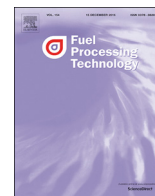




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Research article

The effect of carbon dioxide partial pressure on the gasification rate and pore development of Highveld coal chars at elevated pressures

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ABSTRACT

Char structural changes occurring during gasification are normally only related to conversion and few data is published on the effect of carbon dioxide partial pressure on the extent of pore development. In this study, the char–CO₂ reactivity and consequential pore development of different Highveld coal chars were investigated over a wide pressure range. Reactivity experiments were performed in a fixed bed reactor under reaction controlled conditions. The initial reaction rate was found to be solely a function of temperature and CO₂ partial pressure and was well described by the Langmuir Hinshelwood rate equation.

Surface analyses were performed on fresh and partially converted chars to quantify the effect of CO₂ partial pressure on pore development. It was found that pores development more rapidly with conversion if the CO₂ partial pressure is increased. This outcome has fundamental implications for the interpretations of gasification reaction kinetics. The term describing the total amount of active sites in the Langmuir Hinshelwood equation might not be constant at all partial pressures, and the possible impact of that is shown in this work. More work is required to further understand these effects and incorporate them appropriately into high pressure rate equations.

1. Background and introduction

The gasification of coal is an important process underpinning the chemicals, fertilisers, and energy sectors globally [1]. Commercially, the process is carried out by feeding a mixture of steam and oxygen into large and complex gasifiers, often operated at high temperatures and pressures [2]. Under these conditions, there are many physical and chemical processes occurring in parallel. One of the important processes, which determine how specific feedstocks and their blends will behave, is the conversion kinetics.

The outcomes of kinetic studies of char gasification play an important role in the successful operation of gasifiers, as well as supporting effective process and gasifier design. These studies are usually performed through laboratory scale experiments using different reagent gas mixtures containing H₂O, O₂ and CO₂, sometimes including the presence of reaction products (CO and H₂). While the steam and oxygen reactions are of more practical value to gasifier operation, the reaction with CO₂ is important and also serves as a reference for broader fundamental gasification studies [3].

Numerous studies have investigated coal gasification kinetics and modelling at low pressures (atmospheric pressure and below) [4–10].

The Langmuir Hinshelwood (LH) rate equation shown in Eq. (1) is derived from the commonly-accepted reaction mechanism of the C–CO₂ reaction and has been used to describe reactivity [4–6].

$$r_s = \frac{k_1 p_{CO_2}}{1 + k_2 p_{CO} + k_3 p_{CO_2}} \quad (1)$$

The empirical *n*-th order (power law) equation shown in Eq. (2) has also been used in many studies as it can simplify kinetic analyses over specific ranges of temperature and pressure [7–10].

$$r_s = A \exp\left(-\frac{E}{RT}\right) p_{CO_2}^n \quad (2)$$

Atmospheric pressure kinetic studies are important, and the outcomes of such studies have contributed significantly to the understanding of gasification reaction systems and the application of this through modelling. Given the high operating pressures of many commercial coal gasifiers, however, a need also exists to study gasification reactivity at high partial pressures of reactants. In comparison with atmospheric-pressure studies, there are fewer studies performed at high pressures, in particular when considering South African coals. Studies at high pressure have been carried out for different coal chars [11–16].

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Most authors agree that the empirical power law is only valid up to 10 bar CO₂ partial pressure before pressure-induced modifications to the ‘reaction order’ are required [11, 12]. While the *n*-th order equation can be useful over specific ranges of temperature and pressure, for more widespread application, the Langmuir Hinshelwood model derived from first principles is more suitable for use at high pressure [12–14] as it can explicitly account for such effects based on the reaction mechanism.

The considerable amount of literature regarding the study of char gasification kinetics means that the understanding of the effects of reaction conditions (in particular temperature and pressure) on this kinetics is quite good. However, the overall gasification rate is not only dependent on the reaction conditions but also on the physical char structure and how it changes during reaction [11, 15–17]. Liu and co-workers [16] investigated the physical changes occurring in Australian coal chars during gasification at high pressures and observed significant increases in the micropore surface area. The authors suggest that gasification takes place inside the pores and leads to pore growth as well as the formation of new pores. This is certainly consistent with the generally-accepted mode of reaction of carbonaceous chars. Coetzee and co-workers [17] also observed an increase in surface area from the onset of CO₂ gasification for all pore sizes of a Witbank seam 4 coal char and suggested that the reagent gas had access to most pore sizes and that the difference in individual sized pore development could not solely be explained by gas accessibility.

Kinetic models such as the Langmuir Hinshelwood equation do not have terms that account for structural changes with conversion. The [C_i] term, for example, relates to the number of active sites, and is assumed to be a constant. For this reason, quantification of such terms are usually undertaken at a common extent of conversion, and additional models (for example, the random pore model [18]) are used to estimate how such kinetics might change over time. It has however been suggested that reagent partial pressure significantly affects the char pore development [11]. Roberts and Harris [11] observed that chars reacted to the same extent of conversion at 20 atm generally had a higher internal surface area compared to chars reacted at 1 atm. Further work by the same authors [13] observed that carbon monoxide (CO) partial pressures also had a significant effect on the char surface area after reaction with CO₂ to 10% conversion. The authors inferred that the term describing the total amount of active sites on the char surface (C_T) (which is usually kept constant in the Langmuir Hinshelwood model) may also be changing as a result of pore development. They emphasized the need for deeper investigation regarding the effect of reagent partial pressure on surface area development.

Changes in internal surface areas have fundamental implications for the reaction of CO₂ with coal chars. An improved understanding of these changes is required in order to incorporate them into kinetic rate equations. This study addresses this important but poorly-understood aspect of the char–CO₂ reaction system. The focus is on the quantification and explanation of the effect of high partial pressures of CO₂ on the extent of micro- and mesopore development during CO₂ gasification, in the context of first-of-a-kind measurement of high pressure CO₂ reaction kinetics for South African coals.

2. Materials and methods

2.1. Sample preparation and characterization

The samples used in this work were three South African Highveld coals (2 N, 4 N, 5 N) from different seams (2, 4 and 5). The bulk samples were crushed to a particle size of –8 mm and then split into smaller representative batches. Chars were prepared by heating the coal samples to 950 °C at 10 °C/min under a 1 L_N/min flow of nitrogen with a holding time of 2 h. After charring, the samples were crushed and sieved to a particle size range of –500 μm +425 μm. Parent coals and resulting coal chars were characterized using compositional,

Table 1
Sample characterization results.

Characterization analysis	Coal			Char		
	2 N	4 N	5 N	2 N	4 N	5 N
Proximate analysis (wt% d.b.)						
Ash yield (ISO 1171:2010)	19.5	26.5	30.5	27.0	34.1	40.2
Volatile matter (ISO 562:2010)	24.7	21.9	29.1	1.2	1.2	1.0
Fixed carbon (by difference)	55.8	51.6	40.4	71.8	64.7	58.8
Gross calorific value (MJ/kg a.d.)						
CV (ISO 1928:2009)	24.1	21.5	20.5	22.1	19.9	17.2
Ultimate analysis						
Carbon (ISO 29541:2010)	78.8	77.5	76.7	95.9	96.5	95.2
Hydrogen (ISO 29541:2010)	4.3	3.9	5.6	0.3	0.1	0.3
Nitrogen (ISO 29541:2010)	2.0	2.1	2.1	2.0	2.1	2.0
Oxygen (calculated by difference)	13.8	15.1	14.2	0.0	0.0	1.0
Sulphur (ISO 19579:2006)	1.1	1.4	1.4	1.8	1.3	1.5
Maceral composition (volume % m.m.f.)						
Total vitrinite	23.5	10.5	60.0	ND ^a	ND	ND
Total liptinite	4.9	5.1	11.5	ND	ND	ND
Total inertinite	71.6	84.4	28.5	ND	ND	ND
Total reactivities	79.5	82.2	85.0	ND	ND	ND
Vitrinite reflectance						
Reflectance (%)	0.55	0.66	0.53	ND	ND	ND
Rank (bituminous) ISO 11760:2005	D	C	D	ND	ND	ND

^a ND – not determined.

petrographic and mineral analyses. The compositional analysis was conducted by Bureau Veritas Testing and Inspectors South Africa and the petrographic analysis by Sasol Technology Research and Development. A summary of the characterization results are shown in Table 1.

2.2. Reactivity measurements

A high pressure fixed bed reactor, shown in Fig. 1, was designed and constructed in-house and used to perform reactivity experiments. The reagent gas flow consisted of different concentrations of carbon dioxide (5–30 vol%) with a nitrogen balance. Both gases were instrument grade with 99.9% purity. The char sample (0.2–0.5 g) was loaded onto a porous quartz filter disc with a nominal pore size of 150 μm. The reactor pressure was varied between 1 and 30 bar and controlled by a downstream electronic pressure controller (EL-PRESS from Bronkhorst High Tech®). A vertical split-tube furnace (Carbolite®) was used as a heat source. The temperature range for which Regime I conditions apply was determined separately for each char by varying the char particle size, external diffusion limitations by varying the reagent flow rate and heat transfer limitations by mixing the sample with inert sand particles. After reviewing the results of these tests, the highest temperature where Regime I conditions could comfortably apply was established for each coal char i.e. 2 N: 855 °C, 4 N: 830 °C and 5 N: 800 °C. Gasification was performed at and below these temperatures.

The carbon monoxide concentration in the product gas was measured using a non-dispersive infra-red (NDIR) analyser (MGA3000™ model from ADC Gas Analysis®). During experimentation the CO concentration was low enough as to ensure differential conditions. Through knowledge of the reaction stoichiometry and gas flow rate, the carbon conversion rate (*r_c*) was calculated using Eq. (3):

$$r_c = \frac{y_{CO}}{2} \times \dot{n} \times MW \text{ [g/s]} \quad (3)$$

The amount of carbon remaining in the sample at each time interval was calculated by:

$$m_c(t) = m_{c,0} - \int_0^t r_c dt \text{ [g]} \quad (4)$$

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