P227-WE

LIBERATION OF VOLATILES FROM GREEK BROWN COALS DURING OPEN-SYSTEM NON-ISOTHERMAL PYROLYSIS

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Open-system non-isothermal pyrolysis with on-line analysis of methane (CH_4), carbon dioxide (CO_2), carbon monoxide (CO), hydrogen (H_2) and molecular nitrogen (N_2) has been performed on a series of Greek lignites in order to explore the geochemical characteristics and correlate them with coal petrography. Samples came from the Florina-Ptolemais-Kozani basin in northern Greece and the Megalopolis Basin in southern Greece, the locations of the main Greek lignite deposits.

Huminite was the dominating maceral component of the sample sequence with percentages ranging from 70 to 96 %. Liptinite contents varied from 3 % to 18.5 % and inertinite contents from 0.2 % to 17 %. Huminite reflectance values lay between 0.20 % and 0.43 %. Proximate analysis of the samples revealed ash contents between 11 % and 49 %, volatile matter percentages ranged from 37 to 54 % and fixed carbon contents from 16.3 to 38 %. Sulphur contents, with two exceptions, were below 1.5 % and total nitrogen contents ranged between 0.65 and 1.4 %. All fourteen lignite samples selected for this study were characterised by Rock-Eval pyrolysis. Rock-Eval T_{max} values between 364 and 428°C revealed the immature character of the coals. Hydrogen Index (HI) values extended from 96 to 245 mg HC/g TOC while Oxygen Indices (OI) ranged from 72 to 181 mg CO_2/g TOC.

Pyrolysis was performed at a heating rate of 0.5 K/min from room temperature up to 1100°C in a tubular furnace with helium carrier gas (flow-rate 30 ml/min). The pyrolysis gas was analysed in intervals of 2 minutes by gas chromatography (GC). Hydrogen, N_2, methane and carbon monoxide were separated on a molecular sieve GC column and quantified by means of a Flame Ionisation Detector (FID) while CO_2 was quantified by mass spectrometry. The pyrograms of the individual gaseous products of each lignite sample exhibited characteristic patterns reflecting the type and composition of the precursor entities in the complex polymer structure of the coals. Two examples of these sets of pyrograms are shown in Figure 1. No simple systematic relationship was evident between the pyrograms and the maceral composition or other petrographic features of the coal samples. Carbon monoxide was the major component in the pyrolysis gas with its pyrogram showing complex structures and reaching peak generation rate between 600 and 700°C. Carbon dioxide was the earliest pyrolysis product to be liberated with generation starting around 100 °C and extending beyond 600°C. Characteristic CO_2 peaks around 640°C associated with CO peaks were indicative for small amounts of carbonate. Methane was usually released in the 250 °C to 750 °C range. Shoulders or distinct dual peaks in the pyrogram (Figure 1, bottom) indicate its formation from different precursor structures within the coal. Pyrograms of certain coal samples exhibited very narrow and conspicuous N_2 peaks (Figure 1, top) that must be attributed to a molecular precursor structure with a well-defined thermal stability, possibly the tetrapyrrole structure of porphyrins. Interpretations of the pyrograms will be discussed in combination with ancillary analytical results such as IR spectroscopy.

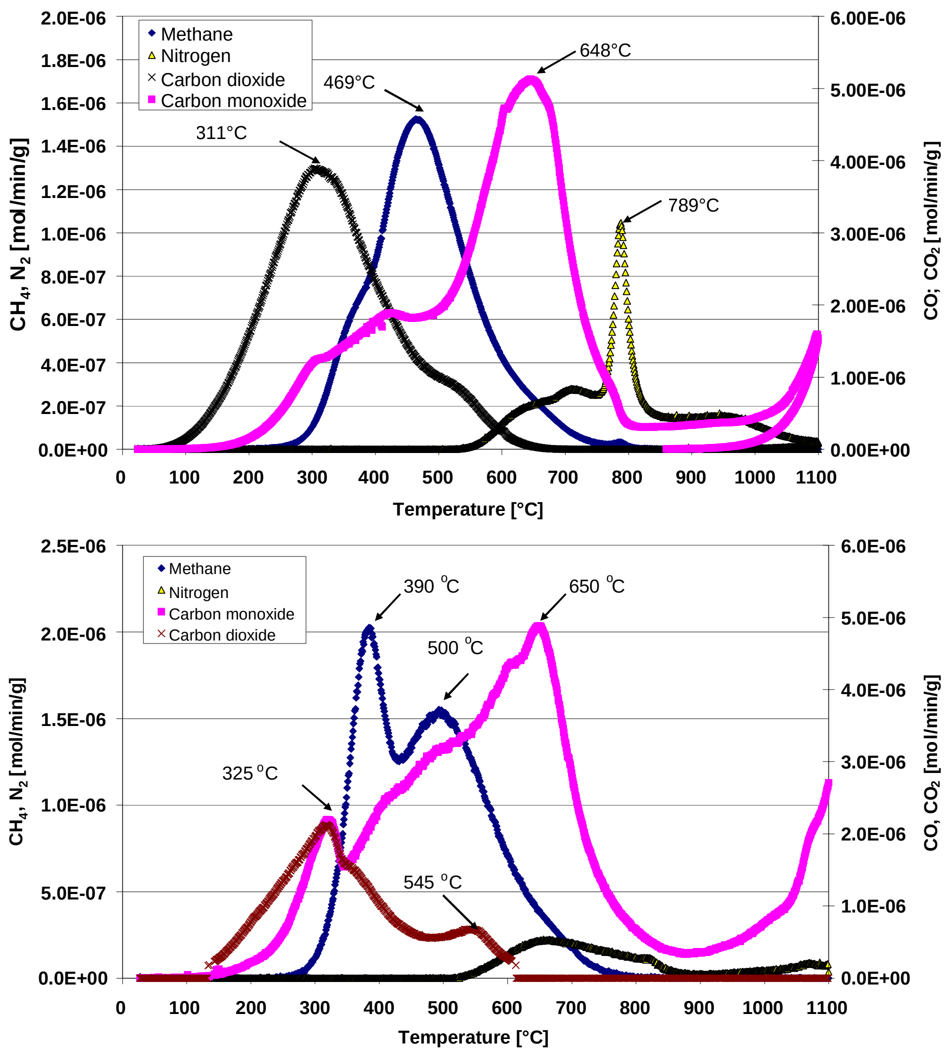

Figure 1. Volatiles liberated from Greek lignites during non-isothermal pyrolysis.