

Study of the distribution of total acid number presents in heavy oils and its fractions

Mariana F. B. Mota^{a,*}, Vinícius M. D. L. de Almeida^a, Majorie M. Malacarne^a, Eustáquio V. R. de Castro^a, Reginaldo B. dos Santos^a, Lílian C. Medina^b, Alexandre de O. Gomes^b

^a Department of Chemistry, University of Espírito Santo, 514, Fernando Ferrari Avenue, Espírito Santo, Brazil.

^b PETROBRAS Development and Research Center (CENPES), University City, Rio de Janeiro, Brazil.

(*sea.mariana@gmail.com)

The incidence of heavy oil is increasing significantly in recent years pointing to a greater need for their study. The heavy oils are more complex handling and processing than the light oil, and generate less noble derivatives. In addition, the heavy oils have high contents of naphthenic acids which are responsible for severe corrosion problems in refineries¹, especially in distillation units and less frequently in catalytic and thermal cracking operations². These factors contribute to the devaluation of the heavy oils in the international market. The Total Acid Number (TAN) determination in petroleum and its products is done using the ASTM D 664 by potentiometric titration with potassium hydroxide.

In view of the presented problems, the objective of this paper was to quantify the TAN present in oil and its distribution in the distilled fractions of three different oils and estimate the TAN of oil through the adding of the TAN value of all fractions and residues reported for this oil and compare with the experimental value.

Three crude oil samples were distilled in a manual laboratory unit following ASTM D 2892 standard. According to the TAN and °API values of these oils, shown in Table 1, they were classified as heavy oil with high acidity.

Oil	IAT (mg KOH/g sample)	°API
1	3.0521	16.3
2	1.6285	22.2
3	0.9834	13.1

The TAN values measured for each fraction in function of average boiling point is shown in Figure 1.

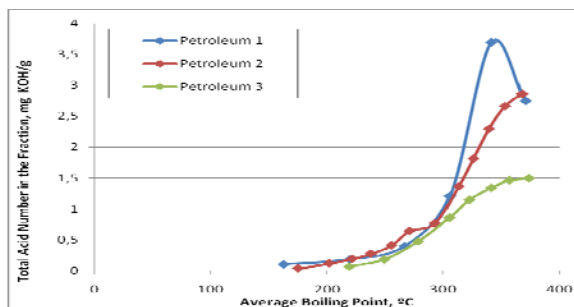


Fig. 1. Acid Curve for fractions

According to the literature the higher acid concentration are usually found in the 371°C to 426°C

TBP range⁴ as could be observed in Figure 1. Lighter fractions tend to be relatively low in acidity.

The curve shows that the petroleum 1 has a major area under the curve than petroleum 2 than petroleum 3, agreeing with their TAN values. Also, the larger area under the curves corresponds to the higher TAN of the samples.

The values of TAN measured in fractions and in the residue were reported to the petroleum according to the Equation 1.

$$TAN_{rep} = TAN_{exp} \cdot \%mass_{exp} \quad (1)$$

where the TAN_{rep} is TAN in fraction or residue reported of oil change, TAN_{exp} is TAN measured in fraction or residue and $\%mass_{exp}$ is the mass percentage of each fraction or residue in the oil change.

The TAN_{rep} calculation values were used to estimate the value of the oil, TAN_{est} , by Equation 2, which is nothing more than the mass balance of the acidity of the distillation.

$$TAN_{est} = \sum TAN_{rep, fraction} + TAN_{rep, residuo} \quad (2)$$

This estimated value and the relative deviation in relation to the experimental value are present in Table 2.

Table 2: Experimental and Estimated oil TAN

Oil	TAN Exp. (mg KOH/g sample)	TAN Est. (mg KOH/g sample)	Relative Deviation
1	3.0521	2.7299	0.1213
2	1.6285	1.6308	0.0014
3	0.9834	1.0494	0.0931

There was no significant loss of acid components of the petroleum fractions. Thus, knowing the distribution of acid in the crude oil as a function of TBP, it is readily possible to predict where high acid concentrations will occur in a distillation unit allowing the optimization of the conversion process of oil to obtain products of high commercial value and minimize the refining losses.

References

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