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**FLASH PYROLYSIS/GC-MS IN INVESTIGATION OF SELECTED
SOUTH AFRICAN COALS**

INTRODUCTION

The main coal strata of the Karoo Basin (South Africa) belong to the Ecca Group (early to late Permian) of terrestrial deposition which developed on a slowly subsiding shelf platform (Ryan, 1968, in: Snyman, 1998). The glacial to periglacial climate was characteristic for the biochemical phase of coals formation. The sediments consist of often thick coal seams enriched in inertinite, especially in the lower part of the succession. The upper coal seams are enriched in vitrinite (up to 60 %) in coal seam No 5 in the Witbank coalfield). The series inorganic sediments consist of coarse fluviodeltaic sandstones of Vryheid Formation altering into shale and sandstone series in Volkstust Formation (Cairncross, 1989, Snyman, 1999).

The typical coal bearing strata in Waterberg subbasin consist a coal zone, thickness of 42 m in places comprising 6 coal seams (Middle Ecca) and a Upper Ecca coal zone about 69 m thick. Both zones are developed as a numerous coal seams and layers intercalated mainly with carbonaceous shale with fine-grained sandstones at the bottom. The whole zone is also defined as a “composite coal seam” in areas where the average ash content is less then 50 % (de Jager, 1976).

The main coal bearing strata of the Soutpansberg subbasin is severely faulted (Upper Ecca Stage). The coal zone is approx. 40m thick and consists of alternating coal seams and carbonaceous shale, resembling the Waterberg coal zone (de Jager, 1976). From the petrographic point of view coals of Waterberg and Soutpansberg subbasins are characterised by high vitrinite and low inertinite content.

AIMS

The main aim of the project was to identify the chemical components of the pyrolysates from the African coals macromolecular fraction in a view of the maceral composition. The main interest was given to the lignin-derived substances.

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EXPERIMENTAL

Coal samples description and preparation

Fifteen samples of coals from different collieries of the Northern province as well as Mpulanga and KwaZulu provinces were chosen for pyrolytical investigation. All samples were provided by Vivien du Cann of South African Bureau of Standards. Powdered samples were exhaustively Soxhlet extracted with a dichloromethane-methanol mixture (4:1; vol.: vol.) to remove their bituminous fraction. Solid residue was analyzed by pyrolysis-gas chromatography-mass spectrometry method to assess the composition of their macromolecules.

Petrographic analyses

Petrographic analyses were carried out on epoxy resin pellets. Vitrinite, liptinite and inertinite groups were distinguished under the cross point in ocular in 500 points using the Swift automatic point counter. Random reflectance of vitrinite (R_{rv}) values are cited after Vivien du Cann in: Pinheiro et al. (1998). The measurements were carried out in non-polarizing reflected light and oil immersion, using Zeiss Universal microscope, equipped in 40x magnifying objective and 10x magnifying oculars were applied as well as the 546 nm interference filter.

Flash pyrolysis/gas chromatography-mass spectrometry

A Curie-point Pye-Unicam pyrolyser, type: 795050, working in 770°C was coupled to a HEWLETT-PACKARD gas chromatograph with a HP-1 column (60 m x 0.32 mm i.d.), coated by 0.52 μ m stationary phase film. The experimental conditions were as follows: carrier gas - He; temp. program: 50°C, heating rate to 175°C - 10°C/min, to 225°C - 6°C/min, to 300°C - 4°C/min, final temperature: 300°C. The mass spectrometer was operated in the electron impact ionisation mode at 70 eV and scanned from 50 to 650 da. Data were acquired in a full scan mode and processed with the Hewlett Packard Chemstation software. All compounds were identified by their mass spectra, and comparison of retention times of their peaks to these of standard compounds and literature data and interpretation of MS fragmentation patterns.

RESULTS AND DISCUSSION

Aliphatic hydrocarbons in pyrolysates

Among acyclic aliphatic hydrocarbons *n*-alkanes dominate in the coal pyrolysates while *n*-alkenes are found in lower concentration (Fig. 1). The presence of *n*-alkane/*n*-alkene doublets from *n*-C₅ to *n*-C₂₄ indicates the presence of aliphatic biopolymers derived from material other than lignin. Generally, two types

of distribution can be recognised. The first one (the 5, 6 and 35 coals) is dominated by light-weight compounds (C_6 - C_8 *n*-alkenes and *n*-alkanes) and the second one by heavier compounds (C_{12} - C_{14} *n*-alkenes and *n*-alkanes). The envelope of the *n*-alkene distribution follows the distribution of *n*-alkanes but in some samples a slight odd-over-even carbon number predominance in the range from C_{14} to C_{24} was found. It may be assumed that aliphatic materials come from micro-organisms or lipids bound to the macromolecular coal structure. There is no an obvious relationship between the coal rank and concentration of *n*-alkane/*n*-alkene doublets.

Pristenes, deriving from the scission of a phytol side-chain from a chlorophyll molecule are absent in these coal pyrolysates.

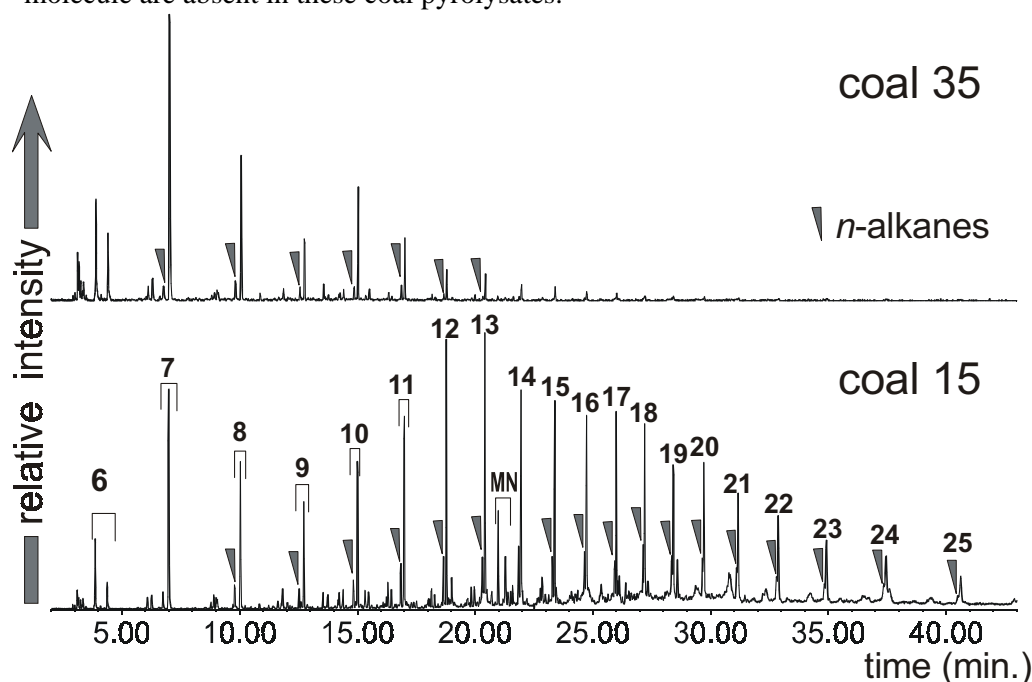


Fig. 1 *n*-Alkane distribution in the pyrolysates of the selected African coals

Lignin-derived compounds

The light-weight compounds constitute a main group in the coal pyrolysates. They are mainly products of thermal destruction of lignin-derived vitrinite. Among them are such phenol derivatives as cresols, ethylphenols, xylenoles, methyl-ethylphenols and aliphatic derivatives of benzenediols present in lower amounts (Fig. 2). Benzene, toluene and xylenes formed from phenol derivatives, increase with the coal rank (Hatcher et al. 1992). The values of benzene/phenol unit ratio calculated for these coals indicate that the ratio can be applied to assess their rank.

Lignin, a rigidifier in woody tissues of vascular plants giving them resistance to gravity and wind, belongs to substances fairly well preserved in geological deposits and can be found in brown coals, soils and marine deposits with land plant input.

There are several lignin types, depend on biochemistry of original plants. Herbaceous, coniferal and angiosperm tree lignins show different chemical composition as a result different requirements of their environments and evolution (Saiz-Jimenez and de Leeuw 1985, Hatcher et al. 1992, Cotrim da Cunha et al. 2001). The main differences lay in type of dominating monomer composing the lignin macromolecule. Coniferal lignins predominantly consist of units of coniferyl alcohol, in herbaceous plants (dicotyledones) the main unit is coumaryl alcohol and in monocotyledones - sinaphyl alcohol.

With increasing coal rank the lignin units undergo significant changes in the structure losing oxygen atoms. The African coals pyrolysates contain numerous compounds formed from lignin alkylphenols such as dibenzofurans formed via condensation of phenols and tetrahydronaphthalenes and naphthalenes formed via cyclization of a four carbon-side chain.

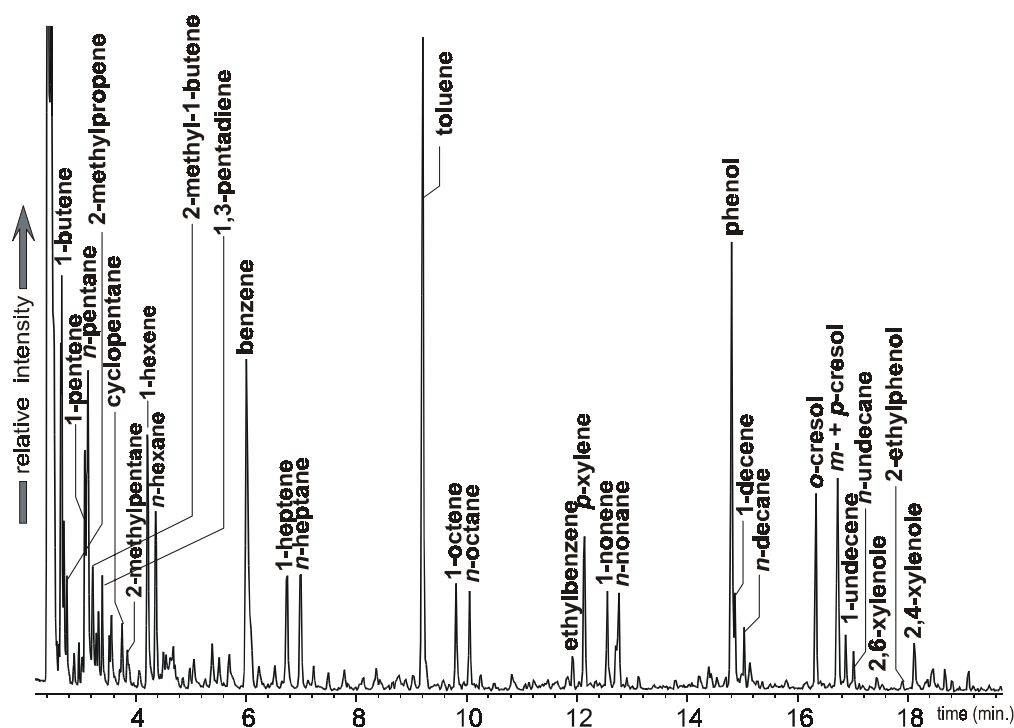


Fig. 2 Identification of the light-weight compounds present in the pyrolysates

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