Evaluation of Time Effects on Precipitated Asphaltene Characteristics Using Atmospheric Pressure Photoionization (APPI) and Laser Desorption Ionization (LDI) Coupled to Magnetic Resonance Mass Spectrometry (MRMS)

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Introduction

Among the several factors that affect asphaltene precipitation, time plays one of the most relevant roles. The appearance of asphaltene flocs outside of the colloidal range (1 m) can take hours and, in some cases, even months after the addition of heptane.[1] Furthermore, time also has a great influence in the characteristics of the deposits. Aging of deposits has a great impact in the easiness to remove them.

Our main goal is to evaluate the evolution of the precipitated asphaltenes during long periods of time in static conditions. Also, the work is focused on the study of a solvent situation close to the stability boundary, this is, a condition where the solvent power was relatively high. It is expected that this state is closer to the real solvent power conditions in industry when asphaltene precipitation begins.

Methods

Asphaltenes were analyzed using a solariX 2xR FT-ICR mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany) equipped with a 7 T refrigerated actively shielded superconducting magnet (Bruker Biospin, Wissembourg, France) and the ParacellTM analyzer cell. Apollo II Dual ESI/MALDI ion source was used. Samples were analyzed using APPI and LDI in positive ion mode with resolving power of 1,300,000 at m/z 400 with quadrupolar detection and adsorption mode processing. Internal mass calibration, spectral interpretation, and export of mass lists were performed using DataAnalysis 5.0 (Bruker Daltonics). The analysis of the data including calculation of molecular formulas and relative abundances of compound classes was performed using PetroOrg 10.0 (Florida State University). Double-bond- equivalence (DBE) values were calculated using the following equation:

$$DBE = c - h/2 + n/2 + 1 \qquad (1)$$

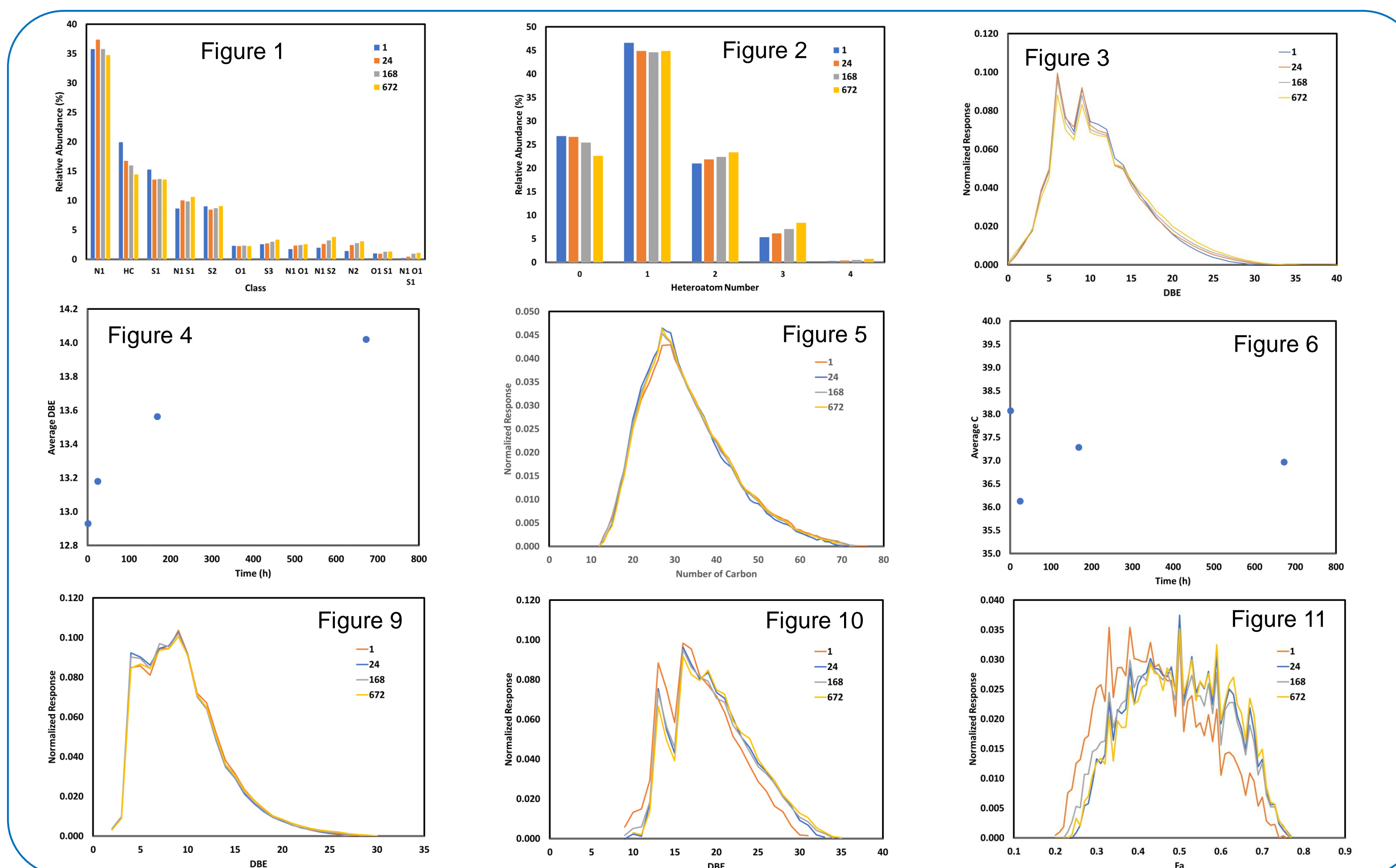For the elemental formula $C_cH_hN_nO_oS_s$.

Fig. 1. Distribution of compound classes using positive ion mode LDI. Fig. 2. Relative abundances for classes containing different numbers of heteroatoms obtained by APPI. Fig. 3. DBE distributions as a function of HCOR . Determined using positive APPI. Fig. 4. Average DBE as a function of time. Determined using positive APPI. Fig. 5. C distributions as a function of time . Determined using positive APPI. Fig. 6. Average C as a function of time. Determined using positive APPI. Fig. 9. DBE distributions for HC class. Determined using positive APPI. Fig. 10. DBE distributions for S3 class. Determined using positive APPI. Fig. 11. Aromaticity (Fa) distributions for S3 class. Determined using positive APPI.

Results

HC classes as well as classes containing one heteroatom become less abundant as time passes. The opposite happens for most classes containing 2 or more heteroatoms. Similar results are found when positive APPI is used. Fig. 2 shows relative abundances for classes containing different numbers of heteroatoms (APPI) as function of time. DBE and C number distributions were calculated for the different times based on weighted relative abundances.

DBE distributions are slightly shifted to the right indicating larger DBEs as shown in Fig. 3. Average DBEs for the distributions are indicate a steady increase as a function of time. C distributions do not show significant changes as a function of time (Fig, 5). Average C numbers for distributions do not have a clear tendency as a function of time. The appearance of molecules with larger DBEs as time goes on indicates a precipitation process where aromaticity of the precipitated material increases

Tendencies for individual classes representative of classes becomming more and less abundant are shown in Figs. 7 and 8. HC class remains almost unchanged as a function of time for carbon and DBE distribution.

In contrast, DBE distributions for S3 class show changes as a function of time as shown in Fig. 10. Changes in C distributions are small. However, changes in aromaticity are significant as shown in Figure 11.
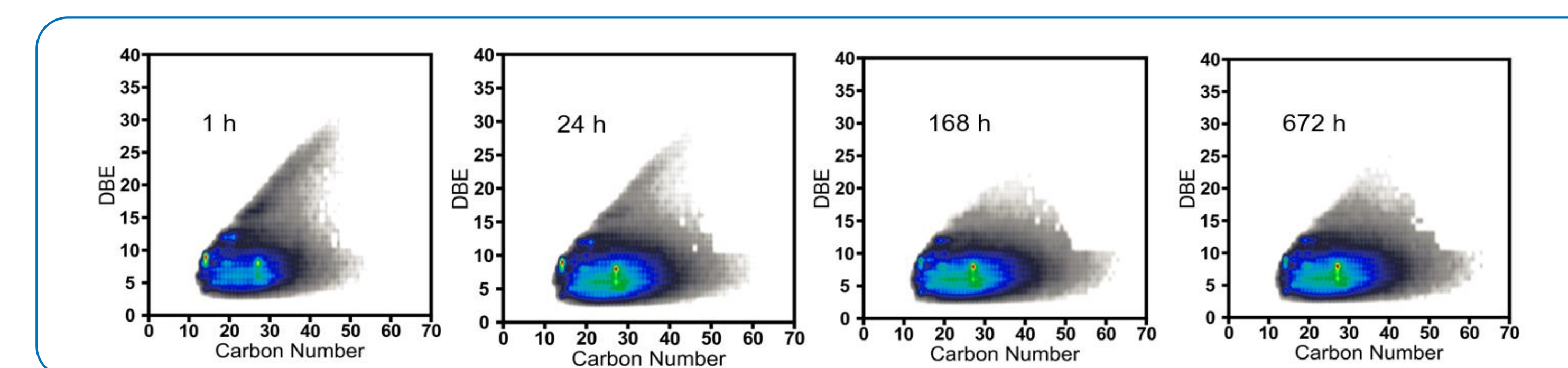

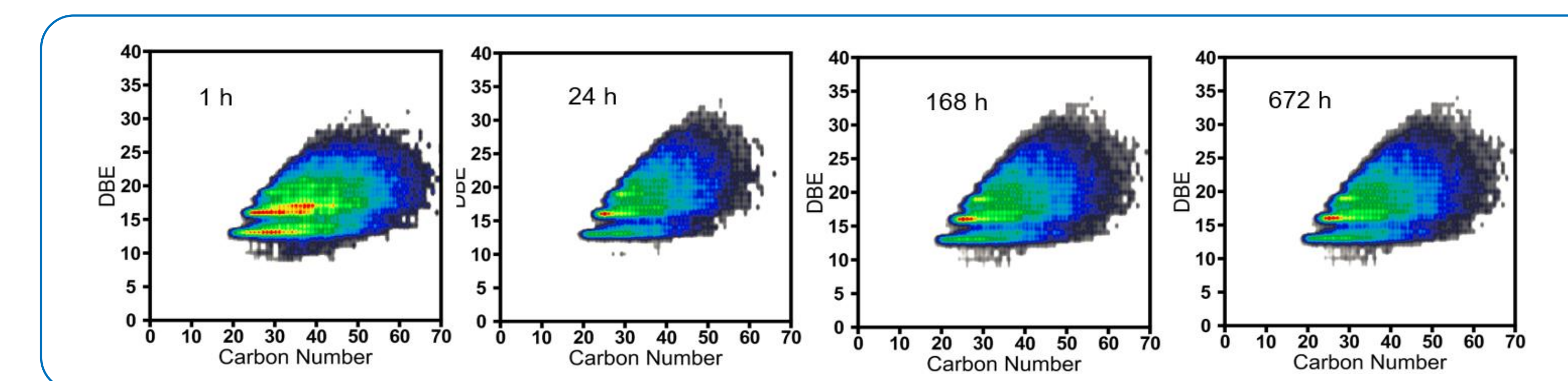Fig. 7. DBE vs C plots for class HC. Determined using positive APPI.

Fig. 8. DBE vs C plots for class S3. Determined using positive APPI.

Separation of Asphaltenes

Asphaltenes were separated from a medium crude oil (30.4 API). The heptane/crude oil ratio (HOCR) of 2 was used to induce precipitation. After blending, solutions were kept in static conditions up to 4 weeks (672 H). Blends were filtered using a Teflon membrane filter (0.2 μ) after 1, 2, 168 and 672 H. The filtered cake was not washed with additional heptane after filtration.

Carbon and Hydrogen analysis of deposits was carried out with a Carlo Erba model 1108 analyzer.

Table 1: Elemental analysis for the asphaltenes as a function of time at a HOCR of 2

Time (h)	Elemental Analysis		
	C (wt%)	H (wt%)	H/C
1	84.62	10.87	1.54
24	84.08	10	1.43
168	83.38	9.85	1.42
672	83.11	9.53	1.38

Conclusions

- Precipitated asphaltenes become more aromatic as a function of time.

- Increases in aromaticity are observed for species containing more than 1 heteroatom.

- Changes as a function of time are less significant than those observed when the nature of the solvent is changed.

- This study provides new information about the nature of the molecules that precipitate under different conditions.

Petroleomics