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UNDER VACUUM DISTILLATION CONDITIONS

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THE INFLUENCE OF NAPHTHENIC ACID AND SULPHUR COMPOUND STRUCTURE ON GLOBAL CRUDE CORROSIVITY UNDER VACUUM DISTILLATION CONDITIONS

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ABSTRACT

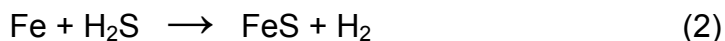
At temperatures between 220 and 400°C, naphthenic acid and sulphur-containing species present in many global crudes are known to cause refinery corrosion. Naphthenic acids are organic acids often described as cycloalkane ring(s) with an attached aliphatic chain having a terminal carboxylic acid group. Elemental sulphur, mercaptan, sulphide and polysulphide species convert to hydrogen sulphide which attacks metal. However, neither total acid contents measured by total acid number (TAN) nor total sulphur contents measured by elemental analyses have been found to correlate well with corrosivity.

A fundamental study of the relationships of molecular structures of organic acid and sulphur compounds to corrosivity has been performed in a test unit that simulates corrosion found under vacuum distillation conditions. The corrosivities of model oil mixtures consisting of specific organic acid compounds in the presence or absence of specific sulphur compounds in white oil were measured. Thermal decomposition studies of the sulphur compounds in white oil assisted with interpretation of the results. The corrosivities of global crudes including Athabasca bitumen are discussed in terms of their contents of different types of organic acid and sulphur species. This work was partially supported by the Canadian Association of Petroleum Producers and Alberta Energy Research Institute.

Keywords: refinery corrosion, naphthenic acids, sulphidic corrosion

INTRODUCTION

It is known that naphthenic (organic)¹ acids and hydrogen sulphide can work independently or together to cause corrosion in refineries at temperatures between 220 and 400°C. In particular, the following mechanisms are active:



Equation (1) describes the interaction of organic acids with iron, resulting in the formation of iron-acid complexes that are oil soluble. Equation (2) describes the interaction of hydrogen sulphide with iron, producing iron sulphides. As iron sulphides tend to be oil insoluble, they can form films on the metal and under low shear conditions can protect the metal surface from further corrosion. Finally, Equation (3) describes the interaction of hydrogen sulphide with iron-organic acid complexes where the acid is regenerated and iron sulphides are formed.

Being able to predict corrosion behavior has been difficult. Zetlmeisl *et.al.* has shown that the classical model for organic acid corrosion, that corrosivity correlates with total acid number (TAN), is inadequate for predicting refinery corrosion due to its assumption that all acid molecules are equally corrosive regardless of their composition and structure¹. Messer *et.al.* proposed that the industrial experience of Athabasca bitumen having low corrosivity, despite its high TAN values, may be explained by its content of “noncorrosive” type acids². As early as 1956, Derungs stated that the size and structure of the organic acid molecules influence corrosion rates of carbon steel³. It has been suggested that a possible explanation for this discrepancy may be found in the differences in chemical compositions and properties of the organic acids found in crude oils, including their structure, boiling point, and molecular weight⁴.

However, work in our lab suggests that sulphidic corrosion mechanisms appear to have more influence than has previously been recognized⁵. It is generally understood that the thermal stability of sulphur compounds varies significantly. In particular, alkyl sulphides are known to undergo thermolysis under relatively mild conditions:



Equation (4) shows that under thermal conditions the two carbon-sulphur bonds are broken creating two olefin hydrocarbon fragments and hydrogen sulphide. Once hydrogen sulphide is formed, it will participate in the corrosion mechanisms outlined in Equations 2 and 3. This will significantly interfere with any attempts to find simple corrosivity relationships based on organic acid contents alone.

¹ We have found that the organic acid species commonly referred to as “naphthenic” acids in crude oils consist of complex chemical structures including all types of carbon (not just naphthenic rings and paraffinic chains), reflecting the complexity of the parent oil. So we have chosen to refer to them by the more general term of “organic” acids.

This paper describes our work towards understanding the relative corrosivities of a set of global crudes including Athabasca bitumen. Previously, we have described corrosion studies of model mixtures of organic acids of known structure and size in white oil⁵. Herein we will use the information learned from the previous study together with sulphur compound thermolysis results to gain insight into the corrosion mechanisms most active for the set of global crudes under the corrosion test conditions chosen.

EXPERIMENTAL PROCEDURE

Model and crude oil descriptions

Corrosion test unit calibration runs were performed with a model oil mixture consisting of commercial naphthenic acids (CMNA) dissolved in white oil (Klearol) having a boiling point range of 225 to 520°C. The organic acids and sulphur compounds used for preparing model mixtures in white oil (Klearol, same as for the CMNA studies) were purchased from a commercial chemical company.

Two types of global crude oils are included in this study. The first type including Athabasca bitumen (ATHB) from the Underground Test Facility (UTF), and two crudes from South America (SA1 and SA2) were received as produced. The second type of crudes is currently sold on the world crude market (commercial products) and include two crudes from Alberta (AB16 and AB17) and two other non-Canadian crudes of undisclosed geographical origins (INT22 and INT30). AB16, AB17 and INT22 were topped to 204°C using the American Society for Testing and Materials (ASTM) method D86⁶ before corrosion testing.

Naphthenic acids, referred to as organic acids in this paper, were quantitatively extracted from the crude oils using QAE Sephadex A-25 acid ion exchange resin according to the ion-exchange separation method developed by Jewell and described by Fan⁷. The extracted organic acids from each crude oil were dissolved in the white oil described above for corrosion testing.

Analytical methods

The densities of the crudes were measured on a helium pycnometer (Micromeritics 1320) using ASTM D2320. Elemental (CHNSO) analyses of the petroleum samples were performed on a Carlo Erba EA 1108 instrument operated using the method recommended by the manufacturer. Total acid number (TAN) was measured using the Canadian Crude Quality Technical Association (CCQTA)-modified ASTM D664⁸. High temperature simulated distillation analyses were run on an Agilent gas chromatograph using Analytical Control software (ASTM D7169).

For the thermolysis of model sulphur compounds study, elemental (CHN) analyses were determined using ASTM D5291 on a LECO CHN-1000 Analyzer. Sulphur analyses of the model oil feedstock and products by gas chromatography (HP 6890) using sulphur chemiluminescence detection (ASTM D5623).

Corrosion testing

A detailed description of the corrosion test unit and a study of the corrosion rates for specific organic acid compounds in white oil has been described previously⁵. Briefly, however, the unit is shown in Figure 1 (A). It is a vacuum distillation unit where coupons are hung either in the liquid or at 3 locations above the liquid, in the vapor phase². Vapors are kept in the system by the condenser at the top of the unit, set at a temperature of -20°C. Figure 1 (B) shows an example of data obtained with the unit where carbon steel (CS1018) coupons were exposed to varying concentrations of CMNA in white oil (TAN= 0.5 to 5mg KOH/g) where the pressure was 30kPa and the temperature was varied to obtain atmospheric equivalent temperatures of 300°C (actual 250°C), 330°C (actual 280C), and 350°C (actual 300°C). Carbon steel coupons and an AET of 300°C (30kPa and actual temperature of 250°C) was used for all other corrosion runs described in this paper. Corrosion tests for CMNA and organic acid compounds in white oil were conducted over a period of 4h while those of the crude oils and their extracted organic acids in white oil, for 24h.

Thermolysis of sulphur compounds

Nine sulphur compounds shown in Table 1 were chosen for sulphur thermolysis experiments. Model oil mixtures were prepared by dissolving the sulphur compound in white oil (0.5wt% sulphur). The thermolysis experiments were conducted in a 316 SS 1L stirred autoclave. The vessel was charged with 300 mL test sample and sealed. It was flushed with nitrogen 3 times at 200 psi (1379 kPa) and then pressure tested at 1500 psi (10342 kPa) for 1h. The pressure was adjusted to approximately 220 psi (1517 kPa) and the vent valve closed. The autoclave was heated to reaction temperature and stirred at approximately 500 rpm. The inside temperature and pressure were continuously recorded at 5s intervals and stored in Excel compatible format (CSV). At the end of the heating period, the autoclave was allowed to cool to room temperature, and then the gas was vented into a gasbag which was analyzed by gas chromatography analysis using standard refinery gas analysis procedures. The oil remaining in the autoclave was drained through a bottom port into a sample collection container. The autoclave was then washed with toluene. The weights of original sample, liquid products and washings were recorded. After evaporation of the toluene, liquid products were pooled and analyzed.

RESULTS

Model mixtures studies

The results shown in Figure 2 have been described in detail previously⁵. However, as the conclusions are very relevant to the discussion of this paper, a brief summary is the following. Figure 2 shows the influence of organic acid boiling point on the corrosion rates of carbon steel coupons at an AET of 300°C. The different organic acid compounds were dissolved in white oil (TAN= 5.0mg KOH/g). The liquid phase results in Figure 2 suggest that as the boiling point increased, the corrosion rate of the coupon immersed in the liquid

² The corrosion rate of the vapor phase coupon having the highest corrosion rate is reported.

decreased. Above 300°C, one-ring naphthenic (1-ring cycloalkane with an alkyl side chain having a terminal carboxyl group) and alkane-carboxylic acid species were more corrosive than two-ring species. For the vapor phase, the boiling point of the organic acid relative to AET was important. The AET of the unit was 300°C. Consequently, those acids whose boiling points were lower than 300°C caused significantly more vapor phase corrosion than those whose boiling points were above 300°C. In vapor phase, the one-ring naphthenic and alkane-carboxylic acid species were more corrosive than the aromatic and two-ring species.

Figure 3 shows a summary of the thermolysis studies of specific sulphur compounds dissolved in white oil. The results were obtained with a residence time of 2 hours at temperatures from 200 to 400°C. To be noted is that at temperatures as low as 200°C, hydrogen sulphide is produced by thermolysis of sulphides (where at least one methylene [CH₂] is attached to the sulphur). As temperature is increased over 300°C, other types of sulphur compounds start to decompose. Severity is determined both by temperature and residence time (for example, see Yan)⁹. This means that very long residence times at lower temperatures will obtain the same conversions to hydrogen sulphide as higher temperatures for shorter periods of time.

In Figure 4, the influence of the presence or absence of sulphur compounds on the corrosivity of CMNA in white oil is shown. The AET was 300°C but the actual temperature was 250°C. The corrosion test was conducted over a 4 hour period. Consequently, it is expected that the octyl sulphide compound should decompose significantly to form hydrogen sulphide. The second sulphur compound chosen, phenyl (also referred to as diphenyl) sulphide is expected to produce little hydrogen sulphide. When octyl sulphide was present in the CMNA-white oil mixture, the corrosion rate of the coupon immersed in the liquid was reduced relative to the control (CMNA in white oil) and there was visible evidence of iron sulphide film formation. These results demonstrate that the metal was protected by the film. When phenyl sulphide was added to the CMNA-white oil mixture, the liquid phase coupon was not protected and the corrosion rate of the vapor phase coupon was significantly greater than the control. This result suggests that having a low content of hydrogen sulphide can be worse than a high content of hydrogen sulphide because with a low content, there is enough hydrogen sulphide to regenerate the acid (i.e. Equation 3) but not enough iron sulphide formed to create a protective film.

Crude oil analyses

Corrosion tests have been performed on a set of global crudes including crudes that were received “as produced” and those which are “commercial products”. Table 2 shows the elemental, density and TAN analyses results for the oils. The “as produced” oils are Athabasca bitumen (ATHB) and two crudes from South America (SA1 and SA2). The four commercial products include two from Alberta (AB16 and AB17) and two non-Canadian crudes of undisclosed geographical origin (INT22 and INT30). This set of crudes was chosen from a larger set included in the study because of their range of sulphur contents and TAN values.

The organic acids were extracted from the crude oils for analysis and model oil studies. The yields of the organic acids from the crudes and their elemental analyses are shown in Table 3. Included as well, is the elemental analysis of CMNA.

The high temperature simulated distillation (HTSD) results for the crudes are shown in Figure 5. The graph in Figure 5A shows the HTSD plots for the “as produced” crudes while the graph in Figure 5B shows those for the commercial products. The curves for ATHB and SA2 are quite similar, as are the curves for AB17 and INT22.

Figure 6 shows the HTSD results for the organic acid samples. The HTSD results for the organic acids extracted from the “as produced” crudes, and CMNA are shown in Figure 6A while those results for the extracted organic acids from the “commercial product” crudes are shown in Figure 6B. CMNA is clearly a lower boiling material compared to all of the extracted organic acids. It is interesting that the HTSD plots for the organic acids extracted from ATHB, SA2, AB17, INT22 and INT30 are all very similar.

Corrosion studies

Figure 7 shows the corrosion rate results for the CMNA in white oil, and the crude oils. AB16, AB17 and INT22 were topped at 204°C prior to corrosion testing. This was done to minimize effects from light ends volatility on the heat management for the corrosion test unit. The TAN values shown are those of the oils tested (whole crude or topped). The sulphur contents shown were those of the whole crudes.

The organic acids extracted from the whole crude oils were mixed with white oil at their yield ratios. The TAN values for the reconstituted oils were similar or slightly lower than the original crudes. Corrosion testing of the reconstituted oils were performed under the same conditions as for the crudes shown in Figure 7 and are shown in Figure 8. The differences between the corrosion rate results for the organic acids in white oil (Figure 8) and the crudes tested (Figure 7) are shown in Figure 9.

DISCUSSION

Organic acid contributions to crude corrosivity

The graph of corrosion rates as a function of TAN value for CMNA in white oil shown in Figure 1B supports the industry assumption that corrosion rates increase as TAN value increases. This is expected when the concentrations of the same organic acids are increased. But this trend is not supported when corrosion rates of organic acids having different structures are measured. For example, the TAN values for the specific organic acids in white oil in Figure 2 were all the same (TAN=5.00mg KOH/g), however the corrosion rates varied significantly. In Dettman *et.al.*⁵, structure was found to be very important for determining the corrosivity of compounds with similar molecular weights³. However, organic acid structure determines its boiling point. When the corrosion rates are presented with respect to boiling points (Figure 2), organic acids that boil above 300°C appear to be significantly less corrosive in both liquid and vapor phases than those that boil below 300°C. Inspection of the HTSD results in Figure 6A shows that approximately one-half of the organic acids in CMNA have boiling points below 300°C. In contrast, only a few weight percent of the acids isolated from the crudes boil below

³ There was a mistake in Dettman *et.al.* (5). In Table 1, the molecular weight of 1,2,3,4-tetrahydro-2-naphthoic acid was reported as 148.20g/mole and should be 176.21g/mole. This changes its position in Figure 3 to be between 1-naphthoic acid and stearic acid.

300°C (Figure 6A and B). It would follow then that the CMNA in white oil should have a relatively high liquid phase corrosion rate compared to the corrosion rates of the crude oils, regardless of their TAN values.

Figure 7 shows that the liquid phase corrosion rate of CMNA in white oil (TAN= 3.00mg KOH/g) is more than 6 times greater than that of the next highest corrosion rate, that of SA2 (TAN= 3.22mg KOH/g). The liquid phase corrosion rates of most of the crudes are very low including the Alberta crudes (ATHB, AB16 and AB17), SA1 and INT22. The liquid phase corrosion rates appear to be higher for SA2 and INT30 which do have higher TAN values. However ATHB has the second highest TAN value but has a lower liquid corrosion rate than SA1 which has the lowest TAN value.

Evidently, as proposed, TAN values do not explain the liquid phase corrosion results of the crudes. While the content of lower boiling organic acids explains why CMNA in white oil has the highest liquid phase corrosion rate, this does not explain why the liquid corrosion rates of SA2 and INT30 are slightly higher than those of the other crudes. The corrosion results for the model compounds in Figure 2 suggest that 1-ring and chain acid species are more corrosive than 2-ring acid species. It is possible that the low boiling organic acids in SA2 and INT30 contain higher contents of 1-ring and chain acid species than the other crudes.

With regards to vapor phase corrosion, the results are even more complex. As with the liquid phase results, the graph in Figure 1B shows that vapor phase corrosion rates increase as TAN values increase, when the contents of the same organic acids increase. Figure 2 suggests that the AET of the corrosion test unit is a “cutoff” temperature for vapor phase corrosion. Only those organic acids whose boiling points are close to or below the AET are able to have enough acid in vapor phase to condense on the vapor phase coupons. Alkane carboxylic (chain) and 1-ring cycloalkane (naphthenic) acids are significantly more corrosive than aromatic and multiple ring acids. The HTSD plot for CMNA in Figure 6A shows that one-half of the organic acids in CMNA have boiling points below the corrosion test AET of 300°C. The HTSD plots in Figure 6A and B for the organic acids isolated from the crude oils show that only 5wt% or less of their organic acids have boiling points in the range of 300°C. Consequently, CMNA in white oil is expected to have the greatest rate of vapor phase corrosion. Figure 7 shows that this is true except for AB16, suggesting that there is another corrosive agent other than organic acids present in this crude.

Sulphidic corrosion contributions to crude corrosivity

A second possible participant in high temperature corrosion is hydrogen sulphide. The graph in Figure 3 shows that thermolysis of sulphur attached to CH₂ groups in the crudes (i.e. Equation 4) is likely to occur during the conditions of the corrosion tests (AET 300, but actual temperature 250°C, for 24 hours). As shown by Equations 2 and 3, hydrogen sulphide would interact with the metal to form iron sulphides, which may form a film to protect the metal. As well, the hydrogen sulphide would regenerate organic acids. Figure 4 shows that a small quantity of hydrogen sulphide can be worse than a large quantity of hydrogen sulphide under the low shear conditions of the corrosion test unit used in these studies. Hydrogen sulphide would be volatile under the corrosion test conditions chosen but would be constantly removed

from the system by the vacuum as the condenser temperature (-20°C) was set above the boiling point of hydrogen sulphide.

To assess the contribution of the oil matrix to corrosion, the corrosion rates of the extracted organic acids dissolved in white oil were measured. Figure 8 shows the corrosion rates of the organic acids in white oil. In Figure 9, the differences between corrosion rates of the organic acids in white oil and that of the crudes are shown. Positive values show that the extracted organic acids in white oil are more corrosive than the original crude, suggesting that some component of the crude matrix is protecting the metal during the crude corrosion tests. Negative values show that the crude oil was more corrosive. This indicates that a corrosive agent in the oil matrix has been removed by replacing the matrix with white oil. If the corrosion rates for the organic acids in white oil are the same as those for the crude, the oil matrix does not contribute to the corrosion. This is illustrated by the difference of "0.0" for CMNA in white oil in Figure 9.

For liquid phase corrosion, the corrosion rates of the organic acids in white oil were greater than those of the crudes. This suggests that there was a little (INT22) to a lot (INT30) of protection of the coupon by the oil matrix. It is likely that iron sulphide formation during the crude oil tests is at least partially responsible for this protection (from inspection of coupons after corrosion tests). The extracted organic acids do contain sulphur (Table 3). However, as the organic acid contents in the crudes (and white oil) range from 1 to 4.8wt% (Table 3), their hydrogen sulphide contribution does not appear to influence the experiments⁴.

The positive differences shown for the vapor phase corrosion rates SA1, SA2 and INT30 indicate that the vapor phase corrosion obtained from the crude corrosion tests is caused by the small content of organic acids boiling close to or below 300°C. That the extracted acids in white oil were more corrosive than the original oil suggests that the vapor phase coupon was partially protected by iron sulphide formation during the crude oil corrosion tests. The negative difference for AB16 shows that the volatile corrosive agent has been removed by replacing the oil matrix with white oil; the liquid and vapor phase corrosion rates of AB16 in white oil are comparable to those of AB17 (Figure 8). This is consistent with the corrosive agent in the oil matrix being hydrogen sulphide. Finally there was no change in the vapor phase corrosion rates for ATHB, AB17 and INT22 which were negligible for the crudes. The small content of organic acids that boil close to or below 300°C in these crudes appears to have low corrosivity. This suggests that there are structural differences between the low boiling (i.e. <350°C) organic acids in SA1, SA2 and INT30, and those present in the Alberta crudes (ATHB, AB16 and AB17), and INT22 where the relative contents of alkane carboxylic (chain) and 1-ring naphthenic acids would be important. These species would be the α - (bad) acids suggested by Messer *et.al.*². Notice as well that the presence of sulphidic protection does not correlate with total sulphur contents. As thermally labile sulphur species are any sulphur atoms attached to CH₂-groups, their content is not easy to quantify but are likely to be present in higher proportions in more paraffinic oils.

⁴ The interactions between the reactions outlined in Equations 1 to 4 will depend upon as yet unknown ratios of reactants.

CONCLUSIONS

Organic acid and sulphidic contributions to crude corrosivity

The results of this study demonstrate that TAN values of crudes do not predict their corrosivity. Crude corrosivity appears to be determined by two factors: the structural nature of the lowest boiling organic acid species in the crude (i.e. <350°C, even if their contents are less than 5 wt% of the organic acids in the crude); and, the content of thermally-labile sulphur species. The formation of hydrogen sulphide from the latter species results in either prevention of corrosion by film formation (in low shear conditions) or increased corrosion. The exact conditions for causing these behaviours are not clear at this time but are likely influenced by the thermal history of the crude. For example, thermal production methods such as steam assisted gravity drainage (SAGD) would crack the most labile sulphur species in the crudes generating hydrogen sulphide. The consequences of this hydrogen sulphide would have immediate impacts at the well site, but should reduce the content of the most labile sulphur species in the oil before reaching the refinery/upgrader. It is not clear whether this would make thermally produced crude more or less corrosive than cold production or mined crude, as it was found that “a little” hydrogen sulphide can be worse than “a lot” of hydrogen sulphide in low shear conditions.

Implications of results on industry practice

Several questions are raised by this work. Since it is clear that TAN does not correlate with crude corrosivity, would it be appropriate to reassess crude pricing formulae that are based on TAN measurements? As well, crude corrosivity will be influenced by its thermal history. More work is needed to understand when corrosivity is enhanced. (i.e. How do the contents of low-boiling 1-ring naphthenic and alkane-carboxylic acids relative to the total acid content, and the contents of thermally-labile sulphur species work together to increase or decrease crude corrosivity?) This last question leads to the following. The usual approach to problem crudes is to blend them with “good” crudes to mitigate problems. The white oil results suggest that with regards to corrosion, blending corrosive crudes with “good” (low TAN and low sulphur content) crude may actually make matters worse due to reducing the content of thermally-labile sulphur and so losing the protection of iron sulphide film formation.

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TABLE 1:
SULPHUR COMPOUNDS USED IN THERMOLYSIS STUDY

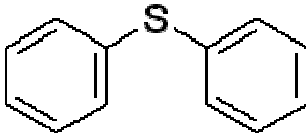
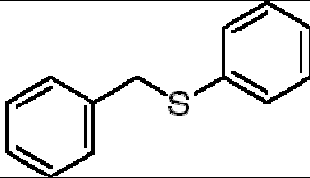
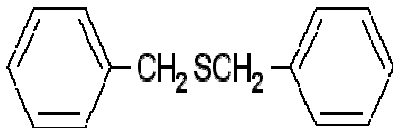
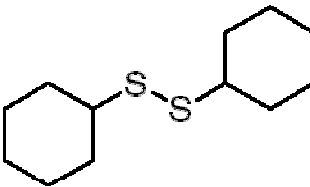
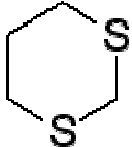
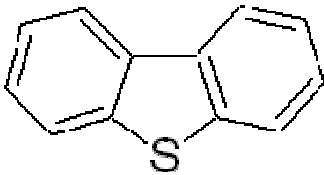
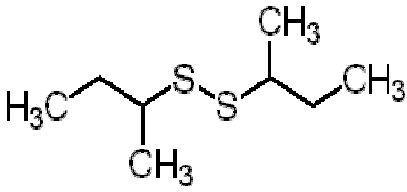
Name	MW	Structure
Octyl sulphide	258.51	$\text{CH}_3(\text{CH}_2)_6\text{CH}_2\text{SCH}_2(\text{CH}_2)_6\text{CH}_3$
Dodecyl sulphide	370.72	$\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{SCH}_2(\text{CH}_2)_{10}\text{CH}_3$
Diphenyl sulphide	186.27	
Benzyl phenyl sulphide	200.30	
Benzyl sulphide	214.33	
Dicyclohexyl disulphide	230.43	
1,3-Dithiane	120.24	
Dibenzothiophene	184.26	
Sec-Butyl disulphide	178.36	

TABLE 2:
ELEMENTAL, DENSITY AND TAN ANALYSES RESULTS FOR CRUDES

Crude Oil	Elemental					Density (g/mL)	TAN (mg KOH/g)
	C	H	N	S	O		
ATHB	83.07	10.51	0.52	4.77	1.14	1.0100	3.39
SA1	86.77	10.64	0.60	0.94	1.05	0.9934	0.60
SA2	83.67	10.31	0.83	3.76	1.43	1.0090	3.22
AB16	81.89	12.66	0.44	3.85	1.16	0.9304	1.04
AB17	84.75	11.70	0.25	2.51	0.79	0.9319	1.27
INT22	86.34	11.77	0.34	0.78	0.76	0.9379	2.11
INT30	86.10	12.29	0.32	0.10	1.19	0.9282	4.15

TABLE 3:
YIELD AND ELEMENTAL ANALYSIS RESULTS FOR ORGANIC ACIDS

Organic Acids	Content in Crude (wt%)	Elemental				
		C	H	N	S	O
CMNA	-	74.35	11.97	0.00	0.00	13.68
ATHB-OA	2.68	78.06	10.29	0.37	3.75	7.54
SA1-OA	0.99	81.18	9.97	0.44	0.99	7.42
SA2-OA	2.22	78.14	10.48	0.82	3.54	7.02
AB16-OA	1.11	78.80	10.15	0.57	3.72	6.76
AB17-OA	1.43	77.96	10.06	0.58	4.75	6.64
INT22-OA	2.37	81.48	10.98	0.36	0.90	6.29
INT30-OA	4.83	81.09	11.66	0.34	0.27	6.64

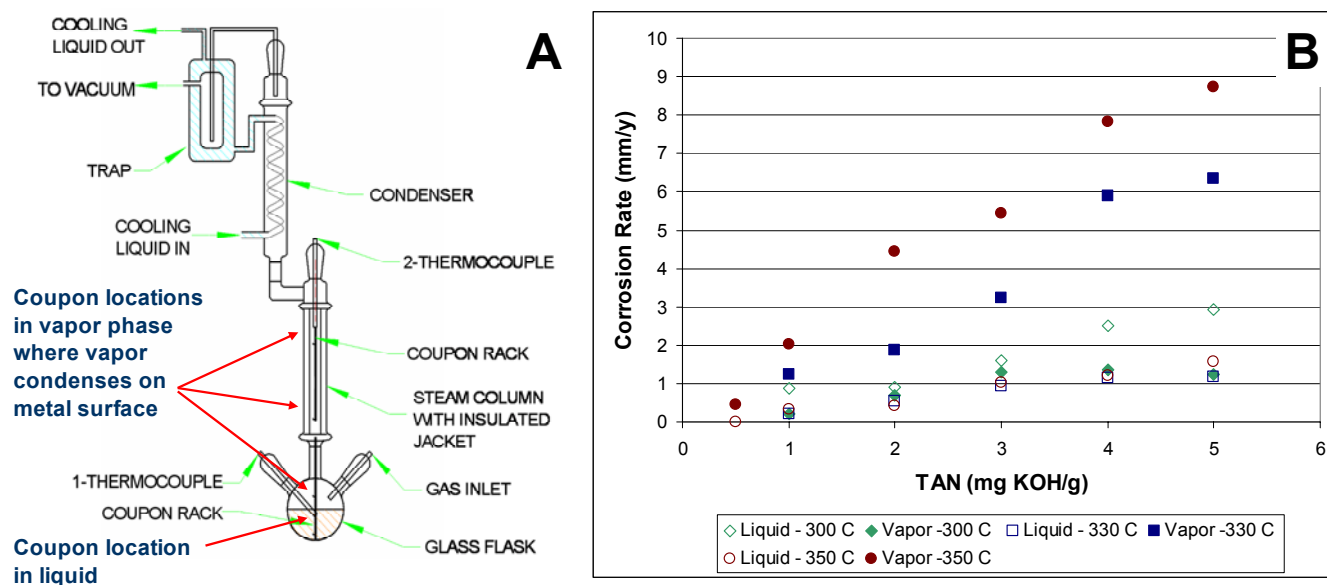


FIGURE 1 – Schematic Diagram of Corrosion Test Unit and Data Demonstrating Test Unit Performance

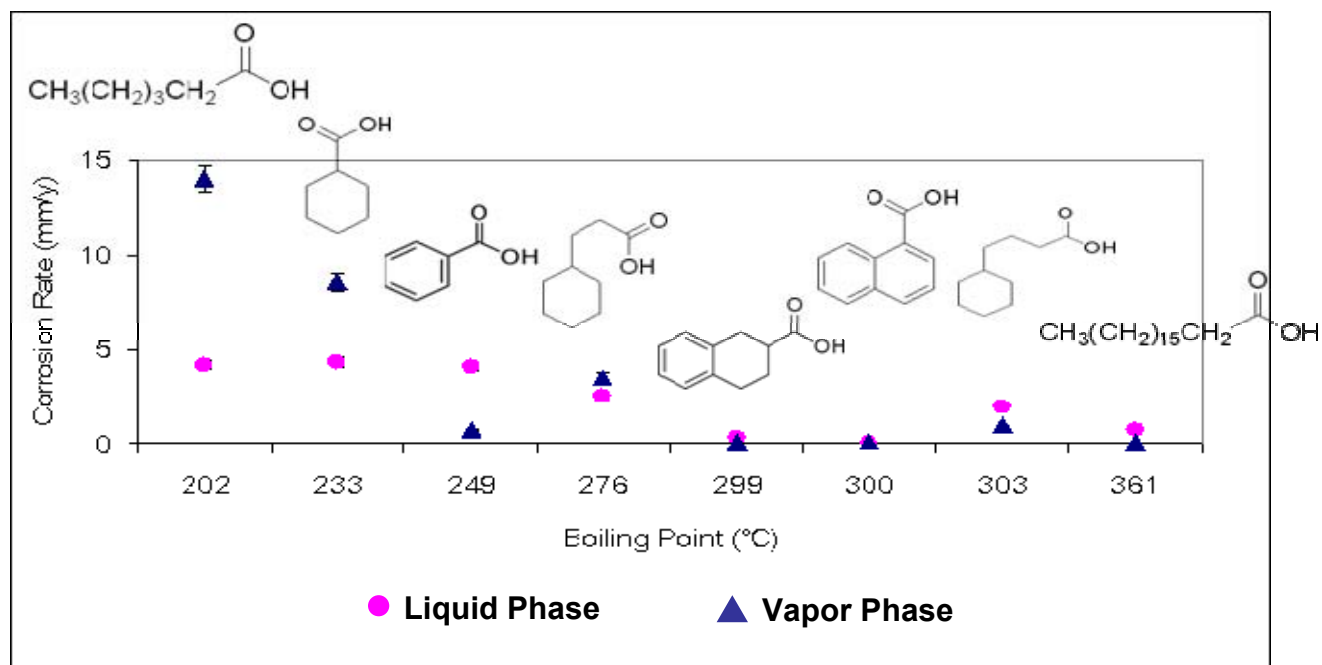


FIGURE 2 – Corrosion Rates of Carbon Steel Coupons for Model Acid Compounds in White Oil (TAN= 5.00mg KOH/g) at AET= 300°C

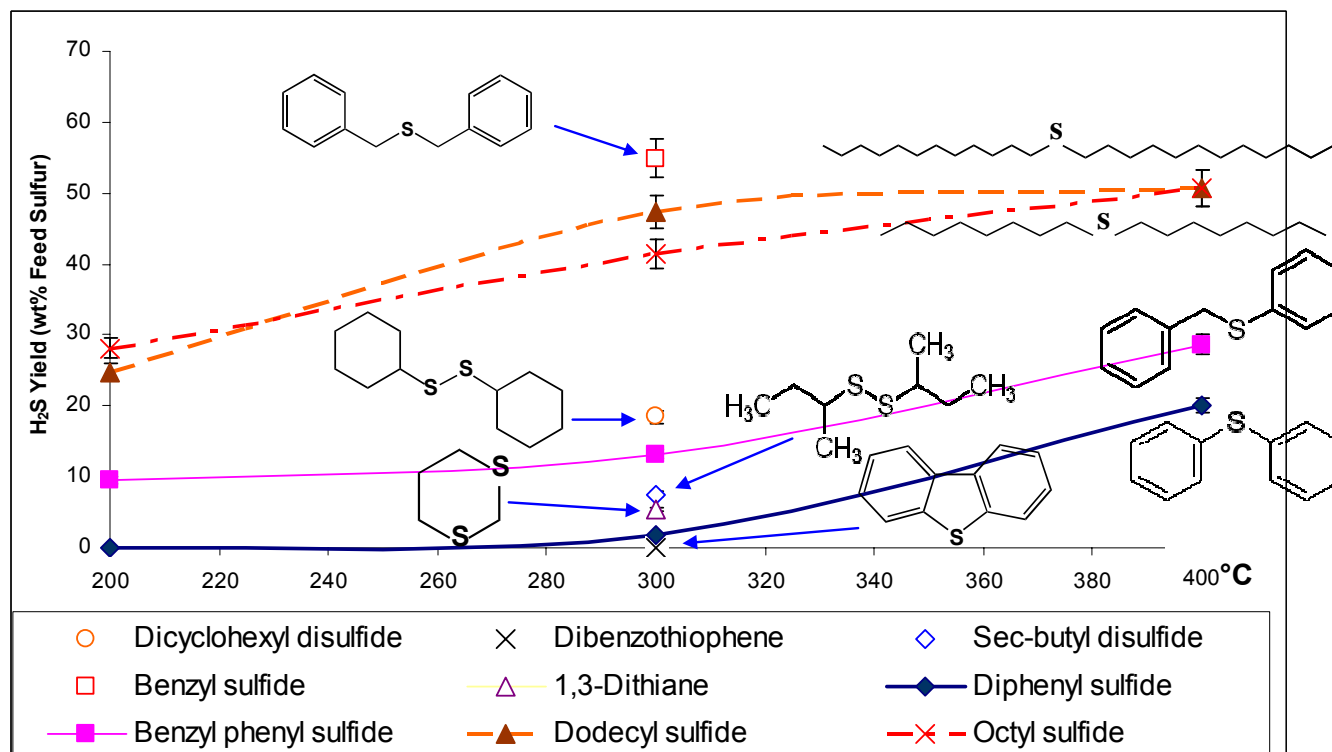


FIGURE 3 – Hydrogen Sulphide Generation from Model Sulphur Compounds in White Oil after Two Hour Residence Time at Elevated Temperatures

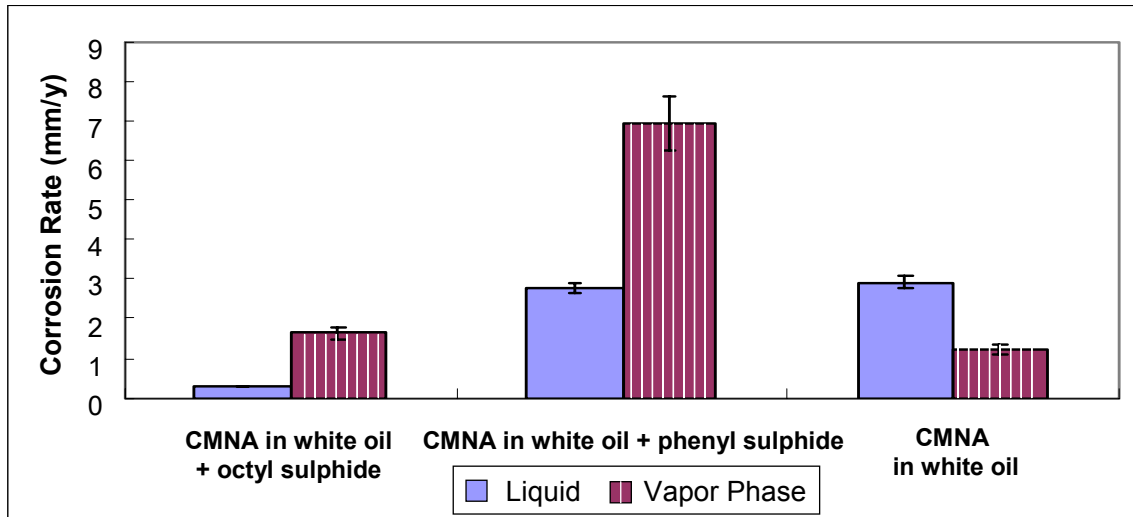


FIGURE 4 – Corrosion Rates of Carbon Steel Coupons for CMNA in White Oil (TAN= 5.00mg KOH/g) with or without Sulphur Compounds (1wt% Sulphur) at AET= 300°C

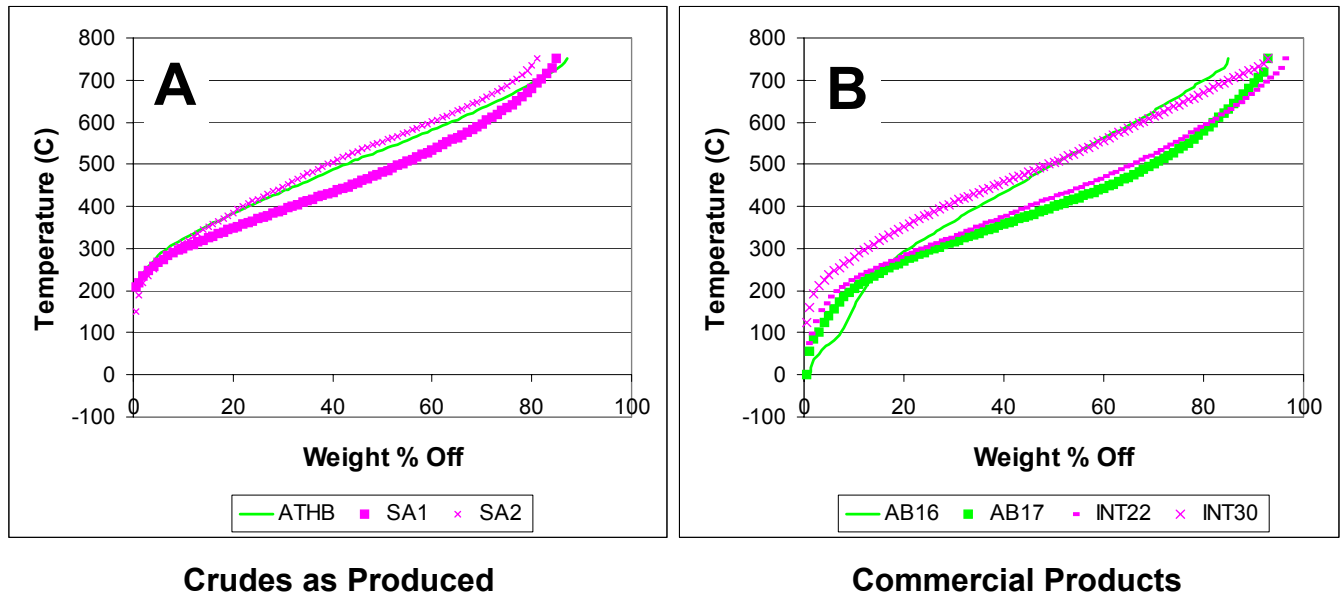


FIGURE 5 – High Temperature Simulated Distillation Results for Crude Oils

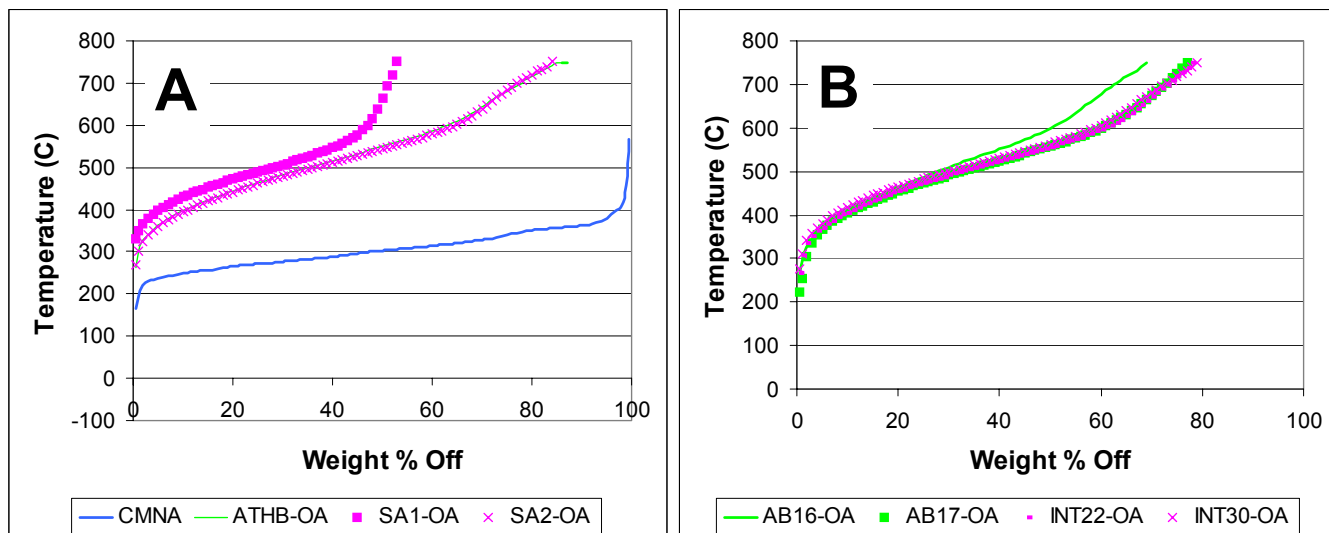


FIGURE 6 – High Temperature Simulated Distillation Results for CMNA and Organic Acids Extracted from Crudes

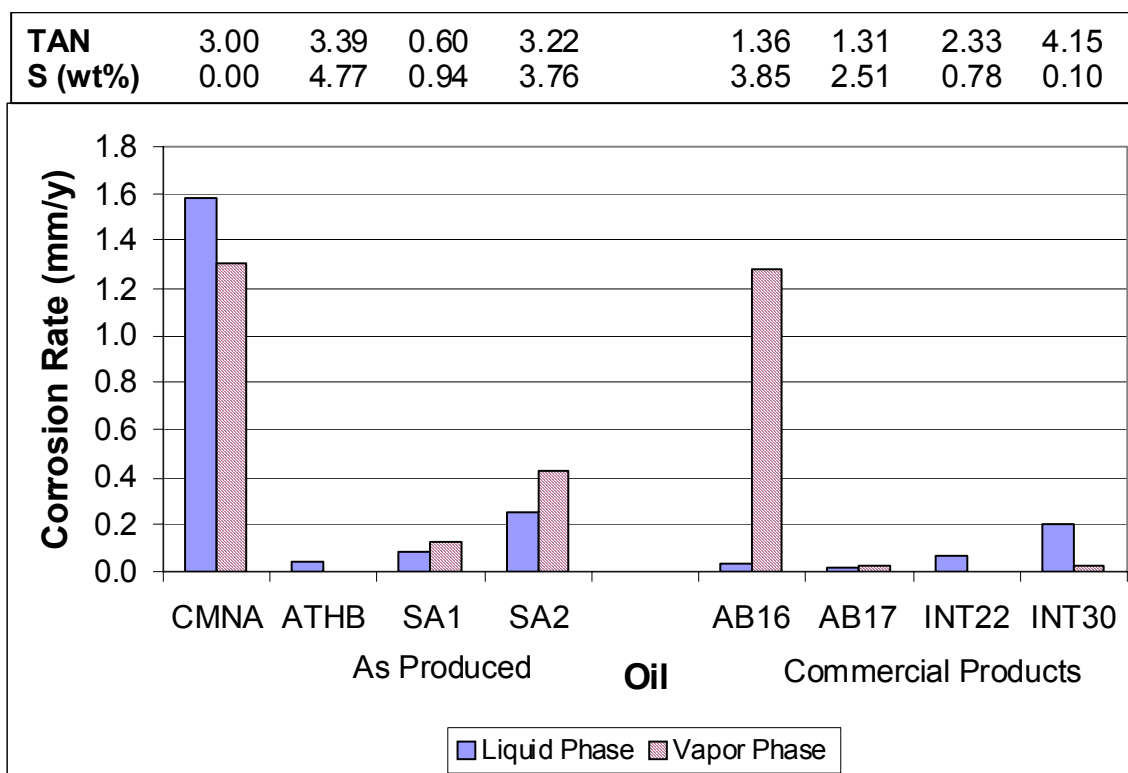


FIGURE 7 – Corrosion Rates of Carbon Steel Coupons for CMNA in White Oil and Crudes (Whole or Topped at 204°C) at AET= 300°C

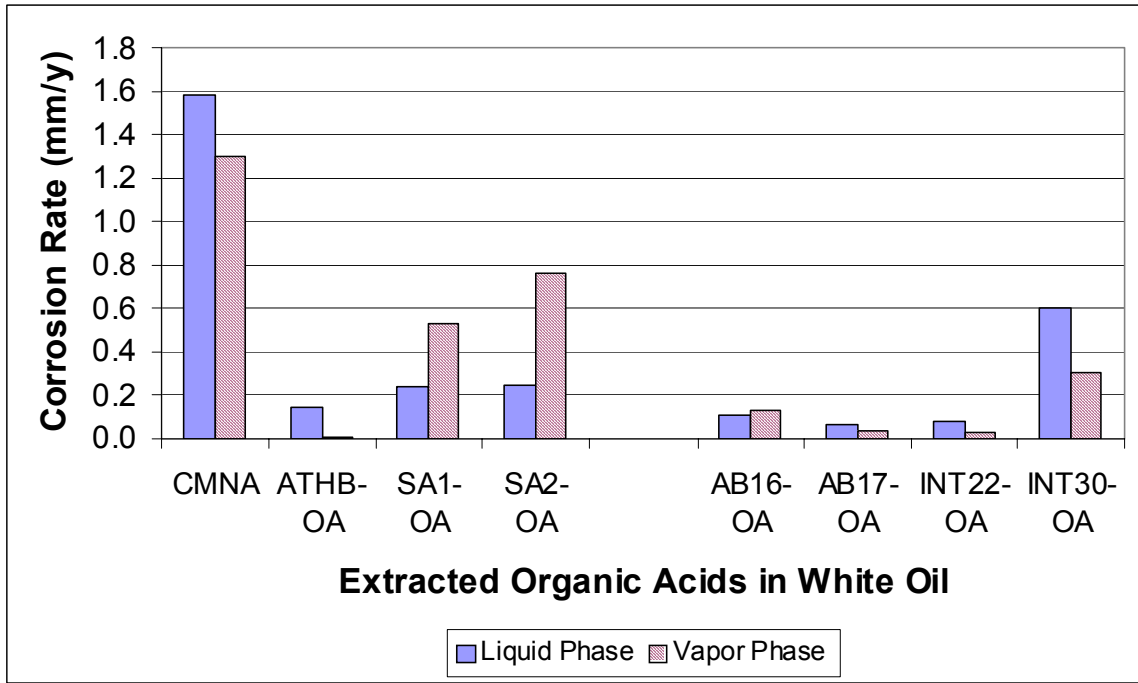


FIGURE 8 – Corrosion Rates of Carbon Steel Coupons for CMNA and Organic Acids Extracted from Crudes in White Oil at AET= 300°C

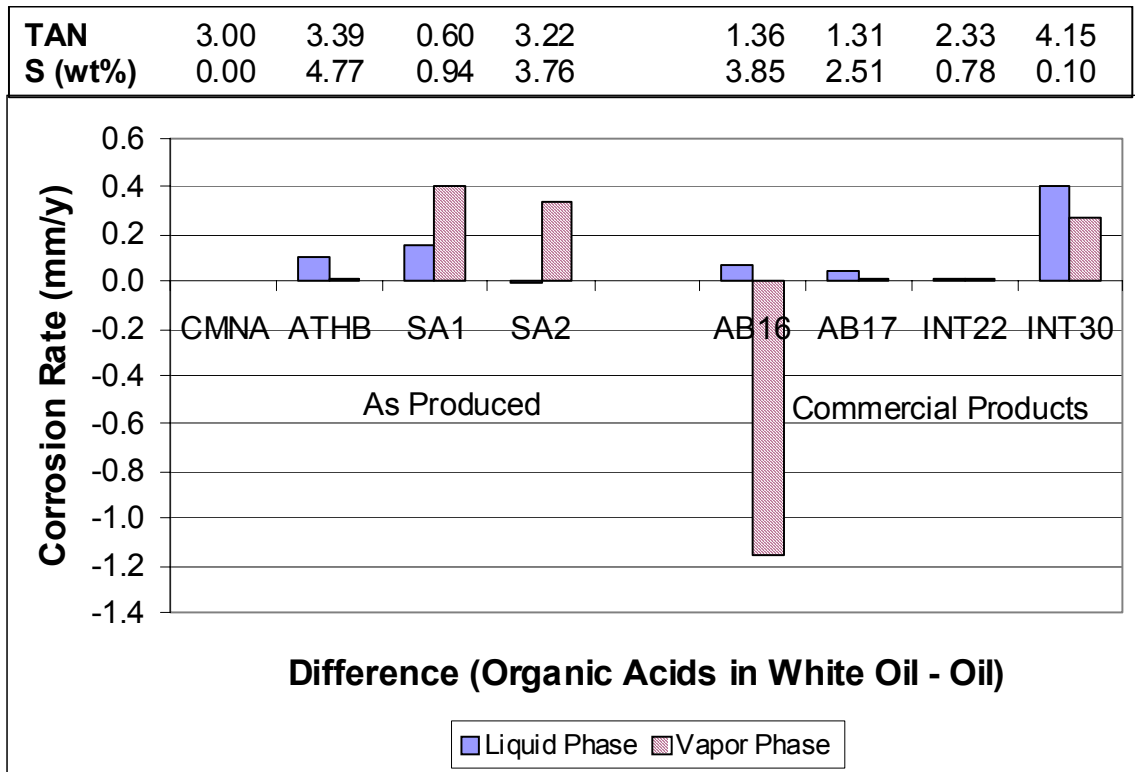


FIGURE 9 – Differences in Corrosion Rates of Carbon Steel Coupons between the Results Shown in Figures 8 and 7

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