

# IDENTIFICATION OF ACIDIC CONSTITUENTS IN A CALIFORNIA HEAVY CRUDE

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## Abstract

Acidic constituents of heavy California crudes cause corrosion in the processing equipment. Many of the smaller acids have been identified, and this paper will focus on the heavier acidic compounds from a San Joaquin Valley crude. The acidic fraction is isolated by base extraction, methylated and analyzed by desorption high resolution mass spectrometry, NMR, and FTIR. The majority of the compound groups have been identified. The effect of mild hydrotreating on the distribution of acidic components will be discussed.

## Introduction

A well known and significant problem in crude oil processing is corrosion due to acidic constituents. It is the goal of this study to first determine the acidic compounds responsible for the corrosion, then develop an online system to treat the crude before it enters the high temperature processes. In this work, we examine the composition of acid fractions in oils before and after mild hydrotreating, a process known to reduce the corrosivity in oils with very little change in composition in other than the acidic fractions. An online system to monitor the process will be the subject of future work.

Samples of pre- and post-treated San Joaquin Valley (SJV) crudes were extracted with base. Prior to methylation, the samples were analyzed by Fourier Transform - Infrared Spectroscopy (FTIR) and by  $C^{13}$  Nuclear Magnetic Resonance (NMR). Then, after methylation, they were analyzed by High Resolution Mass Spectrometry (HRMS); the results of which will be the focus of this paper.

## Description of Samples Used

The oil was sourced from California's San Joaquin Valley, and was desalted in the commercial refinery operation. The hydrotreating consisted of heating the crude to temperatures between 550 and 650 F at hydrogen pressures between 100 and 500 psig over a commercial hydrotreating catalyst in a continuous-flow pilot plant system. Samples were taken throughout the run at various severities.

A common measure of acidity in oils was used to compare samples before and after treatment. This method, known as Neutralization Number or Total Acid Number, involves addition of potassium hydroxide (KOH) to the samples until a neutral pH is achieved, and recording the amount of base required to achieve neutrality as milligrams of base per gram of oil. The Neutralization Numbers for the untreated and treated oils discussed in this paper were 5.18 and 0.87, respectively.

## Extraction

The extraction procedure used is a version of the one developed by Seifert and Howells [1]. It requires a 45 g sample to be dissolved in 67 g of isopentane. The mixture is then extracted ten times with a base solution of 70% ethanol and 1% NaOH, followed by two times with a 70% ethanol solution. The solution is centrifuged after each extraction to separate the layers. Centrifuging often results in three layers, an organic and an aqueous separated by solids, which contain asphaltenes. These solid layers are set off to the side until the extraction of the oil is complete. The solids are then dissolved in xylene and extracted with base. The two base extracts are then combined prior to cleanup and acidification at 0°C. Once acidified, the solution is extracted with ethyl ether. The ether is washed with distilled water to neutrality and dried with  $MgSO_4$ . Approximately 100 mg of

extract is methylated with  $\text{BF}_3$  in MeOH. Percent yields were 4.90% and 2.55% for the crude and the treated oils respectively.

## Results

The samples were analyzed on a 3-sector MS-50 high resolution mass spectrometer [2]. The instrument was run in the electron impact mode. The analysis was performed using low electron voltage (17 eV) at 40,000 resolution. The samples were heated from 200 to 400° C on a probe inserted directly in the source. Mass measurements were a result of averaging the data from all the scans taken throughout the temperature range.

The spectra generated by the HRMS were analyzed by a program written in house. It calculates possible formulas for the masses detected by the instrument and categorizes them according to heteroatom substitution (i.e.  $\text{NO}_x$ ,  $\text{O}_x$ ,  $\text{S}_x$ ...) and hydrogen deficiency. The notation of substitution, such as  $\text{N}_2\text{O}_3$ , only indicates that a compound contains two nitrogen and three oxygen. It is written as such to aid in the ease of presenting the data.

The first change that is evident is the shift in average mass. As can be seen in figure 1, the peak mass in the crude distribution is approximately 580 mass units. In the hydrotreated distribution, the peak mass is around 250 mass units.

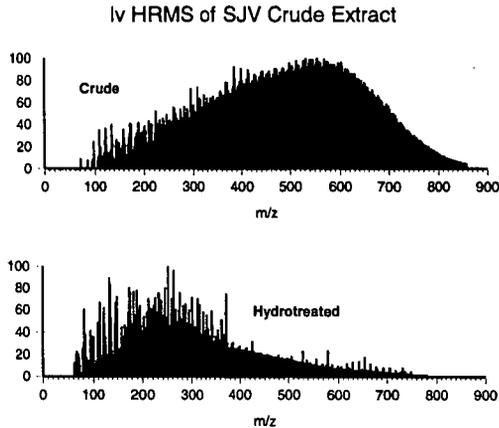


Figure 1. Mass distribution of SJV Crude and most treated product

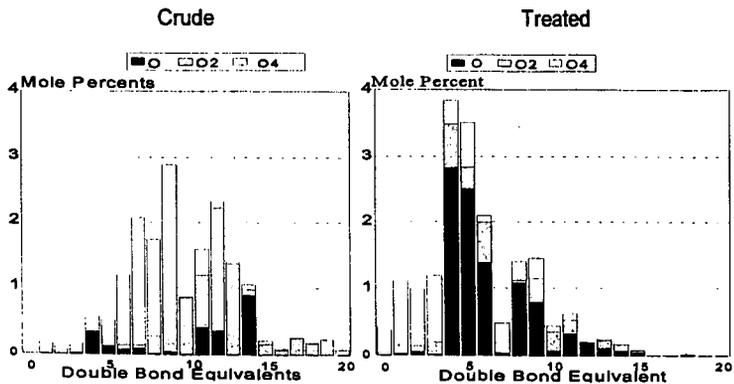


Figure 2. Distribution of oxygen containing species

Looking at figure 2, it is evident that there is a shift in the distribution of the compounds to smaller molecules. There also appears to be a shift from the  $O_4$  functional groups dominating in the crude sample to predominantly single oxygen functional groups in the treated sample without a loss of apparent compound concentration. The groupings of  $O_2$ , and  $O_3$ ,  $O_5$ , and  $O_6$  (not shown in graph) exhibited an overall reduction in concentration and compound size.

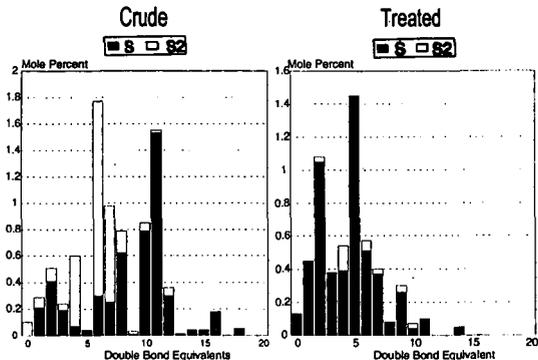


Figure 3. Distribution of sulfur containing species

In figure 3, there is not a significant loss of compounds from the crude to the treated sample. There is, however, an almost complete reduction in  $S_2$  species in the treated sample, thus increasing the concentration of compounds containing one sulfur. There is also a shift towards smaller molecules. In the crude, the compounds are distributed between 0 and 18 DBE, where as, in the treated sample, they are clustered almost entirely below 10 DBE.

Figure 4 shows a significant decrease in the concentration of  $SO_3$  (which designates compounds with a sulfur and three oxygens that are not necessarily together in one functional group) and  $SO_2$  in the treated sample coupled with an increase of  $SO$  containing compounds. There also appears to be a loss of compounds in this group. Though the concentration of the compounds between DBE zero and DBE 10 is not reduced, the compounds above DBE 10 are almost completely gone.

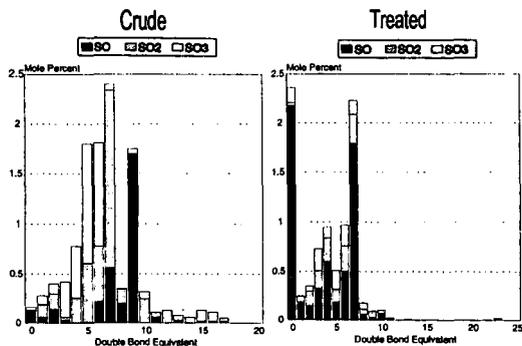


Figure 4. Distribution of  $SO_x$  containing species

For the nitrogen functional groups, in figure 5, there is a sharp reduction in the  $N$  through  $N_2$  moieties coupled with an increase in  $N_3$  groupings in the treated sample. While the distribution across the size of the molecules appears to be intact, there appears to be an overall reduction of compound concentration.

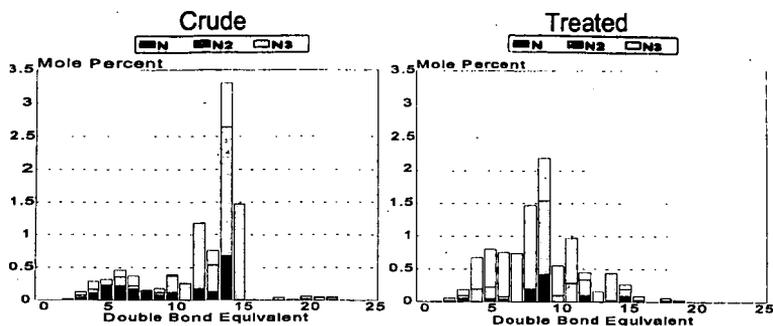


Figure 5. Distribution of nitrogen containing compounds

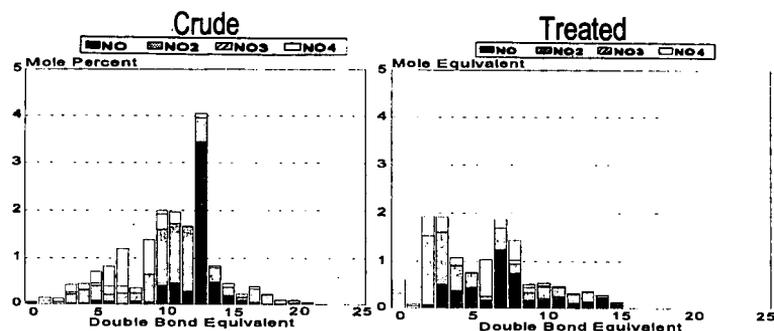


Figure 6. Distribution of  $\text{NO}_x$  containing compounds

Nitrogen-oxygen compounds appear to have had their concentration redistributed (figure 6). In the crude, it appears that the most prevalent class of compounds are those with 13 DBE (mole percent of 3.5), with lesser amounts spread between 3 and 21 DBE. In the treated sample, the distribution shifts to smaller DBE, (i.e. smaller molecule sizes). Looking at the other three  $\text{NO}_x$  moieties, appear to shift to smaller compounds coupled with a slight reduction in overall concentration.

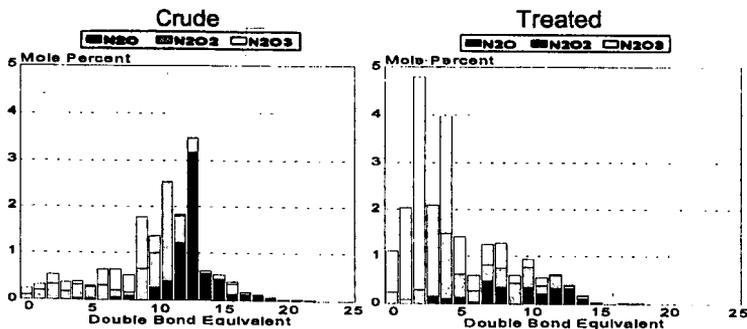


Figure 7. Distribution of  $\text{N}_2\text{O}_x$  containing compounds

The most obvious change in figure 7 is the  $N_2O_3$  grouping. There is a significant increase in the amount of compounds in the treated sample. This change is coupled with a significant a concurrent decrease in  $N_2O$ . The  $N_2O_3$  moieties are only slightly decreased in the treated sample. The redistribution of the entire series is only minor. It is the center of the concentration that is shifted from 13 DBE to 3 DBE.

Not surprisingly, the overall trend appears to be towards smaller compounds. However, while the  $S_x$ ,  $O_x$ , and  $SO_x$  groupings show a tendency towards fewer heteroatoms in the compounds, the  $N_x$  and the  $N_2O_x$  groupings appear to become more complex and keep their larger molecules.

### Conclusions and Future Work

The techniques employed in this study allow us to identify the relative concentrations of various important acidic groups in crude oils and processed products. A broad molecular-weight range of species containing various levels of oxygen, sulfur, and nitrogen are observed. The species identified include aromatic, aliphatic, and phenolic acids. Hydrotreating of acidic crudes to reduce their acid content has different impacts on the different species present. Changes in the number of species with high heteroatom content, and changes in molecular size of certain groups of species have been observed. Our current work applies these techniques to a focused group of samples designed to help understand which components most strongly relate to corrosive behavior in oils, how to facilitate measuring the corrosive species, and how to convert these species to non-corrosive forms.

### Acknowledgement

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### References

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