CHAR-OXIDATION REACTIVITY AT EARLY AND LATE STAGES OF BURN-OFF

Marek A. Wójtowicz, Rosemary Bassilakis, and Michael A. Serio
Advanced Fuel Research, Inc., 87 Church Street, East Hartford, CT 06108, USA

Introduction

Thermogravimetric analysis (TGA) has been employed in coal science to perform a number of characterizations, including char-reactivity determination. TGA data are often helpful in the design of gasification systems by providing insights into the intrinsic reactivity of char, the effects of heat treatment (thermal annealing), catalysis, type of precursor, etc. Low temperature and low burn-off régimes are typically used to minimize heat and mass transfer limitations. The recent emphasis on problems associated with unburned carbon in fly ash points to the need to characterize char behavior at elevated temperatures and at high degrees of burn-off. The objectives of this study are: (1) to examine the relevance of the early gasification data to the description of late stages of burn-off; and (2) to suggest convenient experimental methods of characterizing late stages of oxidation.

A simple approach to the characterization of early char reactivity has been developed at Advanced Fuel Research, Inc. (AFR) and described in several publications [1–5]. The approach is based on the concept of critical temperature, T_{crit}, which is an index of char reactivity related to the concentration of accessible active sites. The determination of T_{crit} relies on a TGA technique, in which the weight loss is measured while the sample is heated at a constant rate in the presence of a reactive gas, e.g., air. T_{crit} is defined as the temperature at which the rate of weight loss reaches 0.065 g/(g min) (high enough to be easily measurable, but low enough to ensure the kinetic-control régime). The measurement is simple, reproducible, and independent of char type. A predictive model based on T_{crit}-TGA data was proposed [2], and good agreement between model predictions and experimental data was found for low, medium, and high rank coals.

Materials and Experimental

Six coals provided by Idemitsu Kosan Co., Ltd. were used in this study: 1AUS, 2AUS, 3AUS, 4AUS, 13AUS, and 5JPN. All samples were sieved to –200 +325 mesh size (particle diameter d_p = 45–75 μm), and elemental analysis was performed by Huffman Laboratories. The results are summarized in Table 1.

A DuPont 951 TGA was used to first pyrolyze the coal precursor in an atmosphere of flowing helium, and then to expose the char to an oxidizing atmosphere (21 vol. % O_2/He). The initial weight of the coal sample was 20–50 mg, and it was verified that the differences in sample sizes and gas flow rates in the ranges used in this work did not affect experimental results.

A typical temperature profile and a weight-loss curve are shown in Figure 1. In general, each TGA run began by heating the sample from room temperature to about 150-200 °C, with a several-minute hold time. The purpose of this step was to drive off the moisture initially present in the sample. The coal was then heated at a heating rate of HR = 10–100 °C/min to a maximum pyrolysis temperature of T_{max} = 1000–1100 °C. The sample was held at T_{max} for 3 minutes, and then the TGA was allowed to cool down to about 200 °C. The arrow in Figure 1 indicates the time at which the oxygen-helium mixture was introduced into the system. As the temperature increased at HR = 30 °C/min, the sample reacted with oxygen and the resulting weight loss was recorder as a function of time. Depending on char reactivity, the critical rate of weight loss (0.065 $g/g_{initial\ carbon}\ min^{-1}$) was reached at a lower or higher temperature (T_{crit}). One can, thus, view $1/T_{crit}$ as an index of char reactivity.

Results and Discussion

Raw TGA weight-loss data, e.g., those shown in Figure 1, can be re-processed to obtain a plot of char reactivity as a function of temperature. Examples of such plots are shown in Figure 2 and Figure 3. The non-smoothness of the reactivity curves is attributed to transient thermal runaways associated with local char-ignition phenomena. It should be pointed out, however, that the determination of T_{crit} is unaffected by the uncertainties in temperature measurement due to the low value of the critical rate of weight loss (0.065 $g/g_{initial\ carbon}\ min^{-1}$).

Data in Figure 2 and Figure 3 illustrate two rather unusual cases: (1) the initial char reactivities are very similar for three coal chars, but the late-stage reactivities are very different (Figure 2); and (2) the initial reactivities for three coal chars differ appreciably, whereas the late stage reactivities are identical (Figure 3). These results lead to the conclusion that the reactivity at high values of burn-off is not necessarily well characterized by char reactivities determined at early stages of char oxidation. Thus, in some cases, T_{crit} may be a good indicator of char reactivity in a gasifier, but a poor loss-on-ignition (LOI) index for a combustion system. In order to obtain more comprehensive char-reactivity characterization, the use of a high burn-off reactivity index is proposed. It could be defined, for example, in a manner similar to T_{crit}, except that the temperature T_L corresponding to the critical rate of weight-loss would be determined on the declining part of the reactivity curve. This concept is illustrated in Figure 2 and Figure 3.

Conclusions

Char-reactivity data collected at early stages of burn-off are not always good indicators of char behavior at high burn-offs. Two simple indices, T_{crit} and T_L, are proposed for more comprehensive char-reactivity characterization. Both indices can be determined in a single TGA run.

Acknowledgments

Financial support of NEDO and CCUJ is gratefully acknowledged. This work was performed under the Brain-C project as a subcontract from Idemitsu Kosan Co., Ltd., which also supplied the coal samples. Dr. Shinji Kambara was the Project Manager at Idemitsu Kosan Co., Ltd.

Table 1. Elemental analysis of coals used in this study. All data are expressed in weight per cent: C, H, N, S, O - dry, ash-free basis; ash - dry basis; oxygen by difference.

Coal	Ash	C	H	N	S	O
1AUS	13.0	84.5	5.21	1.78	0.56	7.99
13AUS	16.0	83.6	5.16	1.67	0.54	9.05
3AUS	7.86	82.9	5.06	1.93	0.37	9.71
4AUS	18.4	81.5	4.79	0.94	1.47	11.3
2AUS	12.6	80.1	6.22	1.59	0.66	11.4
5JPN	10.8	77.8	6.53	1.20	0.27	14.2

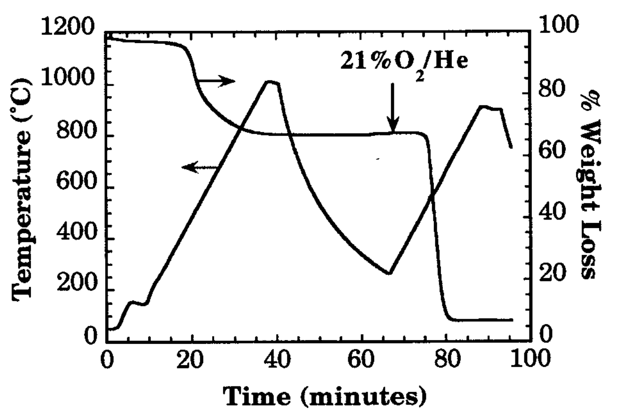

Figure 1. A typical weight-loss curve and temperature profile for an oxygen-reactivity run: 3AUS; HR = 30 °C/min, T_{max} = 1000 °C.

References

1 Serio MA, Solomon PR, Zhang YP, Suuberg, EM. The use of TG-FTIR analysis to determine char combustion properties. Presented at the AIChE Annual Meeting, Chicago, IL, 11-16 Nov., 1990.

2 Charpenay S, Serio MA, Solomon PR. Twenty-fourth symposium (international) on combustion. Pittsburgh, PA: The Combustion Institute. 1992: 1189–1197.

3 Serio MA, Solomon PR, Bassilakis R, Suuberg EM. ACS Fuel Chem. Div. Prepr. 1989;34(1):9.

4 Best PE, Solomon PR, Serio MA, Suuberg, EM, Mott WR, Jr., Bassilakis R. ACS Fuel Chem. Div. Prepr. 1987;32(4):138.

5 Solomon PR, Serio MA, Heninger S. G., ACS Fuel Chem. Div. Prepr. 1986;31(3):200.

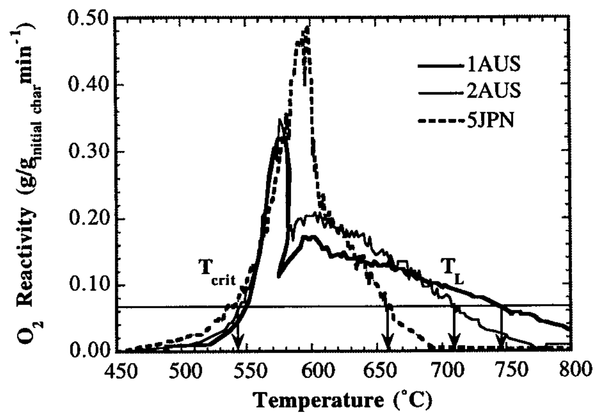

Figure 2. Char reactivity for non-isothermal char oxidation at a heating rate of 30 °C/min; chars pyrolyzed in helium at HR = 30 °C/min and T_{max} = 1100 °C.

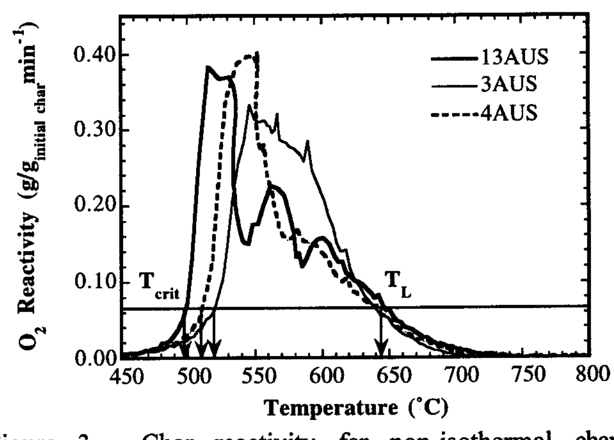

Figure 3. Char reactivity for non-isothermal char oxidation at a heating rate of 30 °C/min; chars pyrolyzed in helium at HR = 30 °C/min and T_{max} = 1000 °C.