



Numerical assessment of Tognotti determination of CO₂/CO production ratio during char oxidation



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ABSTRACT

A review of the experimental investigations of the CO₂/CO production ratio during the high temperature oxidation of carbon reveals a wide variation in this critical parameter for determining the char combustion temperature and burning rate. Of the studies that have been performed, the experiment used by Tognotti et al. [5], with small, laser-heated, electrostatically levitated Spherocarb particles in cool surroundings, appears to be the most promising for giving accurate results. Proper interpretation of the results from Tognotti's study requires assumptions of kinetically controlled combustion behavior, negligible CO conversion either within the particle pores or in the boundary layer, and a uniform particle temperature. To evaluate whether the Tognotti data in fact fulfill these assumptions, we have employed a detailed model of porous particle combustion to simulate the Tognotti experiments. The model results indicate that particle temperatures were uniform and there was negligible oxidation of CO either within the particle or in the particle boundary layer over the range of particle temperatures that was used to determine the Tognotti CO₂/CO production ratio correlations. On the other hand, the model results show that O₂ diffusional resistance became important for temperatures greater than 1050 K in the Tognotti experiments. However, because of the low sensitivity of the observed CO₂/CO production ratio to the local oxygen concentration, computational analysis also shows that the influence of this Zone II combustion behavior on the measured CO₂/CO production ratio is quite minor. Therefore, it appears that the empirical correlation derived by Tognotti et al. [5] to describe the CO₂/CO production ratio during high temperature char oxidation is credible, though its temperature range of empirical validation is limited to less than 1250 K.

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1. Introduction

One of the primary complications in modeling char combustion or in interpreting experimental measurements of char combustion regards the ratio of CO₂ to CO directly produced by heterogeneous char oxidation. This CO₂/CO production ratio is important because of the vastly different amounts of heat released by the two production routes (394 kJ/mol-C_s for CO₂ production versus 110 kJ/mol-C_s for CO production). In addition, the difference in solid carbon consumed per mole of reacting oxygen (1 mole C_s/O₂ for CO₂ production versus 2 moles C_s/O₂ for CO production) can have a profound effect, because high-temperature char oxidation is frequently limited, at least in part, by the diffusion of oxygen to the char surface. Apart from that, the gasification reaction of the formed CO₂ with carbon may contribute to additional char consumption at

high particle temperatures and may lead to misinterpretation of experimental data with respect to oxidation kinetic rates [1]. For these reasons, quantitative knowledge of the CO₂/CO production ratio is almost as critical as the overall kinetic rate constants in determining the burning rate of char particles [2].

A number of experiments over the years, beginning with Arthur [3] and Rossberg [4] in the 1950s, have established that CO₂ is the primary oxidation product of carbon at low temperatures, whereas CO is the primary product at high temperatures. Whereas some char combustion modelers simply choose a single presumed oxidation product, most modelers invoke an Arrhenius expression for the temperature dependence of the CO₂/CO production ratio, typically either that determined by Arthur [3], with an activation energy of -52 kJ/mol, or that determined later by Tognotti et al. [5], with an activation energy of -26 kJ/mol. In addition to these two highly-cited studies, several other investigations have been performed on the CO₂/CO production ratio. Otterbein and Bonnetain [6], Phillips et al. [7], and Du et al. [8] all found effective activation energies for the CO₂/CO production ratio between -25 and -27 kJ/mol, whereas Rossberg [4] found activation energies between -60

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and -78 kJ/mol and Zeng and Fu [9] found a value of -69 kJ/mol. As shown in Fig. 1, these various determinations of the CO_2/CO production ratio show substantial disagreement from one another, particularly at low to intermediate temperatures, where most of the data were actually collected. At high temperatures, all of the obtained expressions asymptote to low fractions of CO_2/CO production, so the choice of the expression that is used is less important.

In addition to the strong temperature dependence of the CO_2/CO production ratio, as evidenced in Fig. 1, a number of researchers have reported a dependence on the O_2 partial pressure on the char surface, with CO_2 production enhanced when there is more O_2 available. This O_2 dependence has generally been expressed in the form of a power law with respect to the O_2 partial pressure. Tognotti et al. [5] found a best-fit oxygen exponent of 0.21 for the CO_2/CO production ratio, which is in good agreement with the results from others that have reported an oxygen dependence: Otterbein and Bonnetain [6] found an oxygen exponent of 0.18, Du et al. [8] determined the oxygen exponent to be approximately 0.23, and Zeng and Fu [9] found the oxygen exponent to be 0.24. The influence of this surface oxygen partial pressure on the CO_2/CO production ratio is shown in Fig. 2. Whereas a surface partial pressure of 0.5 atm of O_2 , as included in Fig. 2, is unrealistic for combustion of coal at atmospheric pressure, for pressurized combustion conditions (especially pressurized oxy-fuel combustion conditions) char surface O_2 partial pressures approaching this value may be experienced.

It should be noted that, in fact, the experiments of Otterbein and Bonnetain [6] were performed at very low pressures (0.12 mmHg and less), such that there is a large extrapolation to partial pressures of oxygen that are of relevance to practical char combustion. At 873 K and 0.12 mmHg (1.6×10^{-4} atm), Otterbein and Bonnetain report a CO_2/CO ratio of 0.37, which is in good agreement with that found by Tognotti et al. at that temperature, but at an oxygen partial pressure of 0.05 atm. Also, it should be noted that Arthur [3] and Rossberg [4] did not observe any oxygen dependence in their measured CO_2/CO production ratios. Arthur [3] varied the oxygen partial pressure from 0.05 to 0.25 atm at approximately 1070 K, while Rossberg [4] varied both the overall gas pressure and the O_2 composition at a fixed pressure. It is unclear why neither of these two investigators detected an influence of the O_2 partial pressure on the measured CO_2/CO production ratios.

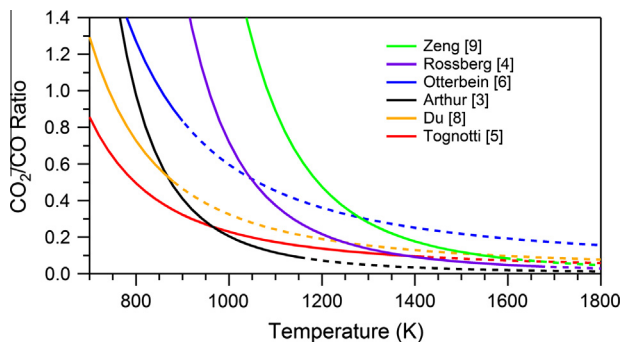


Fig. 1. Reported values of CO_2/CO production ratio from oxidation of carbonaceous particles in 5% O_2 (at particle surface), based on the authors' data correlations. The temperature corresponds to the temperature of the carbon particle surface, and for some of the experiments, under certain conditions, may be substantially greater than the surrounding gas temperature. The solid portion of the line indicates the temperature range where data were actually collected, whereas the dashed portion shows extrapolated results. The Rossberg result shown here corresponds to the first of the two investigated carbons (i.e. the one that generated a lower activation energy).

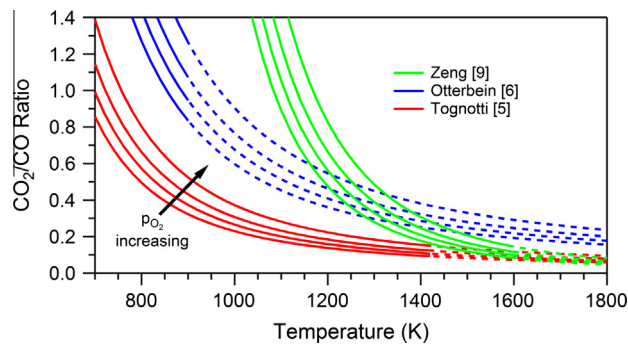


Fig. 2. Dependence of the CO_2/CO production ratio on the partial pressure of oxygen on the char surface, as reported by three studies. The four curves shown for each reference correspond to O_2 partial pressures of 0.05, 0.10, 0.20, and 0.50 atm.

2. Theoretical investigations of co-production of CO and CO_2

The observed dependence on the O_2 concentration may in fact be a surrogate for a dependence of the CO_2/CO production ratio on the concentration of surface oxides on the particle surface (which cannot be easily measured). Walker et al. [10] found evidence that carbon surface oxides can 'combine' to release CO_2 , and this mechanistic route of CO_2 production was recently given support by Radovic's density functional theory (DFT) calculations of surface oxide migration and reaction on graphene surfaces [11]. In addition, isotopic labeling studies by both Tomita's group in Japan [12] and Haynes's group in Australia [13] have shown that CO_2 is produced directly during char oxidation by O_2 -assisted desorption of existing surface oxides. The combination of these two routes of CO_2 production, along with the well-accepted route of CO production via dissociative adsorption of oxygen, followed by desorption of surface oxide, can account for the observed dependence of the CO_2/CO production ratio on temperature and oxygen partial pressure, as shown recently by Geier et al. [14]. Some researchers [e.g., 8,15] have assumed there is a third route for CO_2 production, via the direct formation of $\text{C}(\text{O}_2)$ or $\text{C}_2(\text{O}_2)$ oxides on the char particle surface. Zhuang et al. [16] found evidence for this at 773 K, but Brown et al. [17] found that while the relevant surface oxides may form, particularly at low temperatures, they do not decompose to release CO_2 .

3. Review of reported studies on CO_2/CO production ratio

We have conducted an extensive review of the various reported studies of the CO_2/CO production ratio, which has convinced us that the results from Tognotti et al. [5] are the most relevant and trustworthy for char combustion applications. As discussed below, several of the key studies that have been reported suffer from significant limitations in either the experimental methods or data analysis that was employed.

Arthur [3] measured the production of CO and CO_2 from a fixed column of 1–3 mm diameter carbon particles (either graphite or coal char generated at a low-heating rate) in a tube furnace at temperatures from 750 to 1170 K. Gas mixtures of O_2/N_2 doped with phosphoryl chloride (POCl_3) were passed through the carbon bed. The POCl_3 was used to inhibit the gas-phase conversion of CO to CO_2 at high temperatures, but it was also found to strongly inhibit the low-temperature carbon oxidation. Furthermore, the Arrhenius fit of the CO_2/CO production data used a mixture of data points collected under kinetic control and strong transport control. Given what was later learned regarding the local oxygen-dependence of CO_2/CO production, the higher temperature data (with lower surface O_2 concentrations) would be expected to underestimate the

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