



## MSSV Pyrolysis of Vitrinite - Investigations on Gas Generation and Vitrinite Reflectance

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Vitrinite reflectance is an important parameter for the calibration of thermal history reconstructions in sedimentary basins. Furthermore, since vitrinite generates most of the gas during thermal maturation of coal, it is important to understand its gas generation potential and kinetics, in particular at high temperatures (high maturities). In order to correlate results with established kinetic data sets, the gas generation potential and the changes in reflectance of vitrinites were studied at various heating rates (0.1K/0.7K/5K per minute). Microscale sealed vessel (MSSV) pyrolysis experiments were performed on pure vitrinite particles hand-picked from vitrain layers of a high volatile bituminous coal from the Ruhr area, Germany (0.92%  $VR_r$ ). In a first step, about 25 samples ( $\sim 3\text{mg}$  each) were sealed in quartz glass tubes and heated from  $150^\circ\text{C}$  to  $560^\circ\text{C}$  at the specified heating rates. Between  $300^\circ\text{C}$  and  $560^\circ\text{C}$ , individual samples were removed from the pyrolysis oven at predefined temperatures. The pyrolysis products were analysed in a GC and analysed for their hydrocarbon composition ( $C_1$ - $C_{32}$ ). The same heating procedure was applied to 15 samples ( $\sim 30\text{mg}$  each) that were subsequently used for microscopical analysis (reflectance measurements). In a first evaluation, yields of  $C_2$ - $C_5$ ,  $C_6$ - $C_{14}$  and  $C_{15}$ - $C_{32}$  hydrocarbon fractions and their generation rates as a function of temperature were determined. The peak generation temperature of the  $C_2$ - $C_5$  group increases from  $464^\circ\text{C}$  to  $502^\circ\text{C}$  and  $540^\circ\text{C}$  at heating rates of 0.1, 0.7 and 5.0 K/min, respectively. Temperatures of maximum generation rates for the  $C_6$ - $C_{14}$  group were found to be  $432^\circ\text{C}$ ,  $468^\circ\text{C}$  and  $497^\circ\text{C}$  for these heating rates. The microscopical analysis of the residuum revealed that vitrinite showed almost no increase in reflectance up to  $380^\circ\text{C}$  for all heating rates. A first significant increase in vitrinite reflectance occurred at  $400^\circ\text{C}$ , when values of 1.36%  $VR_r$ , 1.07%  $VR_r$  and

0.97% VR<sub>r</sub> were reached at heating rates of 0.1, 0.7 and 5.0 K/min, respectively. A steady increase in vitrinite reflectance was observed up to temperatures of ~500°C. In this temperature interval, vitrinite reflectance values of the samples from the 0.1 K/min heating rate experiment were found to be higher by roughly 0.3 - 0.4% (absolute) than those from the 0.7 K/min heating rate experiment. The difference between samples from the 0.7 K/min and the 5.0 K/min experiments increases from around 0.2% VR<sub>r</sub> at 400°C up to 0.5% VR<sub>r</sub> from 440 to 480°C. At temperatures above 500°C the vitrinite reflectance increased more slowly, and maximum values of 2.61% VR<sub>r</sub> (at 500°C), 2.53% VR<sub>r</sub> (560°C) and 2.29% VR<sub>r</sub> (560°C) were reached at heating rates of 0.1, 0.7 and 5.0 K/min, respectively. At heating rates corresponding to natural burial, these reflectance values would be reached at temperatures of about 203°C to 215°C (see Barker & Pawlewicz, 1994). The data are used to develop a new kinetic scheme of vitrinite evolution in sedimentary basins as a function of temperature.

Barker, C.E. & Pawlewicz, M.J. (1994). Calculation of Vitrinite Reflectance from Thermal Histories and Peak Temperatures: A Comparison of Methods. in Mukhopadhyay, P.K. & Dow, W.G. (Eds.) *Vitrinite Reflectance as a Maturity Parameter. Applications and Limitations*. ACS Symp. Ser., **570**: 216-229.