

EVALUATION OF ORGANIC MATTER REACTIVITY DURING PYROLYSIS BY MICRO-FTIR TECHNIQUES.

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INTRODUCTION

The understanding of the processes occurring, as well as reacting mechanisms taking place during organic matter maturation and oil generation is of major importance in order to develop models to be used in petroleum exploration. The artificial maturation of organic matter performed in laboratory allows to reduce the duration of experiments and to control the reacting medium components (water, polar compounds, gas, generated hydrocarbons).

Infrared spectroscopy is a well adapted technique for the characterization of organic matter as far as it provides information on the chemical composition (aliphatic, aromatic and oxygenated bearing functions) and functional distribution (hydroxyls, carbonyls, carboxyls, ethers, etc.). Coupling an infrared spectrometer with an adapted microscope and using a diamond anvil compression cell allows to facilitate the sample preparation, to improve the quality of the recorded spectra and to use quantitatively the data obtained from the solid residues. In this study, the reactivity of solid residues and polar compounds related to several artificial maturation series has been investigated thanks to these new transmission micro-FTIR techniques.

ANALYTICAL

Samples: The samples used in this study are polars and solid residues from (i) confined pyrolysis series of an immature vitrinite rich coal from the Mahakam delta¹, (ii) confined and hydrous pyrolysis of Woodford shale², (iii) confined pyrolysis of Kimmeridge Clay³.

Transmission Infrared microspectroscopy: The sample preparation protocols of the solid residues and the polar compounds have been previously described in Ruau et al.⁴ (1996). The micro FTIR analysis were performed on a Nicolet System 800 coupled with a Nic-Plan microscope which was fitted with a 250 μm narrow band MCT detector cooled to 77K. The standard analytical conditions were X 15 infrared objective, 40-60 μm diameter infrared spot, 32 to 128 scans, spectral resolution of 4 cm^{-1} , gain = 4.

Flash pyrolysis - Gas chromatography - Mass spectrometry (Py-GC-MS): Solid residues and polar compounds have been investigated by Py-GC-MS using a CDS 2000 pyrolyser coupled with a HP 5890AII chromatogram and a HP 5972A mass spectrometer. Flash pyrolysis was performed at 620°C for 20 s.

RESULTS AND DISCUSSION

Reactivity of the chloroform extracted solid residue. A detailed inspection of the transmission micro-infrared spectra of the solid residues recorded thanks to the diamond anvil compression cell reveals the presence of interference fringes between 1900 and 2800 cm^{-1} that were used for the sample thickness determination⁴. Thus the band integrations were normalized to a common sample thickness (e.g. 30 μm). This operation allowed the intensity variations of a given band to be directly investigated. The variations of the ν aromatic C-H (3000-3100 cm^{-1}), ν aliphatic C-H (2800-3000 cm^{-1}) and ν C=O (1650-1800 cm^{-1}) normalized to a sample thickness of 30 μm are reported in figure 1.

This figure shows that the removal of the C=O functions and aliphatic moieties follows a rather linear trend while the increase of aromatic CH is rather exponential. Special care was also addressed to the distribution of C=O bearing functions. The results show that the 1650 cm^{-1}

¹ band assigned to conjugated C=O first increases during maturation until 320°C and then decreases. This observation strongly suggests a functional rearrangement within the C=O groups during the maturation. This type of approach facilitates the survey of the chemical modifications the solid residues may undergo during maturation.

Transmission micro-FTIR was applied for the characterization of the fractions issued from other maturation series and particularly to successive pyrolysis-extraction experiments⁵. The results showed that the behavior of the kerogen and the polar fractions (asphaltenes and resins) strongly depends on the presence (or absence) in the reacting medium of polars, hydrocarbons, and generated water. Furthermore, a specific reactivity of polars was clearly evidenced.

Reactivity of the polar compounds. Spectra of the polar compounds can be recorded on the same micro-FTIR system than that used for the solid residues. Then, a comparison of the chemical composition of these fractions as well as their specific evolution along the maturation profile can be made. Spectra reported on figure 2 evidence major differences between the solid and the polar compounds. Generally, the solid residue spectra show more intense bands related to aromatic groups (C=C and aromatic CH), while the spectra of the polar compounds exhibit marked aliphatic CH as well as OH and C=O bands.

Data extracted from the integration of polar compounds and solid residue micro-infrared spectra provide the chemical evolution of each fraction during the artificial maturation. If the solid residue react as previously described with a removal of aliphatic moieties and oxygenated bearing functions, the polar compounds behaviour is somewhat different. The evolution of the aliphaticity of the resins suggests that resins may be considered as the kerogen relay for the hydrocarbon generation. On the other hand, it is shown that asphaltenes undergo an oxidation contemporaneous to the removal of the generated water and to the production of hydrocarbons. These results suggest that asphaltenes are implied in complex and specific reactions during maturation that should be taken into account for the modelisation of the hydrocarbon generation process.

Combined use of micro FTIR and Py-GC-MS techniques. Micro-FTIR results were also compared to PyGCMS data obtained on the solid residues and the polar fractions. This approach provides a molecular insight that is particularly suitable for the elucidation of problems related to organic matter reactivity. Parameters obtained by these two different approaches allow the same process to be evidenced by two ways. The aromatization of the solid residue during the artificial maturation can be depicted by the increase of the ratio aromatic compounds/sum of the compounds (Py-GC-MS) as well as the ratio aromatic CH/Sum of the integrated bands (μ -IRTF) (Figure 3). On the other hand, these two techniques can be used in a complementary way to explain for example the evolution the methyl/methylenes distribution of the aliphatic fraction of the asphaltenes.

CONCLUSIONS

Transmission infrared microspectroscopy appears as an improved routine technique to rapidly record high quality spectra of organic matter. The sample preparation as well as the amounts of studied material can be significantly reduced. The quality of the micro-infrared spectra facilitates the qualitative overview of the gross chemical variations occurring during laboratory simulated maturation of organic matter. Thanks to the diamond anvil compression cell, the micro-infrared spectra of solid residues can be used in a quantitative way in order to follow the chemical evolution of organic matter during maturation. The versatility of the micro-FTIR technique allows the characterization of the polar compounds of the same maturation serie. Then the specific reactivity of each fraction can be underlined. Coupling this technique with the PyGCMS provides converging and/or complementary informations on the chemical composition of the studied samples as well as their reactivity.

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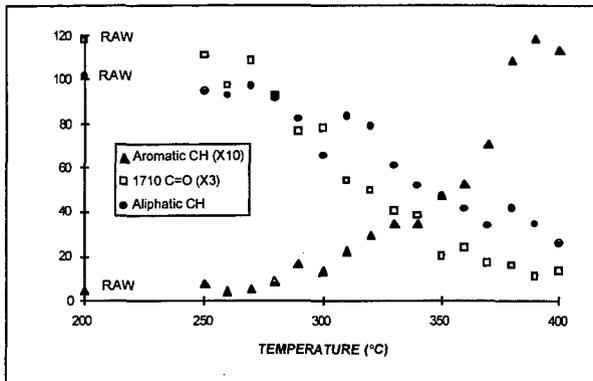


Figure 1 : Evolution of aliphatic C-H ($2800-3000\text{ cm}^{-1}$) integrated area, aromatic C-H ($3000-3100\text{ cm}^{-1}$) integrated area (X 10) and C=O (1710 cm^{-1}) integrated area (X 3), both normalized to a sample thickness of $30\text{ }\mu\text{m}$, with increasing pyrolysis temperature (Confined pyrolysis of a Mahakam coal).

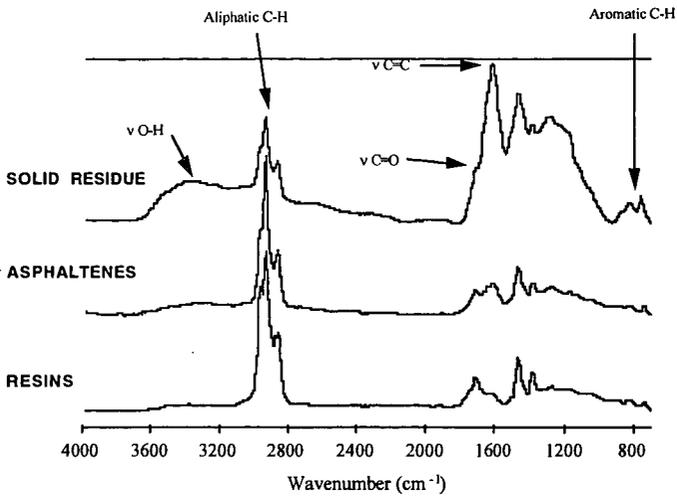


Figure 2 : Comparison between asphaltenes, resins and solid residue obtained by the confined pyrolysis of a Mahakam coal (250°C, 24 h).

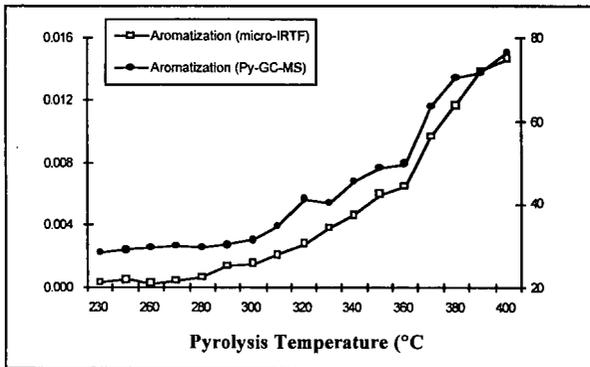


Figure 3 : Aromatization of the solid residue along the artificial maturation evidenced by micro-IRTF and Py-GC-MS data (Mahakam coal).