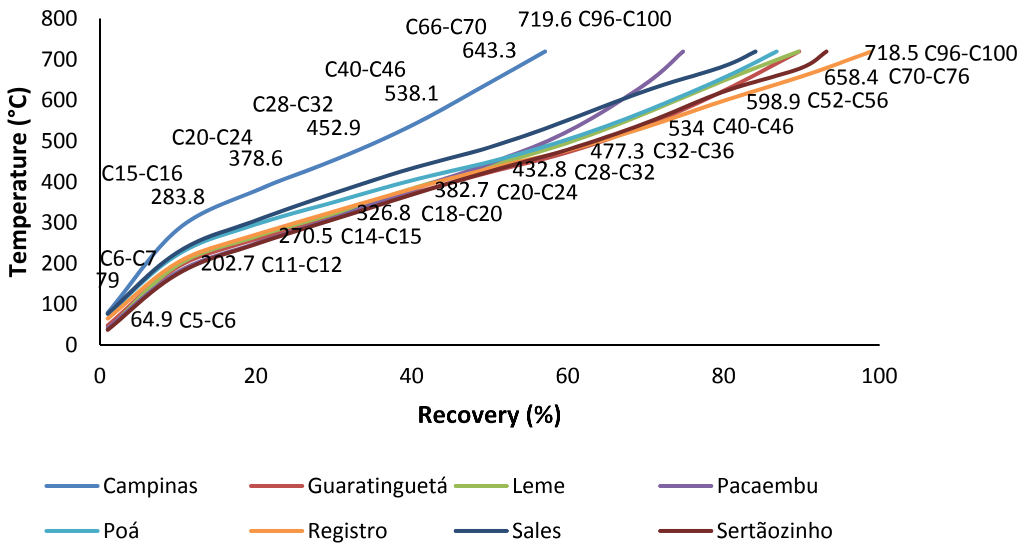

Figure 1: SimDis-HT curves of the 08 samples of oils, highlighting the temperatures and hydrocarbons range of Campinas (lowest recovery) and Registro (highest recovery)

Practically, all oils presented similar results for the TBP curve, with the exception of Campinas. The latter was the oil with the lowest recovery, proving to be the heaviest. Oils with these characteristics allow processing with open vessels or at high temperatures, without undergoing changes. This is possible due to its composition being mostly of heavier components. Although low recoveries can demonstrate the presence of heavier components, it can also indicate the great presence of contaminants (e.g., water, salts, and sediments). Therefore, the characterization of the oil needs to be complete when arriving at the refinery: checking water, salts, and sediments contents, density, and viscosity. These other complementary analyzes help to decide the need for pretreatments, before the oil being processed in the distillation units or other processes in the refinery. Furthermore, Campinas has 50 % of C_{70} or lower and 7.1 % of C_{70} to C_{100}; Guaratinguetá has 80 % of C_{60} or lower, Leme has 80 % of C_{70} or lower, Pacaembu has 70 % of C_{66} or lower, Poá has 80 % of C_{70} or lower, Registro has 90 % of C_{70} or lower, Sales has 80 % of C_{80} or lower, Sertãozinho has 90 % of C_{80} or lower. It is possible to see (Figure 1) that all 08 samples present similar distillation profiles. However, the main differences are related to IBP and FBP of each oil. The evaluation of the distillation profile is important, allowing to draw conclusions about the loss of volatiles during the processing of oils. Since the objective is to ensure that the oils are not mischaracterized in the separation processes, the distillation profile should not change. In addition, knowing the distillation curve of each type of oil before carrying out the conventional distillation processes is crucial before processing them, so it is possible to know more precisely the temperatures of each distillation range. Finally, to emphasize the difference between the lowest and highest recovery oils, Figure 2 brings their chromatograms, demonstrating the necessity to characterize each oil that arrives in the refinery.

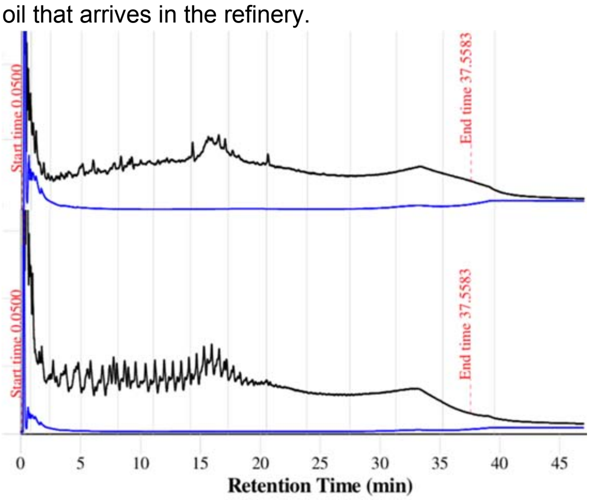

Figure 2: Chromatograms of the lowest – Campinas (up) and the highest – Registro (down) recovery oils

The most common components of crude oils are hydrocarbons, but their range can vary widely from oil to oil, depending on the fields they were extracted from. It is possible to verify that Registro has much more light hydrocarbons than Campinas. Also, the contaminants can impair peak definition, especially for lighter compounds, as can be seen in the Campinas chromatogram.

4. Conclusions

The SimDis-HT analyzes were performed in the original conditions of the oil samples (crude oil), without pretreatment. High (Guaratinguetá, Leme, Poá, Registro, Sales, and Sertãozinho) and low (Campinas and Pacaembu) recovery values were observed, being able to identify them as light and heavy oils, respectively. Determining its IBP is essential for laboratory scale processes, in case of use of high temperatures and open systems (e.g., continuous centrifuges). The analysis of the simulated distillation curves obtained for each of the oils shows that the IBPs of Guaratinguetá, Leme, Pacaembu, and Sertãozinho oils occur around 40 ºC. Thus, these oils may present losses of light fractions in low temperatures, limiting their processing in open and heated systems, without mischaracterizing them. On the other hand, Campinas, Poá, Registro, and Sales oils have the beginning of the loss of light fractions above 65 ºC. Therefore, these oils can be processed at higher temperatures than others, without suffering mischaracterization. It is very important to define the distillation curve of an oil, since it helps to choose the operating conditions before any process. Therefore, if these analyzes would be done after any process, SimDis-HT analysis should provide responses of the loss of volatiles to an open system. Also, this analysis can be used as an indication of the efficiency of the processes, and it is the optimal system for feedstock characterization in the oil refinery process.

Acknowledgments

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