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

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# Mechanisms of Refinery Corrosion

- Refinery corrosion occurs at temperatures between 220°C and 400°C
  - Naphthenic (organic) acids (RCOOH) reach their boiling points and condense on metal surfaces, removing iron [Fe] and eventually causing pits
  - Sulfur-containing compounds decompose to form hydrogen sulfide ($H_2S$), where iron removal causes general corrosion but can form protective films
- Acids and hydrogen sulfide work together:

$$Fe + 2RCOOH \rightarrow Fe(RCOO)_2 \text{ (oil soluble)} + H_2$$

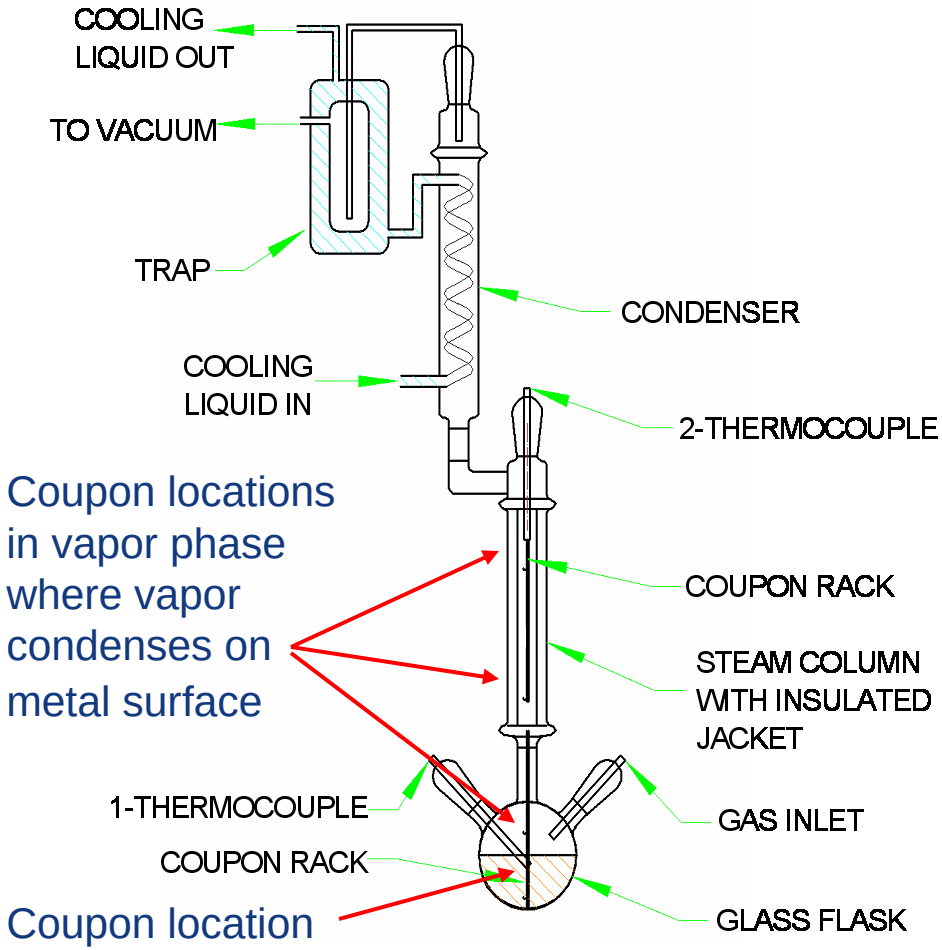
$$Fe + H_2S \rightarrow FeS \text{ (oil insoluble)} + H_2$$

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

# Corrosivity, TAN, and Sulfur

- Corrosivity does not always correlate with total acid number (TAN) (Derungs, 1956; Messer 2004)
  - Are organic acid molecular species in some oils “less active” that those in other oils?
  - Does high sulfide content result in iron sulfide film that protects the plant metallurgy?
  - Another reason?
- This project was conducted to improve the understanding of the contributions of specific structural features of organic acids and sulfur compounds to corrosivity at refinery temperatures

# Corrosion Test Unit

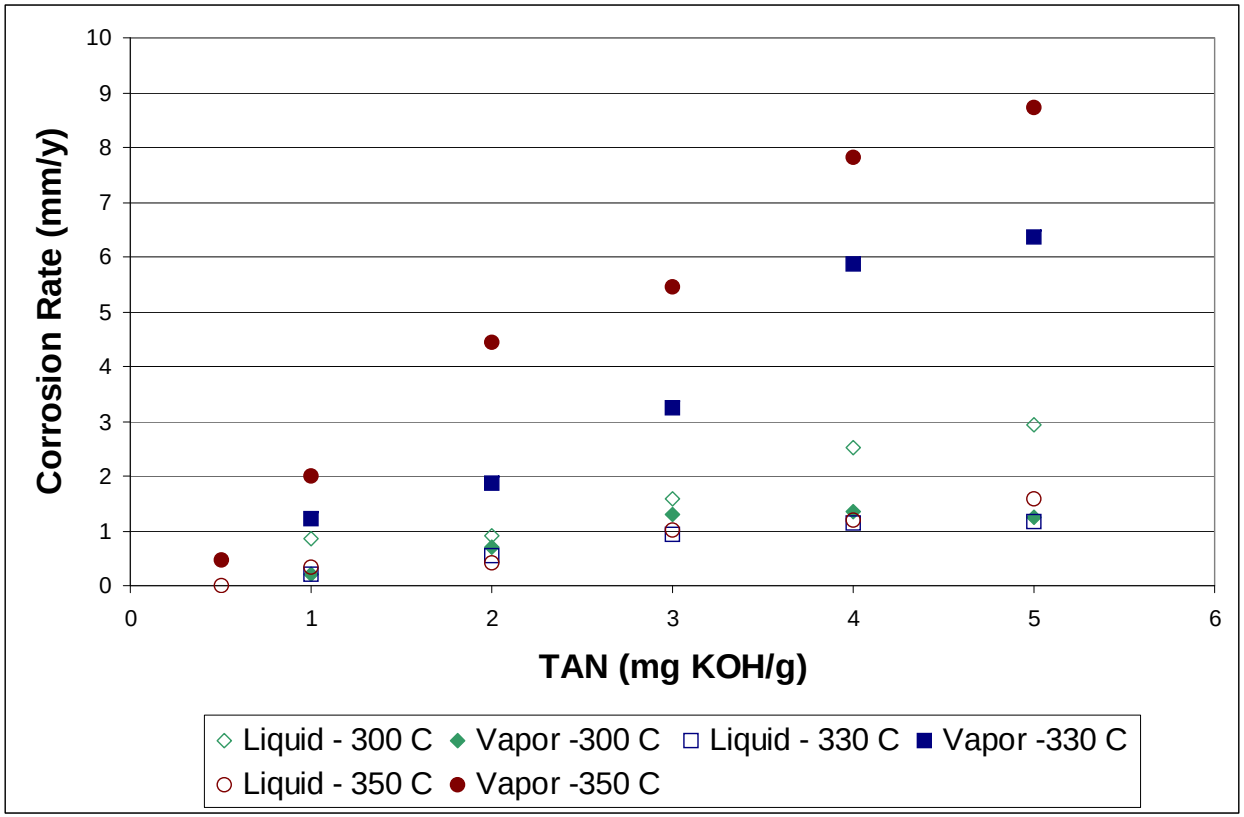



Simulates corrosion in vacuum distillation unit

Features:

1. Volume: 250 mL
2. Charge: Any crude or refinery feed blend
3. No. of coupons: 4
4. Operates under vacuum throughout the temperature range

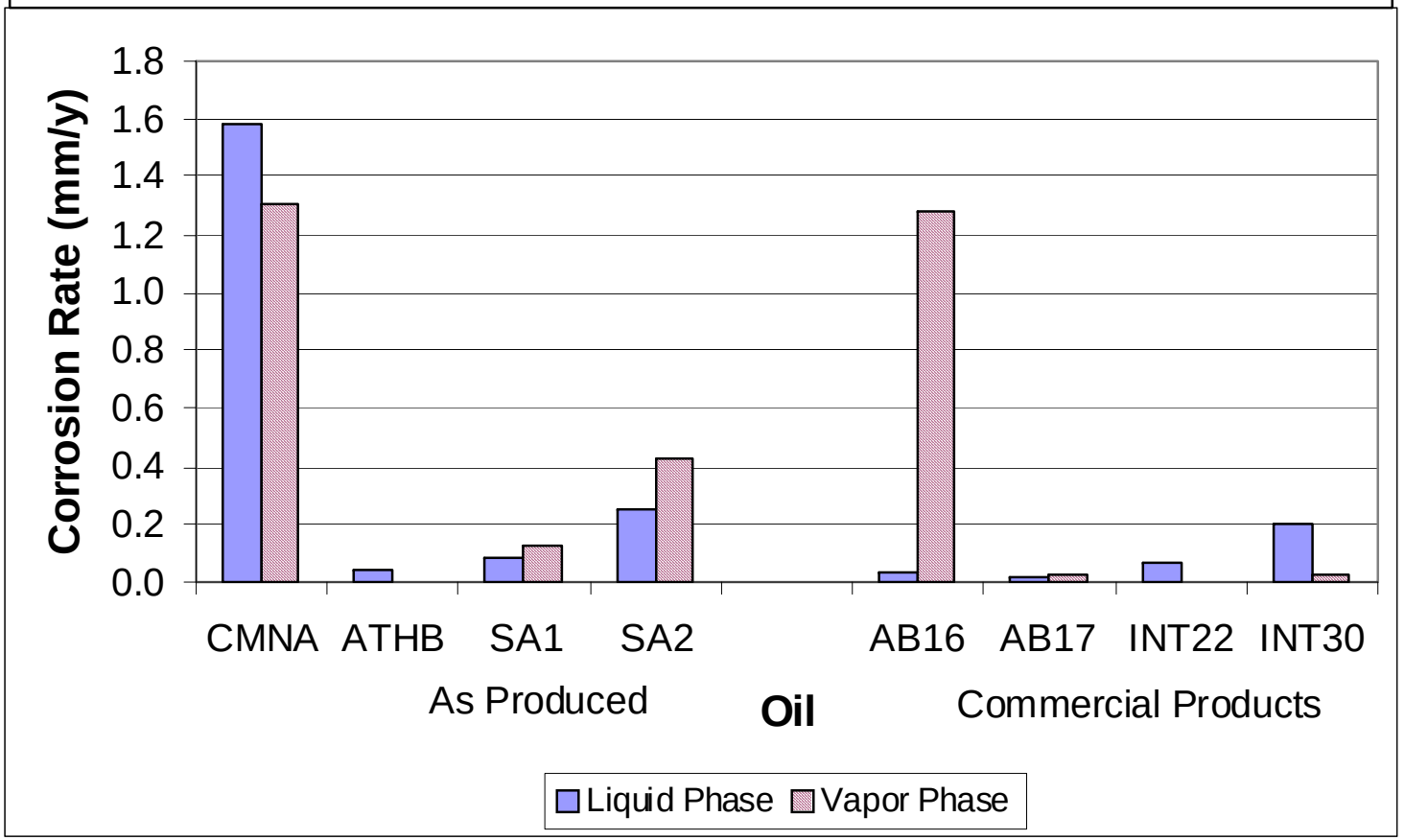
# When Does TAN Correlate with Corrosivity?




TAN correlates with corrosivity when different concentrations of the same acids are tested. (Corrosion rates of carbon steel coupons for commercial naphthenic acids [CMNA] in white oil.)

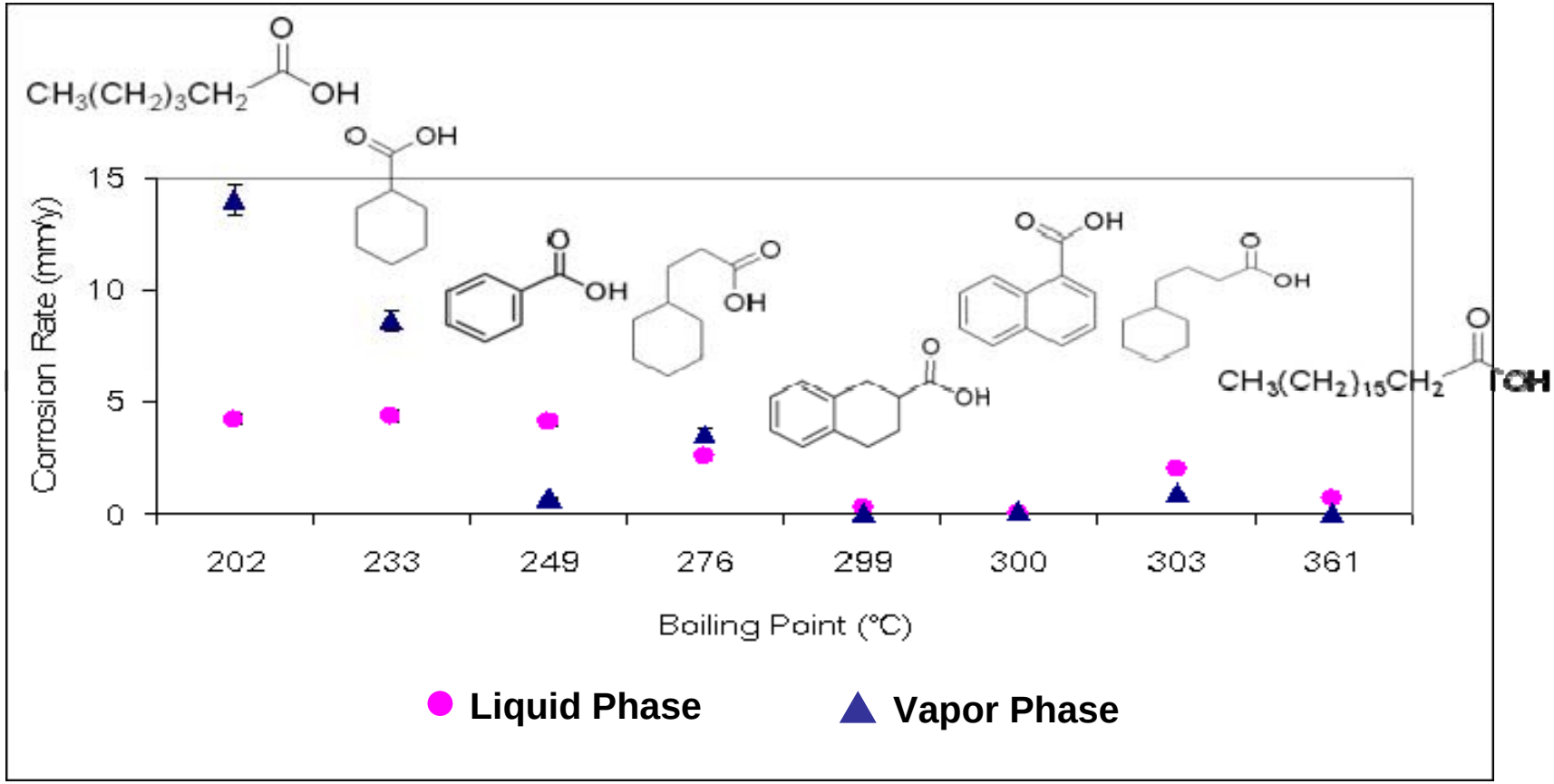
# When Does TAN NOT Correlate with Corrosivity?

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **TAN** | 3.00 | 3.39 | 0.60 | 3.22 | 1.36 | 1.31 | 2.33 | 4.15 |
| **S (wt%)** | 0.00 | 4.77 | 0.94 | 3.76 | 3.85 | 2.51 | 0.78 | 0.10 |




When comparing corrosion rates for different crude oils.....?

# Corrosivity of Organic Acid Compounds

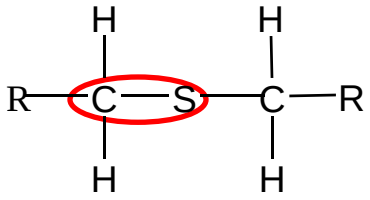



Corrosion rates of carbon steel coupons for organic acid compounds in white oil (TAN= 5.0mg KOH/g) at atmospheric equivalent temperature (AET) of 300°C (250°C actual)

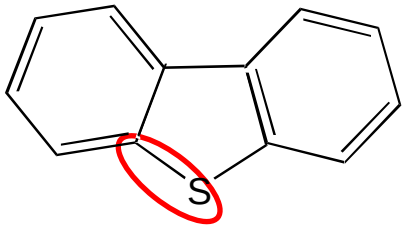
# What about Sulfur?

- Sulfur compounds R-S-R → $H_2S$ + by-products
  - Thermal Cracking
  - Sulfidic Corrosion → FeS

- Model sulfur compounds were chosen to represent the different C-S bonds found in petroleum. For example:



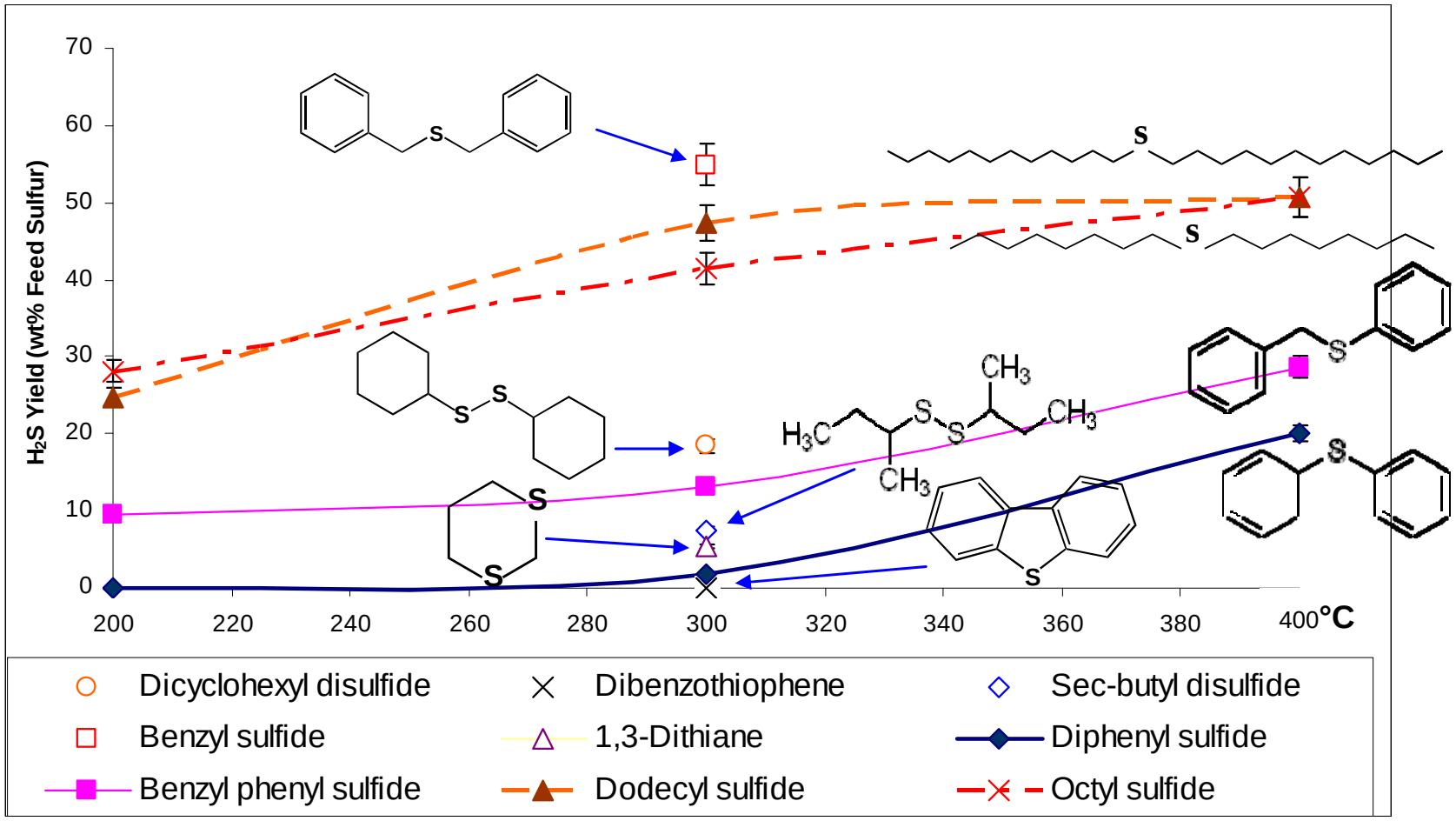

Octyl sulfide




Dibenzothiophene

- Thermal decomposition studies of nine sulfur compounds dissolved in white oil (1 wt% sulfur) were performed

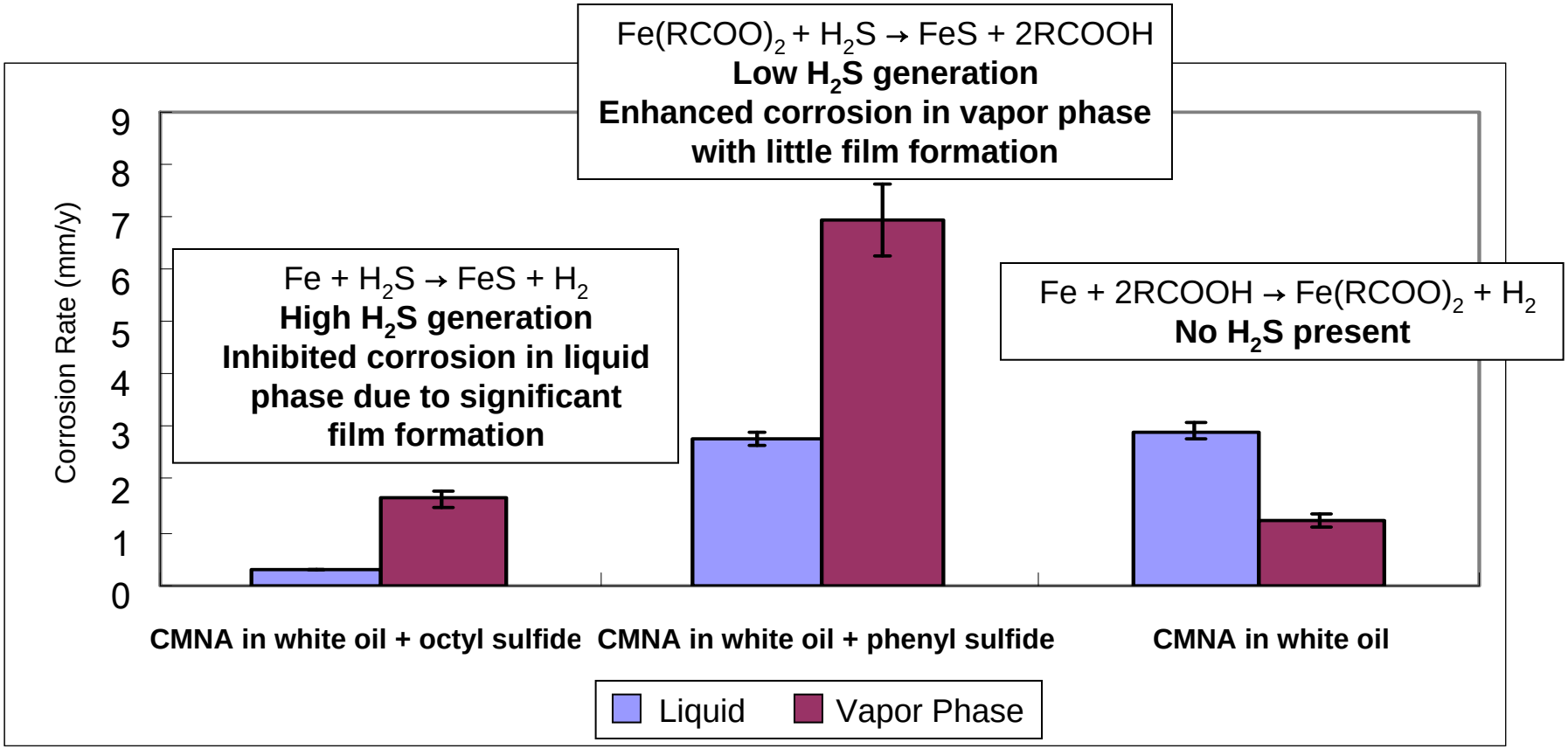
# Thermolysis of Sulfur Compounds




At temperatures as low as 200°C (392°F), within 2 hours -$CH_2$-S- bonds (sulfides) crack and form $H_2S$

# $H_2S$ Effects on Corrosivity of Organic Acids under Refinery Conditions






Influence of presence (1wt% S) or absence of sulfur compounds on the corrosion rates of commercial naphthenic acids (CMNA) in white oil (Total acid number = 5.0mg KOH/g) for carbon steel coupons at atmospheric equivalent temperature of 300°C (250°C actual)

# Why Does TAN Not Correlate with Corrosivity?

Model compound studies show that:

- Small organic acid molecules (boiling point < 300°C) are significantly more corrosive than larger molecules (boiling point > 300°C)
  - In liquid phase, chain and 1-ring acids are the most corrosive; in vapor phase, chain and 1-ring cycloalkane (naphthenic) acids are most corrosive
- Vapor phase corrosion due to organic acids is greatest at temperatures above the boiling point of the acid
- Sulfur compounds can decompose to form hydrogen sulfide at temperatures as low as 200°C; acid corrosion can be inhibited or enhanced depending on how much hydrogen sulfide is present

# Crude Oil Analyses

| Crude Oil | Elemental (wt%) C | H | N | S | O | Density (g/mL) | TAN (mg KOH/g) |
|---|---|---|---|---|---|---|---|
| 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 |

## As produced:

**ATHB** Athabasca bitumen

**SA** South America

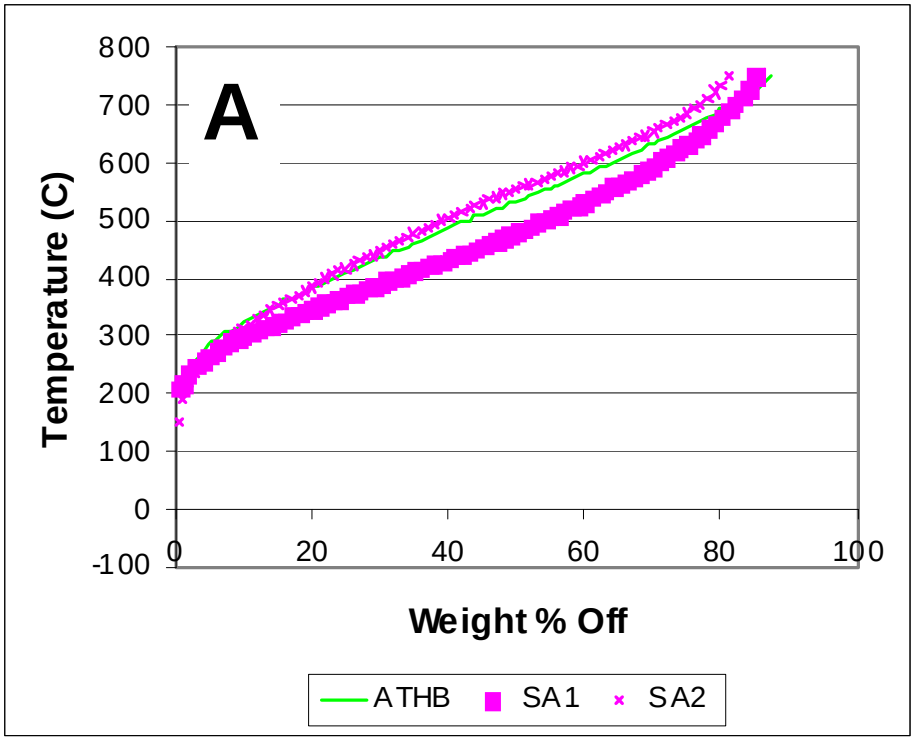
## Commercial products:

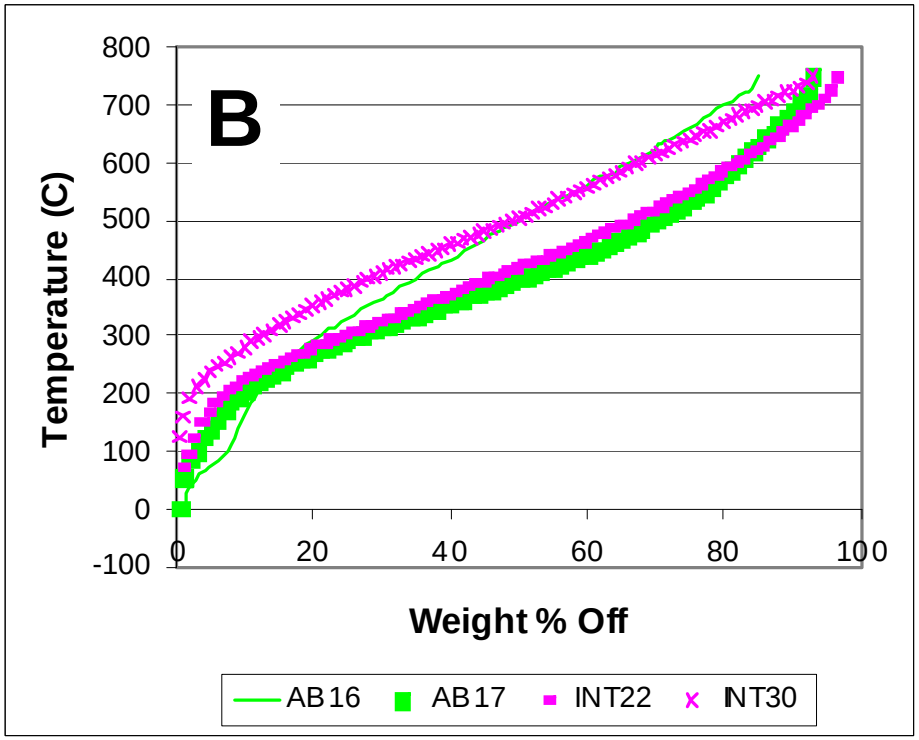
**AB** Alberta heavy oil or bitumen

**INT** Non-Canadian crude of non-disclosed geographical location

*** Crudes were topped at 204°C for corrosion testing**

# HTSD of Crudes




High temperature simulated distillation (HTSD) of:

A – Crudes, as produced

B – Crudes, commercial products

# Analyses of Extracted Organic Acids

| Organic Acids | Content in Crude (wt%) | Elemental (wt%) | | | | |
|---|---|---|---|---|---|---|
| | | 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 |

**CMNA Commercial naphthenic acids**

## Organic Acids Extracted from Crude Oils (Mediaas *et.al., 2003*)

**As produced:**

**ATHB Athabasca bitumen**

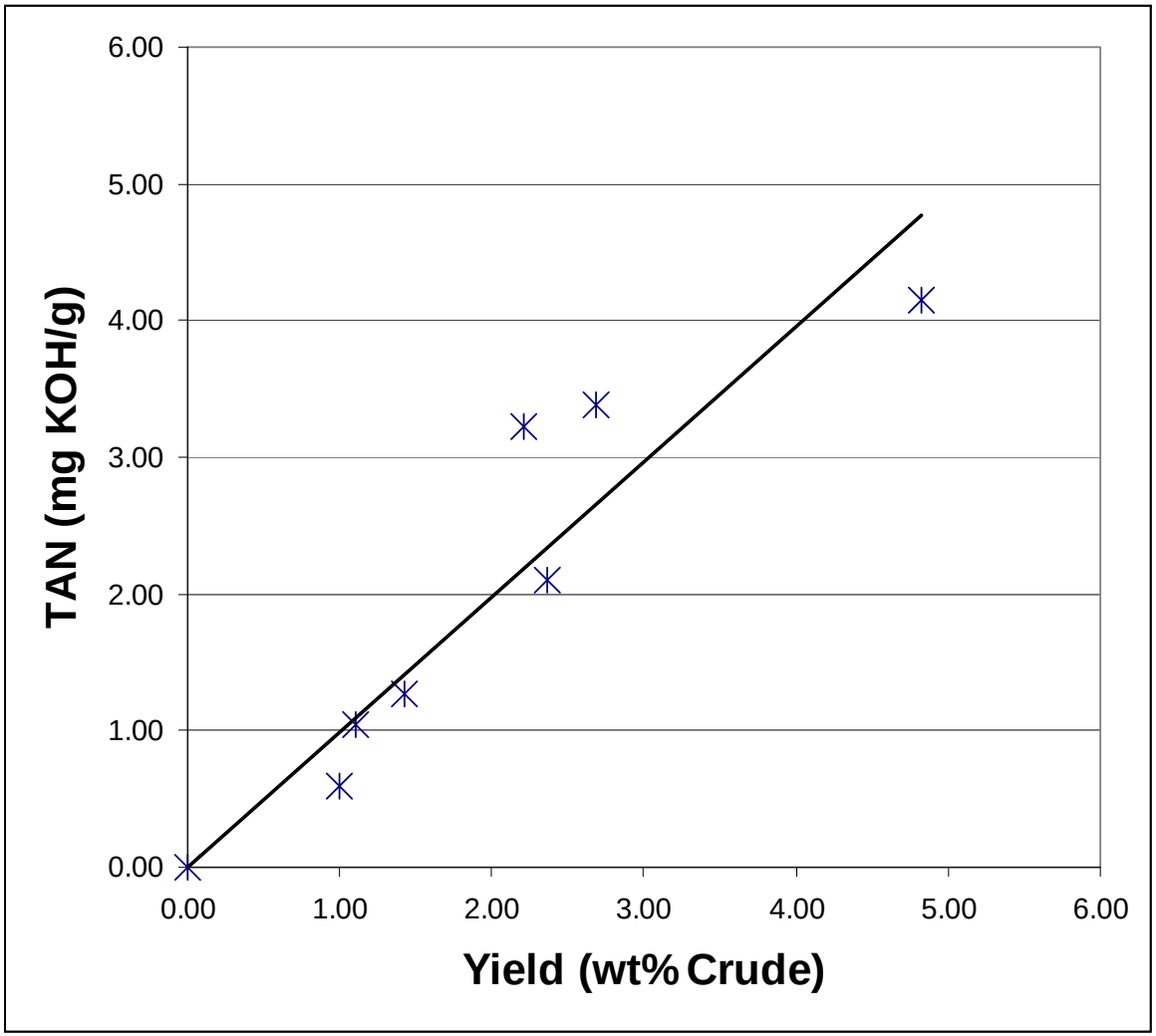
**SA South America**

**Commercial products:**

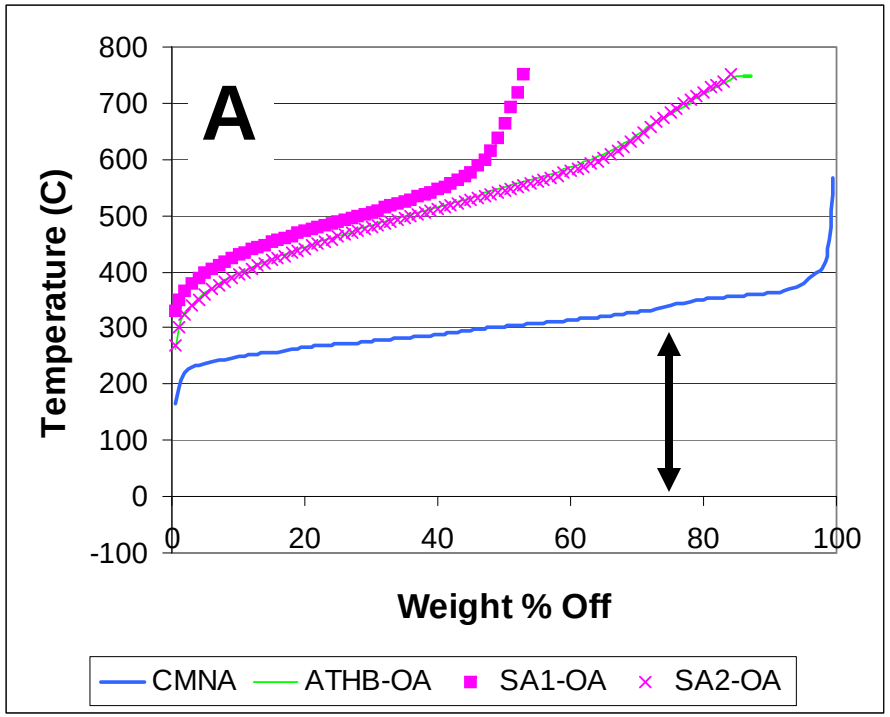
**AB Alberta heavy oil or bitumen**

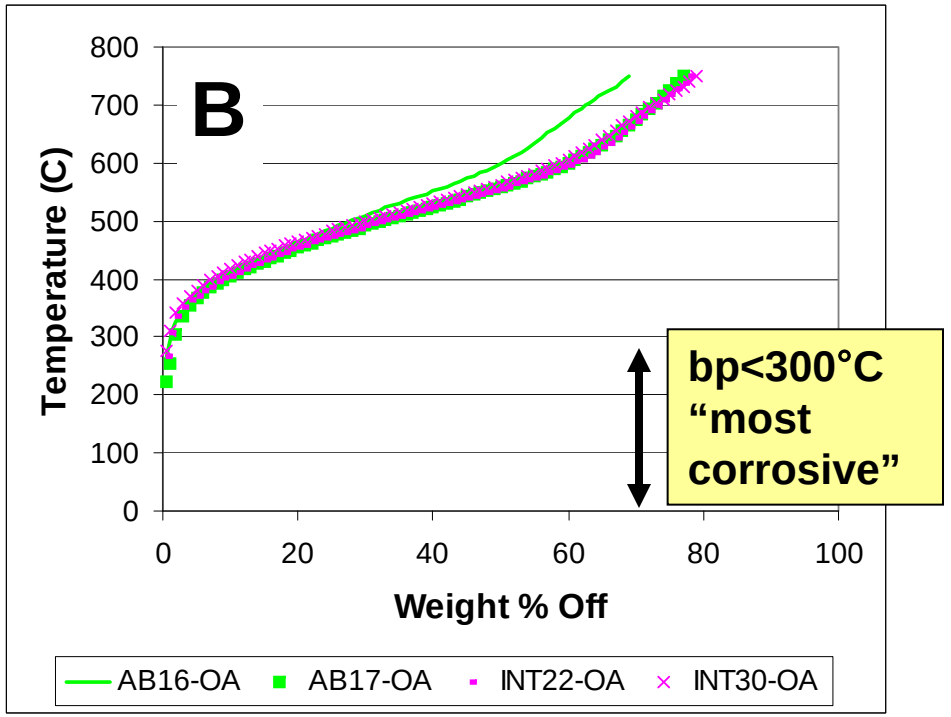
**INT Non-Canadian crude of non-disclosed geographical location**

# Crude Oil TAN versus Organic Acid Yield



# Distillation of Organic Acids from Crudes



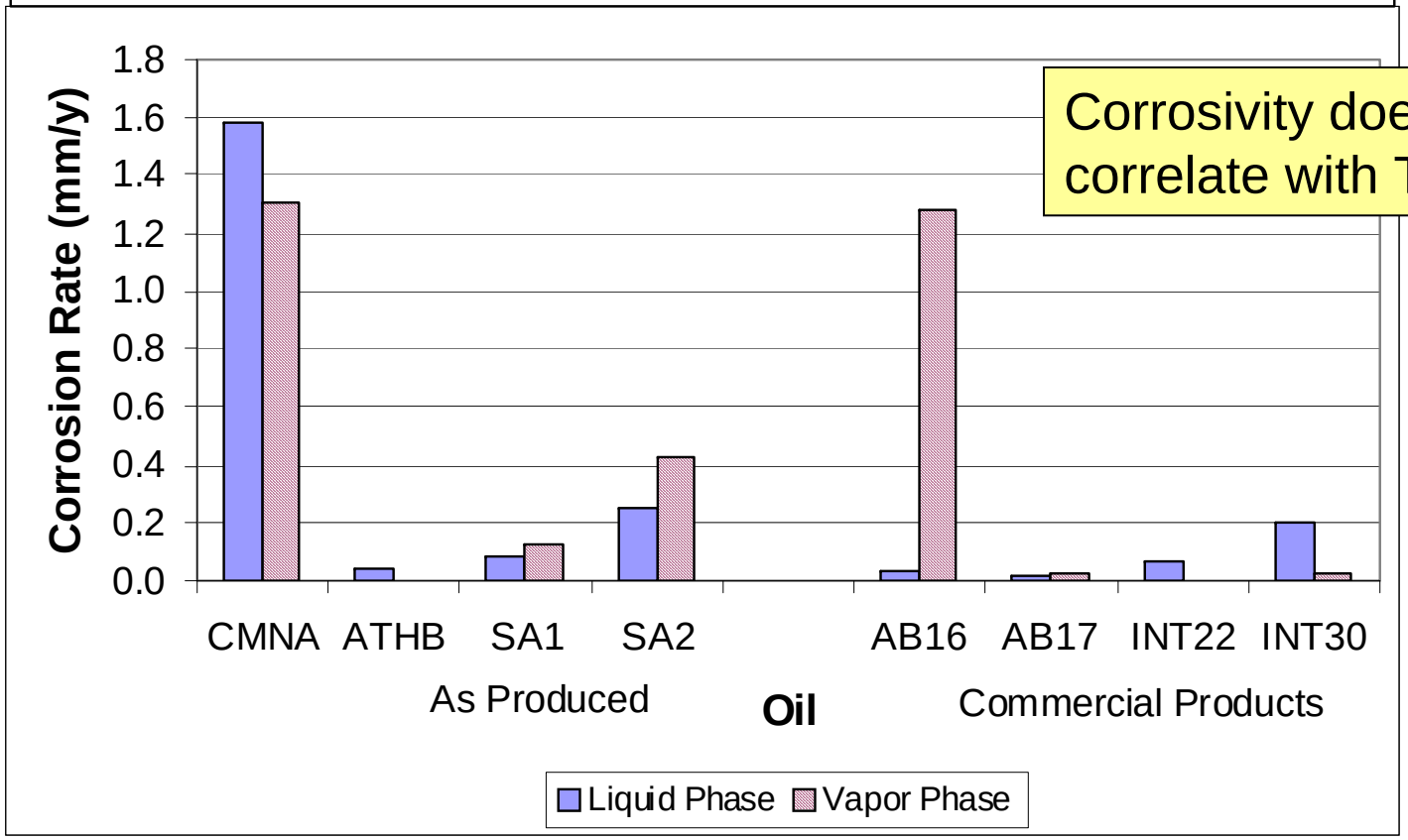

Organic acids from:

A – CMNA and crudes, as produced

B – Crudes, commercial products

# Corrosivity Results – CMNA & Crude Oils

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **TAN** | 3.00 | 3.39 | 0.60 | 3.22 | 1.36 | 1.31 | 2.33 | 4.15 |
| **S (wt%)** | 0.00 | 4.77 | 0.94 | 3.76 | 3.85 | 2.51 | 0.78 | 0.10 |

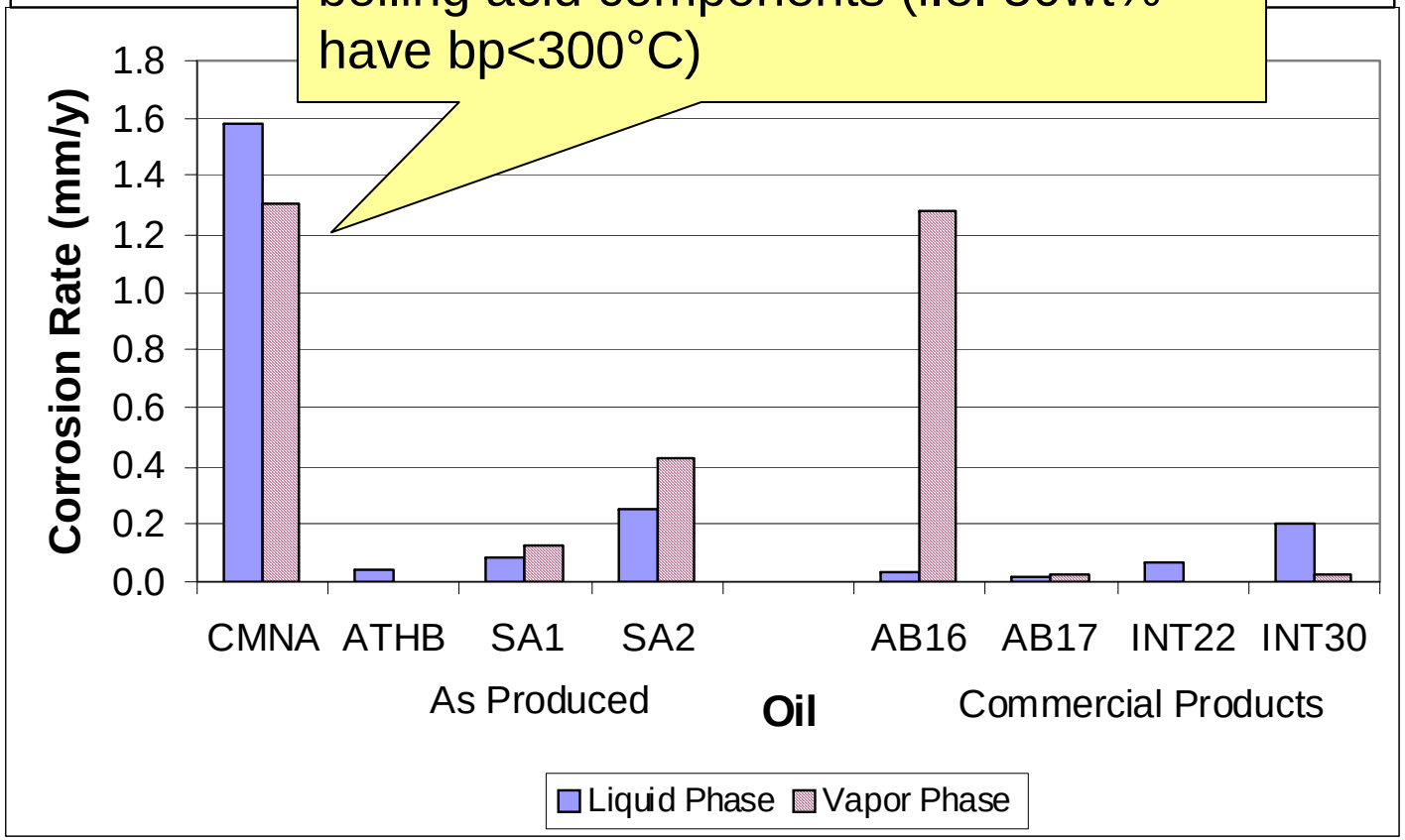



Corrosion rates of carbon steel coupons for CMNA in white oil and crude oils at AET of 300°C (250°C actual)

# Corrosivit… …e Oils

| | | | |
|---|---|---|---|
| **TAN** | 3.0 | | 4.15 |
| **S (wt%)** | 0.0 | | 0.10 |

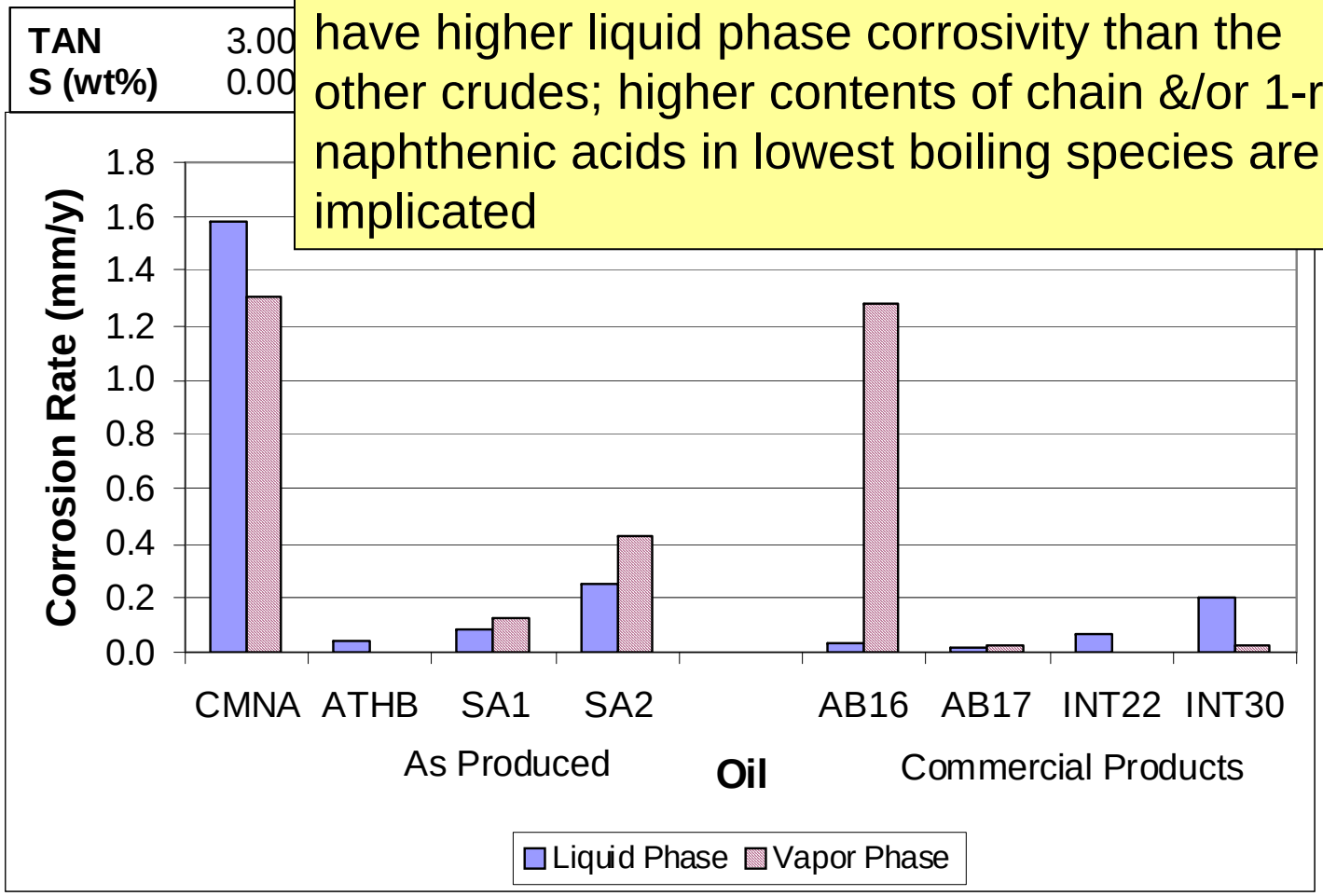
Higher corrosivity of CMNA is explained by its higher content of lower boiling acid components (i.e. 50wt% have bp<300°C)




Corrosion rates of carbon steel coupons for CMNA in white oil and crude oils at AET of 300°C (250°C actual)

# Corrosivit

Boiling point distributions of organic acids in these crudes do not explain why SA2 and INT30 have higher liquid phase corrosivity than the other crudes; higher contents of chain &/or 1-ring naphthenic acids in lowest boiling species are implicated




Corrosion rates of carbon steel coupons for CMNA in white oil and crude oils at AET of 300°C (250°C actual)

# Corrosivity Results – CMNA &

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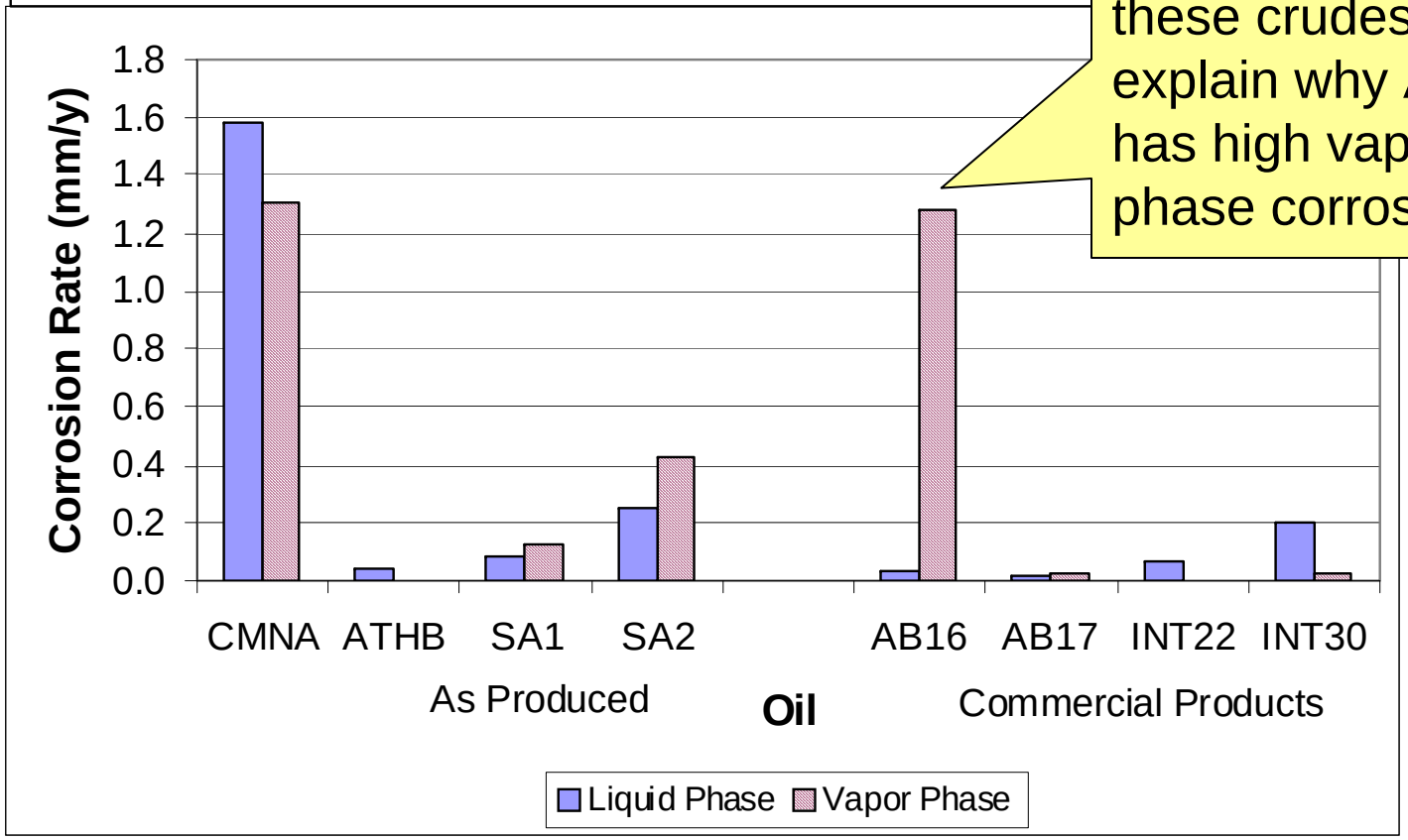


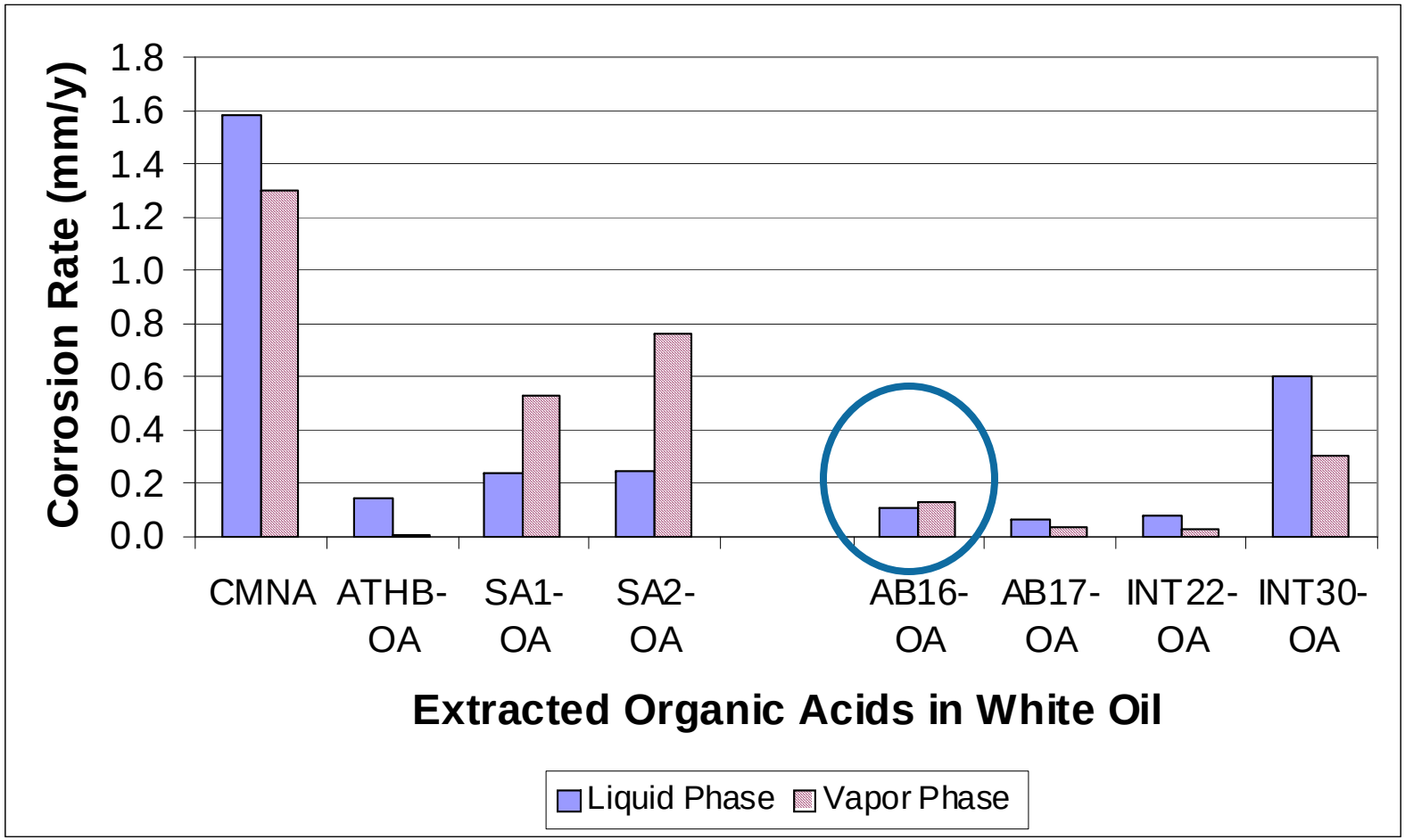

Boiling point distributions of organic acids in these crudes do not explain why AB16 has high vapor phase corrosivity

Corrosion rates of carbon steel coupons for CMNA in white oil and crude oils at AET of 300°C (250°C actual)

# Identification of Sulfidic Corrosion Influences in Crude Oils

- Replace the oil matrix with a sulfur-free medium i.e. white oil
  - Organic acids isolated from each of the Global crudes were dissolved in white oil at TAN values similar or slightly lower than those of the original crude oils tested
  - If the oil matrix has no influence on corrosion, the corrosion rates of the white oil mixtures should be the same as that of the original oil
  - If the oil matrix influences corrosion, the corrosion rates of the white oil mixtures could be either greater or lesser than those of the original oil

# Corrosivity Results – Extracted Acids




Corrosion rates of carbon steel coupons for CMNA and extracted organic acids in white oil at AET of 300°C (250°C actual)

# Differences in Corrosivity Results

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **TAN** | 3.00 | 3.39 | 0.60 | 3.22 | 1.36 | 1.31 | 2.33 | 4.15 |
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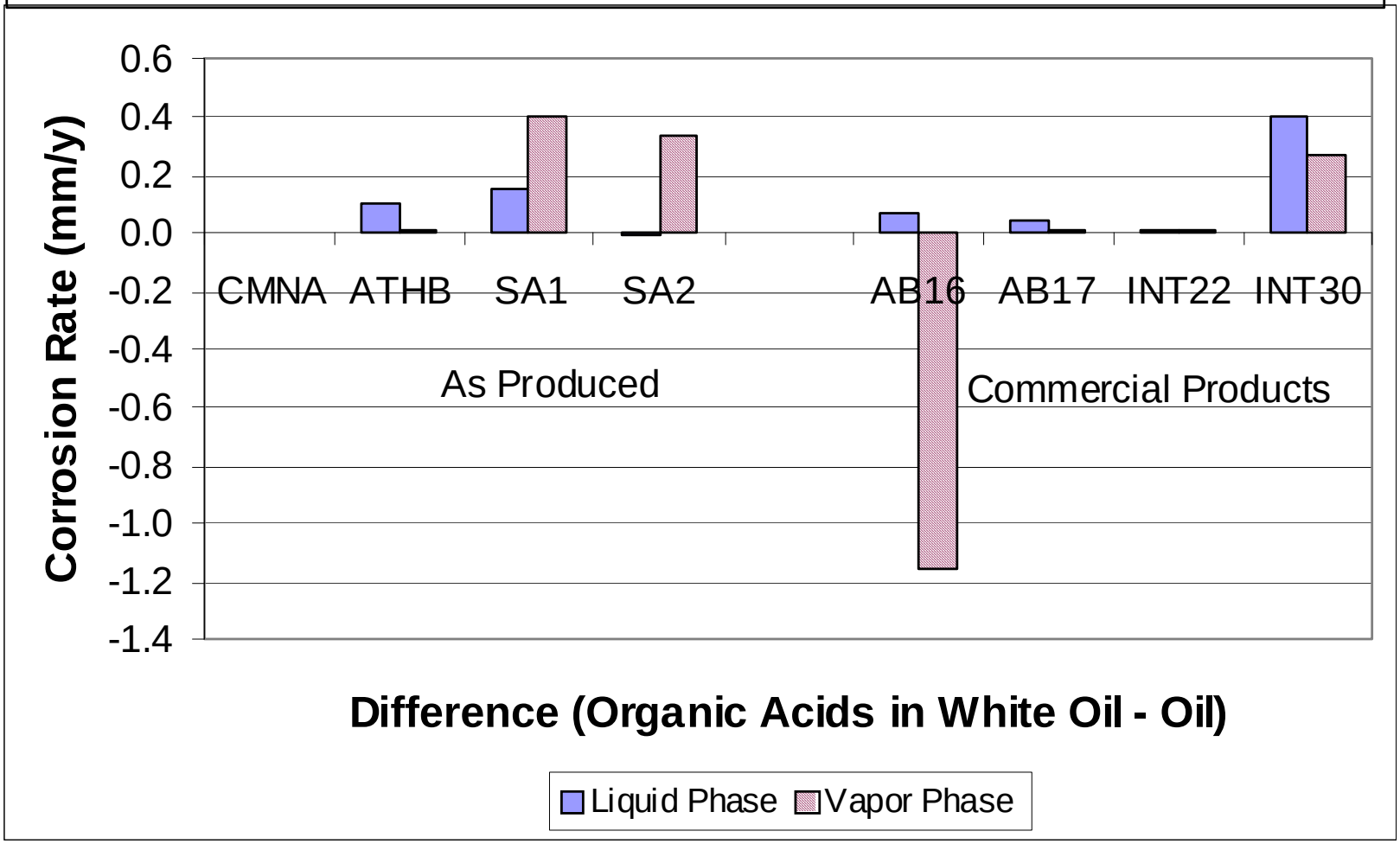

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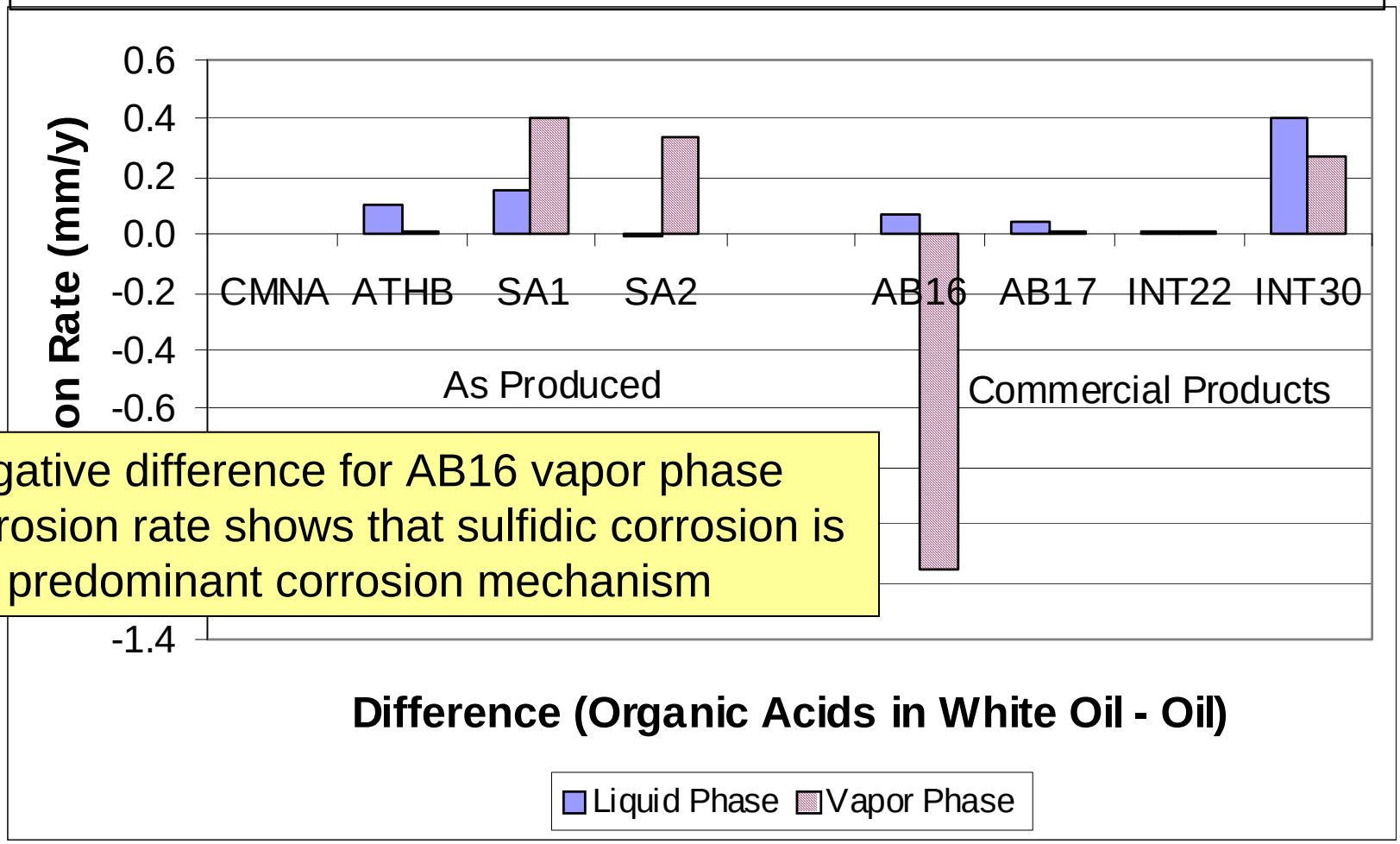


Negative difference for AB16 vapor phase corrosion rate shows that sulfidic corrosion is the predominant corrosion mechanism

# Differences in Corrosivity Results

| | | | | | | | | |
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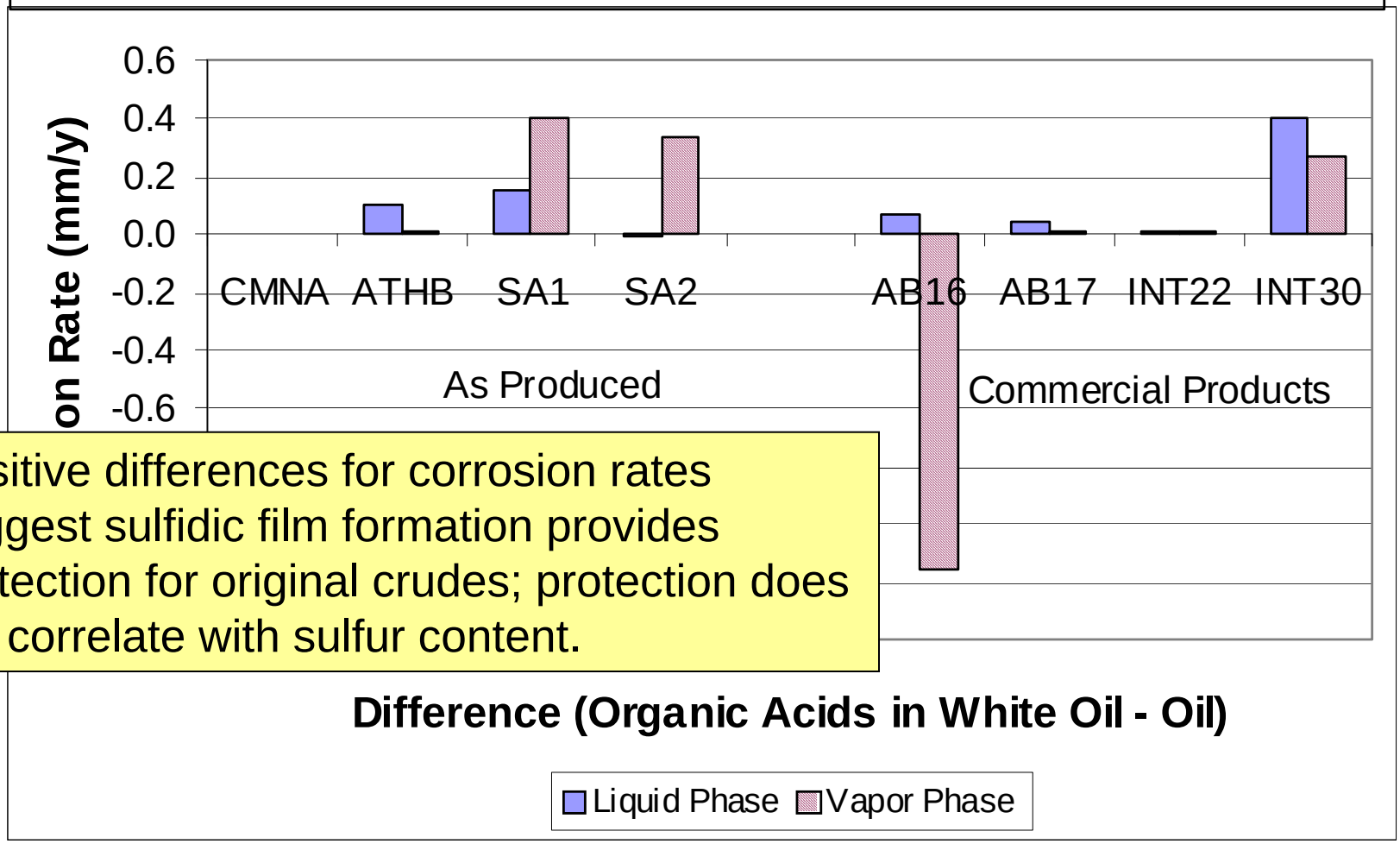


Positive differences for corrosion rates suggest sulfidic film formation provides protection for original crudes; protection does not correlate with sulfur content.

# Differences in Corrosivity Results

| | | | | | | | | |
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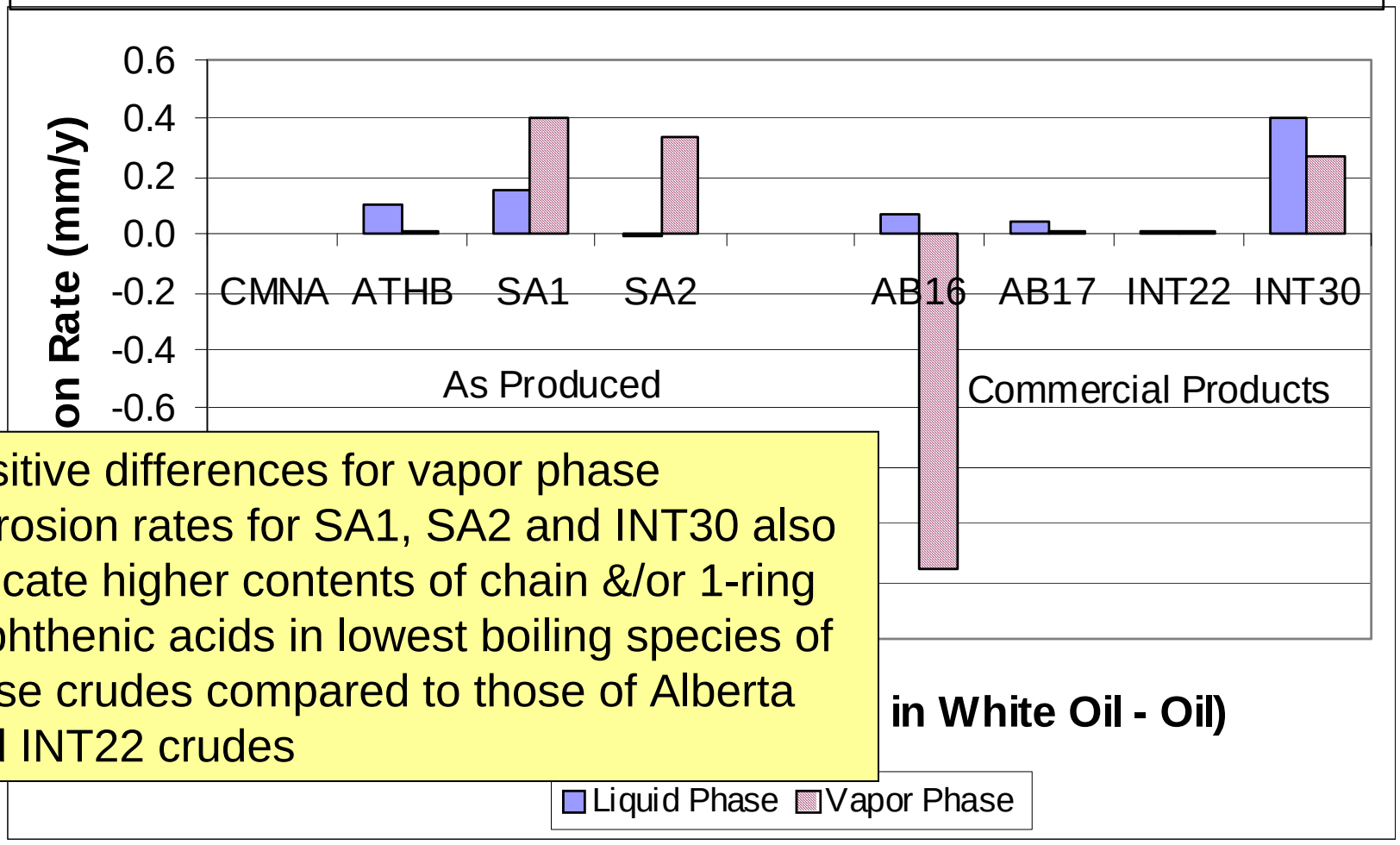


Positive differences for vapor phase corrosion rates for SA1, SA2 and INT30 also indicate higher contents of chain &/or 1-ring naphthenic acids in lowest boiling species of these crudes compared to those of Alberta and INT22 crudes

# CONCLUSIONS

- TAN values of crude oils are not reliable indicators of crude oil corrosivity
- Crude corrosivity appears to be determined by:
  - Low boiling acids (i.e. bp<350°C) where content of chain and/or 1-ring naphthenic acids will be important
  - Content of thermally-labile sulfur species
- Hydrogen sulfide-generating ability of the crude will be influenced by:
  - Content of $CH_2$-S bonds in sulfur species
  - Thermal history of crude oil (field and plant)

# IMPLICATIONS OF RESULTS

- If TAN does not correlate with crude corrosivity, why is it used for setting crude prices?
- How does production method influence corrosivity (i.e. SAGD versus mined?)
  - How does the content of low-boiling chain and 1-ring naphthenic acids compared to the total organic acid content, and the contents of thermally-labile sulfur species work together to influence corrosivity
- When can blending a high TAN crude with a low sulfur, low TAN crude (or diluent?) result in enhanced corrosion?

# Funding Acknowledgements


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