

THE OXIDATION OF FRACTIONS OF FUEL OIL #6 BY DIFFERENTIAL SCANNING CALORIMETRY AND THERMOGRAVIMETRY.

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INTRODUCTION.

Since a few years back, it has been realized throughout the world the need to find new and/or alternative energy sources to replace fossil fuels. Today, however, most of the countries in the world still depend on fossil fuels, and in particular on residual oil to meet their energy requirements. This situation, will continue to be as such for at least the next twenty years, and may be longer. The residual oil, as it is used today for the production of electricity by the utilities, contains sulfur, and trace metals, besides its usual elemental composition. As it is well known, when the residual oil is burned in a big industrial boiler the above mentioned elements, will produce substances which are dangerous for the environment. These substances, also have a high influence in the loss of availability, and efficiency of the boilers due to the formation of deposits within the furnace, and the corrosiveness of some of the products. Moreover, with the utilization of better technologies in crude oil refining processes the residual oil will increasingly have higher amounts of sulfur and metals, and will become heavier. Also, the use of a heavier oil usually leads to an increase in unburned particles, and in polyaromatic hydrocarbons in the flue gas. In order to attain the appropriate protection for the environment, and for the industrial boilers it is necessary to understand how the harmful products are formed, during the combustion of the residual oil. To reach such an understanding, we believe it is necessary to have a better knowledge about the oxidation chemistry of the oil.

In a previous paper(1), we have reported the utilization of differential scanning calorimetry (DSC) to study the thermo-oxidation of fuel oil #6. It was shown, that it is possible to utilize, the techniques in thermal analysis to obtain kinetic information about the oxidation behavior of the fuel. We have also shown(2), that the results from the thermogravimetric analysis (TGA) of the fuel are highly complimentary with the results from the DSC. These two techniques, combined for the study of the oxidation of fuel oil #6, in the temperature range between 200-600°C, have provided us with an insight into the different mechanisms of oxidation of the fuel. In the present work, we have separated the asphaltenes from a sample of mexican residual oil. The oxidation profile of both, the asphaltene, and asphaltene-free fractions was obtained by means of DSC and TGA, between 200°C and 600°C. We also have attempted to obtain kinetic information from the data, and have compared the results with those previously obtained for the fuel.

EXPERIMENTAL.

A sample of a previously studied(1,2) mexican residual fuel oil was chosen for the present work. The asphaltene, or heavy fraction was

separated from the oil by means of extractions with n-pentane. Elemental analysis, and analysis of sulfur and vanadium content were performed on both, the asphaltene and asphaltene-free fractions. Distribution maps of sulfur and vanadium were obtained for the asphaltenes, with an X-ray fluorescence microprobe attachment to a scanning electron microscope (SEM).

The oxidation profile of both fractions was obtained by means of a Perkin-Elmer DSC-2 differential scanning calorimeter, and a TGS-2 thermogravimetric system. The TGS-2 was provided with the signal derivative attachment. Two types of experiments were performed: a) dynamic, and b) isothermic. In the dynamic runs, the sample was charged at room temperature, and the temperature varied at a rate of 10°C/min. In the isothermic experiments, the sample was charged at a given temperature, which was held constant over a period of time, or until the sample weight was depleted. For the asphaltene-free or light fraction the isothermic experiments were run at various temperatures between 230 and 290°C, and between 380 and 460°C. For the heavy fraction, the isothermic runs were made at temperatures between 390 and 480°C. The sample pans in the DSC experiments were made of aluminum, and the sample covers had to be perforated in order to obtain meaningful results. The sample pans in the TGA experiments were made of platinum. All the experiments were performed with a flow of oxygen of ~25 ml/min, and the sample weight was ~1 mg, and ~2 mg for the asphaltene and asphaltene-free fractions, respectively.

## RESULTS AND DISCUSSION.

The fuel oil studied here has an asphaltene content of 14%. Table 1, shows the results of the elemental analysis, the sulfur and vanadium content, and the hydrogen: carbon ratio for the fuel, and the fractions. As expected, all the vanadium remains in the asphaltenes. Approximately 75% of the sulfur from the oil remains in the light fraction. The H/C ratio decreases from a value of 1.5 for the fuel, and the asphaltene-free fraction, to a value of 1 for the heavy fraction. The H/C ratio of the asphaltenes is very typical(3) for this kind of hydrocarbons. This ratio, is close to that found for some coals(4). Thus, this result may speak by itself about the difficulties to obtain adequate conditions for the complete combustion of the asphaltenes. Figures 1, 2, and 3 reveal another interesting feature of the heavy fraction. Figures 2, and 3 are the distribution maps of V, and S respectively of the SEM image for the asphaltenes in figure 1. In these maps, at least some of the sulfur of the heavy fraction seems to be closely associated with the vanadium. Most of the structures proposed for the asphaltenes(3,5), do not include heteroatoms eventhough there usually is a high sulfur content in this fraction. Some of the vanadium in the asphaltenes, is often associated with porphyrin-like structures(6,8) in which sulfur is not included, but very little is known about non-porphyrinic vanadium. Dickson and Petrakis(8), have proposed some possible sulfur environments around a VO system, to account for non-porphyrinic vanadium. The types of system proposed by Dickson and Petrakis are consistent with the results shown in figures 2, and 3. The association of sulfur, and vanadium in the asphaltenes needs to be the object of further investigation since the chemistry of such complexes may be quite different from that of porphyrinic vanadium(7).

Figure 4, shows the DSC results in the region between 200-600°C, for the fuel and its fractions. This plot shows two exothermic

regions, one at  $\sim 300^{\circ}\text{C}$  (zone I), and a second region (zone II) which starts at  $\sim 400^{\circ}\text{C}$ . At the beginning of the zone II, there are several sharp peaks. These peaks, indicate a highly unstable region with respect to the oxidation of the hydrocarbons involved.

The asphaltene fraction, does not show any peaks in the first zone of the thermogram, whereas the light fraction shows the biggest peak within this region. In the second zone we observe that the asphaltenes show the least amount of instability, and they peak earlier in temperature than both, the fuel and the light fraction. The weight of asphaltenes utilized to obtain the thermograms in figure 4, was approximately half of the weight utilized for the fuel and the light fraction. Thus, the asphaltenes also show the biggest area under the peak within the zone II in figure 4. On the other hand, the light fraction gives the smaller peak, and higher temperatures in the second zone. These results, are confirmed by the experimental results with the TGA, which will be discussed later. The differences, in the zone II, among the heavy, and light fractions are not easy to explain. It is possible, that the metals in the asphaltenes are acting as catalysts in the oxidation of this fractions. Therefore, we may have the peak shifted to lower temperatures, with respect to the fuel. In the case of the light fraction, it is possible that the sulfur contained within this fraction is acting as an inhibitor(9) for the oxidation of these hydrocarbons. Thus, an inhibiting mechanism may shift the peak of the light fraction towards the higher temperatures.

Figure 5, shows the typical results for the dynamic TGA experiments, along with the derivative curves (DTGA) of the TGA signals. It is observed in figure 5, the resemblance between the DTGA curves, and the curves in figure 4. Thus, the DTGA thermograms confirm the results obtained for the fuel and its fractions, by DSC. That is, the asphaltene fraction does not show a peak at  $\sim 300^{\circ}\text{C}$ . Also, for the region between  $400\text{--}600^{\circ}\text{C}$  the heavy fraction shows the largest peak at lower temperatures, and the light fraction gives the smallest peak at higher temperatures, with respect to the peak of the fuel. According to the TGA results, there is a mass loss of  $\sim 20\%$  for both, the fuel, and the asphaltene-free fraction up to a temperature of  $\sim 250^{\circ}\text{C}$ . This loss of weight in the samples, has not released or absorbed heat such that it could be accounted for in the DSC experiments. The mass loss before  $250^{\circ}\text{C}$ , could be due to either the evaporation of volatile compounds, or to a very mild oxidation or pyrolysis of the fuel, with the production of volatile species. The TGA, DTGA, and DSC results at  $300^{\circ}\text{C}$  confirm the existence of an exothermic reaction at this temperature in the fuel, and the light fraction. The TGA for the light fraction, in this temperature region shows that the percentage of the mass lost during the reaction is higher than it is for the fuel. This result, explains why the area under the peak in zone I for the asphaltene-free fraction is bigger than the area under the peak of the fuel. These results, indicate that the same type of oxidation reaction is taking place for the fuel and the light fraction in the zone I. However, more material is reacting at these temperatures in the asphaltene-free fraction than it is in the fuel. The end of the first region of oxidation for the fuel and the light fraction is signaled in the TGA plot by a drastic change in the slope of the curve. The new slope indicates a much slower rate in the mass loss. Finally, the TGA curve of the fuel and the asphaltene fraction, shows another change in the slope towards higher rates of mass loss indicating the beginning of the zone II. The new change in slope is more gradual in the light fraction than in the fuel. The TGA curve of the asphaltens, shows almost no change in the weight

of the sample until  $\sim 400^\circ\text{C}$ . At  $\sim 400^\circ\text{C}$ , there is a rapid fall-off of the signal, which indicates a rate of mass loss higher than even that for the fuel, in the same temperature region. The slow rate in the mass loss of the asphaltene-free fraction, and a high rate of mass loss for the asphaltenes within the same temperature region go along with the results in the DSC for both fractions. Therefore, we may argue again that there is an inhibiting mechanism for the oxidation of the light fraction taking place in the zone II. We may also argue that, a catalytic effect is at least partially responsible for the results obtained with the asphaltene fraction.

The isothermic TGA curves have been kinetically analyzed. It was assumed, as it was the case for the fuel(1,2), a pseudo-first order kinetics, which means a first order with respect to the fractions. Figures 6 and 7 present the Arrhenius plots for the zones I and II of the light fraction, respectively. Figure 8 shows the Arrhenius plot for the asphaltenes. In Table 2, we have compared the activation energies( $E_a$ ) for the fuel, and its fractions. The  $E_a$ 's for the fuel, and the light fraction are similar to each other. On the other hand, the  $E_a$  of the asphaltene fraction is considerably higher than the  $E_a$ 's for the fuel, and the light fraction. These are results, which are somewhat expected since the light fraction represents 86% of the fuel. The high activation energy for the asphaltenes, should also be considered as normal due to the oxidation resistance of this fraction. It is probable that the first oxidation zone in the fuel, and the light fraction, is due to the paraffinic content plus some of the lighter aromatic hydrocarbons in the fraction. This observation is based on the low activation energy for the reaction in zone I. However, the results from DSC and TGA show that the heat of oxidation, and the loss of mass are small in this zone. Thus, since the paraffinic content of the fuel is not so small, it is also probable that the degree of oxidation of the reactive species of the fuel, and the fraction in zone I is low.

Another interesting feature of the asphaltene fraction is shown in Figure 9. The curves in figure 9, are the isothermic TGA runs at 470 and 480 $^\circ\text{C}$ . These two curves show a smooth curve for approximately 2.5 and 2 minutes, respectively. After this time, there is a sudden loss of mass until the sample mass is almost depleted. The minute amount of mass remaining after the sudden change continues its oxidation, but at a much slower rate. The sudden change, is an ignition of the asphaltene fraction. The important fact is that at lower temperatures there is no ignition of the sample, but a gradual oxidation of the asphaltenes. Starting at  $\sim 470^\circ\text{C}$  there is an ignition of the sample, but it is preceded by an induction period. This behavior, is not found in the asphaltene-free fraction. In the light fraction, at  $\sim 470^\circ\text{C}$ , there is an spontaneous ignition of the sample without a measurable induction period.

## CONCLUSIONS

- At least some of the sulfur in the asphaltenes, seems to be closely associated with some of the vanadium of this fraction.
- The light fraction shows two regions of oxidation in the temperature range between 200-600 $^\circ\text{C}$ . These regions are similar to those of the fuel, but shifted toward slightly higher temperatures.
- The heavy fraction shows only one region of oxidation in between 400-600 $^\circ\text{C}$ . This oxidation region peaks at slightly lower temperatures than the similar regions in the fuel, and in the light fraction.
- The activation energies of the light fraction are similar to those of

the fuel.

- The  $E_a$  for the asphaltene fraction is considerably higher than the activation energies of the fuel, and the asphaltene-free fraction.
- At 470°C the asphaltenes ignite spontaneously after an induction period of ~2.5 min.
- The light fraction at ~470°C ignites spontaneously without a measurable induction period.

Finally, the overall results of this work, agree well with the idea that the overall behavior of the fuel is an average of the behavior of the two separate fractions. However, some of the differences shown by the DSC, and TGA curves need to be further investigated. Especially, - those features that can be related to catalytic or inhibiting properties of some chemical species within the fuel.

#### ACKNOWLEDGEMENT

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T A B L E 1

ELEMENTAL COMPOSITION OF THE FUEL AND ITS FRACTIONS

	C WT %	H WT %	N WT %	S WT %	V PPM	CENIZAS WT %	H / C ATOMIC RATIO
FUEL OIL	84.7	10.4	0.4	3.8	158	0.05	1.5
ASPHALTENE-FREE FRAC.	84.8	10.9	0.2	3.6	--	--	1.5
ASPHALTENES	83.3	7.2	1.3	6.7	1040	0.42	1.0

T A B L E 2

ACTIVACION ENERGIES FROM THE ISOTHERMIC TGA FOR  
THE FUEL AND ITS FRACTIONS.

FUEL OIL		ASPHALTENE-FREE FRACTION		ASPHALTENES
ZONE I	ZONE II	ZONE I	ZONE II	--
$E_a$ Kcal MoI	$E_a$ Kcal MoI	$E_a$ Kcal MoI	$E_a$ Kcal MoI	$E_a$ Kcal MoI
19.5 ± 0.3	31.6 ± 2.9	23.5 ± 0.5	29.4 ± 0.5	42.6 ± 0.4

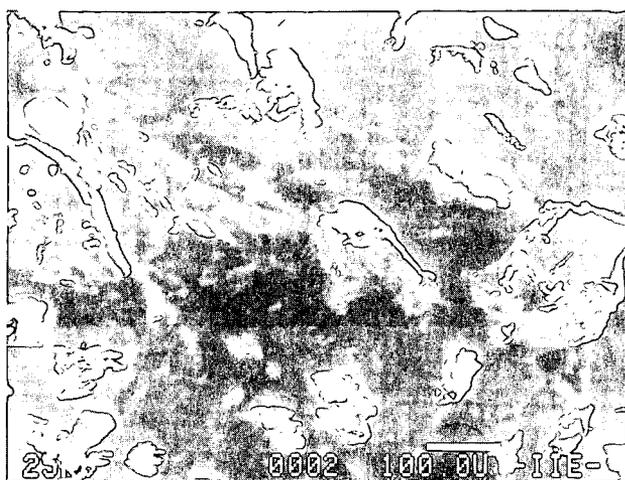


FIGURE 1. SEM IMAGE OF THE ASPHALTENES

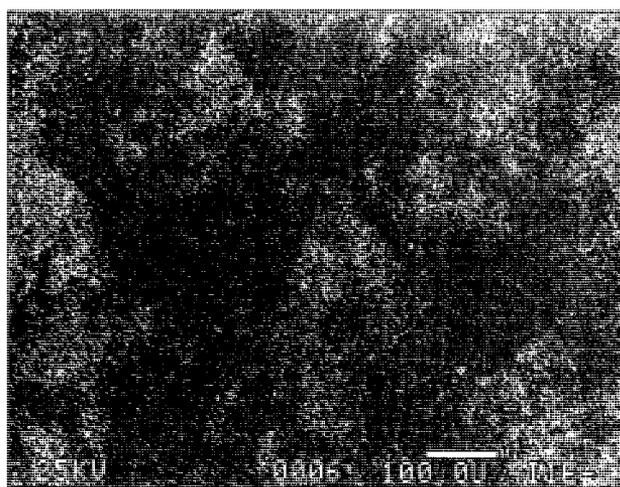


FIGURE 2. VANADIUM DISTRIBUTION IN FIGURE 1

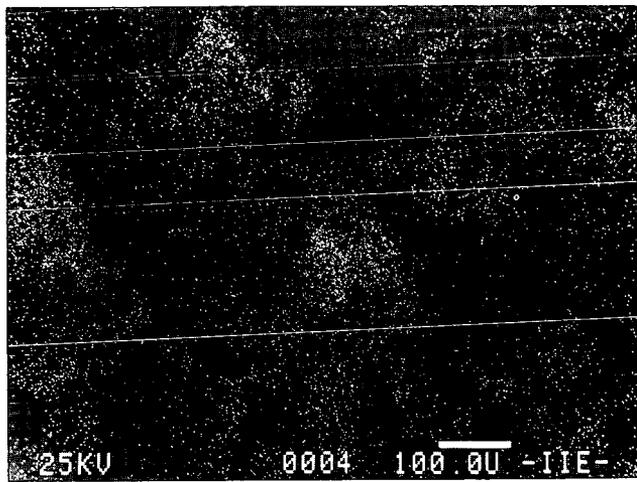


FIGURE 3. SULFUR DISTRIBUTION IN FIGURE 1

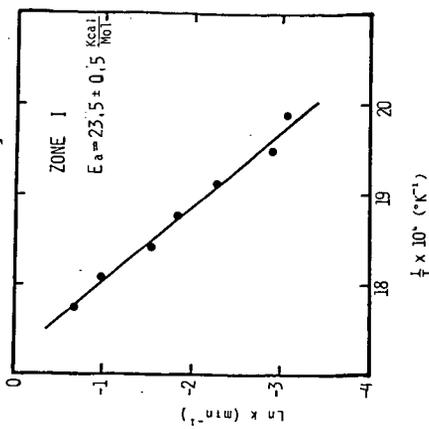


FIGURE 6. ARRHENIUS PLOT FOR THE OXIDATION OF THE ASPHALTENE-FREE FRACTION, ZONE I.

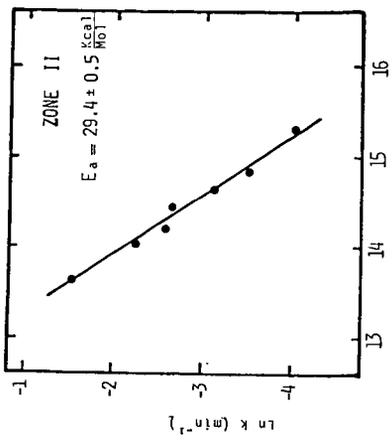


FIGURE 7. ARRHENIUS PLOT FOR THE OXIDATION OF THE ASPHALTENE-FREE FRACTION, ZONE II.

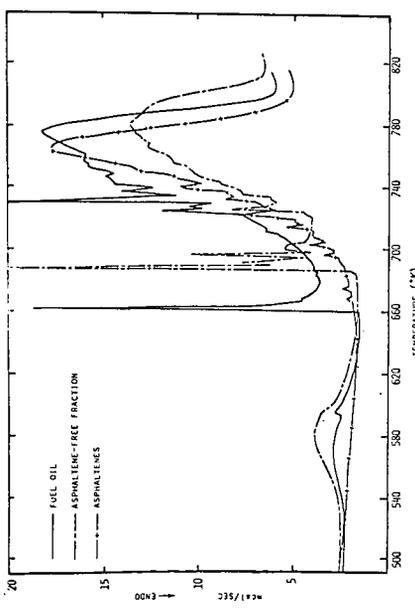


FIGURE 4.- DSC CURVES FOR THE FUEL OIL AND ITS FRACTIONS

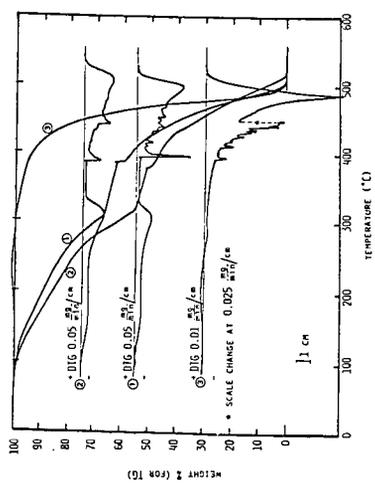


FIGURE 5.- TGA AND DTA CURVES FOR: 1) FUEL OIL (1.8 mg), 2) ASPHALTENE-FREE FRACTION (11.8 mg) AND 3) ASPHALTENES (0.86 mg)

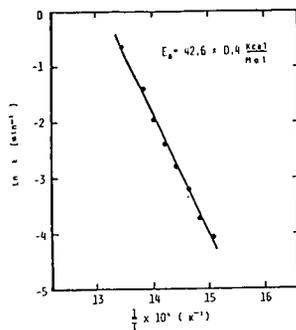


FIGURE 8 .- ARRHENIUS PLOT FOR THE OXIDATION OF THE ASPHALTENES

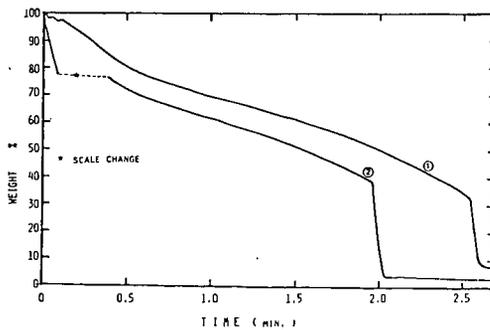


FIGURE 9 .- ISOTHERMIC TGA CURVES FOR ASPHALTENES AT 1).- 470 2).- 480 C.