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Full Length Article

Reaction of volatiles from a coal and various organic compounds during co-pyrolysis in a TG-MS system. Part 2. Reaction of volatiles in the free gas phase in crucibles

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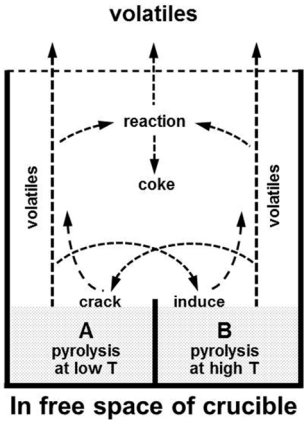
GRAPHICAL ABSTRACT



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ABSTRACT

A low rank bituminous coal and four solid organic compounds were co-pyrolyzed in pairs in a thermal gravimetric analysis coupled online with a mass spectrometer (TG-MS) using specially designed TG crucibles which separate the solid matter from each other while allow their volatiles to mix in the free gas space of different volume (or height) above the sample bed. The TG and DTG curves of co-pyrolysis of each pair of the matter are compared with those obtained from pyrolysis of the individual matter in the same crucible and with that calculated from TG and DTG curves of the individual matter by superposition. The gaseous products, including light paraffinic and aromatic compounds in the co-pyrolysis are also studied. It is found that the volatiles' reaction in all the cases studied decreases volatiles' yield, and the extent of decrease gets large with increasing free gas space height and is affected by the molecular structure of the organic matter. The nature of the volatiles' reaction is discussed with respect to adsorption, cracking, condensation and induction.

1. Introduction

Reaction of volatiles during pyrolysis of solid organic matter, such as coal, plays an important role in yield and quality of liquid and gas products [1–3]. This reaction is particularly important in co-pyrolysis of a coal with low grade hydrogen-rich organic matter because the

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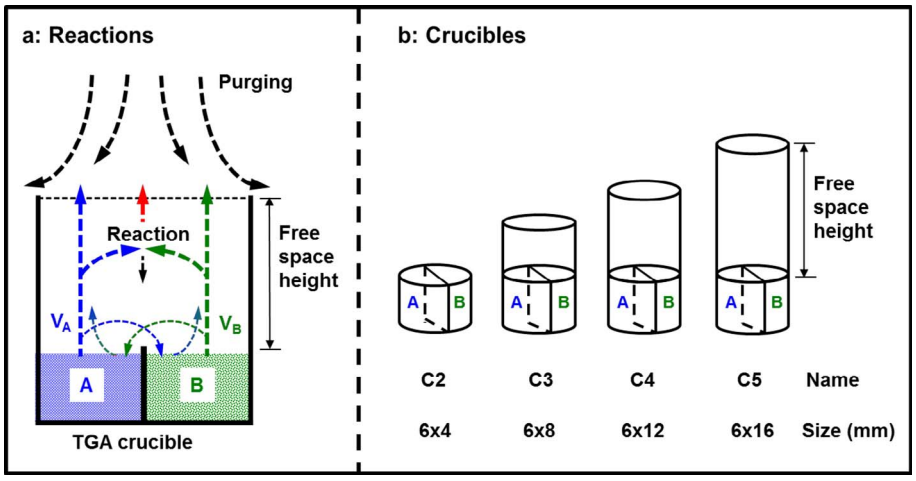

Fig. 1. TG crucibles designed and used in this work.

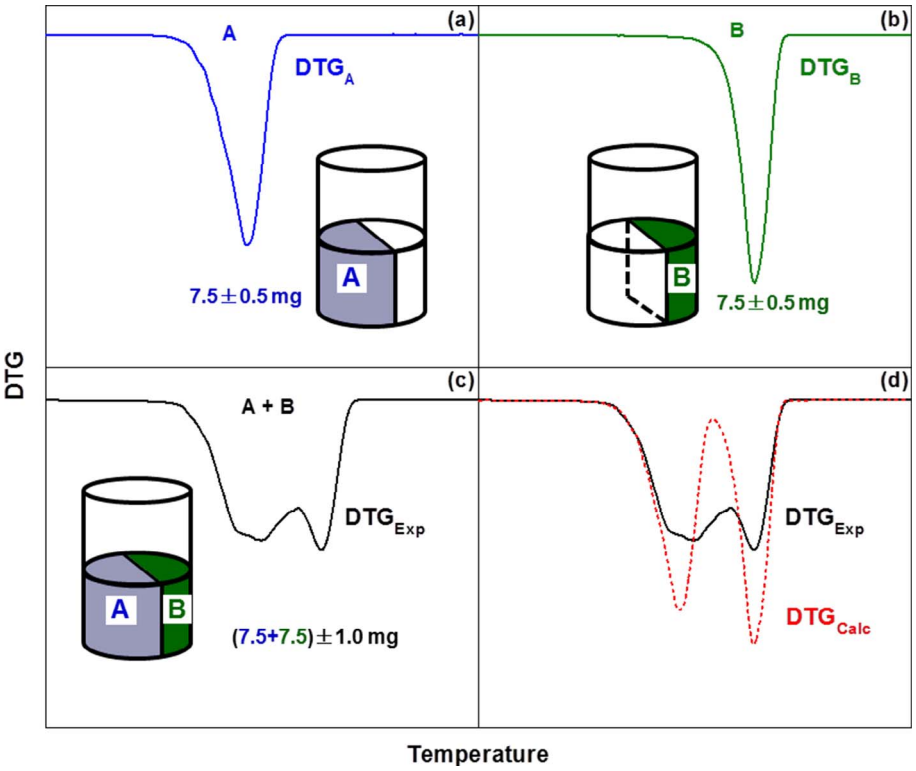

Fig. 2. Determination of reaction of volatiles generated from difference raw matter.

hydrogen-rich volatiles generated from organic matter react with the relatively hydrogen-poor volatiles generated from coal to result in products of increased yield and improved quality. In a pyrolysis reactor the volatiles' reaction occurs in three spaces, inside the pores of solid matter, between particles of solid matter as studied in Part 1 of this series [4], and above the solid matter bed. The volatiles' reaction includes the reaction between volatiles as well as that between volatiles and the solid matter. Part 1 of this series studies the volatiles' reaction in the void space between particles [4]. It shows that the volatiles generated at lower temperatures from one matter adsorb on the other matter that pyrolyzes at higher temperatures. The adsorbed volatiles crack and condensate, and lower the pyrolysis temperature of the adsorbent. These volatiles' reactions generally reduce the volatiles' yield, due to coke formation, and increase the gas yields due to cracking and condensation.

The volatiles' reaction in the space beyond the solid bed has also been studied in the literature. It was reported that the volatiles' reaction in coal pyrolysis in the dilute phase of fluidized-bed reactors decreased the yield and H/C ratio and increased the heavy fraction of tars [5–8]; the volatiles' reaction downstream of a fixed-bed coal pyrolysis reactor decreased the tar yield and increased the gas and coke yields [9,10]. The volatiles' reactions in coal pyrolysis are significant to alter the products yield at temperatures as low as 500 °C [6,10,11], but are significant to alter the tars' coke and radical concentrations at lower temperatures [12–14], as low as 350 °C. However, little study can be found on reaction of volatiles generated in co-pyrolysis of different organic matter.

Following Part 1 of this series, this paper studies the volatiles' reaction of the same pairs of matter in the same thermal gravimetric analysis-mass spectrometer (TG-MS) system using different crucibles. The crucibles are designed to vary the extent of volatiles' reaction in the void space above the sample bed and to monitor the coke and gas formation occurred in the volatiles' reaction. The information obtained is useful in design of co-pyrolysis system, reactor, and operating conditions.