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# Comparison of the first stage of the thermal decomposition of Polish coals by diffuse reflectance infrared spectroscopy

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## ABSTRACT

Diffuse reflectance Fourier transform infrared spectroscopy was applied to study the decomposition of hard and brown coal during mild pyrolysis. The pyrolysis of investigated samples was conducted with a heating rate of 10 K/min up to 673 K under ambient pressure and a nitrogen flow of 4 L/h. Curve-fitting analysis was employed to characterise the coal structures evolving in temperatures ranging from 323 to 673 K. This study gives the information about the degradation of hydrogen bonds and oxygen structure. The comparison of the calculated structural parameters shows that bonds assigned to  $C_{ar}$  in hard coal are more stable at the investigated temperature range than the bonds in brown coal. The same phenomenon was observed for the C–H bonds in aromatic formations. It was noted that during the pyrolysis the first changes in the structural parameters of lignite are visible at temperatures above 423 K and in case of hard coal above 473 K.

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## 1. Introduction

Coal is considered as the most abundant hydrogen resource on earth; therefore, the structure of coal should be well understood for its effective utilisation. During the thermal processing of coal, the first step is always pyrolysis, which takes place due to the heating of coal particles. This step is very important because the rate at which it occurs affects the subsequent steps, so it is critical in any accurate model. Devolatilisation takes place at low temperatures (623–1073 K) and in parallel with the heating of coal particles. The rate of heating of the coal particles influences the way in which pyrolysis occurs, but the main pyrolysis products (composition and amount) are determined by the chemical composition of coal. The pyrolysis behaviour can generally be explained in terms of the presence of weak bonding in the coal macromolecular network and the concentration of side groups, which can be easily broken up during heating. In recent years, much effort has been dedicated to propose a systematic description of coal structures, which could be readily applied to the large variety of coals and the great variability in the chemical properties of different macerals in a single coal. Nevertheless, such a description becomes significant if it is postulated that the chemical properties of coal are determined by a modest number of functional groups common to all coals studied. Coals are then assumed to differ by their content of these functional groups. The reactivity of coal in pyrolysis, hydrolysis and liquefaction can be generally characterised by six classes of functional groups: aromatic nuclei, hydroaromatic structures, alkyl chains, alkyl bridges and oxygen groups. Sulphur and nitrogen groups are important from the standpoint of pollutant formation but do not play noteworthy roles in the thermal reaction mechanisms due to their comparatively low amounts in the coal matter. Knowledge of coal thermal decomposition is particularly important for technologies for capturing  $CO_2$  during the coal combustion and gasification processes. Over many years, infrared spectroscopy has become a widely used method for studying coal structure, giving quantitative and qualitative descriptions of the structure of carbonaceous materials. In recent years, the quantitative accuracy of infrared spectral peaks has increased in the wake of the rapid development of peak separation from overlapping bands [1]. FTIR is currently one of the most powerful techniques for characterisation of coal [2]. This technique allows investigating the contribution of various functional groups – hydroxylic [3–5], aromatic and aliphatic CH [3,6–8], carboxylic COOH [9], hydrogen bonds [11–14] and even mineral matter [10]. As is commonly

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known, hydrogen bonds have negative effects on the conversion of coal (for example, they increase the yields of water and CO<sub>2</sub> cross-linking reactions between hydrogen bonds) [13]. Miura and coworkers found by using FTIR that weak hydrogen bonds were broken at 423–473 K, and the total amounts of CO<sub>2</sub> and water decreased due to the suppression of the aforementioned cross-linking reactions. Due to this observation, they proposed preheating coal before pyrolysis as a method for increasing the efficiency of the pyrolytic products [15]. The onset of covalent bonds cleavage was observed by electron resonance spectroscopy near 583 K for a lignit, rising to 613 K with increasing coal rang [16]. Diffuse reflectance Fourier transform infrared (DRIFT) spectroscopy was first applied to coal investigation in 1978 by Fuller and Griffiths [17]. Currently, this technique is commonly applied to characterise coal blends [18], coal macerals [19,20] and oxidation of coal and carbon materials [21–23].

The aim of this work is to investigate with DRIFT method the thermal behaviour of two different coal samples during the pyrolysis. The changes of coal parameters with temperature increasing can be useful to interpreting their decomposition mechanism.

## 2. Experimental

Two Polish coals, one brown and one hard, were used in this study. The studied coals differed significantly in their rank and were chosen to compare the behaviour of common bands (hydrogen, aliphatic, aromatic, etc.) and coal parameters at the early stage of pyrolysis (up to 673 K). The infrared spectroscopic technique is a powerful method by which chemical changes in materials can be monitored. Diffuse reflectance infrared Fourier transform (DRIFT) spectra were measured by means of a Bruker Tensor 27 spectrometer equipped with a DTGS (deuterated triglycine sulphate) detector and an environmental chamber (Specac), enabling diffuse reflectance measurements to be performed at increasing temperatures. Samples were prepared by weighing 1 mg coal and 200 mg of potassium bromide powder, which were blended by hand for 2–3 min in an agate mortar. KBr is a quite stable ionic compound. It has a melting point of 1007 K and a boiling point of 1728 K. The prepared sample was then transferred to a diffuse reflectance sample cup (13 mm). The cup was filled over, and the surface was flattened with a spatula. The diffuse reflectance spectra were measured at a 2 cm<sup>-1</sup> resolution with 32 total scans from 323 to 673 K, with a heating rate of 10 K/min under a N<sub>2</sub> atmosphere. The DRIFT spectra are presented as Kubelka–Munk functions because they are directly proportional to absorbance. Software processing was used for the baseline corrections of obtained spectra.

### 2.1. FTIR measurement and deconvolution

It is expected that FTIR spectroscopy could show some of the structural changes occurring during pyrolysis. To obtain a semi-quantitative estimation describing the variation of the main structural groups, the evolving areas of the bands from deconvoluted spectra were analysed, and their ratios were calculated. For further interpreting the FTIR data, the peak separations and quantitative calculations were performed using the curve-fitting program Curve Fit, a part of the OPUS software. Selected regions of the FTIR spectra were baseline-linearised by connecting the left and right points of the interval with a straight line. The positions of the bands and the number of bands were established initially from the second derivative of the spectrum. To obtain meaningful results, it is necessary to determine the number of peaks in a given region and to have a good initial estimate of their frequency and intensity. All of the band shapes, heights, and widths were allowed to adjust in initial estimation. In further estimations half peak width and peak position were fixed and only the height of peaks was permitted to adjust. The results were obtained using a Gauss/Lorentz combination of 80%:20% [24]. The Levenberg-Maquardt method was applied to minimise the difference between the fitted curves and the measured spectra, and the algorithm was implemented in the OPUS software. It should be noted that, the position of a peak may be slightly different in the measured spectrum and the corresponding band calculated by curve-fitting, as a result of band overlap.

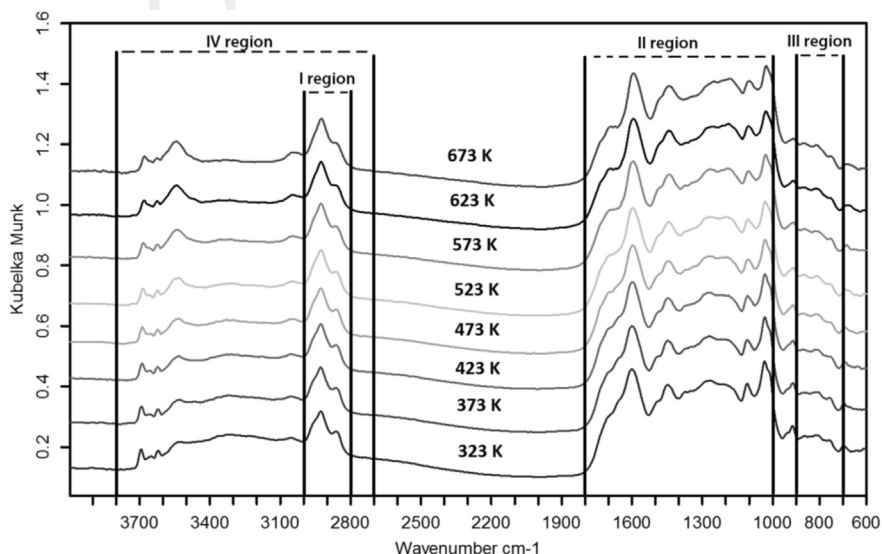


Fig. 1. The effect of temperature on infrared (DRIFT) spectra of the hard coal.

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