

STRUCTURAL HETEROGENEITY OF LIGNITE HUMIC ACIDS AS REVEALED BY ALIPHATIC LIPIDS RELEASED AFTER THERMOCHEMOLYSIS

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Lignite and its alkali-soluble humic acids should not be viewed as some kind of low quality fuels only, but also as a valuable raw material for different chemical applications due to its naturally high content of functional groups which can, among other things, influence the bonding distribution of trace metals in the environment.

In this study we investigate and compare hydrocarbons and fatty acids from humic acids derived from the South-Moravian lignite. Humic acids were obtained following the IHSS procedure (Peuravuori *et al.*, 2006; Klučáková and Pekař, 2005). These compounds were released after solvent extraction (bitumens) or with a preparative thermochemolysis system with different alkylating agents such as TMAH and TEAAc to get structural informations and identification of minor products often hidden in flash pyrolysis (Grasset and Ambès, 1998). Tetraethyl ammonium acetate (TEAAc) is employed for the selective alkylation of free acids without transesterification of esterified ones (Grasset and Ambès, 2002). The products obtained after thermochemolysis, as well as bitumens, were separated and analyzed by capillary GC and GC-MS.

Analyzable compounds were mostly aliphatics. Aromatic units derived from lignous skeletons (known as one of the major constituent of lignite) were detected only as traces and then appear to be recalcitrant to thermochemolysis. Aliphatic compounds released after the solvent extraction of humic acids and after thermochemolysis are principally linear hydrocarbons and fatty acids.

The distribution patterns of fatty acids (C₁₄-C₃₂) present a strong even/odd carbon number predominance in the longer mode with a maxima at C₂₈ (Fig. 1) and attest to a plant origin. Linear fatty acids (methyl esters form) released after TMAH treatment present a greater proportion of the longer mode (originating from higher plants) in comparison with those of fatty acids from TEAAc (ethyl esters form) and of directly extractable one. The presence of FAMES as products from TEAAc treatment shows that some of FAMES released after the TMAH treatment were initially present as FAMES in the studied sample.

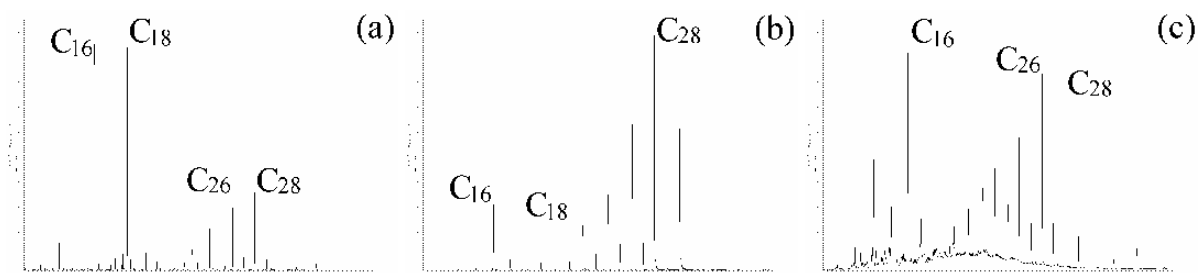


Figure 1. Distributions of fatty acids (as esters) obtained after solvent extraction (a), TMAH (b) and TEAAc (c) thermochemolysis.

Distributions of linear hydrocarbons obtained from the three procedures show sensible differences. The directly extractable hydrocarbons have a typical origin from higher plants with a monomodal distribution from C_{17} to C_{35} members with an odd/even carbon number predominance centered on the C_{29} component. The distribution of linear hydrocarbons obtained after thermochemolysis with TMAH were sensibly different with a slight even/odd carbon number predominance centered on the C_{24} and C_{26} components originating probably from a bacterial activity. The distribution of those obtained after thermochemolysis with TEAAc were centered on the C_{25} and C_{27} members without odd/even preference in the shorter mode ($< C_{24}$).

TMAH and TEAAc thermochemolysis made it possible to discriminate between total and "free" fatty acids. Lipids trapped by macromolecular structures and free, directly-extractable, lipids have not the same origin. The differences observed between compounds released by thermochemolysis and by solvent extraction suggest that these moieties are not "intimately" mixed in humic acids, but forms juxtaposed blocks or "aggregates" of large size, which explains partly their heterogeneous nature.

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