

Impact of finite-rate kinetics on carbon conversion in a single-stage entrained flow gasifier with coal-CO₂ slurry feed

Cristina Botero*, Randall P. Field, Howard J. Herzog, Ahmed F. Ghoniem

Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139

Abstract

Coal-CO₂ slurry feed has been suggested as an attractive alternative to coal-water slurry feed for single-stage, entrained-flow gasifiers. Previous work demonstrated the system-level advantages of gasification-based plants equipped with CO₂ capture and CO₂ slurry feed, under the assumption that carbon conversion remains unchanged. However, gasification in carbon dioxide has been observed to be slower than that in steam. In view of this, the impact of CO₂ slurry feeding on gasification kinetics and ultimately on carbon conversion and oxygen consumption in a pressurized, single-stage entrained-flow gasifier processing Illinois 6 coal is studied here using a 1-D reduced order model. Results show that the CO₂ gasification reaction plays a dominant role in char conversion when the feeding system is CO₂ slurry, increasing the CO content in the products by up to a factor of two. CO inhibition of the gasification reaction and a higher degree of internal mass transport limitations lead to an up to 60% slower gasification rate, when compared to a system based on coal-water slurry. Accordingly, a gasifier with CO₂ slurry feed has a 7%-point lower carbon conversion for a given outlet temperature. The gasifier exit temperature must be raised by 90K in order to achieve the same conversion as in a water slurry-fed reactor; the peak reactor temperature increases by 220K as a result. Net oxygen savings of 8% are estimated for a system with a CO₂ slurry-fed gasifier relative to one with water slurry and the same level of conversion.

Keywords: Coal, CO₂, Slurry, Gasification, Kinetics, Conversion

1. Introduction

Coal-carbon dioxide slurry feed has been suggested as an attractive option to significantly improve the performance of gasification-based plants operating with single-stage slurry-fed entrained flow gasifiers (EFG) and carbon capture [1, 2]. System-level simulations show that an average 15% lower specific oxygen consumption results when substituting water by liquid carbon dioxide in the slurry feeding system of gasifiers processing high and low-rank coal [1]. Coal-CO₂ slurry feeding holds the potential to significantly improve the economics of gasification-based plants through the use of smaller equipment and the advantage of better feedstock flexibility.

Research on the coal-CO₂ slurry feed concept has focused on the assessment of plant-level performance, in particular for Integrated Gasification Combined Cycle (IGCC) power plants [1–3], as well as slurry rheology [4–6] and, most recently, slurry preparation equipment design and characterization [7].

System-level simulations have predicted that coal-CO₂ slurry gasification produces syngas with a significantly higher CO:H₂ ratio, a trend that has been verified experimentally through laboratory-scale experiments [2]. This has been attributed to the increasingly dominant role of CO₂ gasifications relative to steam gasification reactions [1].

The effect of higher CO₂ concentrations on the heterogeneous gasification kinetics and carbon conversion in gasifiers with coal-CO₂ slurry feed has, nevertheless, not been addressed to date. Carbon conversion is one of the key performance measures of a gasifier; incomplete conversion is undesired as it increases the

*Corresponding author

Email address: cbotero@mit.edu (Cristina Botero)

operating costs related to feedstock consumption and ash disposal, as well as capital costs through the need for larger equipment when operating at lower thermal efficiencies.

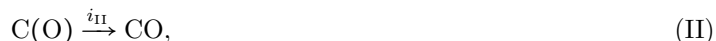
The aim of this work is to assess the impact of using CO₂ slurry feed on the heterogeneous gasification kinetics and ultimately on carbon conversion and oxygen consumption in a single-stage, slurry-fed EFG operating at high pressure. A detailed discussion of the kinetic mechanism of char gasification at high pressure in a mixed gas environment is outside the scope of the present work. Instead, a Langmuir-Hinshelwood kinetic rate expression taken from the literature which can reproduce experimental observations reliably under the conditions of interest is used to model the gasification kinetics in a reduced order model of the gasifier.

This work begins with a brief overview of the main steps in char gasification by H₂O and CO₂. This is followed by a survey of experimental observations of the relative rates of H₂O and CO₂ gasification as well as of observations addressing the question of whether these two gases compete for active sites on the char surface or not. The modeling framework is then introduced, followed by the results comparing the characteristic profiles, conversion, and oxygen consumption in a gasifier using CO₂ slurry feed, relative to one using water slurry feed.

2. Gasification in H₂O and CO₂

2.1. Mechanism

Several mechanisms have been proposed for the char reaction with steam and CO₂. It is believed that the principal steps are the dissociative adsorption of the gasification agent on an active site on the char surface, followed by associative desorption of the surface complex [8–10]. For CO₂ gasification, the reduced mechanism is:



where C_f represents a free site on the char surface, C(O) a chemisorbed atom on a free site, and *i* and *j* are the forward and backward rate constants, respectively. Similarly, the main steps in the reaction of char with steam are:



In these oxygen-exchange mechanisms, the well-known retarding effect by the products CO and H₂ is accounted for via reverse reactions (I) and (III), respectively. Other, more complex, mechanisms which consider additional steps as well as inhibition through different routes such as direct adsorption of the products onto active sites have also been proposed [11–14].

The gasification rate of char in pure CO₂ has been measured to be slower than that in pure H₂O but within the same order of magnitude. A selection of experimental observations comparing CO₂ and H₂O gasification rates under conditions at which the chemical reaction alone controls the rate of reaction is presented in Table 1.

Table 1: Relative rates of CO₂ and H₂O gasification

Feedstock	Partial Pressure	Temperature	Rate		Source
			CO ₂	H ₂ O	
Purified carbon	4-40 bar	800-870°C	1	3-6	Blackwood et al. (1958-60) [12, 15]
Bituminous coal char	< 60 bar	900°C	1	3-4	Muehlen et al. (1985) [16]
Brown coal char	< 1 bar	800°C	1	2	Harris and Smith (1991) [17]
Bituminous coal char	1-30 bar	850-900°C	1	2-4	Roberts (2000) [18]

2.2. Competition for Active Reaction Sites

Extensive work has been performed characterizing the gasification kinetics in the CO_2/CO and $\text{H}_2\text{O}/\text{H}_2$ systems in which the products CO and H_2 have been shown to retard the CO_2 and H_2O gasification reactions, respectively (e.g. [11, 16, 19, 20]). However, the kinetics in a mixed $\text{CO}_2/\text{H}_2\text{O}/\text{CO}/\text{H}_2$ environment typical of commercial gasifiers have not been characterized extensively, in particular at high pressures. Of particular interest here is whether the presence of CO_2 slows down the overall gasification rate in a mixed $\text{CO}_2/\text{H}_2\text{O}$ environment, relative to a system containing only steam; this is especially relevant for gasifiers with CO_2 slurry feed. The underlying question is whether the gasification agents CO_2 and H_2O compete for the same active sites on the char surface or whether they react on separate sites, a topic for which much disagreement still remains.

At atmospheric pressure conditions, this question was addressed independently by Blik [21], Everson et al. [22], and Huang et al. [20] for chars from coals of different ranks. All three groups concluded that the surface mechanism which accounts for the reaction of $\text{C}-\text{CO}_2$ and $\text{C}-\text{H}_2\text{O}$ on separate active sites is best at explaining the experimentally observed rates in a mixture of $\text{CO}_2/\text{H}_2\text{O}/\text{CO}/\text{H}_2$. The overall gasification rate, r , could be successfully predicted by adding the individual rates:

$$r = \frac{k_{\text{CO}_2} P_{\text{CO}_2}}{1 + \kappa_{\text{CO}_2} P_{\text{CO}_2} + \kappa_{\text{CO}} P_{\text{CO}}} + \frac{k_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}}}{1 + \kappa_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}} + \kappa_{\text{H}_2} P_{\text{H}_2}}, \quad (1)$$

where P is the partial pressure of each gas component in the mixture. Here, k_{CO_2} and $k_{\text{H}_2\text{O}}$ correspond to the rate constants i_I and i_{III} in reactions (I) and (III), respectively, whereas κ_{CO_2} , κ_{CO} , $\kappa_{\text{H}_2\text{O}}$, and κ_{H_2} are rate constant ratios whose definition differs between authors depending on the reaction mechanism assumed.

In contrast to the observations above at atmospheric pressure conditions, Roberts and Harris [23] showed that in a pressurized system containing a mix of CO_2 and H_2O , the slower CO_2 gasification reaction inhibits the H_2O gasification reaction by occupying active sites on the char surface, effectively slowing down the overall char gasification rate through competition for active sites. Gasification in a mixed gasifying agent environment with 50 vol.% CO_2 was shown to be up to two times slower than in a pure H_2O under identical conditions. Measurements were carried out for three different bituminous coal chars at partial pressures of up to 10 bar.

Similarly, Muehlen et al. [16, 24] combined all the reaction steps proposed by Blackwood et al. for CO_2 and H_2O gasification at high pressure [12, 15] and assumed single surface coverage to derive a rate expression of the combined form:

$$r = \frac{k_{\text{CO}_2} P_{\text{CO}_2} + k_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}}}{1 + \kappa_{\text{CO}_2} P_{\text{CO}_2} + \kappa_{\text{CO}} P_{\text{CO}} + \kappa_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}} + \kappa_{\text{H}_2} P_{\text{H}_2}}, \quad (2)$$

which succeeded in predicting the reaction rate of a German bituminous coal char in a semitechnical-scale fluidized bed reactor operating at 40 bar in an environment with mixed gasifying agents and products. The rate constants were determined for the binary systems CO_2/CO and $\text{H}_2\text{O}/\text{H}_2$ at pressures of up to 70 bar. Note that squared and hydrogasification terms contained in Muehlen's original work have been neglected in equation (2) since they have been shown to be 3-5 orders of magnitude smaller at the high temperatures characteristic of an EFG [25, 26].

The work conducted by Muehlen et al. is of especial significance. It is still, to date, to the best of our knowledge, the only research group who has published a Langmuir-Hinshelwood (LH) kinetic expression for char gasification at high pressure derived from their own experiments, accounting for the presence of mixed gasifying agent and products, and validated with data from a semitechnical plant.

More recently, Liu [27] determined LH rate constants for the CO_2/CO and $\text{H}_2\text{O}/\text{H}_2$ systems from published high pressure experiments for different chars. Liu found that the rate expression (2) is significantly better than equation (1) at predicting the rates measured by Goyal et al. [28] at high pressure in a mixed $\text{CO}_2/\text{H}_2\text{O}/\text{CO}/\text{H}_2$ environment. In later work, Liu and Niksa [25] conducted an extensive survey of the literature for pressurized coal gasification and used mean rate constants as a basis for the development of the Carbon Burnout Kinetics Model for Gasification (CBK/G). This commercial kinetics package models the gasification rate in a mixed gas environment using an equation of the same form as equation (2) and thus assumes competition between CO_2 and H_2O for active sites.

The observations above indicate that there is no general agreement regarding the role of the competition for active sites between CO_2 and H_2O in char gasification kinetics. Data at ambient pressure tends to support

the independent active site assumption, whereas the competing active site mechanism has been shown by multiple authors to apply at high pressures, where surface saturation is high.

Most recently, an alternative surface mechanism was proposed by Umemoto et al. [29], who found that both the competing and the independent active site mechanisms fail to explain experimental observations for three bituminous coal chars in a mixed $\text{CO}_2/\text{H}_2\text{O}/\text{CO}/\text{H}_2$ environment under atmospheric pressure conditions; the former underpredicts the gasification rate while the latter overpredicts it. According to the proposed mechanism, which proved to be successful at predicting the measured rates, active sites on the char surface are neither independent nor competing but rather shared by CO_2 and H_2O . An analogous study has not been published at pressurized conditions.

3. Methodology

The modeling tool used for the steady-state, 1-D simulations conducted in this study was Aspen Custom Modeler [30]. Langmuir-Hinshelwood kinetics were implemented into a reduced order model (ROM) of an entrained flow gasifier. Simulations were performed for both a water slurry and CO_2 slurry-fed reactor whose geometry and characteristics resemble those of a commercial-scale unit.

3.1. Reduced Order Model of Gasifier

The ROM of the single-stage EFG used in this study was developed by Monaghan et al. and has been described in detail elsewhere [31–33]. It incorporates multiple submodels including fluid mixing and recirculation, particle properties, drying and devolatilization, chemical kinetics, heat transfer, and slagging.

The ROM uses an idealized reactor network model to represent the fluid mixing and recirculation between different regions inside the gasifier. For an axially-fired, swirling, single stage reactor such as the GE gasifier studied here, the network consists of four zones, as schematically illustrated in Figure 1.

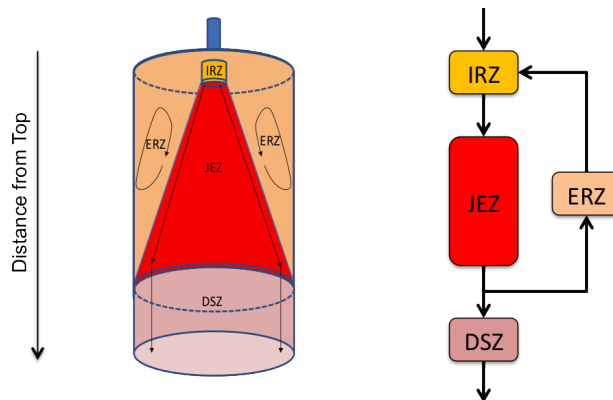


Figure 1: Representation of gasifier through a network of idealized reactors in reduced order model

In the internal recirculation zone (IRZ), which is modeled as a well-stirred reactor (WSR), the inlet streams mix with each other as well as with recirculated gas and particles from the external recirculation zone. The two-phase flow leaving the IRZ expands like a free jet in the jet expansion zone (JEZ), which is modeled as a truncated conical, 1-D plug flow reactor (PFR). A fraction of the flow in the expanding jet is detrained and flows back to the IRZ through the external recirculation zone (ERZ), which is represented by a WSR. The fraction that is not detrained proceeds to the downstream zone (DSZ), which is modeled by a 1-D PFR.

3.2. Intrinsic Heterogeneous Kinetics

Langmuir-Hinshelwood kinetics were selected for modeling the high-pressure intrinsic gasification rate in the ROM:

$$r_1 = \psi \cdot \frac{k_{\text{CO}_2} P_{\text{CO}_2} + k_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}}}{1 + \kappa_{\text{CO}_2} P_{\text{CO}_2} + \kappa_{\text{CO}} P_{\text{CO}} + \kappa_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}} + \kappa_{\text{H}_2} P_{\text{H}_2}}. \quad (3)$$

Here, r_1 is the gasification rate under kinetically controlled conditions (zone I) in inverse time units, and ψ is the relative reactivity factor. The rate constants, k , and rate constant ratios, κ , have Arrhenius-type temperature dependence. Selection of the combined expression (3) was based on the observations by Muehlen [16], Roberts and Harris [23], Liu [27], and Liu and Niksa [25] supporting the competing active site mechanism at high pressures.

In contrast to power-law kinetic expressions, which are strictly empirical, LH kinetics are derived from multistep adsorption-desorption reaction mechanisms and thus have a more mechanistic basis. This kind of rate law is especially attractive for high pressure applications since it is able to reproduce the asymptotic rate behavior caused by surface saturation under those conditions, as well as to account for the inhibiting effect of the reaction products.

The relative reactivity factor ψ in eq. (3) was first introduced by Johnson [34]; it is a feedstock and reactor-specific adjustment parameter which accounts for the difference in char reactivity and morphology resulting predominantly from the parent coal characteristics and the reactor conditions. For a given gasification environment, the gasification rate has been observed to be highest for coals with low carbon content and for slow heating rates during pyrolysis; for low-rank coal, the amount and type of mineral matter in the parent coal is also a key factor [34, 35].

The rate parameters reported by Muehlen [16, 24] were selected for the implementation of expression (3) in the ROM. These are summarized in Table 2 and resulted in the lowest root mean square (RMS) deviation when compared with 124 gasification rate measurements at high pressure taken from the literature, for 17 different chars [28, 36–41]. A similar comparison of the experiments with the rate law parameters by Liu [27] and by Liu and Niksa [25] resulted in an increasingly higher RMS deviation from the experimental data of . The kinetic expression by Roberts and Harris [23] was not considered in the selection process because of the absence of terms accounting for the retarding effect of CO and H₂.

Table 2: Rate constants (k) and rate constant ratios (κ) by Muehlen [16] for use in eq. (3): $k, \kappa = A \exp \frac{E}{RT}$

	A		E	
k_{CO_2}	$2.71 \cdot 10^4$	bar ⁻¹ min ⁻¹	153.1	kJ/mol
$k_{\text{H}_2\text{O}}$	$2.96 \cdot 10^5$	bar ⁻¹ min ⁻¹	154.0	kJ/mol
κ_{CO_2}	$2.06 \cdot 10^{-2}$	bar ⁻¹	-23.0	kJ/mol
κ_{CO}	$3.82 \cdot 10^{-2}$	bar ⁻¹	-48.1	kJ/mol
$\kappa_{\text{H}_2\text{O}}$	$1.11 \cdot 10^1$	bar ⁻¹	29.5	kJ/mol
κ_{H_2}	$1.53 \cdot 10^{-9}$	bar ⁻¹	-209.2	kJ/mol

Figure 2 is a parity plot comparing the gasification rate prediction vs. measurements for the selected rate constants by Muehlen. The narrow confidence interval range indicates that the gasification rate prediction can reproduce the experimental data with reasonable accuracy despite the wide range of feedstocks and conditions and the over four orders of magnitude spread of the rate data. No systematic deviations are observed.

For each of the 17 feedstocks considered, the value of ψ used in Figure 2 represents the average of the reactivity factors determined for the individual experimental runs through adjustment of the prediction to the measurements. The resulting feedstock-specific factors are presented in Figure 3 as a function of the parent coal’s dry ash-free carbon content (C_{daf}). Their magnitudes are within the three order of magnitude range reported elsewhere [35, 42]. The trend of increasing reactivity with decreasing carbon content is correctly represented, though with a wide spread of the data, in particular for low-rank coal. The latter is likely due to the reactor-specific contribution to ψ , which cannot be accounted for by the C_{daf} only, as well as to additional factors such as mineral matter content. Simple char properties alone have been observed to be an unsuitable indicator for char reactivity [35].

3.3. High Temperature Heterogeneous Kinetics

The effectiveness factor approach was used in the ROM in order to account for the transition from the kinetically-limited regime (zone I) into the pore diffusion-limited regime (zone II) at high temperatures. In

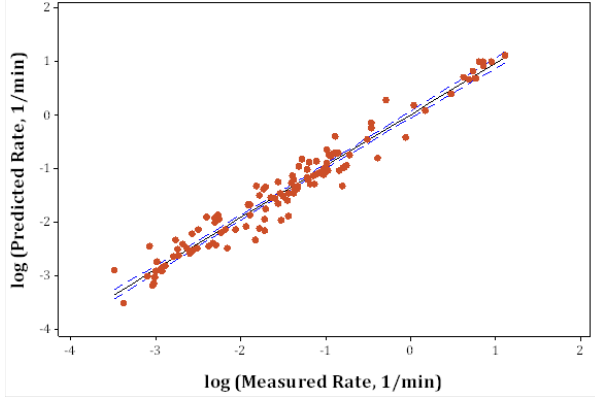


Figure 2: Parity plot comparing gasification rate prediction using equation (3) and Muehlen's rate parameters with experimental measurements from the literature [28, 36–41]; dashed lines indicate the 95% confidence interval. The RMS deviation is 0.23 min^{-1} .

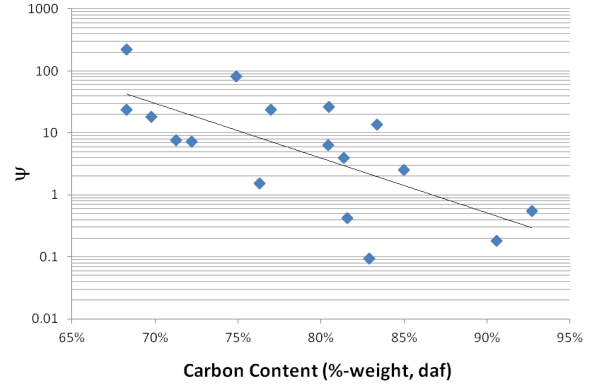


Figure 3: Relative reactivity factor used for each feedstock as a function of dry, ash-free carbon content of parent coal.

this approach, the observed gasification rate in zone II, r_{II} , is estimated from the intrinsic rate r_I and the effectiveness factor η , which is defined as

$$\eta \equiv \frac{r_{II}}{r_I}. \quad (4)$$

The effectiveness factor is, by definition, less than 1 in zone II as a result of internal mass transport limitations. It is calculated from the Thiele modulus (ϕ), which is a measure of the ratio of the surface reaction rate to the rate of diffusion through the pores of the char particle. ϕ is a function of the intrinsic rate parameters as well as of the particle radius (R), $\phi \sim R$, and effective pore diffusivity (D_e), $\phi \sim D_e^{-1/2}$; the latter combines the effects of molecular and Knudsen diffusion and depends strongly on the particle morphology. In the ROM, the calculation of D_e is based on an assumed char particle porosity of 0.25 in combination with an average pore radius estimated from the random pore model [31].

No analytical solution exists for ϕ and η in the case of Langmuir-Hinshelwood kinetics. Approximate values were estimated following the methodology by Hong et al. [43], which requires manipulation of eq. (3) by conducting a mass balance inside the char particle and solving a system of differential equations [44].

Calculation of the observed reaction rate under zone II conditions according to eq. (4) requires extrapolation of r_I to high temperatures, an approach that has been used successfully in the past for combustion applications [45, 46]. Nevertheless, this is one of the factors which contributes most to the uncertainty of the present kinetic analysis. Experimental measurements of high pressure, high temperature gasification kinetics is the topic of current research [45].

3.4. Cases Studied

The main assumptions and characteristics of the gasifier studied are presented in Table 3. The gasifier resembles the GE gasifier used in the Cool Water IGCC Demonstration Project, which has a reported carbon conversion of 96.5% for Illinois 6 coal [47]. A reactivity factor of 8.3 was calculated from the ROM for this reactor and feedstock to achieve the reported conversion; this is within the range expected for the C_{daf} content of this coal, see Figure 3.

The base case operation of the water slurry-fed gasifier was modeled first, whereas the oxygen flow rate was fixed at the value reported for the Cool Water project and the outlet temperature was obtained from the simulations. A gasifier with CO_2 slurry feed operating with the same coal throughput and outlet temperature was subsequently simulated; the oxygen flow rate was adjusted accordingly. The slurry solids loading was assumed to be equal in both cases to allow for an easier comparison; note, however, that the maximum loading in $\text{CO}_{2(l)}$ is expected to be higher than that of water slurry ([4–6]).

Table 3: Characteristics of gasifier studied [47]

Gasifier	
Type	GE
Volume	25.5 m ³ (900 ft ³)
Total Height	8.8 m
Feedstock	
Throughput (dry)	907 tonne/day
Coal type	Illinois 6
Higher heating value	30,506 kJ/kg (dry)
Carbon content	80.5% (daf)
Moisture	10.0%-wt.
Reactivity factor (ψ)	8.3 ^a
Char particle	
Particle radius	50 μm ^b
Porosity	0.25 ^b
Average pore radius	2-8 nm ^c
Base Case Operation	
Slurrying medium	H ₂ O
Slurry solids loading	63.4%-wt.
Oxidant (95 vol.-% O ₂)	842 tonne/day
Pressure	30 bar
Temperature	1,443°C at outlet ^c
Carbon conversion	96.5% (single pass)

^a Adjusted to achieve reported conversion

^b Assumption

^c Simulation result

4. Results

4.1. Gas Phase Composition

The mole fraction of the main gas phase components is presented in Figure 4 along the length of the gasifier for the H₂O slurry and CO₂ slurry cases. The gasifier length is plotted as the distance from the injection point at the top of the reactor, see Figure 1. The profiles begin at the outlet of the IRZ zone, i.e. following the devolatilization and mixing of the inlet streams with the recirculating gasification products. The depletion of oxygen in the figure marks the beginning of the gasification reactions.

The CO₂ content at the beginning of the gasification process is only marginally higher in a reactor with CO₂ slurry feed. There are two reasons for this; firstly, the mass flow of CO₂ replacing H₂O in the slurry represents a smaller contribution on a mole basis due to the high molecular weight of CO₂. Only about 60% of the liquid inlet to the gasifier is CO₂, on a mole basis, while the remaining 40% is coal moisture. Secondly, CO₂ produced in the initial, heating section of a CO₂ slurry-fed gasifier is an estimated 30% lower than in a reactor with water slurry feed. CO₂ heats up and vaporizes more readily than water so less oxidation of volatiles and char is required to heat up the feed to the operating temperature.

The largest difference in the gas phase composition for a gasifier with CO₂ slurry is its H₂O and CO content. The fraction of H₂O to which the char is exposed during gasification decreases by almost half when the feed is CO₂ slurry, as the figure shows. Less water in the feed and less oxidation of the hydrogen-containing volatiles are the main causes for this, analogous to the discussion above for CO₂.

The almost two times higher concentration of CO in a CO₂ slurry-fed gasifier indicates that the CO₂ gasification reaction, eq. (I)-(II), plays a more important role in the overall carbon conversion process when CO_{2(l)} is used in the feeding system. For the case of water slurry, on the other hand, conversion is strongly dominated by the steam gasification reaction, eq. (III)-(IV), as a result of the very high ratio of H₂O to CO₂. This ratio decreases by a factor of two when the feeding system is based on CO_{2(l)}, thus increasing the contribution of the CO₂ gasification reaction.

4.2. Temperature Profile

The heat of reaction for CO₂ gasification is about 30% higher than that of steam gasification. Overall, gasification in a reactor with CO₂ slurry is thus more endothermic than in a reactor with water slurry. This

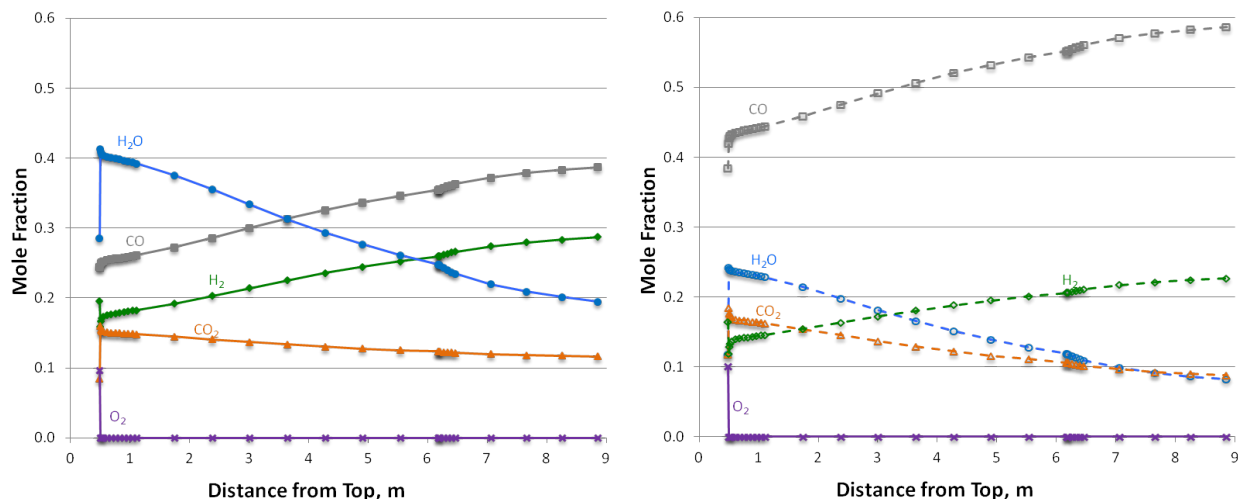


Figure 4: Mole fraction of main components in gas phase along the reactor for a gasifier with H₂O slurry feed (left) and CO₂ slurry feed (right). The profiles begin at the IRZ zone outlet, so the combined effects of devolatilization and gasification product recirculation are observed.

can be seen in Figure 5, where the temperature profile inside the gasifier is shown. For the base outlet temperature of 1,443°C, an almost 100K higher peak temperature is required in the gasifier with CO₂ slurry to provide enough heat for the endothermic gasification reactions.

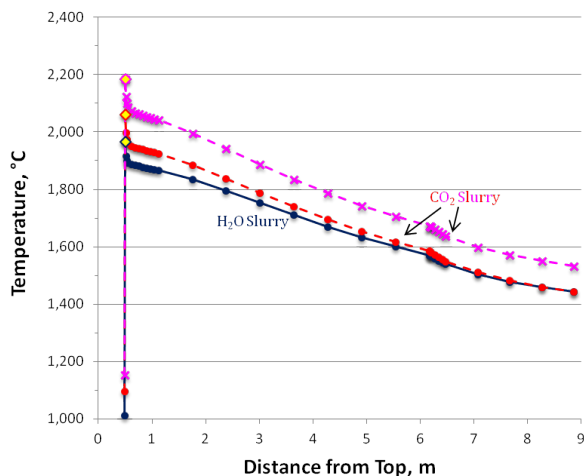


Figure 5: Temperature profiles for gasifier with H₂O slurry (—) and CO₂ slurry feed (---) for the base outlet temperature of 1,443°C (●) and an increased outlet temperature of 1,534°C (×). The peak reactor temperature is indicated in each case (♦).

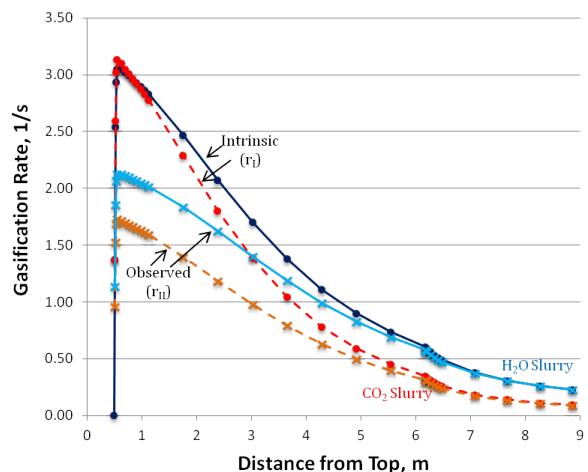


Figure 6: Intrinsic (●) and observed (×) reaction rate for a gasifier with water slurry (—) and CO₂ slurry (---) feed

4.3. Gasification Rate

The higher contribution of the CO₂ gasification reaction to the overall carbon conversion in a reactor with CO₂ slurry feed raises questions related to how this reaction will affect the process outcome. Of particular interest is whether the trend of the slower kinetics of CO₂ gasification observed at low temperatures (see Table 1) will apply at higher temperatures and the degree to which higher CO concentrations will inhibit the gasification reaction.

The intrinsic and observed gasification rate profiles obtained from the ROM simulations are plotted in Figure 6. The results show that for both water slurry and CO₂ slurry, internal mass transport limitations play an important role in the early gasifier stages, where the temperature is highest and the kinetics fastest: the observed reaction rate is up to 2 times lower than the intrinsic rate. The role of internal mass transport limitations diminishes along the reactor as the intrinsic reaction rate drops with the temperature and with product accumulation; the process becomes fully kinetically controlled by the time the syngas leaves the gasifier.

The observed reaction rate for a system with CO₂ slurry feed is 20-60% lower than one with water slurry feed. This is true both in the pore diffusion-limited regime near the gasifier inlet, where the intrinsic rates are nearly equal, and in the kinetically limited region near the outlet. The results thus indicate that CO₂ slurry has a detrimental effect on both the intrinsic kinetics and the mass transport processes taking place inside the char particle.

Intrinsic gasification kinetics in pure CO₂ and H₂O

A comparison between the intrinsic reaction rate of Illinois 6 char in pure H₂O and pure CO₂, as predicted by the Langmuir-Hinshelwood kinetic expression used in this study, is presented in Figure 7. The normal probability density functions (PDF) shown were constructed from the RMS deviation between prediction and experiments in Figure 2.

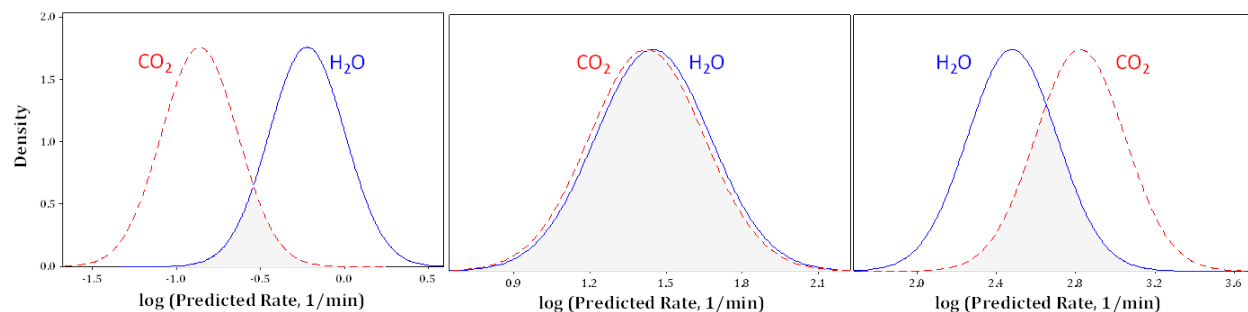


Figure 7: Probability density function of intrinsic gasification rate in pure H₂O (—) and pure CO₂ (---) at 30 bar and 900°C (left), 1,400°C (middle), and 2,000°C (right) as predicted by eq. (3) with $\psi = 8.3$

The results in the figure show that the predicted gasification rate (mean of PDF) is about 4 times slower for CO₂ than for H₂O at low temperatures. This result agrees well with experimental observations under similar conditions, see Table 1.

For the conditions inside the entrained flow gasifier considered, however, the situation is somewhat different. The intrinsic gasification rate in pure CO₂ is predicted to be the same or higher than in pure H₂O in the range 1,400-2,000°C. This can be attributed to the slightly higher temperature dependence of the CO₂ gasification rate constant in the rate expression used, a fact that is supported by multiple experimental observations (e.g. [17]).

For practical purposes and in view of the large areas of overlap in Figure 7, the intrinsic rates of CO₂ and H₂O gasification can be considered to be nearly equal at entrained flow gasifier conditions. Observations of slower intrinsic reaction kinetics for CO₂ gasification at low temperatures can therefore not be extended to high temperature conditions in order to explain the slower intrinsic rates in Figure 6 for gasification of coal-CO₂ slurry.

CO Inhibition

Given that the partial pressure of CO is almost two times higher in gasifiers with CO₂ slurry feed, CO inhibition of the gasification reactions is considered to be a potential cause for the slower intrinsic gasification kinetics observed for this feeding system.

While both CO and H₂ are known to inhibit the intrinsic gasification reaction (e.g. [11, 12, 15, 19]), CO has been reported to have a stronger effect than H₂ [48, 49]. This trend is correctly reproduced by the kinetic expression used in this study, as shown in Figure 8, where the predicted inhibitory effect of CO and H₂ are compared at different temperatures for a fixed partial pressure of the gasifying agents.

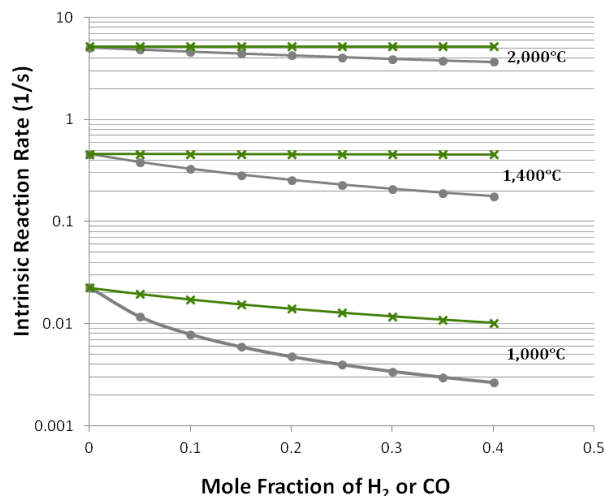


Figure 8: Inhibition of intrinsic gasification rate by CO (●) and H₂ (×) at different temperatures and a total pressure of 30 bar as calculated with eq. (3). The mole fraction of H₂O and CO₂ in the mixture is assumed to be 0.2.

As illustrated in the figure, the intrinsic reaction rate is inhibited more strongly in the presence of CO than in H₂. Product inhibition is predicted to decrease with increasing temperature, as expected [50]. For the temperatures above 1,400°C relevant to entrained flow gasifiers, H₂ inhibition is negligible compared to CO inhibition. Inside the gasifier, inhibition by CO is augmented by the higher concentration of this gas, relative to H₂. This is particularly true for gasifiers with CO₂ slurry feed, for which the ratio of CO to H₂ is twice as high than in gasifiers with water slurry feed.

Pore Diffusion Limitations

The increased concentration of CO₂ and CO relative to H₂O and H₂ in a gasifier with CO₂ slurry feed proved to also affect the degree of internal mass transport limitations. Near the gasifier inlet, where this effect is most significant, Figure 6 shows that the ratio of intrinsic to observed reaction rate, i.e. the effectiveness factor, is about 20% lower in a reactor with CO₂ slurry feed despite the fact that the intrinsic reaction rate is almost the same. This result can be attributed to the compositional change of the gas phase in gasifiers with CO₂ slurry feed, in combination with the fact that CO₂ and CO have a lower diffusivity than H₂O and H₂.

4.4. Carbon Conversion and Oxygen Consumption

The slower gasification rate in a reactor with CO₂ slurry feed results in a reduction of the carbon conversion achieved for a given exit temperature. The results in Figure 9 show that when the gasifier outlet temperature is maintained at its base value of 1,443°C, carbon conversion drops from 96.5% for water slurry to 89.8% for CO₂ slurry.

To quantify how significant the estimated conversion reduction is, the gasifier throughput was adjusted to achieve the base case conversion of 96.5%. The simulation results show that a 45% throughput reduction would be necessary to outweigh the slow kinetics in a reactor with CO₂ slurry.

Because the reaction rate near the gasifier outlet proved to be limited by the intrinsic gasification kinetics, the conversion in a CO₂ slurry-fed gasifier can be increased by raising its operating temperature. The results of this study showed that a 90K increase is necessary in order to achieve the same conversion as with a water slurry fed reactor. As shown in Figure 5, this increase leads to a 220K higher peak gasifier temperature near the inlet, relative to a reactor with water slurry feed, and could thus compromise the integrity and lifetime of the refractory and burner.

Previous work for a similar feedstock and slurry loading as those used here reported oxygen savings of an estimated 10% for a gasifier with CO₂ slurry feed; the gasifier temperature and carbon conversion were assumed to remain unchanged, relative to a gasifier based on water slurry [1]. However, this study shows

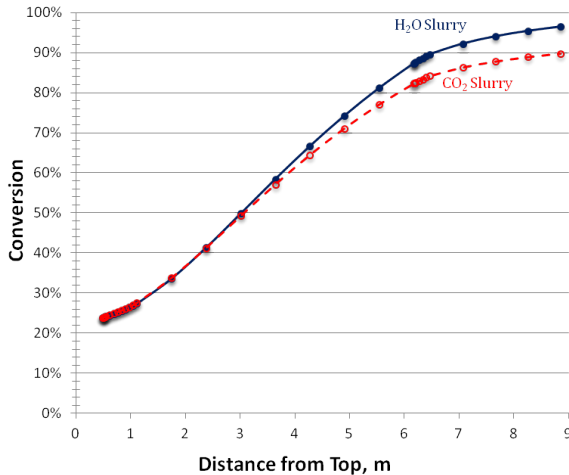


Figure 9: Carbon conversion in a gasifier with CO₂ and H₂O slurry for a fixed outlet temperature of 1,443°C.

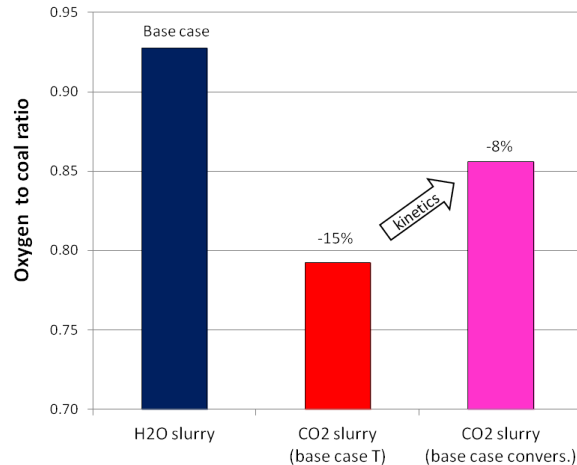


Figure 10: Oxygen consumption comparison of a gasifier with water slurry feed and one with CO₂ slurry feed and the same outlet temperature of 1,443°C, but reduced conversion, or the same conversion at a higher outlet temperature of 1,534°C.

that previous assumptions are not realistic since carbon conversion will decrease significantly in a gasifier with CO₂ slurry feed if the operating temperature is kept constant.

Results in Figure 10 show that once the conversion reduction is accounted for, the estimated oxygen consumption in a system based on CO₂ slurry is 15% lower than in a system with water slurry feed for the base case operating temperature of 1,443°C. However, if the base case conversion of 96.5% is to be maintained in a gasifier with CO₂ slurry feed, the net oxygen savings account for 8%, relative to a case with water slurry feed, as a result of the required 90K increase in the outlet temperature.

5. Conclusions

In this work, accurate heterogeneous gasification kinetics were used for a gasifier with coal-CO₂ slurry feed in order to assess the impact of this alternative feeding system on carbon conversion and oxygen consumption inside the reactor. A Langmuir-Hinshelwood intrinsic rate expression from the literature, which was developed at high pressure and validated in an environment of H₂O/CO₂/CO/H₂, was selected based on its ability to reproduce a wide range of experimental observations at high pressures. This expression accounts for the competition between CO₂ and H₂O for active sites on the char surface. Moreover, an effectiveness factor approach was used to account for internal mass transport limitations at high temperatures.

The results show that a gasifier with CO₂ slurry feed produces up to two times more CO than one with water slurry feed as a result of the higher CO₂:H₂O ratio in the feed and hence higher contribution of the CO₂ gasification reaction to the overall conversion process. The observed gasification rate is up to 60% lower: the CO₂ slurry feed penalizes the intrinsic reaction rate, through CO inhibition, and reduces pore diffusive transport, through the lower diffusivities of CO and CO₂ relative to H₂O and H₂.

As a result of the slower gasification rate, a gasifier operating with coal-CO₂ slurry will have a 7%-point lower conversion than one with water slurry if the exit temperature of the reactor is left unchanged. A 90K temperature rise at the exit is required in order to achieve the same conversion as in a water slurry fed gasifier, increasing oxygen consumption relative to previous estimates which assumed unchanged conversion and operating temperature. In reality, an oxygen consumption saving of 8% is estimated if the temperature increase required to maintain conversion at its base value is accounted for. Additionally, the peak reactor temperature increases by 220K, which could compromise component integrity.

6. Outlook

Future work will study the possibility of injecting small amounts of steam to gasifiers with CO₂ slurry in order to improve kinetics and thus conversion. This measure will raise carbon conversion, however, the oxygen consumption and cold gas efficiency will be compromised. The tradeoff between these performance variables will be studied.

Acknowledgments

The authors would like to acknowledge BP for the funding and Aspen Technology, Inc. for the simulation software.

References

- [1] Botero C., Field R. P., Herzog H., Ghoniem A. F., Impact of coal rank, slurry loading, and syngas cooling technology on the performance of an IGCC plant with carbon capture and coal-CO₂ slurry feed, Manuscript Submitted for Publication, 2012.
- [2] Dooher J. P., Castaldi M. J., Rubin D., Phillips J. N., Schoff R., Evaluation of low rank coal/liquid CO₂ slurries for generic, single-stage, slurry-fed gasifiers, in: 35th International Technical Conference of Coal Utilization and Fuel Systems, Clearwater, Florida (USA), 2010.
- [3] McNamee G. P., White G. A., Use of lignite in texaco gasification-based-combined-cycle power plants, Technical Report AP-4509, Prepared by Energy Conversion Systems, Inc. for Electric Power Research Institute (1986).
- [4] Peirson J. F. J., Burje W. J., Santhanam C. J., Investigation of low-rank-coal-liquid carbon dioxide slurries, Technical Report EPRI AP-4849, Prepared by Arthur D. Little, Inc. for Electric Power Research Institute (1986).
- [5] Dooher J., Phillips J., Program on technology innovation: Advanced concepts in slurry-fed low-rank coal gasification. liquid CO₂/coal slurries and hot water drying, Technical Report 1014432, Prepared by Dooher Institute of Physics and Energy for the Electric Power Research Institute (2006).
- [6] Dooher J. P., Physio-chemical properties of low rank coal/liquid CO₂ slurries as gasifier feedstocks, in: 34th International Technical Conference of Coal Utilization and Fuel Systems, Clearwater, Florida (USA), 2009.
- [7] U.S. Department of Energy's National Energy Technology Laboratory (NETL) , Carbon dioxide coal slurry for feeding low-rank coal to gasifiers, Project Fact Sheet, Project No.: DE-FE0007977 (2011).
- [8] Hurt R., Calo J., Fletcher T. H., Sayre A., Fundamental investigation of fuel transformations in pulverized coal combustion and gasification technologies, Technical Report DE-FG26-OONT40815, Prepared by Brown University for the U.S. Department of Energy (2005).
- [9] Roberts D. G., Harris D. J., Char reactivity in gas mixtures: Towards an understanding of the C-CO-CO₂ reaction system, Technical Report TN35, CSIRO Energy Technology (2008).
- [10] Roberts D. G., Harris D. J., A kinetic analysis of coal char gasification reactions at high pressures, *Energy & Fuels* 20 (6) (2006) 2314–2320.
- [11] Gadsby J., Long F. J., Sleightholm P., Sykes K. W., The mechanism of the carbon dioxide-carbon reaction, *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences* 193 (1034) (1948) 357–376.
- [12] Blackwood J. D., Ingeme A. J., The reaction of carbon with carbon dioxide at high pressure, *Australian Journal of Chemistry* 13 (2) (1960) 194–209.
- [13] Liu G.-s., Tate A. G., Bryant G. W., Wall T. F., Mathematical modeling of coal char reactivity with CO₂ at high pressures and temperatures, *Fuel* 79 (10) (2000) 1145–1154.
- [14] Huettinger K. J., Merdes W. F., The carbon-steam reaction at elevated pressure: Formations of product gases and hydrogen inhibitions, *Carbon* 30 (6) (1992) 883–894.
- [15] Blackwood J., McGrory F., The carbon-steam reaction at high pressure, *Australian Journal of Chemistry* 11 (1) (1958) 16–33.
- [16] Muehlen H. J., van Heek K. H., Juengtgen H., Kinetic studies of steam gasification of char in the presence of H₂, CO₂ and CO, *Fuel* 64 (7) (1985) 944–949.
- [17] Harris D. J., Smith I. W., Intrinsic reactivity of petroleum coke and brown coal char to carbon dioxide, steam and oxygen, *Symposium (International) on Combustion* 23 (1) (1991) 1185–1190.

- [18] Roberts D. G., Intrinsic reaction kinetics of coal chars with oxygen, carbon dioxide and steam at elevated pressures, Ph.D. thesis, University of Newcastle (2000).
- [19] Gadsby J., Hinshelwood C. N., Sykes K. W., The kinetics of the reactions of the steam-carbon system, Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences 187 (1009) (1946) 129–151.
- [20] Huang Z., Zhang J., Zhao Y., Zhang H., Yue G., Suda T., et al., Kinetic studies of char gasification by steam and CO₂ in the presence of H₂ and CO, Fuel Processing Technology 91 (8) (2010) 843–847.
- [21] Bliiek A., Mathematical modeling of a concurrent fixed bed coal gasifier, Ph.D. thesis, Twente University of Technology, The Netherlands (1984).
- [22] Everson R. C., Neomagus H. W. J. P., Kasaini H., Njapha D., Reaction kinetics of pulverized coal-chars derived from inertinite-rich coal discards: Gasification with carbon dioxide and steam, Fuel 85 (78) (2006) 1076–1082.
- [23] Roberts D. G., Harris D. J., Char gasification in mixtures of CO₂ and H₂O: Competition and inhibition, Fuel 86 (17-18) (2007) 2672–2678.
- [24] Muehlen H. J., Zum Einfluss der Produktgase auf die Kinetik der Wasserdampfvergasung in Abhaengigkeit von Druck und Temperatur (*Influence of product gases on the kinetics of steam gasification as a function of pressure and temperature*), Phd thesis, University of Essen (1983).
- [25] Liu G.-S., Niksa S., Coal conversion submodels for design applications at elevated pressures. Part II. Char gasification, Progress in Energy and Combustion Science 30 (6) (2004) 679–717.
- [26] Walker Jr P. L., Rusinko Jr F., Austin L. G., Gas reactions of carbon, in: D.D. Eley P. W. S., Paul B. W. (Eds.), Advances in Catalysis, Vol. Volume 11, Academic Press, 1959, pp. 133–221.
- [27] Liu G.-S., Mathematical modelling of coal char reactivity in a pressurised entrained flow gasifier, Ph.D. thesis, The University of Newcastle, Australia (1999).
- [28] Goyal A., Zabransky R. F., Rehmat A., Gasification kinetics of western kentucky bituminous coal char, Industrial & Engineering Chemistry Research 28 (12) (1989) 1767–1778.
- [29] Umamoto S., Kajitani S., Hara S., Modeling of coal char gasification in coexistence of co₂ and h₂o considering sharing of active sites, Fuel (In Press).
- [30] Aspen Technology, Inc. , Aspen Custom Modeler, Version 7.3 (2011).
- [31] Monaghan R. F. D., Ghoniem A. F., A dynamic reduced order model for simulating entrained flow gasifiers: Part I: Model development and description, Fuel 91 (1) (2012) 61–80.
- [32] Monaghan R. F. D., Ghoniem A. F., A dynamic reduced order model for simulating entrained flow gasifiers: Part II: Model validation and sensitivity analysis, Fuel 94 (0) (2012) 280–297.
- [33] Monaghan R. F. D., Ghoniem A. F., Simulation of a commercial-scale entrained flow gasifier using a dynamic reduced order model, Energy & Fuels 26 (2) (2011) 1089–1106.
- [34] Johnson J. L., Kinetics of Coal Gasification, John Wiley & Sons, Inc. 1979.
- [35] Miura K., Hashimoto K., Silveston P. L., Factors affecting the reactivity of coal chars during gasification, and indices representing reactivity, Fuel 68 (11) (1989) 1461–1475.
- [36] Sha X.-Z., Chen Y.-G., Cao J., Yang Y.-M., Ren D.-Q., Effects of operating pressure on coal gasification, Fuel 69 (5) (1990) 656–659.
- [37] Adanez J., Miranda J., Gaviln J., Kinetics of a lignite-char gasification by CO₂, Fuel 64 (6) (1985) 801–804.
- [38] Zevenhoven R., Hupa M., Characterization of solid fuel at pressurized fluidized bed gasification conditions, in: 23rd international technical conference on coal utilization and fuel systems, Clearwater, FL, USA, 1998.
- [39] Kajitani S., Hara S., Matsuda H., Gasification rate analysis of coal char with a pressurized drop tube furnace, Fuel 81 (5) (2002) 539–546.
- [40] Nozaki T., Adschiri T., Fujimoto K., Coal char gasification under pressurized CO₂ atmosphere, Fuel 71 (3) (1992) 349–350.
- [41] Roberts D. G., Harris D. J., Char gasification with O₂, CO₂, and H₂O: Effects of pressure on intrinsic reaction kinetics, Energy & Fuels 14 (2) (2000) 483–489.
- [42] Radovic L. R., Steczko K., Walker Jr P. L., Jenkins R. G., Combined effects of inorganic constituents and pyrolysis conditions on the gasification reactivity of coal chars, Fuel Processing Technology 10 (3) (1985) 311–326.

- [43] Hong J., Hecker W. C., Fletcher T. H., Improving the accuracy of predicting effectiveness factors for nth order and langmuir rate equations in spherical coordinates, *Energy & Fuels* 14 (3) (2000) 663–670.
- [44] Roberts G. W., Satterfield C. N., Effectiveness factor for porous catalysts. Langmuir-Hinshelwood kinetic expressions, *Industrial & Engineering Chemistry Fundamentals* 4 (3) (1965) 288–293.
- [45] Harris D. J., Coal gasification reactivity: Measurement and application, in: *Pittsburgh Coal Conference*, Johannesburg, South Africa, 2007.
- [46] Valix M. G., Harris D. J., Smith I. W., Trimm D. L., The intrinsic combustion reactivity of pulverised coal chars: The use of experimental pore diffusion coefficients, *Symposium (International) on Combustion* 24 (1) (1992) 1217–1223.
- [47] Electric Power Research Institute, Cool Water coal gasification program: Final report, Technical Report GS-6805 (1990).
- [48] van Heek K. H., Muehlen H.-J., Juentgen H., Progress in the kinetics of coal and char gasification, *Chemical Engineering & Technology* 10 (1) (1987) 411–419.
- [49] Wall T. F., Liu G.-s., Wu H.-w., Roberts D. G., Benfell K. E., Gupta S., et al., The effects of pressure on coal reactions during pulverised coal combustion and gasification, *Progress in Energy and Combustion Science* 28 (5) (2002) 405–433.
- [50] Kajitani S., Suzuki N., Ashizawa M., Hara S., CO₂ gasification rate analysis of coal char in entrained flow coal gasifier, *Fuel* 85 (2) (2006) 163–169.