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Identification of Naphthenic Acids and Other Corrosivity-Related Characteristics in Crude Oil and Vacuum Gas Oils from a Mexican Refinery

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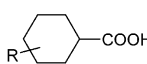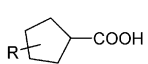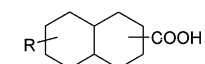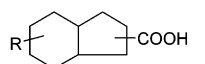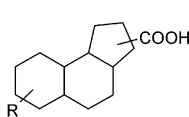
To understand the relationship between total acid number and sulfur content, relative to corrosivity, a complete characterization of these parameters along the distillation curve of a desalted crude oil was performed. Naphthenic acid identification and a complete physical and chemical characterization of crude oil, light vacuum gas oil, and heavy vacuum gas oil samples are also presented. The results found in this work show that there is a relationship between total acid number and corrosivity in the distilled fractions of a sample of desalted crude. Sulfur content is not directly related to the corrosive properties of the same fractions. In addition, negative fast atom bombardment (FAB) ionic spectrums of the crude oil, light vacuum gas oil, and heavy vacuum gas oil show that a more-complex mixture of naphthenic acids may not be directly associated to the total acid number or corrosivity.
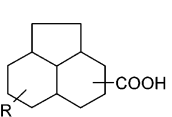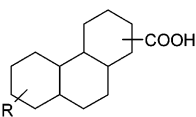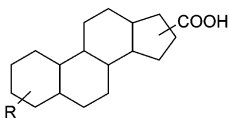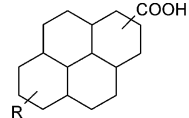
Introduction

A well-known problem in crude oil processing is corrosion associated with acidic constituents.[1] To understand the source of this corrosive behavior, it is very important to know the full range of species that may be responsible. Naphthenic acids present in crude oils found in many countries are currently considered as being part of the problem.[2–9] Table 1 is illustrative of this type of organic acids.[10] At the operating temperatures relevant to the refinement of crude oil, these acids can be corrosive and the form of attack is called "naphthenic acid corrosion". However, crude oils are complex mixtures and sulfur species and chlorides may be present, which can influence the nature and extent of the corrosion in different ways.[8]

Hydrolysis of the chloride salts contained in the crude releases hydrogen chloride, which causes chloride corrosion.[11] Calcium chloride and magnesium chloride contribute significantly to hydrogen chloride corrosion,

Table 1. Major Naphthenic Acid Types

because they are not stable thermally and hydrolytically. Hydrolysis begins at 120 °C and accelerates at

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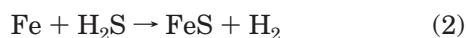(10) Fan, T. *Energy Fuels* **1991**, *5*, 371.

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temperatures of >175 °C. Sodium chloride is stable to ~400 °C and does not contribute notably to the release of hydrogen chloride. One rule of thumb states that, to avoid corrosion problems, a recommended maximum of 1 lb of salt/1000 bbls of oil should be present in crude oil.[11]

The sulfur content in crude oils varies from 0.2 to 2.5 wt %, but it can be as high as 6 wt % in some crude oils. However, the reported total sulfur in crude oil is not a true indication of how corrosive a crude oil will be. The establishment of crude oil corrosivity is dependent on the thermal decomposition of the several organic sulfur species, as a result of the liberation of hydrogen sulfide (H_2S). This type of decomposition begins at temperatures of >230 °C, with the majority of the decomposition occurring in the range of 260−500 °C; these are conditions generally found in atmospheric and vacuum column furnaces.[10] Direct reaction of H_2S with iron forms a protective layer; however, high turbulence can shear away this film to expose new surfaces for corrosion.[4]

Naphthenic acid corrosion was observed for the first time during the distillation process of certain types of crude oils since 1920.[5] According to recent reports naphthenic acid corrosion have been found in China, India, Venezuela, Eastern Europe, Russia, and the United States.[5,7] In the past, certain difficulties were encountered in 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.[2,5,6] This type of corrosion generally is higher when the crude oil processed has a TAN of >0.3; however, experience reveals that, although such a test may be sufficient for providing an indication of whether a given crude may be corrosive, it is a poor quantitative indicator of the severity of the expected corrosion. It has been observed that the corrosive behavior of oils with fairly low TANs were comparable to others with high TANs, whereas other oils with high TANs have been observed to be less corrosive than their TANs might indicate. A Indonesian light crude[8] with a TAN value well below 0.5 mg KOH/g and a Nigerian crude with a neutralization number slightly higher than 0.3 and a sulfur content of 0.24%[5] have proved to present naphthenic acid corrosion problems. A suspected explanation for this observation is that corrosion is not caused by the total acids, but rather by a select group of acids. Slavcheva et al.[10,11] reported that significant variations in corrosivity can be obtained at the same TAN values, depending on the chemical structure of the naphthenic acids.

Naphthenic acid corrosion occurs mostly when the boiling point distillation temperature is in the range of 220−400 °C and the fluid rate is high. Sulfur content in a crude oil is an important factor in naphthenic acid corrosion, mainly because of the competition between the two types of processes (naphthenic attack and H_2S attack), according to the following reactions:[7,8]

$$Fe + 2RCOOH \rightarrow Fe(RCOO)_2 + H_2 \quad (1)$$

$$Fe + H_2S \rightarrow FeS + H_2 \quad (2)$$

$$Fe(RCOO)_2 + H_2S \rightarrow FeS + 2RCOOH \quad (3)$$

Table 2. Methods Used for the Characterization of the Samples

property	method(s)
specific gravity 60/60 °F	ASTM D-1298
API gravity (°)	ASTM D-287
salt content (lb salt/bbl oil)	ASTM-3230
bromine number (gr Br/100 g)	ASTM D-1159
acid number (mg KOH/g)	ASTM D-664, ASTM D-974
total sulfur (wt %)	ASTM D-4294
total nitrogen (wppm)	ASTM D-4629
basic nitrogen (wppm)	UOP-313
distillation curve	ASTM D-1160

Reaction 1 represents the direct attack of naphthenic acid on iron (carbon steel), whereas reaction 2 represents the corrosion by hydrogen sulfide. A highly significant difference is that, the corrosion product—iron naphthenate—is very soluble in oil, whereas iron sulfide has a tendency to form a protective film on the metal. Reaction 3 represents the case where hydrogen sulfide reacts with the soluble iron naphthenate to produce iron sulfide, which is precipitated in the oil. Note that naphthenic acid is regenerated by this reaction. To form the protective layer, crude oils must have a sulfur content of 2−3%, if this film is not removed.[5]

To develop a better understanding of the corrosion problems that are involved in processing certain types of crude oils, a fair amount of work has been conducted in regard to naphthenic acid characterization.[10,12−19] A serious problem that Mexican refineries recently have faced is the very high corrosive behavior observed during the processing of an Isthmus/Maya (90/10) crude oil blend (IMCO). The objective of this work was to obtain the TAN and the total sulfur content along the distillation curve and, using a conventional procedure that has already been described elsewhere,[10] the detailed naphthenic acid characterization and total salt content of this blend, in an attempt to relate these properties to its observed corrosive behavior. In addition, because of the high corrosivity observed in the top of the vacuum column, where the processing of this crude oil is occurring, detailed characterizations (TAN, sulfur content, salt content, type of naphthenic acid, and corrosivity) of light vacuum gas oil (LVGO) and heavy vacuum gas oil (HVGO) are also presented.

Experimental Section

The properties of the samples of a desalted crude oil and LVGO and HVGO obtained from a Mexican refinery processing a 90% Isthmus/10% Maya crude oil blend were obtained following the ASTM and UOP methods listed in Table 2. Separation of the crude oil sample in 50 °C fractions was performed in Older Shaw distillation equipment, following

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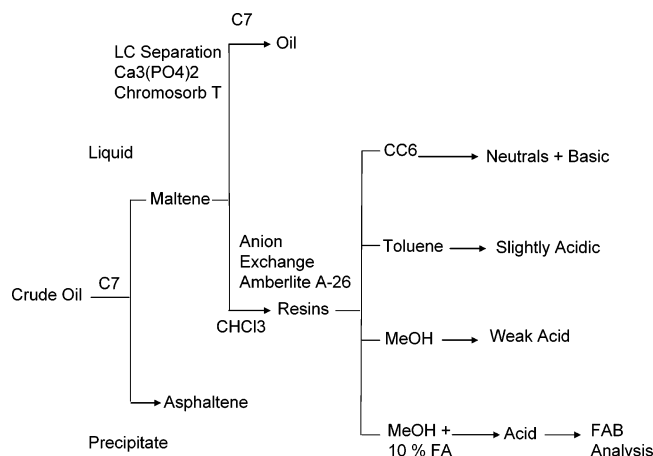
Figure 1. Sample preparation scheme for separating naphthenic acids from crude oil using preparative ion-exchange column chromatography (from ref 4).

ASTM D-2892, "Standard Test Method for Distillation of Crude Petroleum (15-Theoretical Plate Column)".

TAN values were obtained according to ASTM Methods D 664 ("Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration") and D 974 ("Standard Test Method for Acid and Base Number by Color-Indicator Titration").

The total sulfur content values were obtained according to ASTM D 4294 ("Standard Test Method for Sulfur in Petroleum and Petroleum Products by Energy-Dispersive X-Ray Fluorescence Spectrometry").

The commercial sample of naphthenic acids for mass spectroscopy (MS) evaluation was purchased from Fluka. Naphthenic acids were isolated from the desalted crude oil, LVGO, and HVGO samples, using the ion-exchange separation method that was developed by Jewell and described by Fan.[10] The resin fraction, which contained the naphthenic acids, was first isolated from the crude oil, followed by anion-exchange column separation, as shown in Figure 1. The components were eluted into four fractions, on the basis of acidity, using four solvents of increasing polarity. Naphthenic acids were observed only in the acid fraction eluted with acidic methanol.

Identification was accomplished using a JEOL model JMS-AX-505 WA mass spectrometer. The instrument was operated in negative ion mode at an acceleration voltage of 3 kV. A xenon ion beam at 20 mA (ion current) and 3 kV (kinetic energy) was used for ionization. The neat acid extract was first dissolved in toluene, in a proportion of ~1:5. One microliter of the solution was then mixed with triethanolamine (TEA) and loaded on the FAB probe. The scanning rate was 30 s per decade, from 100 to 1200 amu at a resolution of $M/D_M = 2000$. Normally, 10−20 scans were acquired and a representative spectrum was obtained by averaging 5−10 scans.

Corrosion tests were made according to NACE TM0169, Item 3003, "Laboratory Corrosion Testing of Metals for the Process Industries". The parameters followed in the tests included temperature (180 and 300 °C), time (48 h), and quiescent flow conditions and a nitrogen atmosphere (to prevent oxidation).[20] Carbon steel coupons were used (1 in. × 0.5 in. × 0.003 in.) with a total surface area of 1.1246 in^2 (7.2556 cm^2). A coupon surface/sample volume ratio of 10 cm^2/250 mL was used for all samples. The uniform corrosion rate, in millimeters per year (Mpy), is measured by weight lost in the test, after the corrosion product film has been carefully removed by bead blasting:

$$Mpy = \frac{534\Delta w}{AtD_M} \qquad (4)$$

where Δw is the weight lost (in milligrams), A the exposed

surface area of the coupon (in square inches), t the time, and D_M the metal density (in units of g/cm^2).

Following the methods developed by Craig,[20] the corrosive acid numbers (CANs), the corrosive acid percentage (CA%), and the naphthenic acid corrosion indexes (NACIs) were also calculated, using the following equations:

$$CAN = \frac{1.0048 \times Mpy}{MW_{KOH}} \qquad (5)$$

$$CA\% = \frac{100 \times CAN}{TAN} \qquad (6)$$

and

$$NACI = \frac{Mpy \times A}{W_{CP}} \qquad (7)$$

where MW_{KOH} is the molecular weight of potassium hydroxide and W_{CP} is the weight per unit area of corrosion product film (W_{CP} is determined by cleaning and drying the coupon after the test and weighing it with the corrosion product intact). The film then is removed by bead blasting and the bare coupon is reweighed. The difference in weight is used to calculate the weight of corrosion product that adheres to the metal after the test. According to Craig,[20] different NACI values are an indication of the type of corrosion presented. NACI values of 5−6 indicate corrosion by sulfidation or oxidation; NACI = 10−100 indicates moderate naphthenic attack, perhaps inhibited by sulfidation; and NACI ≥ 100 indicates severe naphthenic attack.

Results and Discussion

Physical and Chemical Characterization of the Complete Samples. Physical and chemical characterizations of the samples (IMCO, LVGO, and HVGO) are presented in Table 3. The TAN values in IMCO, LVGO, and HVGO are 0.05 mg KOH/g in all the samples tested. In all cases, TAN < 0.3; therefore, corrosion related only to this parameter could be discarded.[2−8]

The sulfur contents in IMCO, LVGO, and HVGO are 1.81%, 2.10%, and 2.07%, respectively. According to the literature, crude oils that have a sulfur content of 2−3% form a protective layer against naphthenic acid corrosion.[5] Therefore, the Isthmus/Maya blend does not seem to be protected very well.

The crude oil tested has a very high salt content (3.0 lbs of salt/1000 bbls of oil). To avoid chloride corrosion problems, this amount of salt must not be higher than the recommended value of 1 lb of salt/1000 bbls oil.[11]

Naphthenic Acid Characterization in Crude Oil, Light Vacuum Gas Oil, and Heavy Vacuum Gas Oil. The scheme for the extraction of the naphthenic acids in the samples is shown in Figure 1. The method is based on the use of an ion-exchange resin for the fractionation of the petroleum components. After the resin fraction that contains the naphthenic acids is separated, the other components are eluted into four fractions, based on acidity, using four solvents of increasing polarity. Material balances of these separations are shown in Tables 4 and 5.

Figure 2 shows the negative-ion FAB spectrum of a naphthenic acid standard mixture. The major series of carboxylic acid homologues are identified and labeled

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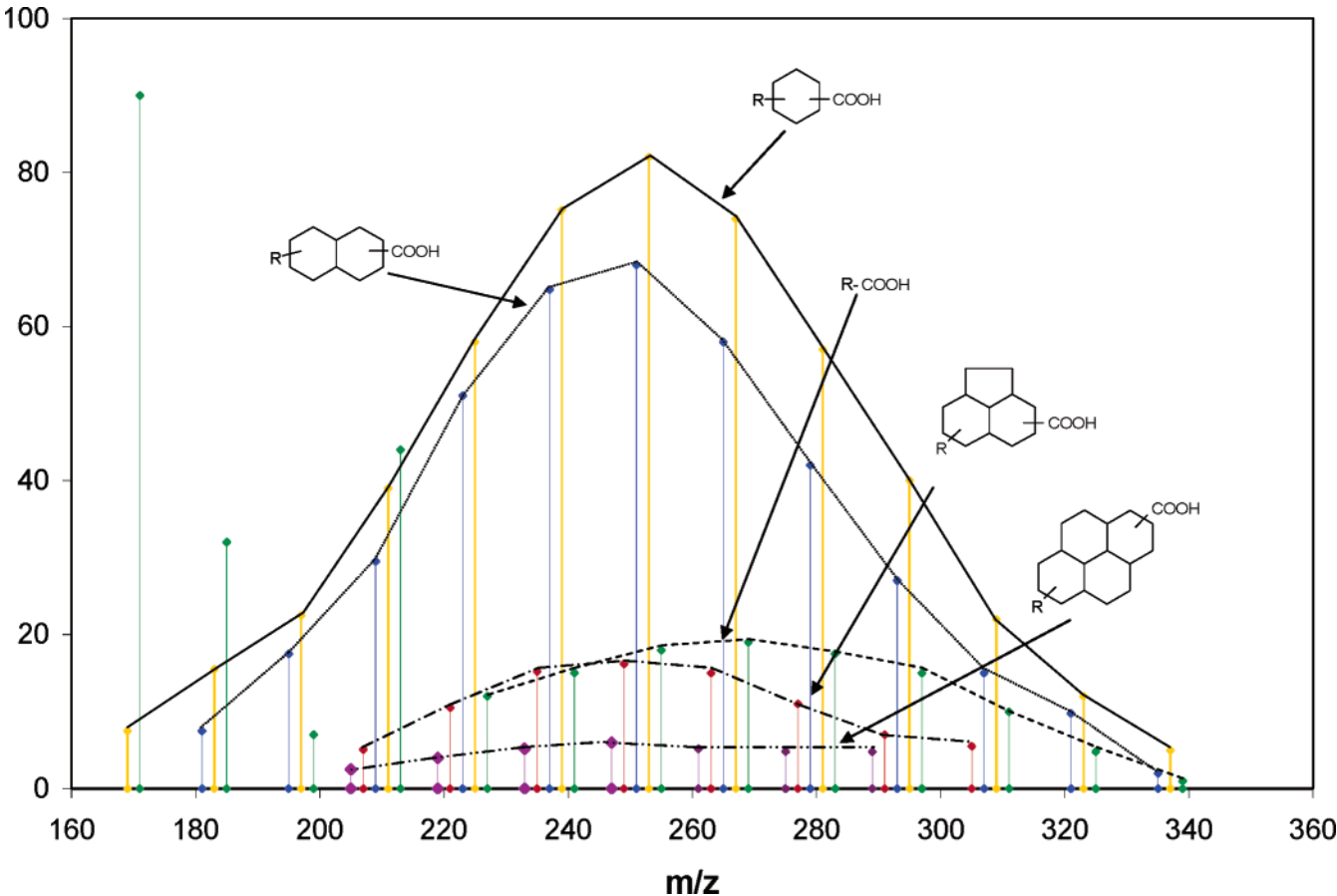
Figure 2. Negative-ion fast-ion bombardment (FAB) of a naphthenic acid standard.

Table 3. Chemical Characterization of the Desalted Crude Oil, Light Vacuum Gas Oil, and Heavy Vacuum Gas Oil

	Value		
property	desalted crude oil	light vacuum gas oil	heavy vacuum gas oil
specific gravity	0.8777	0.9123	0.9278
API gravity (°)	29.19	23.13	20.52
salt content (lb salt/bbl oil)	3.0	<0.45	<0.45
bromine number (gr Br/100 g)	8.77	6.94	9.21
acid number (mg KOH/g)	0.05	0.05	0.05
total sulfur (wt %)	1.8137	2.1008	2.0656
total nitrogen (wppm)	1435	670	1300
basic nitrogen (wppm)	342	221	343
ASTM distillation (°C)			
IBP/10	32/113	155/257	425/448
30/50	187/278	320/346	461/479
70/90	365/471	367/387	499/540
95/FBP	503/538	393/400	547/558

Table 4. Asphaltene and Maltene Contents in the Desalted Crude Oil

	Asphaltenes		Maltenes		
sample mass (g)	mass (g)	(wt %)	mass (g)	(wt %)	yield (%)
5.0	0.0144	0.4	3.6022	99.6	92.3

Table 5. Maltene Fractionation (Oil and Resin) of the Desalted Crude Oil, Light Vacuum Gas Oil (LVGO), and Heavy Vacuum Gas Oil (HVGO)

Sample		Resin		Oil		Yield
	mass (g)	mass (g)	wt %	mass (g)	wt %	yield (%)
crude	0.5070	0.3410	67.26	0.1659	32.74	100.0
LVGO	0.5212	0.4925	96.21	0.0194	3.79	98.0
HVGO	0.5421	0.4720	89.20	0.0571	10.80	97.6

in the figure. Only (M-1)⁻ ions are observed in the spectrum. Ion m/z 148 corresponds to the deprotonated molecular ion of the TEA matrix. Table 6 indicates the percentage composition of each compound found in the standard naphthenic acid sample determined by the relative abundance of each naphthenic acid ion. Only the peaks at the characteristic naphthenic acid m/z ratios had been considered. It was assumed that all z homologues have equal ionization sensitivities. The observed compound distribution correlates well with the

negative FAB spectrum of a Fluka naphthenic acid standard that has already been reported elsewhere.[10,13,14]

FAB spectra of the acidic fraction separated from the IMCO sample are shown in Figure 3. Following the same procedure already described for the standard sample of naphthenic acid, Tables 7, 8, and 9 were prepared to show the percentage composition of naphthenic acid components by z number and by carbon number.
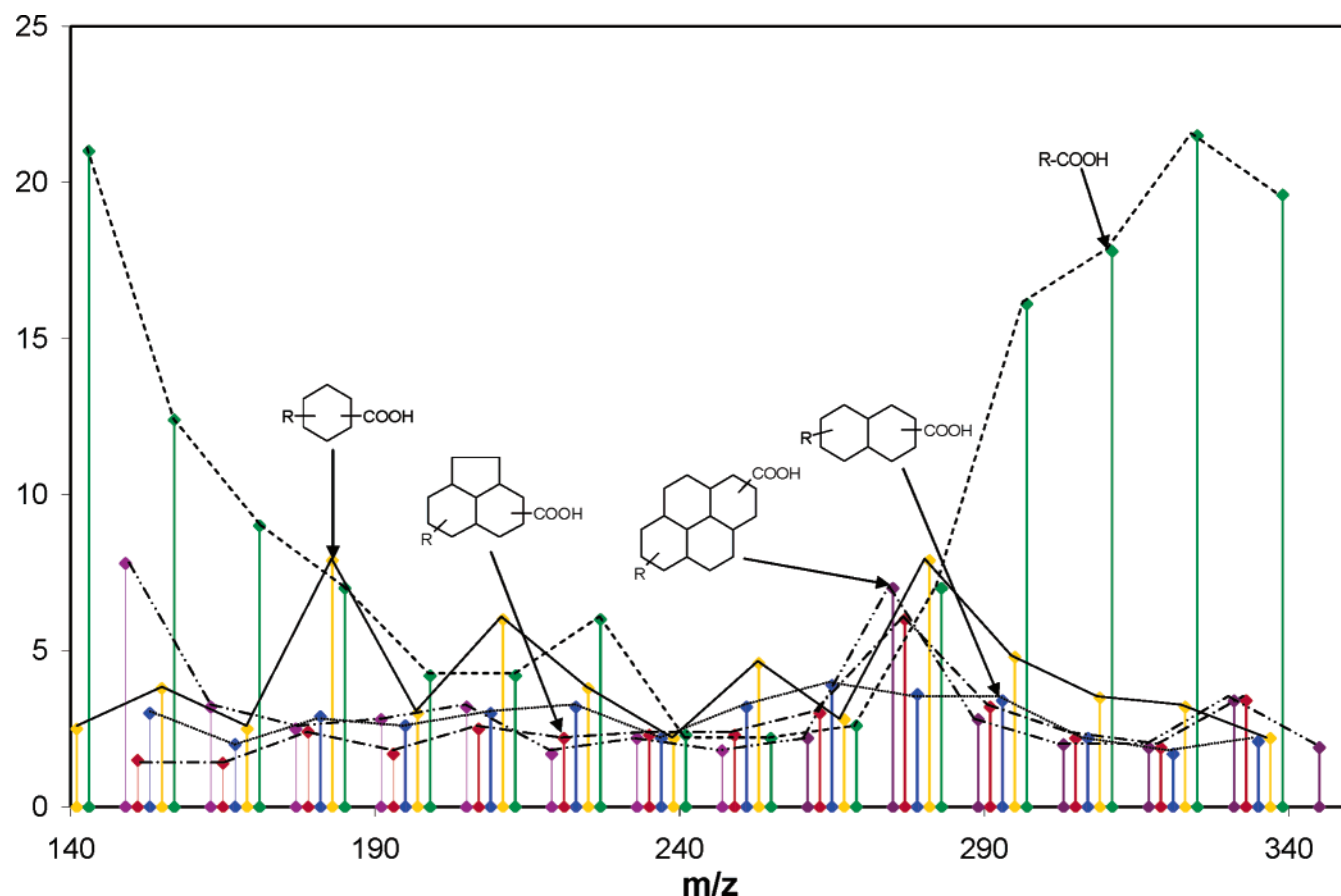
Figure 3. FAB spectrum of the acid fraction separated from a crude oil (90% Isthmus/10% Maya, IMCO).

Table 6. Percent Determination of Naphthenic Acid Components by z and Carbon Numbers Identified in the NA Standard

carbon number	Percentage of Naphthenic Acid, by z Number					percentage, by carbon number
	$z = 0$	$z = 2$	$z = 4$	$z = 6$	$z = 8$	
10	6.90	0.57				7.47
11	2.45	1.19	0.57			4.21
12	0.54	1.72	1.34			3.60
13	3.37	2.99	2.26	0.39	0.19	9.20
14	0.92	4.44	3.91	0.80	0.31	10.38
15	1.15	5.75	4.97	1.16	0.40	13.43
16	1.38	6.28	5.21	1.24	0.46	14.57
17	1.46	5.67	4.44	1.15	0.40	13.12
18	1.34	4.37	3.22	0.84	0.37	10.14
19	1.15	3.07	2.07	0.54	0.37	7.19
20	0.77	1.69	1.15	0.42		4.02
21	0.37	0.92	0.75			2.04
22	0.08	0.38	0.15			0.61
total	21.82	39.05	30.05	6.55	2.49	100.00

Table 7. Percent Determination of Naphthenic Acid Components by z Number and Carbon Number Identified in a Crude Oil (90% Isthmus/10% Maya)

carbon number	Percentage of Naphthenic Acid, by z Number					percentage, by carbon number
	$z = 0$	$z = 2$	$z = 4$	$z = 6$	$z = 8$	
8	5.89	0.70				12.62
9	3.48	1.07	6.03	0.42	2.19	7.99
10	2.52	0.70	0.84	0.39	0.90	5.08
11	1.96	2.22	0.56	0.67	0.70	6.37
12	1.18	0.84	0.81	0.48	0.79	4.01
13	1.18	1.68	0.73	0.70	0.90	5.30
14	1.68	1.07	0.84	0.62	0.48	4.74
15	0.65	0.62	0.90	0.65	0.62	3.14
16	0.62	1.29	0.62	0.65	0.50	3.96
17	0.73	0.79	0.90	0.84	0.62	4.07
18	1.96	2.22	1.09	1.68	1.96	8.84
19	4.52	1.35	1.01	0.90	0.79	8.50
20	4.99	0.98	0.95	0.62	0.56	7.77
21	6.03	0.90	0.62	0.53	0.53	8.47
22	5.50	0.62	0.48	0.95	0.95	8.61
23					0.53	0.53
total	42.89	17.03	16.97	10.10	13.02	100.00

The naphthenic acid distribution in the IMCO is quite simple (see Figure 3 and Table 7). The FAB spectrum is dominated (43%) by aliphatic carboxylic acid ($z = 0$). Note that these signals are primarily located at both edges of the spectrum, presenting signals at *m/z* 143 ($C_8H_{16}O_2$) and *m/z* 157 ($C_9H_{18}O_2$) for the low-molecular-weight compounds and *m/z* 283 ($C_{18}H_{36}O_2$), *m/z* 297 ($C_{19}H_{38}O_2$), *m/z* 311 ($C_{20}H_{40}O_2$), *m/z* 325 ($C_{21}H_{42}O_2$), and *m/z* 339 ($C_{22}H_{44}O_2$) for the high-molecular-weight derivatives. In the FAB spectrum, only small proportions of the $z = -2$, $z = -4$, $z = -6$, and $z = -8$ type compounds are observed.

According to Figure 4 (and Table 8), the most pronounced signals for the LVGO sample are those associ-

ated with the $z = 0$ species (31%). Signals at *m/z* 185 ($C_{11}H_2O_2$), *m/z* 255 ($C_{16}H_{32}O_2$), and *m/z* 297 ($C_{19}H_{38}O_2$) are the most important. Other signals at C11 (*m/z* 183) and C18 (*m/z* 275), which belong to $z = -2$ and $z = -8$ type compounds, are observed. Even distributions (C10−C20) of the $z = -2$ (21%), $z = -4$ (14%), $z = -6$ (16%), and $z = -8$ (18%) naphthenic acids are present.

The naphthenic acid distribution in the HVGO is more complicated (see Figure 5 and Table 9). In the FAB spectrum, signals for the $z = -2$ type compounds are the most prominent (29%), followed by the $z = 0$ (25%) and the $z = -4$ (23%) type compounds. Note that, in
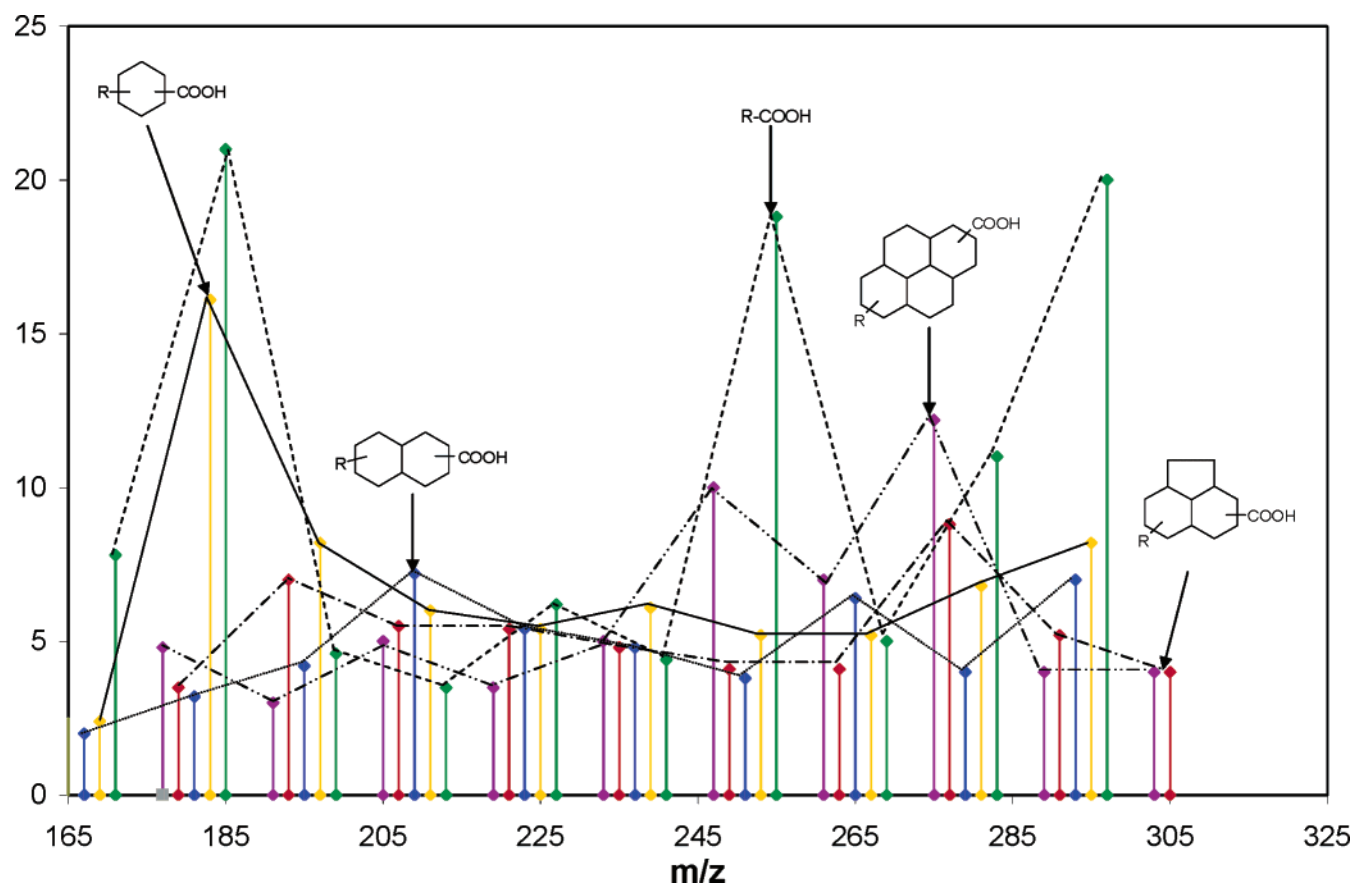
Figure 4. FAB spectrum of the acid fraction separated from a light vacuum gas oil (LVGO).
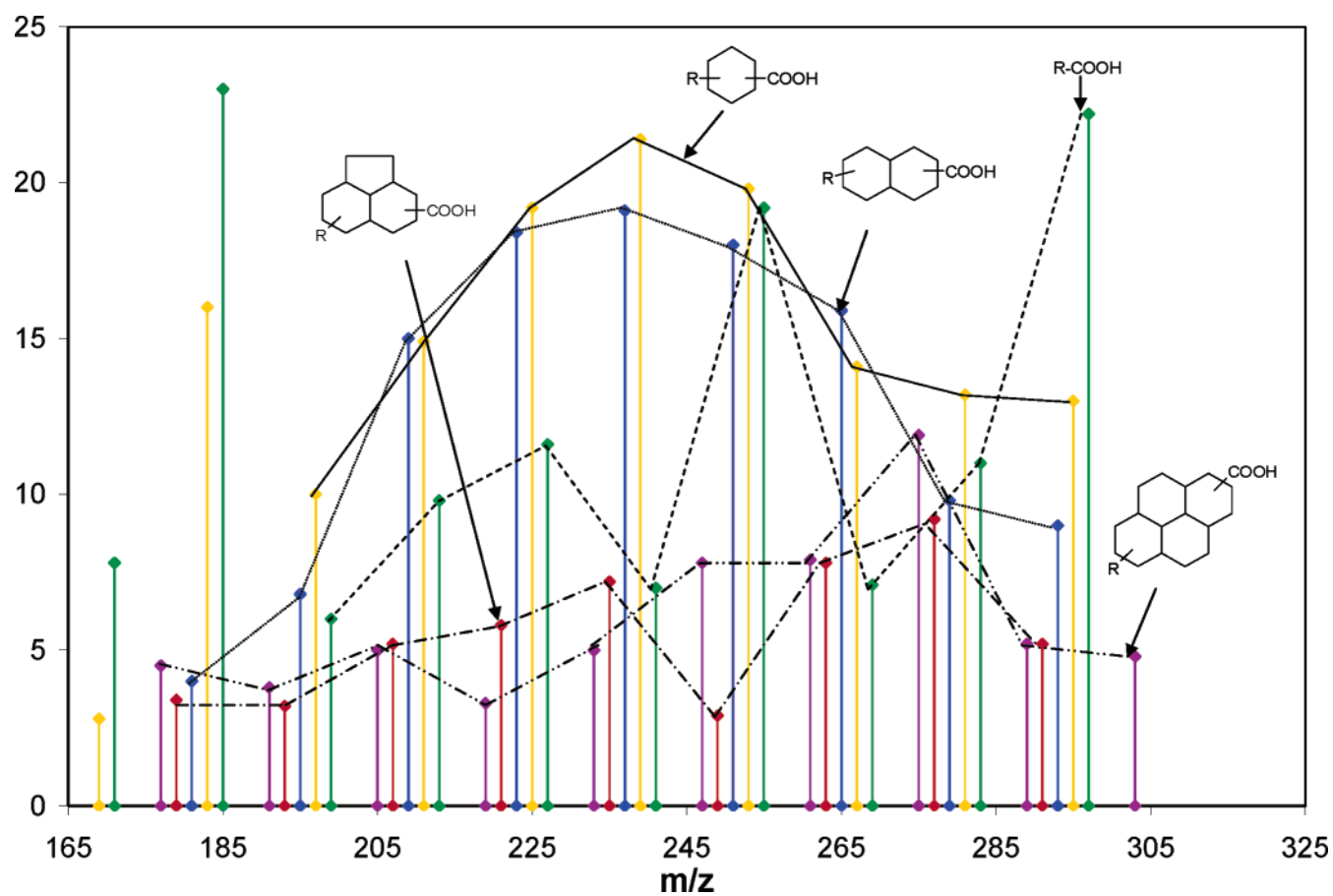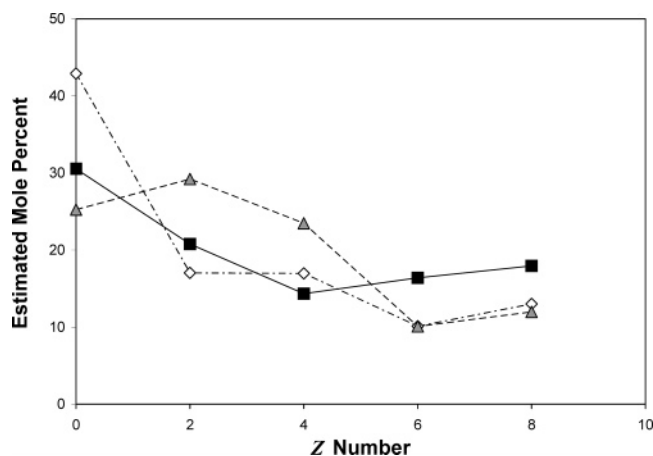

Figure 5. FAB spectrum of the acid fraction separated from a heavy vacuum gas oil (HVGO).

Figure 6. Comparison between the estimated mole percent and the z number in ($\diamond$) the Isthmus/Maya crude oil (IMCO), ($\blacksquare$) LVGO, and ($\blacktriangle$) HVGO.

Table 8. Percent Determination of Naphthenic Acid Components by z Number and Carbon Number Identified in a Light Vacuum Gas Oil (HVGO)

carbon number	Percentage of Naphthenic Acid, by z Number					percentage, by carbon number
	$z = 0$	$z = 2$	$z = 4$	$z = 6$	$z = 8$	
10	2.33	0.72	0.60	0.75	0.48	4.87
11	6.27	4.81	0.96	1.05	1.43	14.51
12	1.37	2.45	1.25	2.09	0.90	8.06
13	1.05	1.79	2.15	1.64	1.49	8.12
14	1.85	1.61	1.61	1.61	1.05	7.73
15	1.31	1.82	1.43	1.43	1.49	7.49
16	5.61	1.55	1.13	1.22	2.99	12.51
17	1.49	1.55	1.91	1.22	2.09	8.27
18	3.28	2.03	1.19	2.63	3.64	12.78
19	5.97	2.45	2.09	1.55	1.19	13.26
20				1.19	1.19	2.39
total	30.55	20.78	14.33	16.39	17.95	100.00

Table 9. Percent Determination of Naphthenic Acid Components by z Number and Carbon Number Identified in a Heavy Vacuum Gas Oil (LVGO)

carbon number	Percentage of Naphthenic Acid, by z Number					percentage, by carbon number
	$z = 0$	$z = 2$	$z = 4$	$z = 6$	$z = 8$	
10	1.58	0.57				2.14
11	4.65	3.24	0.81	0.69	0.91	10.30
12	1.21	2.02	1.38	0.65	0.77	6.03
13	1.98	3.01	3.04	1.05	1.01	10.10
14	2.35	3.89	3.72	1.17	0.67	11.80
15	1.42	4.33	3.86	1.46	1.01	12.08
16	3.89	4.01	3.64	0.59	1.58	13.70
17	1.44	2.85	3.22	1.58	1.60	10.68
18	2.23	2.67	1.98	1.86	2.41	11.15
19	4.49	2.63	1.82	1.05	1.05	11.05
20					0.97	0.97
total	25.23	29.22	23.47	10.10	11.98	100.00

this spectrum, the most important signals are located at the center of the spectrum, presenting a peak at C15, $m/z = 239$ (belonging to $C_{15}H_{28}O_2$ naphthenic acid) ($z = -2$) and at $m/z = 237$ (from $C_{15}H_{26}O_2$ naphthenic acid) ($z = -4$).

In Figure 6, a comparison between the z distributions versus the estimated mole percent of the desalted crude oil, LVGO, and HVGO shows that naphthenic acids of the $z = 0$ type distills primarily at the LVGO fraction, whereas $z = -2$ and $z = -4$ appear at the HVGO fraction. LVGO and HVGO present similar carbon
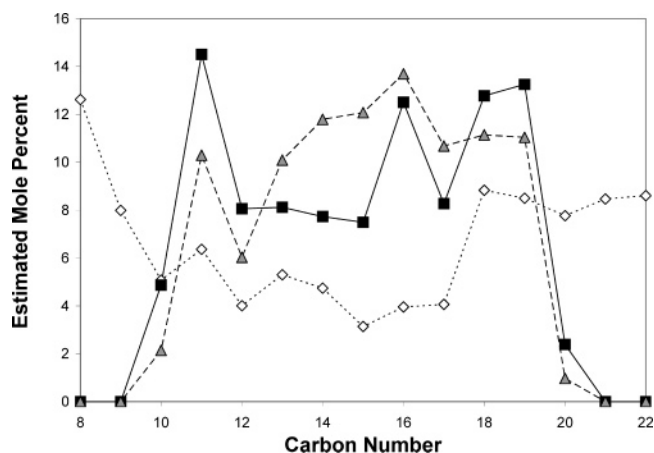
Figure 7. Comparison between the estimated mole percent and the carbon number in ($\diamond$) the Isthmus/Maya crude oil (IMCO), ($\blacksquare$) LVGO, and ($\blacktriangle$) HVGO.
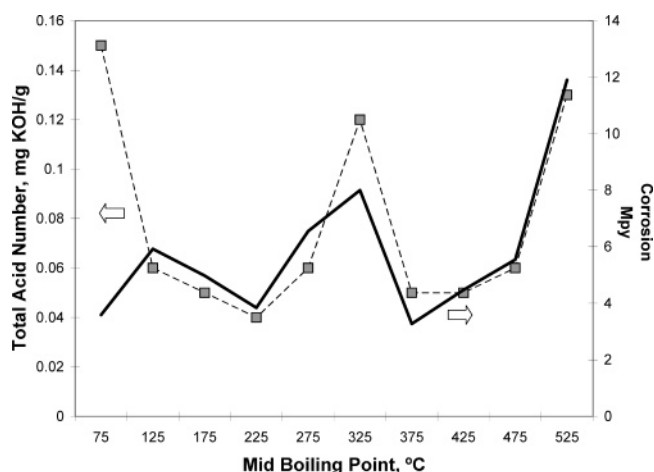
Figure 8. Total acid number (TAN) and corrosion of a crude oil (90% Isthmus/10% Maya, IMCO).

**Table 10. Characteristics of the Desalted Crude Oil and Its Distillation Fractions**

characteristic	yield (wt %)	acid number (mg KOH/g)	total sulfur (wt %)
IBP−50 °C BP range	0.67	2.84	0.53
51−100 °C BP range	4.04	0.15	0.024
101−150 °C BP range	7.52	0.06	0.043
151−200 °C BP range	8.37	0.05	0.125
201−250 °C BP range	7.82	0.04	0.321
251−300 °C BP range	8.80	0.06	0.938
301−350 °C BP range	7.14	0.12	1.454
351−400 °C BP range	8.09	0.05	1.795
401−450 °C BP range	7.82	0.05	1.819
451−500 °C BP range	6.73	0.06	2.044
501 °C−FBP BP range	4.06	0.13	2.590
residue	27.64	0.04	3.372
losses	1.30		
material balance	100.0	0.077	1.692
real value		0.05	1.8137

number distributions, versus the estimated mole percent, as shown in Figure 7.

TAN and Total Sulfur Distributions in the Desalted Crude Oil. Table 10 (Figure 8) shows that the TAN values along the distillation curve present three peaks, at mid boiling points of 75, 325, and 525 °C. The sulfur content increases as the boiling point increases (Figure 9).

Corrosion Results. Corrosion results for the complete samples of crude oil, LHGO, and HVGO are shown
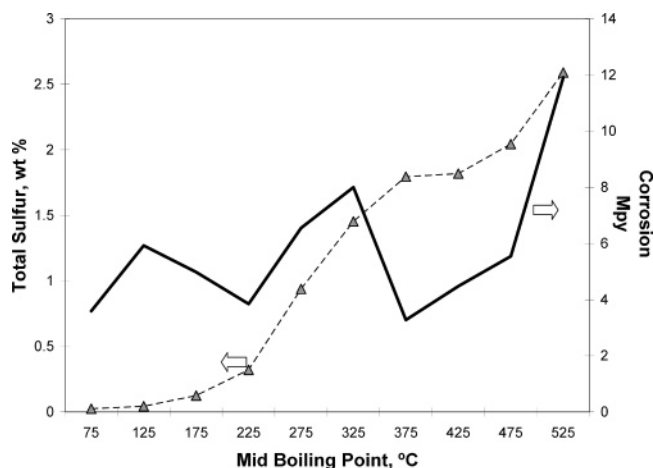
Figure 9. Percentage total sulfur and corrosion in a sample of crude oil (90% Isthmus/10% Maya, IMCO).

Table 11. Carbon Steel Corrosion of Crude Oil, Light Vacuum Gas Oil, and Heavy Vacuum Gas Oil

	corrosion (Mpy)	CAN (Mg KOH/g)	CA%	NACI (Mpy/mg/cm^2)
		180 °C		
crude oil	1.13	0.0029	5.8	N.D.
LVGO	0.8821	0.000245	0.5	N.D.
HVGO	0.8821	0.000245	0.5	N.D.
		300 °C		
crude oil	6.175	0.0156	31.2	N.D.
LVGO	8.002	0.02341	46.82	7.9
HVGO	3.024	0.00764	15.28	8.8

in Table 11. According to these results, the three samples are relatively noncorrosive at 180 °C; however, the rates become significant at 300 °C. The order of the corrosion rates of the samples at this temperature are as follows: LVGO > desalted crude > HVGO. The NACI values obtained were not high enough to correlate corrosion with moderate naphthenic acid attack, inhibited by sulfidation.[20]

Finally, corrosion results of the fractions from the distilled crude oil are presented in Table 12. A three-

Table 12. Carbon Steel Corrosion of Crude Oil and Its Fractions

temp (°C)	corrosion (Mpy)	CAN (Mg KOH/g)	CA%	NACI (Mpy/mg/cm^2)
IBP−50	3.0	0.0075	0.41	
51−100	3.591	0.009	6.06	7.24
101−150	5.923	0.015	29.7	7.22
151−200	4.978	0.012	23.84	15.05
201−250	3.843	0.0097	25.92	11.86
251−300	6.552	0.016	32.31	13.4
301−350	8.002	0.020	15.82	38.7
351−400	3.276	0.0083	16.42	13.2
401−450	4.474	0.0113	22.31	8.5
451−500	5.545	0.014	27.65	7.81
501−FBP	11.909	0.03	23.73	9.0
residue	N.D.	N.D.	N.D.	N.D.

peak distribution is observed, at 125, 325, and 525 °C. This three-peak behavior correlates well with the TAN distribution (see Figure 8) and very poorly with the sulfur content (see Figure 9). NACI values in the 151−400 °C range (for LVGO) indicate that the corrosion type was a moderate naphthenic acid attack, inhibited by sulfidation.[20]

Conclusion

According to our results, the total acid number (TAN) correlates well with the corrosivity found in a desalted crude oil from a Mexican refinery (90% Isthmus/10% Maya crude oil blend). No relation between corrosivity and sulfur content was observed. In addition, negative fast-ion bombardment (FAB) ionic spectra of the crude oil, vacuum light gas oil, and heavy vacuum gas oil samples show that a more-complex mixture of naphthenic acids may not be directly associated with the TAN or corrosivity.