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Artificial maturation of a high volatile bituminous coal from Asturias (NW Spain) in a confined pyrolysis system

Part II. Gas production during pyrolysis and numerical simulation

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Abstract

The objective of this work is to estimate the hydrocarbon production in the Central Asturian Coal Basin (NW Spain) by using the results of artificial maturation and the numeric maturation modeling taking into account the thermal evolution of the maceral composition, the vitrinite reflectance, the T_{max}, and the gas production.

A confined pyrolysis was carried out inside gold cells under a pressure of 700 bar at several temperatures (330, 360 and 400 °C) and duration (24, 120 and 720 h).

The kinetic model METAGAZ-1D was used to simulate hydrocarbon production. Methane production begins at $\%R_r = 0.7$ and increases with reflectance.

Vitrinite reflectance, and T_{max} were calculated from the model by describing the kerogen transformation under the action of typical temperature of burial. From the spatial distribution of the vitrinite reflectance, and after the depth, the importance of the hydrocarbon production was estimated by the simulation and artificial maturation and compared with the gas quantities adsorbed by coal. Two mechanistic pathways relating to CH_4 production and CH_4 adsorption from coal were built to estimate the real exploitable gas proportion as function of depth and the geographical location of the coal seams in the basin.

Keywords: Artificial maturation; Confined pyrolysis; Kinetic simulation; Coal gas; Central Asturian Coal Basin

1. Introduction

The stratigraphy of the Central Asturian Coal Basin was studied by Gutiérrez-Claverol and Luque-Cabal [1]; and Fuente-Alonso and Sáenz de Santa-María Benedet [2], among other authors. Colmenero and Prado [3], and Alonso and Brime [4] reported some data related to the maturation of the region, and Piedad-Sánchez et al. [5–8] studied the petrography and regional thermal gradient in this basin.

Piedad-Sánchez et al. [9] described the petrological and geochemical results of the artificial maturation for the Central Asturian Coal Basin. This paper was focused on the artificial evolution of a high volatile bituminous coal selected from the Pumarabule coal mine. The main objective of this second paper is to compare the results of gas production during pyrolysis with the simulation of gas generation and production using the METAGAZ-1D kinetic model [10].

2. Methodology

2.1. Gas characterization

Petrographic analysis, geochemical and molecular characterization, and confined pyrolysis [30–46] used on a vitrinite-rich coal with $\%R_r = 0.78$ of Pumarabule mine from the Central Asturian Coal Basin. Detailed procedures on the

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methodology were previously described by Piedad-Sánchez et al. [7–9].

One technique developed in the G2R laboratory helped to evaluate the gaseous products of the solid residues from artificial maturation (C_1–C_{30}, H_2O, CO_2, H_2S, CO, and N_2) by using the thermodesorption-multidimensional gas chromatography (TD-MDGC). The TD-MDGC was created to quantitatively evaluate in one injection the gas content. A detailed description of this method is found in Landais et al. [11,12], Gérard et al. [13], Mansuy [14], and Landais and Gérard [15]. The gold cell in which the coal has been pyrolysed is placed into a piercing device located in a thermodesorption oven. The system is closed, evacuated and heated at 250 °C before the gold cell is pierced. The thermovaporizable content of the gold cell expands into the evacuated system and fills the sample loop of a Valco Valve. After an equilibration tie of 30 min and measurement of the effluents pressure, 0.5 ml of effluents is injected via the Valco Valve into gas chromatograph. Two columns and two detectors were used to analyse the complex thermodesorbed gas mixture: first, a thermal conductivity detector (TCD) for the Ar, CO, CO_2, H_2S, H_2S, H_2O, N_2 and C_1–C_6 fraction; and finally, a flamme ionisation detector (FID) for the C_7–C_{30} fraction. Data acquisition and processing directly performed on adapted software for personal computer. After each run, the gold cell is collected and weighted in order to determine the total weight loss [11–15].

3. Results and discussion

3.1. Kinetic simulation

Artificial maturation on an Asturian coal showed that the chemical composition was thermally transformed with increasing temperature and time (Fig. 1). High measured R_r values for these solid residues also suggested the influence of the expulsion phenomena [9].

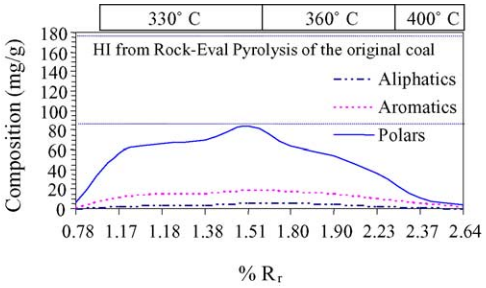

Fig. 1. Calculated composition of artificial maturation of one coal sample from Pumarabule mine (Central Asturian Coal Basin, NW Spain).

Models of hydrocarbon formation, primary migration and thermal evolution are based on first-order kinetics according to the Arrhenius equation [16–19]. In general, the kinetic models used for maturation assessment assume that the reactions are controlled by time and temperature but it ignores the effect of pressure on endothermic volume expansion reactions, e.g., maturation and hydrocarbon generation [20]. In addition, the modeling of the petroleum generation from coals presents some additional problems to those found with marine source rocks, apparently related to structural rearrangements of the macromolecular network [21]. Therefore, the structural rearrangements have significant implications for the kinetic modeling of the petroleum generation from coals [22,23,21], and they may be taken into account in the results.

In this context, a kinetic model called METAGAZ-1D (Fig. 2; [10]) was used. In this model the thermal transformations are function of the temperature, time, pressure and subsidence (i.e. uplift phenomena). In using METAGAZ-1D for some samples of Central Asturian Coal Basin, it is possible to calculate the activation energy of

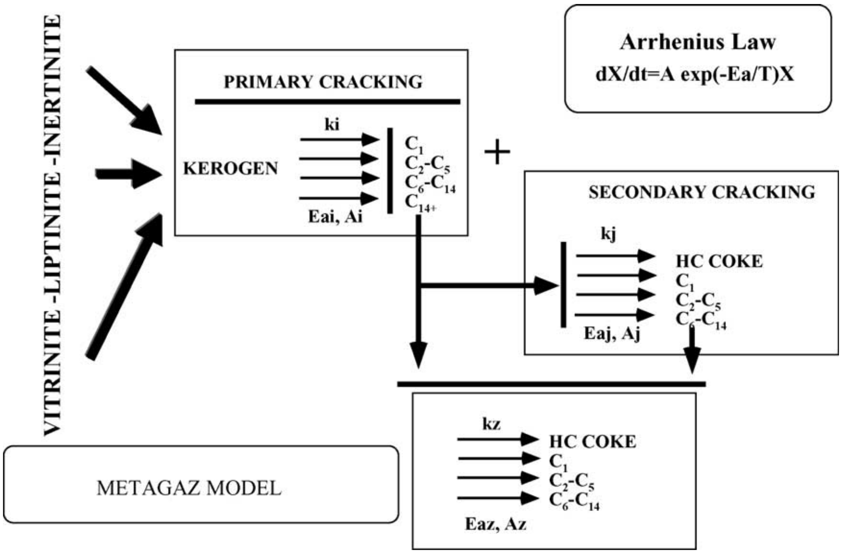

Fig. 2. Schematic diagram of the METAGAZ model.