A mechanistic char oxidation model consistent with observed CO_2/CO production ratios

M. Geier [a], C.R. Shaddix [a,*], F. Holzleithner [b]

[a] *Sandia National Laboratories, Livermore, CA 94551, USA*
[b] *Vienna University of Technology, Vienna A-1060, Austria*

Abstract

Reliable prediction of char conversion, heat release, and particle temperature during heterogeneous char oxidation relies upon quantitative calculation of the CO_2/CO production ratio. This ratio depends strongly on the surface temperature, but also on the local partial pressure of oxygen and thus becomes more important in simulations of oxy-fuel or pressurized combustion systems. Existing semi-empirical intrinsic kinetic models of char combustion have been calibrated against the temperature-dependence of the CO_2/CO production ratio, but have neglected the effect of the local oxygen concentration. In this study we employ steady-state analysis to demonstrate the limitations of the existing 3-step semi-global kinetics models and to show the necessity of using a 5-step model to adequately capture the temperature- and oxygen-dependence of the CO_2/CO production ratio. A suitable 5-step heterogeneous reaction mechanism is developed and its rate parameters fit to match CO_2/CO production data, global reaction orders, and activation energies reported in the literature. The model predictions are interrogated for a broad range of conditions characteristic of pressurized, oxy-fuel, and conventional high-temperature char combustion, for which essentially no experimental information on the CO_2/CO production ratio is available. The results suggest that the CO_2/CO production ratio may be considerably lower than that estimated with existing power-law correlations for oxygen partial pressures less than 10 kPa and surface temperatures higher than 1600 K. To assist with implementation of the mechanistic CO_2/CO production ratio results, an analytical procedure for calculating the CO_2/CO production ratio is presented.
© 2012 The Combustion Institute. Published by Elsevier Inc. All rights reserved.

Keywords: Char oxidation; CO_2/CO production ratio; Pressure effects; Intrinsic reaction kinetics

1. Introduction

The rate of CO_2 production at the char surface during high temperature char combustion is typically quantified as being less than 15% relative to the production rate of CO [1]. Despite the apparent small magnitude of the CO_2/CO production ratio, it has a significant impact on the particle temperature and therefore on the char combustion rate, because of the substantially higher heat release upon formation of CO_2 (394 kJ/mol-C_s) instead of CO (110 kJ/mol-C_s). The dependence of the CO_2/CO production ratio on particle temperature has been studied at low to intermediate temperatures by many researchers, beginning with Arthur [2] and Rossberg [3] over half a century ago. At high

* Corresponding author.

E-mail addresses: mgeier@sandia.gov (M. Geier), crshadd@sandia.gov (C.R. Shaddix), franz.holzleithner@tuwien.ac.at (F. Holzleithner).

temperatures, determination of the CO_2/CO production ratio is very difficult, on account of the rapid conversion of heterogeneously formed CO to CO_2 in oxidizing atmospheres. These experimental investigations of the CO_2/CO production ratio have frequently shown that this ratio is not only a strong function of temperature, but indeed also depends on the oxygen concentration at the char surface [4–9]. This oxygen dependence has usually been expressed in the form of a power law together with an Arrhenius-type expression to capture the dependence of the production ratio on temperature. The most noteworthy of these investigations was the seminal study conducted by Tognotti et al. [6] of levitated, laser-heated Spherocarb particles surrounded by a cold gas atmosphere (to quench any CO that left the particle surface). Experiments were performed for bulk oxygen concentrations of 5%, 20%, and 100% by volume for a range of temperatures (up to 1670 K). Both particle mass loss and the CO_2/CO production ratio were measured. From this data, a correlation was developed for the dependence of the CO_2/CO production ratio on temperature and local oxygen partial pressure:

$$CO_2/CO = 0.02 p_{O_2,s}^{0.21} \exp(3070/T) \qquad (1)$$

where $p_{O_2,s}$ is the oxygen partial pressure at the surface (atm), and T is the surface temperature (K). Similar relationships have been established by other researchers, but Tognotti's experiments covered a temperature and pressure range closest to practical combustion conditions. The oxygen dependence found by Tognotti et al. is in good agreement with that determined by Otterbain and Bonnetain [4], Du et al. [7,8] and Zeng et al. [9], all of whom found an effective reaction order of approximately 0.2. The effective activation energy of the CO_2/CO production ratio (which is in fact equal to the difference in activation energy of CO_2 production and CO production) determined by Tognotti et al. (of -25 kJ/mol) is also in good agreement with those found by Otterbein and Bonnetain [4], Phillips et al. [10], and Du et al. [7]. Arthur [2], Rossberg [3], and Zeng et al. [9] found much greater differences in activation energies, ranging from -51 kJ/mol to -76 kJ/mol. Phillips et al. [10] postulated that the high activation energies derived in those studies resulted from experiments with high O_2 pressures over a wide range of temperatures, yielding a wide variability of surface site characteristics.

Over the past 20 years various semi-detailed heterogeneous reaction mechanisms have been proposed to describe the complex characteristics of char oxidation during typical conditions of pulverized coal combustion (e.g. [7,11–14]). The rate constants in these mechanisms were chosen to match the results from specific sets of experimental measurements and, in most cases, were also chosen

to match a data set for the variation in the CO_2/CO production ratio as a function of temperature (typically either the Arthur or Tognotti data sets). However, in no case was a proposed semi-detailed mechanism tested for its predictions of the oxygen-dependence of the CO_2/CO production ratio. Furthermore, for the shorter mechanisms, it is easy to show that the dependence on oxygen predicted by the mechanism contrasts with the findings of Tognotti and other researchers (as will be shown in the next section). This neglect of proper treatment of the O_2-dependence of the CO_2/CO production ratio may yield acceptably small errors for conventional coal char combustion, wherein the total extent of variation of surface O_2 content is small, but for application to either oxy-fuel combustion or pressurized combustion a much wider range of surface oxygen concentrations may be applicable and the quality of predictions is likely sensitive to accurate estimation of the CO_2/CO production ratio.

In the present work we discuss the development of a semi-global reaction mechanism with particular emphasis on the predictive capability concerning the joint temperature-oxygen dependence of the CO_2/CO production ratio. To this end, we first derive the relationship for the CO_2/CO ratio assuming steady-state char consumption and a small number of commonly utilized pseudo-elementary reactions. After a brief theoretical discussion, we discuss a relatively simple mechanism fitted to the CO_2/CO data of Tognotti et al. [6]. This newly developed mechanism represents an improvement over other semi-global mechanisms, and it is used here to explore implications for the global reaction order, degree of surface coverage, and CO_2/CO production ratio, over a wide range of conditions. Certainly, model predictions for conditions beyond the model validation range must be treated with caution, but, similar to other empirical models, the expression by Tognotti et al. is commonly extrapolated beyond its original range of validity, and it is therefore instructive to compare these predictions with those from an advanced, mechanistic model.

2. Development of a semi-global kinetics model

Constrained by the requirement of compactness and computational practicality, we seek to develop a simple but appropriate semi-global intrinsic mechanism for char surface oxidation at high temperatures. Rather than reducing a complex mechanism consisting of a large number elementary reaction steps, we have chosen to assemble the mechanism from a small number of defensible reaction steps that can match predictions and experimental evidence.

The development of such a mechanism is facilitated by knowledge of the nature of surface