TOTAL ACID NUMBER DISTRIBUTION IN A BRAZILIAN REFINERY OIL SAMPLE AFTER EXPOSURE TO DIFFERENT LEVELS OF HEATING IN THE PROCESS UNITS

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Introduction

Naphthenic acid corrosion was observed for the first time during the distillation process of certain types of crude oils since 1920. According to recent reports naphthenic acid corrosion has been found in China, India, Venezuela, Eastern Europe, Russia, and the United States. In the past, certain difficulties were encountered with regard to differentiating if the observed corrosion at high temperatures was due to naphthenic acids or sulfur. Now, it is known that naphthenic acid corrosion is associated with the total acid number (TAN), temperature, and fluid rate [(1)].

The total acid number (TAN) is defined by the American Society for Testing and Materials (ASTM) as the quantity of base, expressed as milligrams of KOH, required to neutralize the acidic components in 1 g of oil. It is basically a measure of all acidic components, including naphthenic acids and sulfur compounds. High TANs typically tend to give crudes a “bad name” and result in discounted prices. Often high TAN crudes are heavy, with densities in the 900-1000 kg/m^3 range, which includes most heavy oils and bitumens [(2)]. Here in Brazil, we find crude oils with TAN up to 10.0 mg KOH/g.

The presence of relatively high levels of naphthenic acids in crude oils is a bane of petroleum refiners; and more recently, of producers as well. Essentially, these acids, which are found to greater or lesser extent in virtually all crude oils, are corrosive, tend to cause equipment failures, lead to high maintenance costs and may pose environmental disposal problems [(3)].

Previous tests run at Petrobras Development and Research Center’s (CENPES) laboratories showed that crude oils had their TAN distribution curves modified when exposed to high temperatures for a period 5.5 to 24.5 hours[(4)].

In addition, it has been recognized that TAN measurement at the high boiling range can be distorted due to the thermal decomposition of naphthenic acids during the distillation [(5)].

In order to obtain a better understanding of corrosion problems when processing different blends of crude oils in a Brazilian refinery, in these paper we obtained the TAN along the distillation curve by means of a conventional procedure following ASTM D 2892 and ASTM D 5236 to produce the true boiling point (TBP) curve, cuts and residues, which have the TAN values measured by ASTM D 664 method. According ASTM D 664 method, in new and used oils, the constituents that may be considered to have acidic characteristics include organic and inorganic acids, esters, phenolic compounds, lactones, resins, salts of heavy metals, salts of ammonia and other weak bases, acid salts of polybasic acids, and addition agents such as inhibitors and detergents. So, to known the naphthenic acid contribution in TAN results from samples 2 and 6, Naphthenic Acid Number (NAN) was determined using a FT-IR in-house method.

Experimental

Five samples received from the refinery were studied: crude oil after desalting (sample 2), crude oil after pre-heating exchangers (sample 3), crude oil before pre-flash oven (sample 4), reduced crude oil before atmospheric distillation tower (sample 6) and atmospheric residue (sample 10). Figure 1 shows the refining scheme.

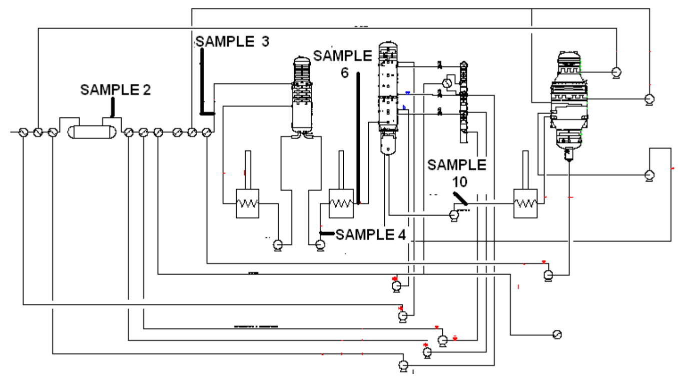

Figure 1: Refinery Scheme

The separation in 25ºC cuts of samples 2, 3, 4 and 6 was carried out in a Gecil MVD Distillation Unit using the ASTM D-2892 Standard Test Method for Distillation of Crude Petroleum (15-Theoretical Plate Column) up to residue 300ºC (or 307ºC in sample 6). The residue was taken to a Gecil Pot Still Unit which meets the ASTM D 5236 Standard Test Method and the separation in 25 ºC (or 15ºC above 500ºC) cuts was carried out as well as residue 530ºC. In all samples, the TAN values were obtained according to the ASTM Method D 664 Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration.

Results and Discussion

When crude oil samples are exposed to high temperatures for long period of time, the TAN peaks usually come to a lower boiling point, suggesting conversion of high molecular weight acids into lower weight acids, as shown in Figure 2.

Once more, these tests were done in CENPES, to see the degree of thermal degradation in different periods of time [(5)].

Table 1 shows the characterization by GC-MS of the fraction 123-146ºC from the oil sample that was exposed to 24.5 hours, whose TAN curve is shown in Figure 2. As can be seen, there is an evidence of many acids of low molecular mass appeared.

So, we decide to investigate real samples from a refinery. The TAN values are very similar in the oil samples 2 (1.02 mg

KOH/g), 3 (1.05 mg KOH/g) and 4 (1.08 mg KOH/g). Oil Samples 6 (1.23 mg KOH/g) and 10 (1.27 mg KOH/g) presented higher values, suggesting that acids species are being concentrated, whereas sample 6 had undergone a pre-flash tower and, as it was said before, sample 10 is an atmospheric residue.

The samples were distilled and the cuts and residues obtained. All of these products had their TAN measured. Table 2 shows the results and Figure 3 presents the TAN curves. All the oil samples exhibited the same pattern, with slight differences.

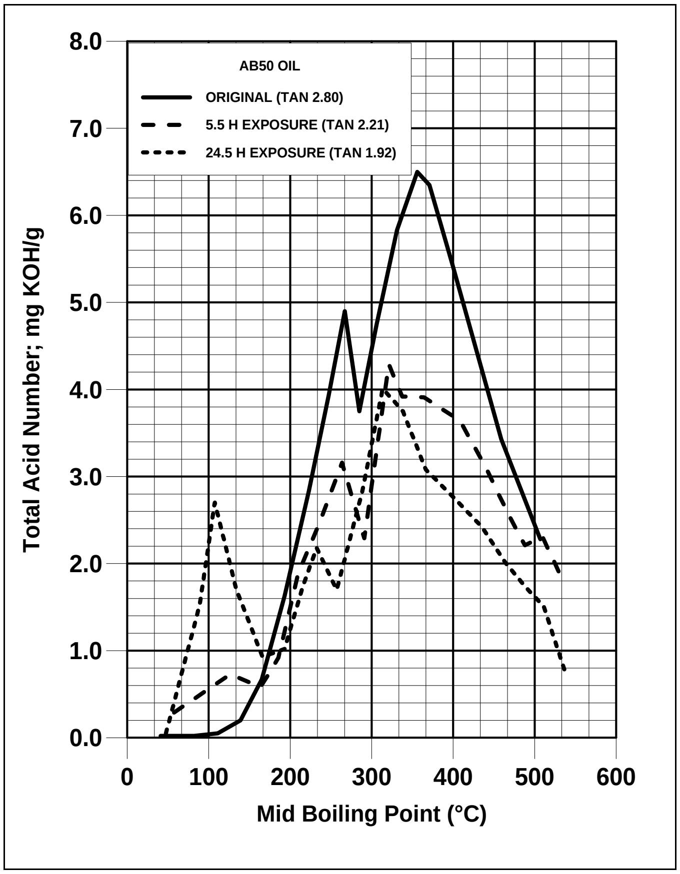

Figure 2: TAN distribution from Oil Sample AB50 and for the same sample exposed to 350ºC for 5.5 and 24.5 hours.

Table 1 – GC-MS results from AB50 oil exposed 24.5 hours

Extract from a cut from AB50 Oil 24,5H/350ºC	GC/MS Analysis
Cut 123-146ºC	Propanoic Acid, Methyl butanoic acid, Pentanoic acid, Methyl pentanoic acid, Dimethyl butanoic acid, Hexanoic acid, Methyl hexanoic acid, Heptanoic acid

TAN values are higher above 400ºC. Comparing these patterns, we do not note expressive differences, indicating that no significant thermal degradation occurred, at least the way that was detected in previous tests showed in Figure 2. We shall remember that sample 2 was collected just after desalting (process temperature nearly 160ºC) and sample 6 just before atmospheric distillation tower. So sample 6 passed through pre-heating exchangers, pre-flash oven (nearly 250ºC) and atmospheric oven (370ºC).

Based on the different thermal exposure, we decided to measure NAN in the fractions (when possible) from sample 2 and 6. Table 3 show de values and Figure 4 exhibits the TAN and NAN profiles these two samples.

We can see that the naphthenic acid contribution for TAN values in sample 6 is greater than in sample 2, mainly above 400ºC (752ºF). We can suppose that some others components that are interfering in ASTM D 664 method measures, were thermal degraded or evaporate in the pre-flash and/or atmospheric systems.

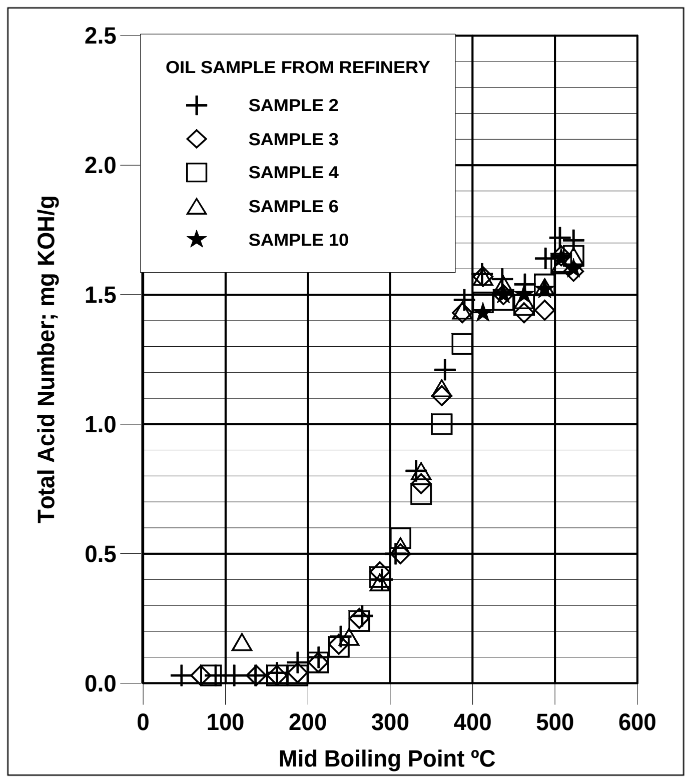

Figure 3 – TAN distribution of refinery samples

We also compared the TAN distribution from sample 2 and the refinery products. The results from the laboratory are similar to the results from the refinery. Table 4 shows the TAN results from the refinery products (TAN Refinery) and calculated in laboratory (TAN Laboratory).

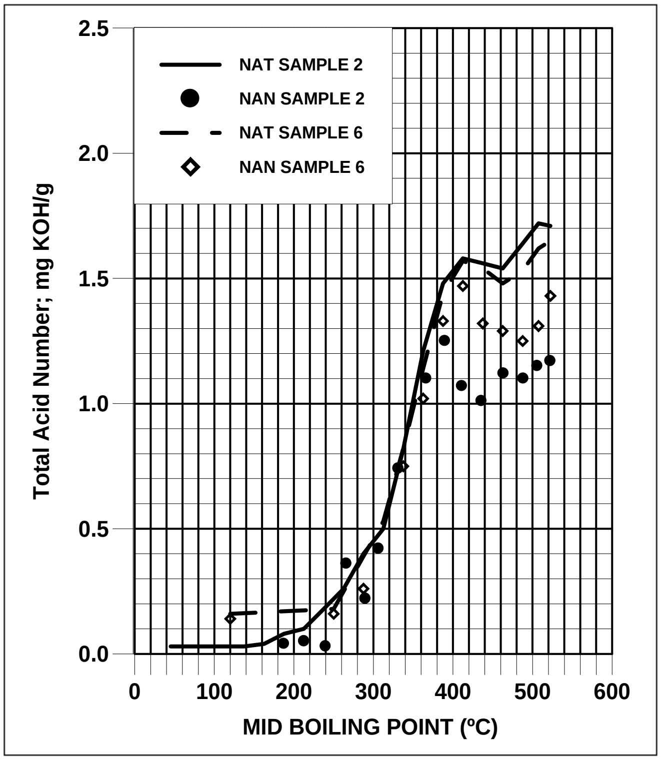

Figure IV – TAN and NAN distribution from samples 2 and 6.

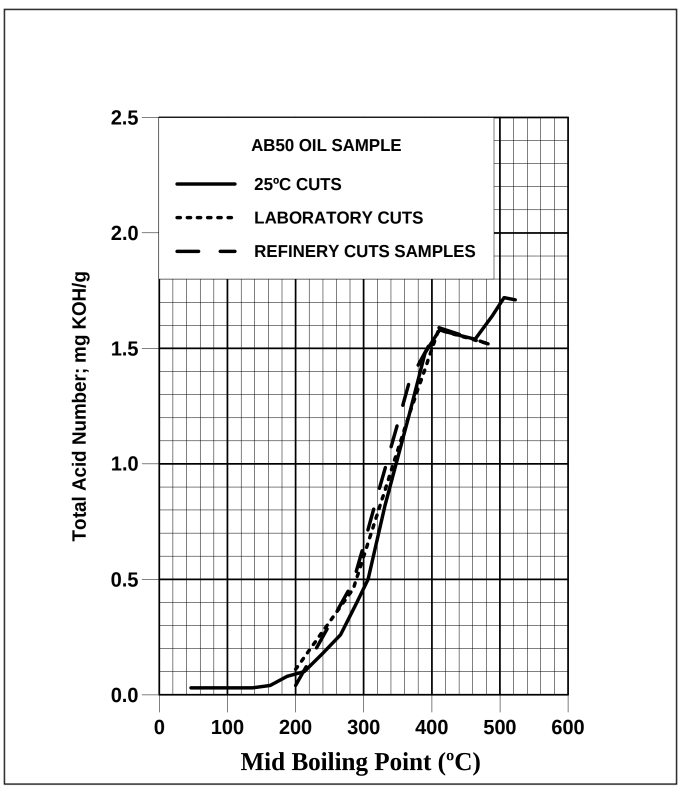

Figure V – Acids distribution curve from refinery and laboratory cuts

Table IV – Tan results for cuts from the refinery and from laboratory

	Refinery Cuts Temperature (ºC)	TAN (mg KOH/g) Laboratory	TAN (mg KOH/g) Refinery
Petroleum	--------------	1,02	1,02
Kerosene	160-240	0,11	0,04
Light diesel	240-330	0,46	0,49
Heavy diesel	330-405	1,22	1,36
LGO	405-415	1,58	1,59
HGO	415-550	1,52	1,52

The TAN Laboratory is based in the refinery products temperature range and TAN curve from sample 2, showed in Table 2. The full line shows the TAN values from the cuts obtained in ASTM D 2892 and ASTM D 5236 methods. These results are in Table 2. The dot line shows the TAN values from the cuts calculated in the laboratory, based on the refinery cuts temperatures. Finally, the dash line exhibits the TAN values from the refinery samples. The results agree very well. So we can conclude that the laboratory processes are representing the industrial process. The possible thermal degradation, if occurred, happened in the same intensity in both cases.

Conclusion

The refinery samples showed the same TAN distribution profiles. These profiles do not indicate any significant thermal degradation from acids of high molecular mass to low molecular mass, as we saw in previous long time tests.

There is a great contribution of naphthenic acids in TAN measures in samples 2 and 6.

When we compared the laboratory cuts results with the refinery cuts, the results agree very well.

References

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Table 2 – Cuts and residues TAN values and temperatures

TAN Values, mg KOH/g									
Cuts (ºC)	Sample 2	Cuts (ºC)	Sample 3	Cuts (ºC)	Sample 4	Cuts (ºC)	Sample 6	Cuts (ºC)	Sample 10
15-75	0,03								
75-100	0,03								
100-125	0,03	15-125	0,03						
125-150	0,03	125-150	0,03	15-150	0,03				
150-175	0,04	150-175	0,03	150-175	0,03				
175-200	0,08	175-200	0,04	175-200	0,03				
200-225	0,10	200-225	0,08	200-225	0,08				
225-250	0,18	225-250	0,15	225-250	0,14	15-225	0,16		
250-275	0,26	250-275	0,25	250-275	0,24	225-275	0,18		
275-300	0,40	275-300	0,43	275-300	0,41	275-307	1,24		
Residue 300	1,25	Residue 300	1,19	Residue 300	1,15	Residue 307	0,39		
300-325	0,50	300-325	0,50	300-325	0,56	307-325	0,53		
325-350	0,82	325-350	0,77	325-350	0,73	325-350	0,82		
350-375	1,21	350-375	1,11	350-375	1,00	350-375	1,14		
375-400	1,48	375-400	1,43	375-400	1,31	375-400	1,44	15-400	1,16
400-425	1,58	400-425	1,57	400-425	1,47	400-425	1,57	400-425	1,43
425-450	1,56	425-450	1,5	425-450	1,48	425-450	1,54	425-450	1,50
450-475	1,54	450-475	1,43	450-475	1,46	450-475	1,48	450-475	1,50
475-500	1,64	475-500	1,44	475-500	1,54	475-500	1,53	475-500	1,52
500-515	1,72	500-515	1,65	500-515	1,62	500-515	1,62	500-515	1,64
515-530	1,71	515-530	1,59	515-530	1,65	515-530	1,65	515-530	1,60
Residue 530	0,89	Residue 530	0,64	Residue 530	0,67	Residue 530	0,51	Residue 530	0,83

Table 3 – TAN and NAN values for samples 2 and 6

Sample 2			Sample 6		
Mid Boiling Point (ºC)	TAN (mg KOH/g)	NAN (mg KOH/g)	Mid Boiling Point (ºC)	TAN (mg KOH/g)	NAN (mg KOH/g)
46,5	0,03	-------------	120	0,16	0,14
88,0	0,03	-------------	250	0,18	0,16
110,5	0,03	-------------	287,5	0,39	0,26
136,5	0,03	-------------	312,5	0,53	____
162,5	0,04	-------------	337,5	0,82	0,75
187,5	0,08	0,04	362,5	1,14	1,02
213,0	0,10	0,05	387,5	1,44	1,33
240,0	0,18	0,03	412,5	1,57	1,47
266,0	0,26	0,36	437,5	1,54	1,32
290,0	0,40	0,22	462,5	1,48	1,29
306,5	0,50	0,42	487,5	1,53	1,25
331,5	0,82	0,74	507,5	1,62	1,31
366,5	1,21	1,10	522,5	1,65	1,43
390,0	1,48	1,25			
411,5	1,58	1,07			
436,0	1,56	1,01			
463,5	1,54	1,12			
488,5	1,64	1,10			
506,0	1,72	1,15			
522,5	1,71	1,17			