Communication

Comparison of Temperature Programmed Char Combustion in CO₂ – O₂ and Ar – O₂ Mixtures at Elevated Pressure

Gábor Várhegyi* and Ferenc Till
Research Laboratory of Materials and Environmental Chemistry, Chemical Research Center, Hungarian Academy of Sciences, P. O. Box 17, Budapest 1525, Hungary
Email: varhegyi.gabor@t-online.hu or gvarhegyi@gmail.com

SUMMARY: A pressurized thermobalance (TGA) system was built. The role of CO₂ was studied in the controlled temperature combustion under pressurized conditions. Particular care was taken to employ low sample masses in thin layers, to avoid self-heating phenomena and ensure kinetic control. It was found that a CO₂ partial pressure of 0.57MPa at a 0.6 MPa total pressure had no effect on the overall reaction rate of a temperature programmed combustion.

KEYWORDS: High pressure thermogravimetry, char, combustion, effect of carbon dioxide.

In a previous work the authors studied the temperature programmed combustion of coal chars by atmospheric pressure thermogravimetry (TG) and found that the mass loss rate did not depend on the CO₂ content of the ambient gas.¹ Future combustion systems, however, may be based on combustion at high pressures with a large concentration of CO₂ in the combustion environment.² To study the role of CO₂ under pressurized conditions, we repeated the key experiments of our earlier work in a pressurized TG system. Particular care was taken to employ low sample masses in thin layers, since our earlier studies proved it necessary to avoid self-heating phenomena and ensure kinetic control. In the present communication we wish to demonstrate that a CO₂ partial pressure (P_{CO₂}) of 0.57MPa at P=0.6 MPa total pressure has no effect on the overall reaction rate of a temperature programmed combustion.

Saastamoinen at al.² reported minor effects of CO₂ on the combustion rate in a pressurized entrained flow reactor at P_{CO₂}= 0.05 – 0.2 MPa and P= 0.2 – 0.8 MPa. Their reaction temperatures, however, were higher and other experimental conditions also differed from those in the present work.
In high-pressure thermogravimetry, turbulence and fluctuation phenomena hinder the precise weight measurement. Probably this is the cause of the relatively high sample masses (15 – 1000 mg) employed in high-pressure TG studies.\textsuperscript{3-8} Recognizing the importance of low sample masses\textsuperscript{1}, we focused our work on finding an experimental setup suitable for the accurate measurement of char samples around 3 mg. A Hiden IGA high pressure microbalance system was equipped with an alumina furnace enclosed in a stainless steel housing. The temperature of the furnace is programmed by a Eurotherm 906 EPC programmer. Elevated pressure gas is led to the furnace so that the pressure surrounding the furnace is identical to the pressure inside. The pressure is regulated with an Aalborg PSV-1 proportional solenoid valve and an Omega CN 76163-PV programmer unit. The gas flow rate is controlled at the outlet of the system by an ASM AFC-260 flow controller, which was set to a constant flow rate of 600 ml/min at room temperature and atmospheric pressure. Test measurements showed that the apparatus can accurately measure 2 – 3 mg samples at 6 MPa pressure. The samples are distributed on a sample pan of 6 mm diameter, resulting in ca. 0.1 mm layer thickness. The schematic of the equipment is shown in Figure 1.

We studied the same chars as in our earlier work.\textsuperscript{1} They were prepared at 950°C from two typical European high-volatile bituminous coals (Arkadia and Westerholt) and a French lignite from the Gardanne region. The effect of CO\textsubscript{2} was determined by carrying out experiments in gas flows of high purity 95% Ar – 5% O\textsubscript{2} and 95% CO\textsubscript{2} – 5% O\textsubscript{2}, respectively, at 0.6 MPa pressure. Since the transport properties of these gas mixtures are similar (due to the similar mass of the CO\textsubscript{2} molecules and argon atoms), and all other experimental conditions were strictly identical, the comparison of the results were hoped to show clearly the effect of CO\textsubscript{2} on the kinetics.
The results are shown in Figure 2. The Ar – O2 and CO2 – O2 experiments are denoted by solid and dashed lines, respectively. The sample mass (m) and mass loss rate (-dm/dt) were normalized by the initial sample mass. There is a good agreement between the m(t) curves measured in Ar – O2 and CO2 – O2. The small differences in the derivative curves are not significant in this type of experiments. The only exception is the high-temperature part of panel c, which shows the thermal decomposition of the calcium carbonate content of the lignite char in the absence of CO2.\(^1\) The reaction rate of this process strongly depends on P\(_{\text{CO}_2}\).

![Graphs showing mass and mass loss rate for different experiments](image)

**Figure 2.** Sample mass and mass loss rate of the temperature programmed combustion of 2.5 mg Arkadia (a), 3 mg Westerholt (b), and 3 mg Gardanne (c) chars in 95% Ar – 5% O2 (——) and 95% CO2 – 5% O2 (- - -) gas mixtures at 0.6 MPa pressure.

The similarity of the Ar – O2 and CO2 – O2 experiments reveals that the kinetics of the char + O2 reaction is not influenced by a high amount of CO2 under the given experimental conditions. This may be explained by the following factors: (i) the char + CO2 reaction has much lower rate than the char oxidation; (ii) the CO2 does not participate in the elementary reactions of the oxidation; and (iii) changes in ambient CO2 concentrations do not materially affect the concentration of evolved CO2 at the molecular level.

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