The Effect of Total Sulfur Content and Total Acid Number (TAN) on Small Scale Oil Refinery

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Abstract. Corrosion is one of major problems in refinery industry which leading to mechanical failure of equipments. Corrosion mechanism and rate depend on the corrosive substance, temperature, and material of equipment. Refinery feedstock commonly is a blending of different oils contains different corrosive substance. One of corrosive substance, Sulfur Content and TAN, can cause thinning of material surface at high temperature. This research aims to study the effect of sulfur content and TAN on corrosion mechanism and rate of equipment and piping in small scale refinery. Corrosion mechanism and rate for several refinery feedstocks, containing various sulfur content and TAN, were determined using API-581RP. Mass and energy balance for small scale refinery consists of distillation unit, sulfur removal unit, and platformer unit was done based on process simulator. Materials concerned in this research were carbon steel, alloy steel, and stainless steel. The result showed most of the mechanism in distillation column was thinning high temperature sulfidic/naphthenic corrosion while in sulfur removal and platformer were thinning high temperature H₂S/H₂ corrosion. The change of sulfur and acid content caused change corrosion rate in non-linear way. These results can be used as prediction for future corrosion assessment based on sulfur and TAN composition.

1. Introduction
Corrosion is major problems in industry especially oil refinery [1]. Corrosion is natural phenomenon and cause material depletion of equipment because of its interaction with its environment [2]. Corrosion can cause many casualties and economical loss, even endanger worker safety [3]. There are many refinery explosions caused by corrosion in one of the equipment which lead to leaking or explosion [4]. Corrosion analysis is needed to prevent major accident caused by corrosion [5]. Prevention of corrosion is key point to assure process safety in the refinery and petrochemical industry [6]. Corrosion analysis can be used to predict lifetime of equipment and prepare the replacement to be installed at plant turnaround [7]. Corrosion analysis can be done by using API 581 to predict corrosion mechanism and rate based on impurities, temperatures, and equipment materials [8].

In general, small scale refinery consists of three main units: distillation, desulphurization unit, and platformer [9]. Distillation unit is used to separate raw crude into several product; naphtha, kerosene, diesel, etc. Distillation unit has impurities such as sulfur organic, TAN, salt, and water which sulfur
organic and TAN cause thinning at high temperature while salt can cause localized corrosion such as pitting even at room temperature [10]. Desulphurization unit is used to convert organic sulfur into H₂S and lower the corrosion potential. In Desulphurization unit beside sulfur and TAN, impurities such as H₂S, hydrogen, ammonia, water can also cause localized and general corrosion [11]. Platformer is used to increase gasoline octane number by reforming lower octane number hydrocarbons into higher octane number using catalyst. This process is done at high temperature in environment rich of hydrogen. This can cause high temperature hydrogen attack, which is one types of corrosion that can be dangerous [12].

The impurities in small scale refinery units are very diverse and complicated. Small change in hydrocarbons or impurities content can cause major change of corrosion severity [13]. Thus, a study to predict the effect of impurities or hydrocarbons composition to corrosion in small scale refinery must be done. This study aim to analyze the effect of different crude, in which contains different impurities, to corrosion mechanism and rate in small scale refinery plant. The output hopefully can be used as basic prediction for future corrosion in refinery.

2. Experiment Methods

The methodology for this study is shown by figure 1. Initially, by using crude assay, mass and energy balance of small scale refinery plant is calculated. From mass and energy balance, the data needed for corrosion analysis can be extracted. In corrosion analysis, corrosion mechanisms and rates are checked for individual equipment. Each corrosion rate is labeled by different colors to indicate how severe the damage is. Then every analysis for equipment is combined into corrosion mapping followed by evaluation.

This study is done by using three types of crudes: crude that contains most heavy hydrocarbons (Crude A); crude that contains most light hydrocarbons (Crude B); and mixture of both Crude A and Crude B in ration 50:50 (Crude C). Each crude contains different sulfur and TAN content, which shown in table 1. Crude B which contains most light hydrocarbons has higher sulfur and TAN content than the others. The mass and energy balance calculation is done for three crude assays. Mass and energy balance calculation is carried out by using Process Simulation Software.
Table 1. Sulfur and TAN content in three types of crudes

| Impurities       | Crude A | Crude B | Crude C |
|------------------|---------|---------|---------|
| Sulfur content (%-wt) | 0.31    | 1.56    | 0.94    |
| TAN content (mg KOH/g)  | 0.04    | 0.13    | 0.09    |

Process Simulation Software used crude assay as input to construct different types of hydrocarbons based on its boiling point. The impurities such as sulfur and TAN were added by using compound model such as carboxylic acid or sulfur organic. For this study, the compound models used for sulfur are thionaphthene (boiling point 219°C) as light sulfur and 1-octadecanethiol (boiling point 360°C) as heavy sulfur. For TAN, the compound models used are pentadecanoic acid (C_{15}H_{30}O_2) and eicosanoic acid (C_{20}H_{40}O_2). Those compounds are used because sulfur and TAN content are much concentrated in two boiling points; around 200 – 230°C and 320 – 360°C [14].

Small scale refinery consists of three main units: Crude Distillation Unit or CDU, Naphtha Hydrotreater or NHT, and Platformer or PTU [9]. Process flow diagrams of each unit are shown in figure 2. Each units consist of different number of equipment which shown in table 2. There are three types of equipment material used in each unit; there are carbon steel, stainless steel, and low alloy carbon steel.

Table 2. Number of equipment contained in each unit

| Equipment Types | CDU | NHT | PTU |
|-----------------|-----|-----|-----|
| Columns         | 4   | 1   | 1   |
| Reactor         | 0   | 2   | 3   |
| Heat Exchanger  | 2   | 10  | 7   |
| Vessels         | 24  | 2   | 3   |
| Furnace         | 1   | 1   | 3   |
| Total Equipment | 31  | 16  | 17  |

Corrosion analysis is based on API 581. In API 581, determining corrosion mechanism and rate needs concentration and types of impurities in each stream, equipment materials, and temperature. In this study which mass and energy balance is done by simulation, there are only three types of corrosion can be determined. First, the impurities are TAN and sulfur organic which cause Thinning High Temperature Sulfidic/Naphthenic Acid Corrosion at high temperature (>400°F). Second, the impurities are H2S and H2 which cause Thinning High Temperature H2S/H2 Corrosion at high temperature (>400°F). Last, hydrogen gas at high temperature (>400°F) in carbon steel or low alloy steel can cause High Temperature Hydrogen Attack (HTHA).

Corrosion mapping severity level is based on four colors; green for low, blue for moderate, yellow for high, and red for severe. Based on API 581, boundary limits of corrosion rate for each mapping colors are shown in table 3.

Table 3. Number of equipment contained in each unit

| Colors | mpy | mmpy |
|--------|-----|------|
| Low    | Green | < 2  | < 0.05 |
| Moderate | Blue | 2–20 | 0.05–0.51 |
| High   | Yellow | 20–50 | 0.51–1.27 |
| Severe | Red | > 50 | > 1.27 |
Figure 2. Process flow diagrams
3. Results and Discussion

3.1. Crude assay analysis for early prediction

Figure 3 shows hydrocarbon composition inside each crude based on its boiling points. Crude A contains more hydrocarbons with boiling points above 300°C while Crude B contains more hydrocarbons with boiling points below 200°C. Thus, Crude A is categorized as heavy crude and Crude B is categorized as light crude. Crude C is a mixture between Crude A and B in 50:50 ratio, thus the composition is rather even between each boiling point.

It is expected, that Crude A will have heavier product, such as diesel and atmospheric residue rather than light product such as naphtha or kerosene. This means, in distillation column the flow of hydrocarbons is mostly headed toward bottom columns. While in Crude B, the flow of hydrocarbons is mostly headed toward top columns. Sulfur and TAN content is distributed mostly towards bottom columns, thus near bottom columns sulfur and TAN content should be higher [15]. The concentration of sulfur and TAN in Crude A at bottom columns should be lower than Crude B because Crude A has more heavy hydrocarbons which can dilute sulfur and TAN concentration. This means, Crude A should have lower corrosion severity than Crude B. In addition of that, Crude B contains more sulfur and TAN than Crude A. In Crude C, because the hydrocarbon composition is spread evenly, corrosion severity became more unpredictable. The corrosion severity will depend strongly to sulfur and TAN concentration which tied to hydrocarbon movement inside columns.

![Figure 3. Hydrocarbons composition based on boiling point for each crude assays](image)

3.2. Corrosion Mapping Results and Analysis

The corrosion mapping results for each unit are shown in figure 4 – 7.
Figure 4. Corrosion mapping of Crude Distillation Unit (CDU)
Figure 5. Corrosion mapping of Naphtha Hydrotreater (NHT)
Figure 6. Corrosion mapping of Platformer (PTU)
Figure 7. Number of equipment damaged by corrosion and its severity
Between these three units, Crude distillation Units or CDU have the highest number of equipment that damaged by corrosion. This happens because CDU is the first unit that raw crude enters. The impurities in CDU are higher than any other units. NHT has less corrosion damage because NHT feed comes from heavy naphtha product around the top column of CDU. Sulfur and TAN are mostly concentrated in bottom columns [15]. Thus, this heavy naphtha contains very little sulfur and TAN to cause significant corrosion. PTU feed also comes from NHT, thus the corrosion damage is also low.

In CDU, the corrosion mechanism happened is only Thinning High Temperature Sulfidic/Naphthenic Acid Corrosion, while in NHT only Thinning High Temperature H₂S/H₂ Corrosion, and PTU only High Temperature Hydrogen Attack. Thinning corrosion due to sulfidic/naphthenic acid is only happened at CDU because in NHT sulfur organic is converted into H₂S. Conversion of sulfur organic into H₂S in NHT process is usually very high, around 90-99% [16]. Thus, resulted no sulfur carried throughout NHT and PTU. However, H₂S produced from the reaction also will cause thinning at high concentration in NHT. In PTU, the reaction is conducted in high temperature (500°C) which raised HTHA probability to happen [17]. Because only HTHA happened, the corrosion damage should relatively same between each crude.

In NHT, Crude B and C do not cause any corrosion to equipment while Crude A does. Crude A contains heavier hydrocarbons which cause most hydrocarbons concentrated in bottom column product. This causing product in top of column contains higher concentration of sulfur and TAN than the other crudes. Because the concentration of sulfur is higher than other crudes, then the reaction of sulfur to H₂S will also give higher concentration of H₂S than other crudes.

On the contrary, in CDU, Crude B causes corrosion with highest severity. This happens because two things. First, crude B contains more sulfur and TAN than any other crude. Second, Crude B contains mostly light hydrocarbons thus less heavy hydrocarbon in bottom columns product. Fewer heavy hydrocarbon make sulfur dan TAN concentration is higher than other crudes. This cause the severity is the highest among other crudes which is shown by red colors. On the other hand, by using Crude A, several equipments, which colored as red in Crude B, are colored as yellow.

The interesting thing from this result is corrosion behavior using Crude C. Crude C has the lowest severity among other crudes. This could mean that the hydrocarbon is separate evenly in top and bottom column in which case cause the concentration of sulfur and TAN to the lowest. To prove this hypothesis, in figure 8, sulfur concentrations along the column are shown.

![Figure 8. Sulfur concentrations along the main distillation column in CDU](image)
Figure 8 shows the concentration of sulfur at near bottom column in crude B is the highest among the other. This proved the discussion before that heavier hydrocarbon make concentration sulfur and TAN at bottoms column and vice versa. Meanwhile, in Crude C, sulfur concentration is separated and concentrated near two points in tray number 17 and 35. Figure 8 also shows temperature profile along the column. It shows that tray number 17 temperatures is around 220°C and tray number 35 is around 330°C. According to literature, sulfur and TAN content are usually concentrated in two boiling points; around 200–230°C and 320–360°C [18]. This means because Crude C has hydrocarbons composition even at boiling point 200 until 360°C, the sulfur movement follows the common average temperature of light sulfur and heavy sulfur. The separation is very clear due to this study only modeled sulfur as two kinds; heavy and light. Thus the heavier sulfur will go to hydrocarbons around 330°C and the lighter goes to hydrocarbons around 220°C.

This phenomenon clearly can be seen in corrosion mapping (figure 4). Sub-column distillation and reboiler near bottom column of main distillation has distinguished color in each crude. In Crude A, the color is mostly yellow, while in Crude B is mostly yellow and red, and in Crude C is mostly blue. This means, the corrosion damage in Crude A is high, Crude B is severe, and Crude C is moderate. This sub-column has feed comes from the 27th tray of main distillation column. From Figure 7, in tray 27 the sulfur concentration for Crude C is the lowest than other crudes. This proves that different types of hydrocarbon can effect strongly to corrosion severity.

4. Conclusion
This study presents corrosion analysis for small scale refinery. The results showed that the change of sulfur and TAN composition on crude oil could cause significant change in corrosion rate in nonlinear way especially in Crude Distillation unit which has the highest number of equipment damaged by corrosion with the most severity. These results can be used as prediction for future corrosion assessment based on sulfur and TAN composition.

5. References
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