



# Competitive or additive behavior for H<sub>2</sub>O and CO<sub>2</sub> gasification of coal char? Exploration via simplistic atomistic simulation

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## ABSTRACT

Here, a large-scale char atomistic structure (41,438 carbon atoms) and simple simulation approaches explored char gasification behavior for H<sub>2</sub>O and CO<sub>2</sub> — comparing their mixture with one gas being passive (non-reactive) and the dual reactive mixture. Reactivity was captured through simplistic atomistic simulations via an automated sequence of gas diffusion, close-contact determination for gas (es) to reactive edge sites, then “reaction” via atom deletion. The higher reactivity of H<sub>2</sub>O was captured by a reaction probability function. For the reactive mixture (where both gases are reactive), the char consumption rate was 14% higher than with H<sub>2</sub>O alone, but lower (~80%) than the sum of the individual gases (where only one gas is reactive), demonstrating *competitive behavior*. The H<sub>2</sub>O out competed the CO<sub>2</sub> molecules and contributed ~83% to the char consumption — with the reaction rate being similar to that of H<sub>2</sub>O independently. The pore size development for individual gases also differed with H<sub>2</sub>O favoring development in the smaller pore sizes in comparison to CO<sub>2</sub>. With fewer gas molecules (using 10% to capture a lower pressure), the *competitive behavior* was muted and became much closer to *additive behavior*. These simple simulations are consistent with the emerging rationalization of contributing factors to char gasification.

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## 1. Introduction

Gasification of coal, petcoke, or biomass fuel is used for power generation (integrated gasification combined cycle power plant), steam generation, and for chemicals/fuel production. The conversion of coal in a gasifier is generally divided into three main processes: drying, devolatilization, and char gasification. It is the char gasification that is the rate limiting step and this has been examined for >50 years [1]. Char gasification is endothermic, with the heat of absorption being 131 and 172 kJmol<sup>-1</sup> respectively for char-H<sub>2</sub>O and char-CO<sub>2</sub> reaction [2]. The common activation energies under kinetic control (zone I) are ~220–280 kJmol<sup>-1</sup> [1]. However, under zone II conditions, the reactivity is also influenced by the transport of gases through the char pores and the apparent

activation energies are ~160–220 kJmol<sup>-1</sup> [3–6]. The H<sub>2</sub>O gasification rate is higher than CO<sub>2</sub>, due to a much lower bond dissociation energy [2] and a higher diffusion rate. At 900 °C, the rate is ~5 × 10<sup>-4</sup>–10<sup>-2</sup> s<sup>-1</sup> for H<sub>2</sub>O gasification, and about half of that for CO<sub>2</sub> gasification for a coal char [3–5,7,8]. The rate is dependent on the temperature with the CO<sub>2</sub> gasification rate being more sensitive (increases by 37 times from 800 to 1000 °C but only 18 times for H<sub>2</sub>O [3]).

The simple Langmuir-Hinshelwood (L-H) mechanism describes the kinetic reaction rate of char gasification in pure gases (H<sub>2</sub>O or CO<sub>2</sub>, or one reactant gas in inert gas as diluent) from atmospheric to 3 MPa gas pressures [4,8–10]. In practice however, the char is exposed to the mixture of H<sub>2</sub>O and CO<sub>2</sub>. These experimental data are conflicted over the extent of (negative or positive) synergy when these gases are combined [4,8,10–14]. In some cases, there is evidence of *additive behavior*, where the gasification rate in the mixture gas can be represented as the sum of the two individual gases [4,11,15]. Thus, it is suggested that H<sub>2</sub>O and CO<sub>2</sub> react with “separate” active sites and there is no synergy. Roberts and Harris showed the reaction rate of char with 0.5 MPa H<sub>2</sub>O is higher than

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that with the mixture of 0.5 MPa H<sub>2</sub>O and 0.5 MPa CO<sub>2</sub> [16]. There the presence of CO<sub>2</sub> inhibited the H<sub>2</sub>O reaction. Assuming that the active sites are fully accessible to H<sub>2</sub>O and CO<sub>2</sub>, they successfully described the relationship between the gasification rate of the mixture gas and that of the individual gases by the L-H mechanism. Others have suggested that the active sites are partly [10,12] or fully “shared” [5,14], as the reaction rate with the mixture gas is lower than the sum of that with individual gases. These observations are collectively termed by *competitive behavior* between the gases, where the synergy is negative and reduces the overall rate.

Roberts and Harris reviewed the literature and observed that H<sub>2</sub>O and CO<sub>2</sub> were competing for the same reaction sites [1]. Those studies supporting the *additive behavior* were mostly conducted at relatively low reactant partial pressures (~0.05 MPa and below), and under those conditions the occupation of char active sites by the reactants are far from being saturated. Therefore, gases would react independently (when both are present) and the total reaction rate is the sum of individual gases. The *competitive behavior* will be present with increasing partial pressure of reactant gas (up to 3 MPa), where access to the active sites becomes competitive [1].

This “active sites saturation” theory is in agreement with most of the experimental data, and Li et al. demonstrated the char reactivity behavior for the gas mixture was dependent on the reactants partial pressures [8]. In addition, the extent of the competition will also depend on the pore structure as it controls the access to the bulk of the active sites in most chars. Thus, the more porous biomass chars [17] are more likely to exhibit the “*additive behavior*” [4,11,15], while the less porous bituminous coal chars had “*competitive behavior*” [5,12,16]. These outcomes support the theory that the gasification mechanism in a mixture is dependent on the char active sites saturation extent. Wang and Bell [14] observed the “*competitive behavior*” under atmospheric pressure, and suggested that when the partial pressure of H<sub>2</sub>O is sufficiently high to reach the surface saturation (0.05 MPa in his study), the addition of CO<sub>2</sub> will not impact the reaction rate, and the rate was the same as when only H<sub>2</sub>O was present. Thus, there H<sub>2</sub>O was dominating the competition for active sites. Chen et al. had similar observations [18]. Guizani et al. [3] investigated the influence of reaction temperature and char particle size with the mixed gases, and found that an increase in either reaction temperature or particle size caused the reaction rate to shift gradually from *additive* to *competitive behavior*. This further supports the surface saturation influence, since both impact diffusional limitations.

In addition to the *competitive* or *additive behavior*, there is a third case where the char reactivity in the mixture atmosphere is higher than the sum of that in the two individual gases (positive synergy) [7,19,20]. This behavior is attributed to the catalytic effect of CaO to the char-CO<sub>2</sub> reaction under the presence of H<sub>2</sub>O. The positive synergy was only observed at lower temperatures (<900 °C), as CaO sinters at high temperature [7].

The evolution of char surface morphology and pore structure with different gasification reactant gases has also been evaluated [21–24]. The char surface morphology and pore structure evolution during gasification with H<sub>2</sub>O were different in comparison to the CO<sub>2</sub> case, indicating the reaction pathways of the two gases differed [21,22,24]. Bai et al. considered a positive interaction exists with H<sub>2</sub>O and CO<sub>2</sub> in developing char pore structure during the gasification in mixture gas, that H<sub>2</sub>O creates porous structure on char surface to promote the diffusion of CO<sub>2</sub> further into the pore structure [22]. This difference in char specific surface area development has been included in relative reaction rate models [11,16].

It is evident that char gasification behavior occurring with both H<sub>2</sub>O and CO<sub>2</sub> is complicated. The relationship between the reaction rate of the mixture and that in individual gases is influenced by experimental conditions, such as pressure, temperature, particle

size, the char pore structure, char structure, ash, and catalytic influences. It is very difficult to separate the competing influences experimentally. As listed in Table 1, the community has differing experimental observations with both additive and competitive behavior being observed.

Atomistic simulations are an approach to explore the reaction behaviors. Both Density Functional Theory (DFT) [25,26] and ReaxFF [27,28] approaches show reasonable results (compared to experimental observation) and provided additional insights into char reactions. Unfortunately, these methods are quite expensive and will often limit their application to small scale structures. Small scale systems lack the influence of the pore structure and its development upon reactivity in zone II gasification conditions. Carbon char models (~4000 carbon atoms) have also been constructed with a molecular dynamic annealing approach — with activation being simulated by stepwise removal of the higher energy carbons [26]. An edge recession approach has also been used with a simplistic coal char representations (~4000 carbon atoms) without consideration of pore influences [29]. There gasification was simulated with reactive probabilities and included recognition of zig-zag and chair reactive sites.

In our earlier work, a large-scale char structure (41,438 carbon atoms) was obtained by a rapid construction strategy [30], and an automated atomistic simulation method was proposed, to cost-effectively explore the char reactivity and behavior [31]. The char reactivity and behavior during oxy-fuel combustion was investigated via this simplified atomistic simulation approach [31,32]. Here, the simplistic atomistic approach was amended and adopted using the large-scale atomistic char model (where the char structure, ordering, and pores size distribution can be directly controlled), to determine the relative H<sub>2</sub>O and CO<sub>2</sub> reactivities individually and combined, to identify if additive or competitive behaviors are present, and to explore the differences in the pore distribution development. By excluding the influence of catalysis or ash, the atomistic simulation method could provide a more direct observation of some microscopic phenomena, which is helpful to gain a deep insight on the reaction mechanism of char reaction in mixture of H<sub>2</sub>O and CO<sub>2</sub>.

## 2. Methods

### 2.1. Large-scale char structure

The char structure was constructed in earlier work to conform with the experimental data of Sharma et al. [33] for a subbituminous pyrolysis char generated at 800 °C at a heating rate of 30 °C/min. An image-guided approach was used to quantify the stacking, polycyclic aromatic hydrocarbons (PAH) distribution, and the orientation from HRTEM lattice fringe micrographs. The HRTEM and XRD trends are similar for coal chars [34,35]. The two techniques measure slightly different components, corrected values however show similar values [34,35]. The large-scale char structure was constructed using the in-house Fringe3D [27,36–38] and Vol3D [36,38] scripts. The stacks and single (flat) PAH molecules were created in Fringe3D and then Vol3D packed those entities into a user defined volume without rotation or optimization. In this manner large-scale structures are created with minimal computational expense but retain the observed stacking and regional order. The atomistic structure was placed within a 100 × 100 × 100 Å cube. It contains 41,438 aromatic carbon atoms without heteroatoms, cross-links, or curvature. The H/C ratio is ~0.26 (close to the experimental result of ~0.24) and the structural properties are close to experimental values for helium density (1.93 g/cm<sup>3</sup>), average layers number per stack (~3.6), and average fringe layer length/PAH size (~1.5 nm). The PAH molecular weight distributions range from

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