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EFFECT OF REACTANT PENETRATION ON INHIBITION OF COAL CHAR GASIFICATION

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Resumen

Se utilizó un modelo para partícula individual que incluye reacciones homogéneas para estudiar el efecto de la penetración del reactivo en la acción inhibitoria del CO y el H_2 durante la gasificación del semicoque con CO_2 y H_2O. Los resultados obtenidos con el modelo sugieren la existencia de un rango te tamaño de partícula preferido donde la inhibición es mínima. El modelo también identifica condiciones experimentales en las cuales la información de reactividad disponible en la literatura no es adecuada para predecir la velocidad de gasificación de carbón a alta temperatura y propone mediciones experimentales que buscan corregir esta falla.

Palabras Clave: gasificación, carbón, reactividad, inhibición

Abstract

A single particle model with homogeneous reactions was used to study the effect of reactant penetration on the inhibitory effect of CO and H_2 during char gasification with CO_2 and H_2O. The results suggest the existence of a preferred size range where inhibition is minimal. The modeling exercise identifies experimental conditions in which the current reactivity data available in the public literature is not adequate to predict the char gasification reaction at high pressure and proposes experimental measurements aimed to correct this lack of available information.

Keywords: gasification, coal, reactivity, inhibition

1. INTRODUCTION

Recent estimates (Sekar et al, 2007) consider that coal gasification technologies, such as Integrated Coal Gasification Combined Cycle (IGCC), may become the cheapest technology for power generation if carbon penalties are imposed. This implies that, for the first time, gasification will be the economically-preferred option for power production. Previously, environmental and efficiency-related considerations have been the main motivations for the use of coal gasification for power generation.

Coal gasification has various analogies to coal combustion. In both processes, a high-temperature environment sets off coal pyrolysis, a process that yields a solid matrix, named char. Char subsequently heterogeneously reacts with oxygen (coal combustion) or CO_2 and/or water vapor (coal gasification).

Differences between coal gasification and combustion are also evident. Depending on the technology, particle sizes tend to be larger during gasification than for combustion. And, more noticeable, char reactivity, not a critical factor in coal combustion due to the fast reaction rates of coal oxidation, becomes an important design parameter for coal gasifiers.

The low reactivity observed during char gasification has motivated numerous experimental studies (Agarwal and Sears, 1980; Miura et al., 1986; Adschiri et al., 1986; Kasaoka et al., 1987; Hüttinger, 1988; Goyal et al., 1989; Molina and Mondragón, 1998, Lussier et al., 1998) aimed to evaluating kinetic parameters for char gasification.

One particularity of coal gasification is that H_2 and CO are products and inhibitors of the char/CO_2 and char/H_2O gasification reactions. During high pressure char gasification, the radial concentration of reactants (CO_2 and H_2O) and products (H_2 and CO) in the boundary layer and inside the particle is a function of the total gas pressure and reactant penetration. Given the relative low reactivity of char towards H_2O and CO_2, penetration of reactants into the particle is significant (low Thiele modulus). This implies the concurrent presence of significant concentrations of reactants and inhibitors inside the particle.

The mechanism of coal gasification inhibition has been constantly interpreted by Langmuir-Hinshelwood expressions (see, e.g., Lussier et al., 1998, and Hüttinger, 1988). However, recent computational tools (Lee et al. 1995; Goel et al., 2002; Molina et al. 2002), allow a more detailed analysis of the system that considers penetration of reactants inside the particle as well as distribution of surface site complexes. These computational tools allow a good description of the effects that inhibitor concentration inside the particle can have on char conversion.

In this paper we utilize a single particle model with homogeneous reactions to study the effect of reactant penetration on the inhibitory effect of CO and H_2 during char gasification with CO_2 and H_2O. We show, by detailed modeling of the gasification of coal char, how particle size affect the penetration of CO_2 and H_2O inside the particle and how these changes in penetration affect the inhibitory effect by H_2 and CO. We use this modeling exercise to (1) identify experimental conditions in which the current reactivity data available in the public literature is not adequate to predict the char gasification reaction at high pressure and (2) to propose experimental measurements aimed to correct this lack of available information.

2. COMPUTATIONAL STRATEGY

The literature available on inhibition by H_2 and CO_2 is mainly focused on obtaining empirical expressions, typically of the form Langmuir-Hishelwood, that describe the reduction of the gasification rate by the presence of the inhibitor. Few studies consider a detailed mechanism with elemental reactions.

2.1. Inhibition by H_2

For H_2 inhibition, three mechanisms have been identified: i. Dissociative hydrogen adsorption (R 1), ii. Reverse oxygen exchange (R 2) and, iii. Associative hydrogen adsorption.

$C(\_) + \frac{1}{2}H_2 \leftrightarrows C(H)$	R 1
$C(O) + H_2 \leftrightarrows C(\_) + H_2O$	R 2
$C(\_) + H_2 \leftrightarrows C(H_2)$	R 3

The effect of associative hydrogen adsorption (R 3) on char gasification is normally considered minimal because, as TPD experiments (Lussier et al., 1998) show, the amount of hydrogen desorbed in TPD experiments at low temperatures (< 1050 K) is minimal. The other two mechanism of inhibition play important roles. At early stages of char gasification, dissociative hydrogen adsorption (R 1) becomes important as H_2 saturates active sites. However, once steady-state is obtained and there is no more blockage, H_2 inhibition mostly occurs by reverse oxygen exchange (R 2) (Lussier et al., 1998).

2.2. Inhibition by CO

The primary CO inhibition effect comes through reversibility in the CO_2 dissociative adsorption reaction (Molina and Mondragón, 1998):

$$\mathrm{C(\_)} + \mathrm{CO_2} \rightleftarrows \mathrm{C(O)} + \mathrm{CO} \qquad \text{R 4}$$

However, some authors (Hüttinger, 1988) consider that the reversible desorption of C(O) complexes (R 5) can affect the CO_2/char reaction because C(O) complexes saturate the char surface decreasing the reaction rate.

$$\mathrm{C(O)} \leftrightarrows \mathrm{CO} \qquad \text{R 5}$$

This last reaction has been widely studied as it is part of the char/O_2 reaction. Montoya et al., 2002, report a kinetic expression for the desorption of C(O) sites found by ab initio calculations.

2.3. Heterogeneous model

Modeling was performed with the University of Sydney's Skippy (Surface Kinetics in Porous Particles) computer program (Ashman and Haynes, 1999). This program calculates steady-state species and temperature profiles for the reaction of a porous solid in a reacting gaseous environment. Skippy has proven a valuable tool for understanding char oxidation kinetics (Molina et al., 2002; Molina et al., 2004).

GRI-3.0 MECH (Smith et al., 2006) was used for the gas phase chemistry. However, the effect of the homogenous mechanism was found negligible in the temperature range studied and most simulations were performed without homogeneous chemistry.

2.4. Heterogeneous mechanism

As a first approximation, the heterogeneous mechanism considered a reversible step of H_2O/char reaction and CO desorption:

$$\mathrm{C(\_)} + \mathrm{H_2O} \leftrightarrows \mathrm{C(O)} + \mathrm{H_2} \qquad \text{R 6}$$

$$\mathrm{C(O)} \leftrightarrows \mathrm{CO} \qquad \text{R 7}$$

H_2 inhibition was assumed as occurring by oxygen reverse exchange (R 2). Although dissociative hydrogen adsorption (R 1) should be important during the first stages of char gasification at the conditions of this study, it was assumed that the effect of a reduction of reactivity because of active site saturation by H_2 could be represented by reaction R 2 when steady-state was achieved. Lussier et al., 1998, state that this is a good approximation for steady-state analysis, such as that performed by Skippy. Char gasification by CO_2 (R 4) was not considered in this approximation. Original rate expressions were taken from Yang and Yang, 1985, and Montoya et al., 2002 for reactions R 6 and R 7 respectively. The model was calibrated according to the experimental data of Goyal et al., 1989, as described bellow.

3. RESULTS

3.1. Mechanism calibration

The kinetic mechanism was calibrated with the experiments carried out by Goyal et al., 1989, for char collected from a pilot gasification plant working with Kentucky bituminous coal with a typical size (particle radius)of 0.032 cm. The simulations considered constant density and constant diameter cases. It is known that heterogeneous reactions should lie somewhere between these two cases. The heterogeneous mechanism was, however, the same for all cases.

The original rate expressions were modified until the best fit to the char conversion profiles reported by Goyal et al., 1989, was obtained. Figure 1 through Figure 3 show a comparison of the experimental data (as lines with open circles) with the best fit simulations (closed an open squares for the constant diameter and constant density cases respectively).

Although not perfect, the simulations agree with experimental data collected for the different temperatures and gas compositions. Major differences between simulations and experimental data are observed at high conversion levels. Agreement between experiments and simulation was slightly better for the constant diameter model than for constant density model.

Table 1 shows the kinetic parameters found after optimization. The data in Table 1 differs in more than one order of magnitude from the original expressions reported by Yang and Yang, 1985, and Montoya et al.,

2002. Furthermore, some of the values, such as an equal activation energy for reactions R 6 and inverse R 6 cannot be explained from a chemical point of view. The parameters in Table 1 are, therefore, empirical fits to the experimental data and do not provide any chemical insight into the process. Nevertheless, they can be used to understand the effect of particle size and species concentration profiles on char reactivity, as long as the calculations are performed within the temperature and pressures used for the calibration of the model.

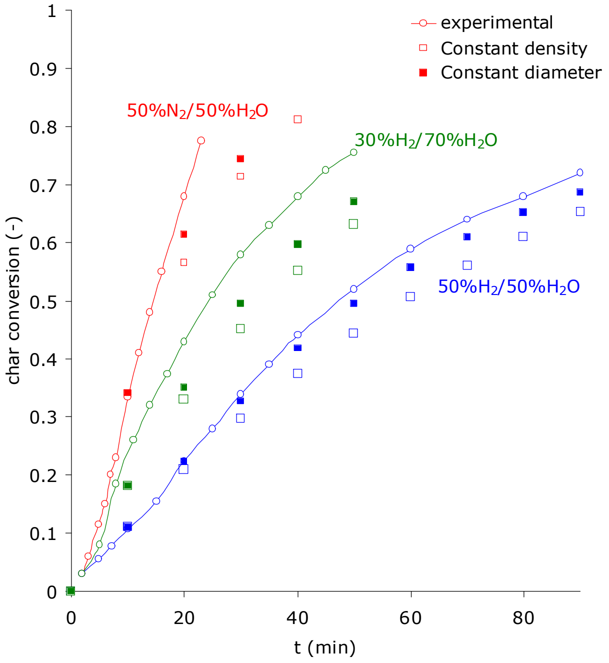

Figure 1. Comparison of calculated char conversion profiles according to constant density (open squares) and constant diameter (closed squares) with experiments (lines with circles) from Goyal et al.[6] for char gasification at 1200 K and 14 atm with water vapor.

Table 1. Kinetic parameters found after calibration (cal, mol, cm, s units)

Reaction No.	k_o	b	Ea
R 6	1.0×10^{13}	1.0	54 000
Inverse R 6	2.2×10^{13}	1.0	54 000
R 7	5.5×10^{07}	0.0	40 000

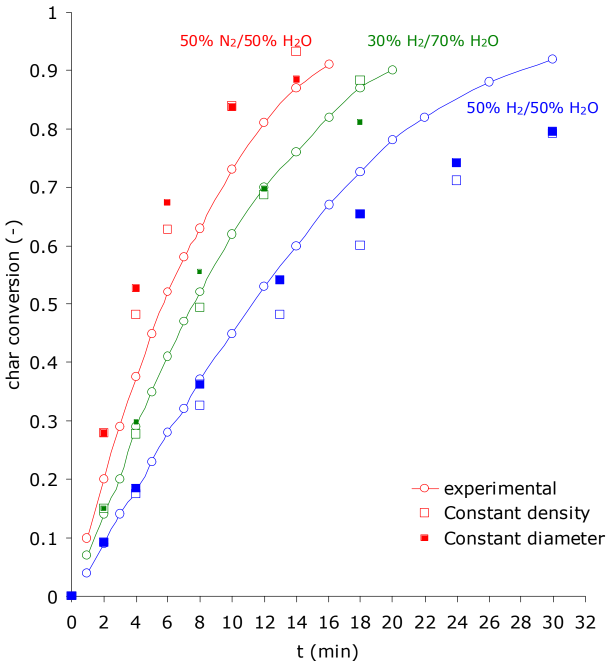

Figure 2. Comparison of calculated char conversion profiles according to constant density (open squares) and constant diameter (closed squares) with experiments (lines with circles) from Goyal et al.[6] for char gasification at 1310 K and 14 atm for different $H_2O/N_2/H_2$ mixtures.

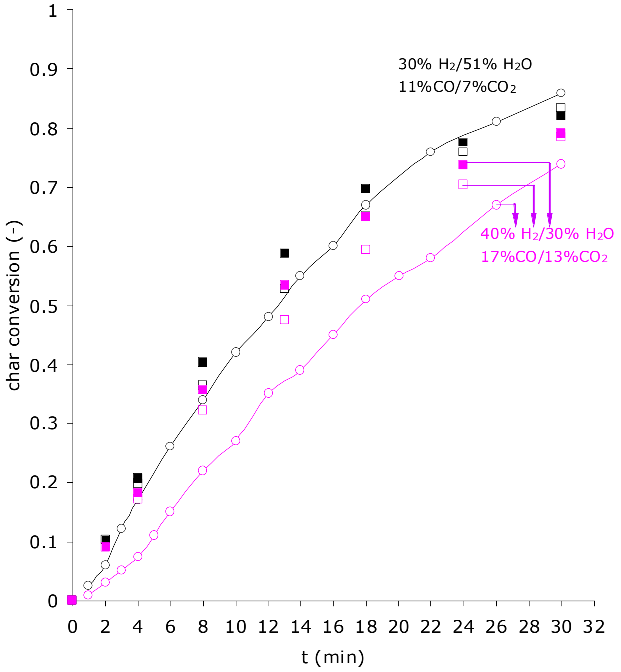

Figure 3. Comparison of calculated char conversion profiles according to constant density (open squares) and constant diameter (closed squares) with experiments (lines with circles) from Goyal et al.[6] for char gasification at 1310 K and 14 atm with $H_2O/N_2/H_2/CO$ mixtures

3.2. Effect of particle size on gasification rate

The validated mechanism was used to predict the initial gasification rate for a gas with composition typical of oxy-blown gasification 42% CO, 28% H_2, 19% H_2O, 9% CO_2 and 2% N_2 and T= 1310 K, P = 14 atm. The simulation shows a decrease in reaction rate as particle size increases (Figure 4).

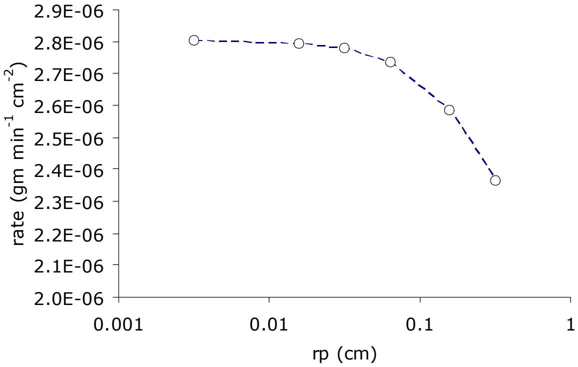

Figure 4. Variation of initial gasification rate with particle size as predicted by the model for a gas composition of 42% CO, 28% H_2, 19% H_2O, 9% CO_2 and 2% N_2 and T= 1310 K, P = 14

The reduction in the reaction rate as the particle size increases can be explained by a higher concentration of inhibitors (H_2 and CO) inside the particle and/or a lower concentration of reactant (H_2O). Other effects, such as a reduction on external surface area as particle size increases are consider minor given that during char gasification, most of the reaction occurs on the particle pores, represented by the particle surface area, that is mostly invariant with particle diameter.

Figure 5 shows the concentration profiles along the particle radius. The results suggest that for the mechanism used in these simulations, a lower H_2O concentration has a higher effect on decreasing the gasification rate than the higher inhibitor concentration.

For the typical particle size of 0.032 cm, the variation of concentration inside the particle is minimal, suggesting that the reaction occurs mostly through a constant diameter mechanism at the conditions of the simulation

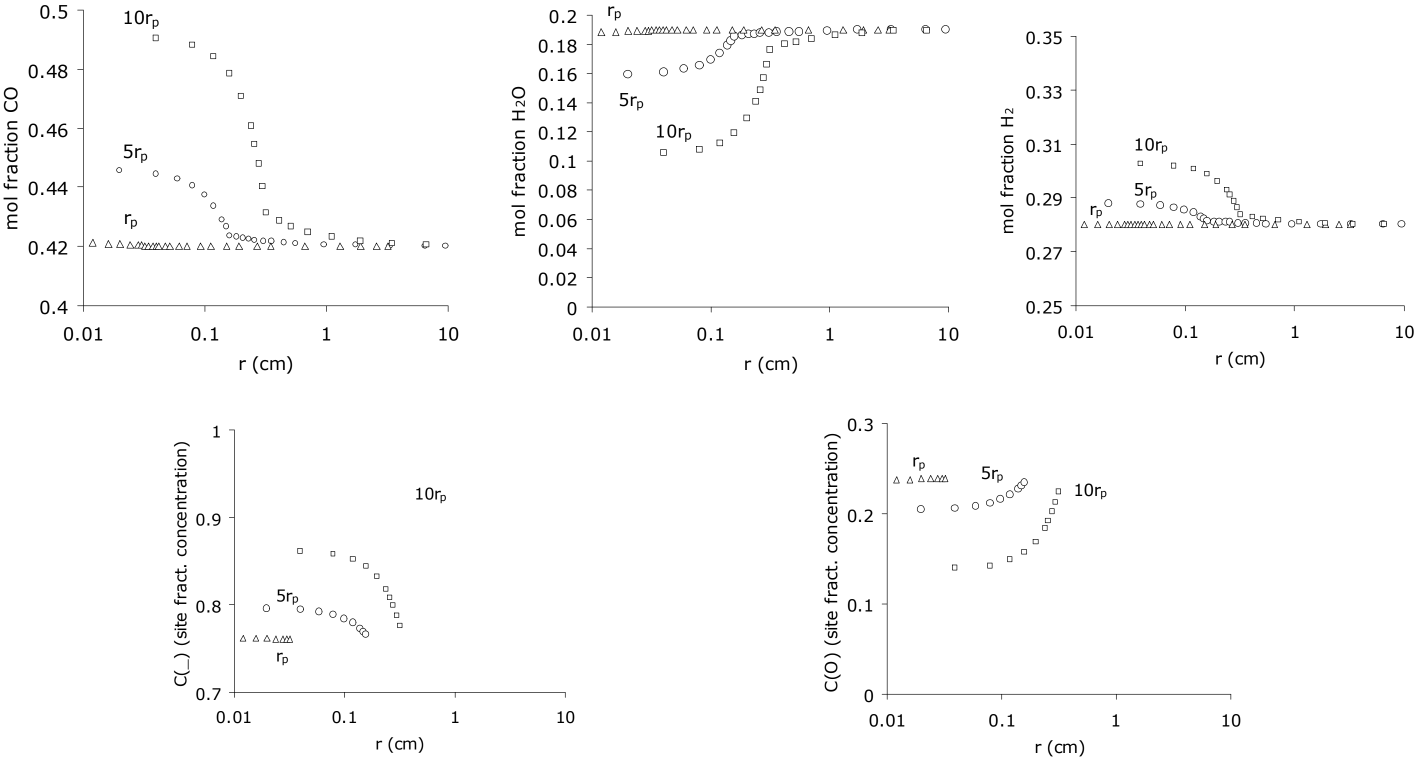

Figure 5. Predicted concentration profiles along particle and boundary layer during char gasification for different particle diameters. Gas composition 42% CO, 28% H_2, 19% H_2O, 9% CO_2 and 2% N_2 and T= 1310 K, P = 14 atm. Nominal particle radius (r_p) is 0.032 cm

4. CONCLUSIONS

The information available in the open literature for the gasification reactions, particularly for the inhibition by CO and H_2, is scarce and dominated by Langmuir-Hinshelwood expressions that are difficult to translate to detailed heterogeneous systems. When the available kinetic expressions are calibrated with existent experimental data, the resulting model captures the trends of reduction in reaction rate by inhibitors.

Major discrepancies between models and experiments occur at higher char conversion, possibly because of the crude system used to model the changes in physical properties.

As the particle size increases, the model predicts a reduction in the reaction rate that is caused by a lower concentration of H_2O inside the particle. This effect is more important than the higher inhibitor concentration inside the reactor.

Future research on char gasification at high pressure should study the effect of inhibitor penetration inside the particle and determine kinetic expressions suitable for the use in detailed heterogeneous models.

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