Multivariable optimization of reaction order and kinetic parameters for high temperature oxidation of 10 bituminous coal chars

Oskar Karlström [a,*], Anders Brink [a], Mikko Hupa [a], Leonardo Tognotti [b,c]

[a] Process Chemistry Centre, Åbo Akademi University, Biskopsgatan 8, 20500 Turku, Finland
[b] Dipartimento di Ingegneria Chimica, Universitá di Pisa, Via Diotisalvi 2, 56100 Pisa, Italy
[c] International Flame Research Foundation, Via Salvatore Orlando 5, 57123 Livorno, Italy

ABSTRACT

In industrial pulverized fuel combustion, char oxidation is generally limited by the combined effects of chemical reactions and pore diffusion. Under such conditions, char oxidation is frequently predicted by power law models, which despite their simplicity, are widely used in the comprehensive CFD modeling of pulverized coal boilers. However, there is no consensus on the apparent reaction order given by such models. This study developed a systematic approach which gives consistent values over a range of conditions. Apparent reaction orders for 10 bituminous coal chars were investigated with three different oxygen concentrations, ranging from 4 to 12 vol.%, and a gas temperature of 1223 K for each char. Experimental burnout profiles of the chars were obtained by means of an Isothermal Plug Flow Reactor operating at industrially realistic heating rates (10^4 K/s). For various reaction orders between 0.05 and 2.00, kinetic parameters were independently determined, following numerical procedures recently suggested in the literature. The resulting values were incorporated into an empirical power law model and compared to experimental data for the 10 chars, over a burnout range of 0–75%. The best fit to the experiments occurs with apparent reaction orders of around one for all the chars.

© 2011 The Combustion Institute. Published by Elsevier Inc. All rights reserved.

1. Introduction

The development of kinetic char oxidation models comprising more than one explicit reaction step is important for deriving the correlations needed to design combustion systems [1]. Although there have been many studies on realistic char oxidation mechanisms [2–11], identifying the most appropriate and fundamentally realistic form for the rate remains an elusive goal [1]. Partly because of this, empirical power law models continue to play a vital role [1]. Taking into account variations in particle properties such as diameter and reactivity [12] and also various deactivation phenomena, these models can accurately predict char combustion under many industrially significant conditions and are, therefore, useful for CFD modeling [13–17]. However, there is no consensus regarding the apparent reaction order n given by such models, especially under industrially significant regime II conditions [11] in which particle rates are limited by the combined effects of chemical reactions and pore diffusion. Under regime II conditions, according to the conventional Thiele analysis, the apparent reaction order lies between 0.5 and 1 [13]. Consequently, it has

generally been suggested that the reaction order lies within these ranges [13]. One of the many reasons for the scatter in the reported values is the relationship between the reaction order and the kinetic parameters [13,18]. Young and Smith [19] demonstrated the existence of such a relationship by comparing apparent reaction orders of 0.5 and 1 for a pulverized coal char of various sizes. Using different kinetic parameters for the two cases, they showed that the calculated rates were similar. In addition, Hurt and Calo [11] pointed out another case in which the same experimental data had been used to derive various reaction orders.

Recently, Murphy and Shaddix [13] presented an approach for determining the reaction order that takes into account the relationship between the reaction order and the kinetic parameters: conversion rates modeled with various reaction orders are compared to experimental rates, and for each reaction order, kinetic parameters are independently optimized using a comprehensive optimization method. Fundamentally it may be argued that the real activation energies are independent on the reaction orders. However, it is reasonable to suppose that the apparent activation energy is dependent on the apparent reaction order, since all elementary char oxidation steps are lumped together to one step in the apparent kinetic model they use. Their analysis shows that the apparent reaction order for two bituminous coal chars is around 0.1 under near-surface diffusion limited oxidation

---

* Corresponding author.
  E-mail address: oskar.karlstrom@abo.fi (O. Karlström).

conditions at gas temperatures between 1300 and 1800 K in an entrained flow reactor, and 6–12 vol.% O_2 in the surrounding gas. Since both the kinetic parameters and the reaction order are allowed to vary freely, it is evident that their methodology provides a reliable reaction order. However, this approach has not been tested for a large number of coal chars oxidized under regime II conditions, with all the experimental data came from the same facility.

In the current study, apparent reaction orders for the oxidation of 10 bituminous coal chars are determined under regime II conditions following the approach of Murphy and Shaddix [13]. One of the main issues is whether the apparent reaction order is constant or whether there are differences for the various bituminous coal chars. This has not yet been considered under relevant combustion conditions for a large number of chars produced and analyzed using a homogeneous approach. The oxidation of the chars is modeled with a kinetic/diffusion power law model, and the reaction orders for each char are varied. Apparent kinetic parameters are independently determined based on the modeled burnout profile from the range of 0% to 70% burnout that best fits the experimental measurements for each apparent reaction order and each char. The measurements are taken from the Isothermal Plug Flow Reactor, a 4 m drop tube reactor, at 1223–1473 K, with oxygen concentrations of 4–12 vol.% and heating rates typical of pulverized fuel systems. The experimental data used in this study come from the IFRF solid fuel database [20]. This kind of analysis has not previously been applied to this database.

2. Experiments

Table 1 lists the 10 bituminous coal chars that were investigated. The experimental data were taken from the IFRF solid fuel database, which contains the ultimate and proximate analyses, initial diameters, and densities of the chars [20]. The fixed-carbon content of the parent coals varied between 59% and 72%, and the initial mean particle diameters varied between 19 and 107 μm. While drop tube experiments have been carried out using several initial mean diameters for some of the chars, in this study, a maximum of two sizes were considered for each char. The burnouts of the 10 chars were assessed in a drop tube reactor (IPFR) with various residence times. The database contains burnout versus time data for the coals and for the chars derived from the coals. A detailed description of the setup can be found in a previous work [21]. A brief description of the reactor is given below.

The IPFR consists of a 4 m long tube in which the combustion takes place. The tube contains eight modules which can be controlled and electrically heated independently. A K-tron sample feeder provides a continuous mass flow of pulverized fuel, and the furnace is equipped with ports at different levels through which the fuel is fed to achieve different residence times. Partially burned particles are collected by a sampling probe and immediately quenched at the bottom of the reactor. The solids probe consists of a water-cooled jacket with a nitrogen quench. Reactor gas is aspirated into the probe tip isokinetically and quenched with nitrogen in approximately 1 ms to a temperature of about 300 °C. The parent coals were devolatilized in N_2 at 1473–1673 K, usually with a small amounts of oxygen (less than 0.5%), to prevent tar condensation on char particles [21]. The remaining chars were collected for combustion tests. The particle heating rates, both during the devolatilization and the oxidation tests, were in the range 10^4–10^5 K/s. For each char, the particle burnout fractions at different residence times are obtained using the ash tracer method: the measured ash contents are related to the initial ash contents of the original chars. The ashes are assumed thermally stable in the oxidation tests, i.e. the possible volatilization of the ash is not taken into account. The fuel feeding rate for the char combustion tests was set to achieve a maximum relative oxygen drop of 10% over the reactor length. For each set of experimental conditions, 4–7 fuel samples were taken.

The 10 bituminous coal chars analyzed in this study were combusted at three or more oxygen concentrations ranging from 4 to 12 vol.% at 1223 K. However, for the chars that were combusted at more than three oxygen concentrations, only three oxygen concentrations were considered in the analysis. In addition, tests were carried out at two temperatures above 1223 K, typically 1473 K and 1673 K. In many cases, the oxygen concentrations were the same during the experiments at the higher temperatures. Since the goal was to compare the effect of oxygen concentration on the oxidation rate, only one set of conditions with temperature above 1223 K was selected for each char. The experimental matrix is listed in Table 1, and Fig. 1 gives an example of the raw data for three bituminous coal chars obtained by IPFR at 1223 K and 8 vol.% O_2. Here, U is the fractional degree of char burnout starting at 0 and increasing throughout the conversion. Generally, the experimental burnout data indicate that char oxidation begins within a few ms after the particle injection into the reactor system, which is expected, based on the particle heating time at the heating rates the device provides. In some cases, however, there seems to be a

Table 1
Parent coals, experimental conditions, kinetic parameters of chars, apparent reaction orders of chars, and differences between objective functions.

Coal	FC%[a]	A%[b]	d[c]	Exp. conditions[d]	E_a[e]	A_a[e]	n_{opt}[e]	$f - f1$[f]	$f - f2$[f]
1. Colombian coal	59	11	44	1223/4,8,12 1473/4	56	5.33E−04	0.74	0.003	0.011
2. Economy	70	16	61	1223/4,8,12 1473/6	52	1.93E−05	1.1	0.001	0.029
3. Polish 5600	64	12	107	1223/4,6,8 1473/6	51	6.96E−04	0.77	0.001	0.004
4. Enel Coal 2001	59	11	35	1223/4,8,12 1673/4	72	2.02E−05	1.36	0.018	0.059
5. Polish	64	9	24	1223/4,8,12 1473/4	61	4.23E−04	0.79	0.003	0.007
6. Kleinkopje	68	14	19	1223/4,8,12 1473/4	72	1.35E−03	0.73	0.003	0.008
7. South African	63	11	42	1223/4,8,12 1473/4	70	1.90E−04	1.08	0.001	0.032
8. Kellingley 45	67	19	21	1223/4,8,12 1473/4	84	2.06E−03	0.86	0.003	0.018
9. Polish	67	4	38	1223/4,8,12 1473/4	93	1.73E−03	1.03	0.001	0.023
10. Kellingley coarse	62	8	72	1223/4,8,12 1473/4	63	7.85E−04	0.89	0.001	0.018

[a] Fixed-carbon content of parent coal (daf).
[b] Ash content of parent coal (db).
[c] Initial mean particle diamater (μm).
[d] Experimental conditions, e.g., Colombian coal char experiments were performed at the following reactor temperatures and oxygen concentrations in the gas: 1223 K/4% O_2; 1223 K/8% O_2; 1223 K/12% O_2; and 1473 K/4% O_2.
[e] Optimized apparent activation energy (kJ/mol) and apparent pre-exponential factor (kg/m² s Pa^n) for the optimized apparent reaction order n.
[f] f, $f1$, and $f2$: least squares-based objective functions calculated for modeled and experimental burnout data according to the experimental conditions (in Table 1) using $n = n_{opt}$, $n = 1$, and $n = 0.5$.