

# MAYA PETROLEUM ASPHALTENE IMAGING BY SCANNING TUNNELING MICROSCOPY: VERIFICATION OF STRUCTURE FROM $^{13}\text{C}$ AND PROTON NUCLEAR MAGNETIC RESONANCE

G. W. Zajac\*, Amoco Corporation, N. K. Sethi and J. T. Joseph, Amoco Petroleum Products, P. O. Box 3011, Naperville, IL 60566.

Keywords: scanning tunneling microscopy, NMR structure, Maya asphaltene

## Introduction

Petroleum resids are generally upgraded to higher value products by hydroprocessing. This process, however, is very demanding because of the highly aromatic nature of the constituent molecules, high metal and heteroatom content. Most of the problems associated with resid upgrading are attributed to the presence of asphaltenes. Asphaltenes are generally believed to be the precursors of coke formation during resid processing, limiting the kinetics and economics of the process.

Asphaltene structure has been extensively investigated in the past (Speight, 1980; Strausz et al., 1992; Herzog et al., 1988; Ravey et al., 1988; Sheu et al., 1992; Storm, 1991). These studies have provided a global picture of asphaltene structure, which explains general asphaltene reactivity under thermal and catalytic conditions. Because of the dependence of the asphaltene structure on the origin of the crude oil, we performed a detailed study of this particular Maya asphaltene. This work describes a study focused on Maya asphaltenes, using carbon-13 and proton NMR and scanning tunneling microscopy.

## NMR - STM Analysis - Experimental, Results & Discussion

The asphaltene sample used in this study was obtained by heptane precipitation from Maya vacuum resid and its preparation has been discussed in detail previously (Zajac, Sethi and Joseph 1994). The virgin asphaltene sample was analyzed by carbon-13 and H-1 NMR in solution on a Varian VXR-300 spectrometer operating at 300 Mhz proton frequency. Deuterated chloroform was used as the solvent. The asphaltene sample was completely soluble in chloroform. The solubility was confirmed by filtration through a 1  $\mu\text{m}$  millipore filter that left no residue. The details of the analysis are discussed in our previous work (Zajac, Sethi and Joseph, 1994).

The average aromatic cluster parameters for virgin Maya asphaltene (heptane insolubles) were estimated from combined high resolution H-1 and C-13 NMR and atomic H/C data. Possible structural features of the virgin asphaltene molecule that include cyclic and linear aliphatic carbon atoms are illustrated in Figure 1. Three possible structural units of the virgin asphaltene are shown where the aliphatic sidechains repeat units range from  $n=1-5$ . Though no direct evidence of the precise structure groups that contain heteroatoms, N, S, O etc., is available, these are assumed to be part of the ring structure, e.g., thiophenic functional groups for S. These NMR derived structural models form the basis of input for the scanning tunneling microscopy study.

The precipitated virgin asphaltene was diluted in THF to a concentration of 1-5  $\mu\text{g/ml}$  which at the average molecular weight for the asphaltenes corresponds to a submonolayer coverage on an appropriate substrate if agglomeration does not occur. We have employed freshly cleaved highly oriented pyrolytic graphite (HOPG) as a substrate. Several microliters of the dilute solution are micropipetted on the surface and dried in dry nitrogen. A Digital Instruments Nanoscope II equipped with a side viewing stereo microscope is employed. The tunneling tips are electrochemically AC etched tungsten (250  $\mu\text{m}$ ) in 1 M KOH which are subsequently rinsed in distilled water and stored in alcohol. The tunneling conditions were typically 100-600 mV bias voltage and 0.5-2.0 nA tunneling current.

Scanning tunneling microscopy is a direct real space probe of structure. The structure of adsorbates on model surfaces resolved at the molecular level has been applied to a number of systems (see e.g. Chiang, 1992). In an ambient environment, STM studies of the adsorption geometry of alkylcyanobiphenyl on graphite has resolved the individual aromatic groups and alkyl chains (Smith et al., 1990; Mizutani et al., 1990). Previous STM imaging of Rawati asphaltenes (Watson and Barteau, 1994) at high concentrations ( $1, 5 \times 10^{-2}$  wt%) in pyridine has indicated the self-assembly nature of the alkyl sidechains with large regions of self-assembled asphaltenes.

A typical 140  $\text{\AA}$  image of a cluster of asphaltenes is shown in Figure 2. The atomically resolved graphite substrate is visible and a group of asphaltenes are observed as the higher contrast regions. The dimensions are measured as full widths of the observed current perturbations. In Fig. 2, a typical measurement sets the scale of such features  $\sim 13 \text{\AA}$ . Another view of 102  $\text{\AA}$  STM

image of a similar cluster of several asphaltenes is presented in Figure 3, the highlighted feature is of order  $\sim 12$  Å. Because of the heterogeneous nature of this material it is difficult to distinguish aggregates versus individual structural units. Despite this difficulty we attempted a detailed measurement over twenty-four separate entities which were clearly isolated structures in approximately ten individual images yielding an average full width dimension of  $10.4 \text{ Å} \pm 1.9 \text{ Å}$ . A comparison is made to a random set of ten measurements from the possible NMR-derived asphaltene structural units shown in Figure 1, excluding the aliphatic sidechains. The measurements were made by calibration of the C-C bond length at  $1.42 \text{ Å}$  and making several measurements across the condensed ring portion of the three structural units presented. The average NMR dimension derived in this manner is  $11.1 \text{ Å} \pm 1.4 \text{ Å}$  for the condensed ring portion of the possible structural models. The reasonable agreement obtained between the NMR structural models and the STM observation argues in favor of the NMR molecular models.

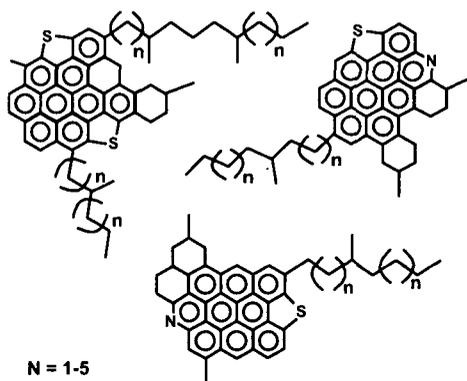
An example of the heterogeneity in the distribution that we observe by STM is shown in Figures 4 & 5 where we find small structures in the presence of much larger structures. The larger structure shown in Fig. 4 of a  $62 \text{ Å}$  field of view is interesting for it appears to be comprised of three separate structural units which are individually  $< 20\text{-}30 \text{ Å}$ . It is not clear if the large structure is an aggregate of three smaller units or a single structure connected by aliphatic linkages. Although we do not have evidence for the existence of aliphatic sidechains, there is weak fine structure existing in the vicinity of many of the structures that we observe. At low bias voltages aromatic structures would be emphasized and aliphatic regions suppressed, hence we might be biasing our observations toward the aromatic structures.

### Summary and Conclusions

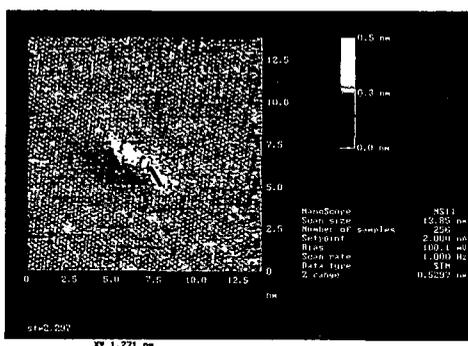
The C-13 and proton NMR analysis predicts small 6-9 ring condensed aromatic ring structural units with aliphatic sidechains for the virgin Maya asphaltene. The comparison of NMR structural models and STM direct observation reveals an agreement between the distribution of aromatic cluster sizes predicted and observed. The broad distribution ranges from several condensed rings to large macromolecular structures in excess of  $30\text{-}50 \text{ Å}$ . This study works in a very dilute limit ( $1\text{-}5 \times 10^{-3}$  wt%). During hydroprocessing NMR has shown condensation reactions to occur and that the average aromatic cluster size grows in size and number. One is tempted to extrapolate to the high concentration regime where very large aggregates and self-assemblies might dominate and form the basis of coke precipitation during the hydroprocessing process.

### References

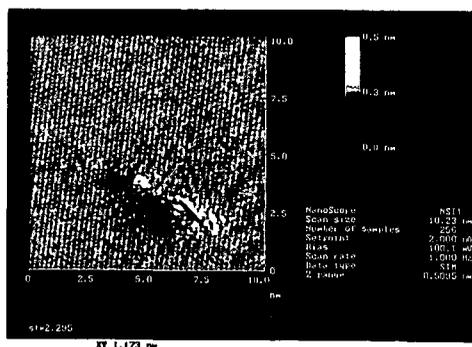
- Chiang, S. Molecular Imaging by STM in *Scanning Tunneling Microscopy II*, H. J. Guntherodt and R. Wiesendanger (Eds.) Springer-Verlag, New York, 1992, 181.
- Herzog, P.; Tchoubar, D. and Espinat, D. Macrostructure of asphaltene dispersions by small angle x-ray scattering. *Fuel* 1988, **67**, 245.
- Mizutani, W; Shigeno, M.; Ono, M. and Kajimura, K. Voltage-dependent scanning tunneling microscopy images of liquid crystals on graphite. *Appl. Phys. Lett.* 1990, **56**, 1974.
- Ravey, J. C.; Ducouret, G. and Espinat, D. Asphaltene macrostructure by small angle neutron scattering. *Fuel* 1988, **67**, 1560.
- Sheu, E. Y.; DeTar M. M.; Storm, D. A. and DeCanio, S. J. Aggregation and kinetics of asphaltenes in organic solvents. *Fuel* 1992, **71**, 299.
- Smith, D. P. E.; Horber J. K. H.; Binnig, G. and Nejh, G. Structure, registry and imaging mechanism of alkylcyanobiphenyl molecules by tunneling microscopy. *Nature* 1990, **344**, 641.
- Speight, J. G. *The Chemistry and Technology of Petroleum* Marcel Dekker, New York, 1980.
- Storm, D. A.; Barresi, R. J.; DeCanio, S. J. Colloidal nature of vacuum residue. *Fuel* 1991, **70**, 779.
- Strausz, O. P.; Mojelsky, T. J.; Lown, E. M. The molecular structure of asphaltene: an unfolding story. *Fuel* 1992, **71**, 1355.
- Watson, B. A. and Barteau, M. A. Imaging Petroleum Asphaltenes using Scanning Tunneling Microscopy. *Industrial and Engineering Chemistry Research*, 1994 **33**, 2358.
- Zajac, G. W.; Sethi, N. K. and Joseph, J. T., Molecular Imaging of Petroleum Asphaltenes by Scanning Tunneling Microscopy: Verification of Structure from  $^{13}\text{C}$  and Proton Nuclear Magnetic Resonance Data, *Scanning Microscopy*, 1994, **8**, 463-470.



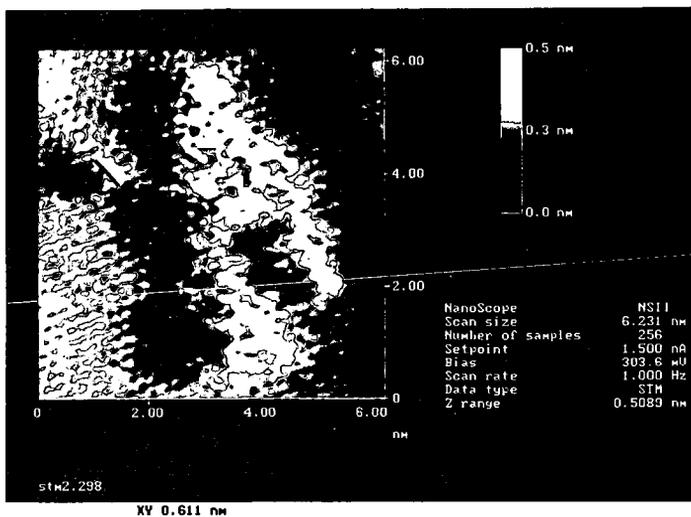
**Figure 1**  
The  $^{13}\text{C}$  and proton NMR derived average structural units in Maya asphaltenes.



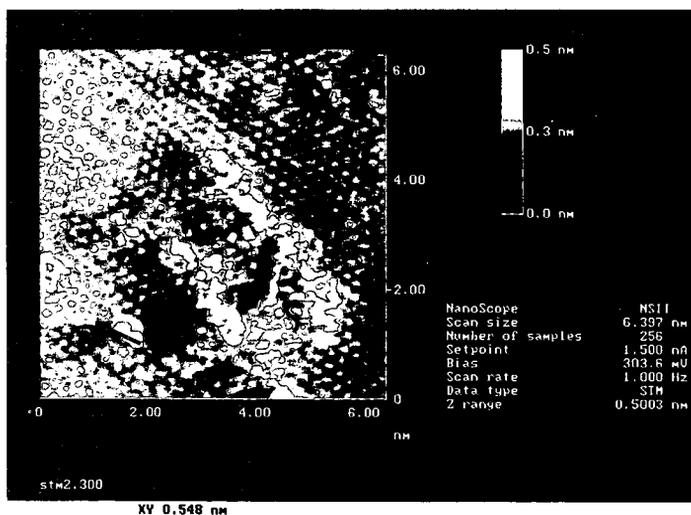
**Figure 2**  
A constant current STM 140Å view of graphite at atomic resolution with a cluster of asphaltenes appearing as bright current spots ( $V_T=100\text{mV}$ ,  $I_T=2.0\text{ nA}$ ). The white line marker indicated at bottom measures  $\sim 13\text{Å}$ .



**Figure 3**  
A constant current STM 102Å view of graphite at atomic resolution with a cluster of asphaltenes, ( $V_T=100\text{mV}$ ,  $I_T=2.0\text{ nA}$ ). The marker indicates a dimension of  $\sim 12\text{Å}$ .



**Figure 4**  
 A constant current STM 62Å view of a large aggregated cluster of asphaltenes, ( $V_F=304\text{mV}$ ,  $I_F=1.5\text{ nA}$ ). The marker indicates an isolated structure of  $\sim 6\text{Å}$ .



**Figure 5**  
 A constant current STM image of 64Å field of view on graphite of another asphaltene cluster, ( $V_F=304\text{mV}$ ,  $I_F=1.5\text{ nA}$ ). The marker measures an isolated structure of  $\sim 5.5\text{Å}$ .