Fuel 140 (2015) 17–26

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

The properties of large coal particles and reaction kinetics of corresponding chars

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HIGHLIGHTS

- The chemical, petrographic and physical properties of coal particles of different sizes and densities were determined.
- The distribution of properties depended on the densities of the particles.
- The combustion reaction rates for large particles and for different particles sizes and densities were measured.
- The combustion rates were characterised with a shrinking core with diffusion controlled mechanisms only.

ARTICLE INFO

Article history:
Received 26 July 2013
Received in revised form 6 February 2014
Accepted 11 September 2014
Available online 27 September 2014

Keywords:
Large coal particles
Particle size
Particle density
Devolatilization
Combustion

ABSTRACT

An investigation was undertaken to determine the distribution of chemical-, petrographic- and mineralogical properties of large coal particles of different sizes and densities and to evaluate a suitable reaction rate model for combustion of corresponding chars. This was undertaken in order to contribute to the knowledge of the combustion kinetics of large particles in fluidized bed combustion and moving bed combustion/gasification. The study was confined to a mineral rich (24.1 wt%) and inertinite rich (74 wt%) parent coal (precursor) that was separated into different sizes and density fractions. The combustion reactive properties of chars prepared at 1100 °C and at a reaction temperature of 1000 °C were determined using a horizontal tubular furnace with the associated on-line analysers and temperature controllers. Coal particles in the size range of 0.50–53 mm diameter and density from 1.4 g cm^{-3} to 2.0 g cm^{-3} were studied. The characterisation of the different coal samples consisting of ash content, maceral content, fuel ratios and calorific values showed that the parameters did not vary significantly over the particle size ranges, but were different for the different density fractions. Combustion studies showed that particle size and density influenced the time required for complete conversion of the chars. The smaller particles and low density particles reacted faster and the modeling of the experimental data showed that the isothermal shrinking un-reacted core model with film and ash layer diffusion was applicable. The effective ash layer diffusion becomes more prominent as the density increased and the mass transfer coefficients correlated well with published results.

1. Introduction

It is well-known that the particle properties of coal have a significant influence on its devolatilization, combustion and gasification behaviour and needs to be examined in greater detail for the optimisation of future coal conversion processes. These properties include particle size, physical structure (morphology), chemical-, petrographic- and mineral composition [1–8]. The overall density which depends on the physical structure and composition of minerals and macerals distributed within the particle has also been considered as a useful property [6,7,9–11]. Results from studies consisting of devolatilization, combustion and gasification involving the abovementioned properties have been published extensively for mostly pulverized and small particles (less than 1 mm) [6–11], which however needs to be extended to large particles as used in fluidized bed (1–6 mm) and moving fixed bed (up to 75 mm) operation [3,4,12]. The distribution of minerals and macerals between different particle sizes and different density fractions has been considered by many investigators and its effect on structural changes and reactivity have been reported [6,7,10]. For large particles, diffusion of mass and heat becomes important and can be

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http://dx.doi.org/10.1016/j.fuel.2014.09.038
0016-2361/

Nomenclature

b	stoichiometric coefficient (carbon oxygen reaction) (−)	N_{Re}	Reynolds number Ud_p/υ
B	carbon (−)	R_p	particle radius (m)
C_{Ag}	concentration of reactant gas (mol m^{-3})	t	time (s)
d_p	particle diameter (m)	U	gas velocity (m s^{-1})
D_e	effective ash layer diffusion coefficient (m^2 s^{-1})	X_B	conversion of carbon B (−)
k_g	film mass transfer coefficient (m s^{-1})	ρ_B	molar density of carbon B (kmol m$^{-3)}$
M_B	molar weight of carbon B (g mol^{-1})	υ	kinematic viscosity of air (m^2 s^{-1})
M_{AB}	molar weight of diffusing gas (g mol^{-1})		

expected to effect the overall reaction rate and has been shown by some investigators to be rate controlling [2,13,14]. The minerals present can also have a major influence on the overall reaction kinetics and needs to be considered in detail especially for mineral-rich (greater than 20 wt% ash content) coal which is characteristic of deposits occurring in South Africa. [12,15,16]. The effects include: (1) the volatiles formed as a result of the decomposition of certain minerals in addition to volatiles formed from the macerals [17,18], (2) the calorific value of the coals will be lowered as a result of the heats of mineral transformation (endothermic) [17], (3) the slagging properties especially at high temperatures [19,20], (4) thermal cracking can occur as a result of differential thermal conductivity properties causing shattering, [21] and (5) the reaction rate is influenced as a result of inherent catalytic properties of minerals containing calcium, magnesium and iron [22,23]. The behaviour of pure macerals consisting of liptinite, vitrinite and inertinites are well known [1,24,25], however in the presence of minerals, the carbominerites present needs to be considered [6,18]. The effect of high concentrations of minerals and inertinites on reactivity has been examined in detail [26,27] for small particles; the combustion kinetics of which can be described adequately with a reaction–diffusion model. The influence of inert macerals can be summarised as follows [1,24,18,26]: (1) a low swelling property which contributes to the formation of low porosity structures, (2) a lower ratio of hydrogen to carbon affecting the yields of hydrogen in the volatiles, and (3) the tendency to form carbominerites with the minerals present causing it to become more inert. It has been established that both the mineral and maceral distribution within particles vary significantly with particle density, which obviously will have an impact on the overall reaction kinetics [6].

The reaction rate modeling for large particles can be expected to consist of diffusion mechanisms around the particle (film/boundary layer), through as ash layer and inside pores together with surface (intrinsic) chemical reactions. Reaction rate models for reaction rate controlled systems, essentially for fine coal particles, have been proposed and validated which include the shrinking core model and the random pore model [28–32]. These models can be extended to incorporate diffusion through an ash layer (high ash coal) according to the shrinking core model concept, or within the pores occurring in the coal/char structure according to the random pore model. The film diffusion depends on the gas flow used which needs to be assessed relative to the ash layer diffusion for a complete description.

Thus, in order to contribute to the understanding of the use of large particles for combustion, an investigation was undertaken to examine the properties of different size particles and density fractions and to assess the overall reaction kinetics. The purpose of this paper is: (1) to present results showing the distribution of results obtained from proximate, ultimate petrographic and mineralogical analyses for different size particles and different density fractions, and (2) to show the validity of the isothermal shrinking core model involving experimental and detailed modeling results.

2. Experimental

2.1. Preparation of samples

Samples for the characterisation and combustion experiments were prepared according to a systematic procedure involving essentially the separation of a typical South African coal batch (parent coal) into different density fractions followed by separation into different particle size ranges as shown in Table 1. The particle sizes chosen are in the range of particles used in combustion and gasification in fluidized (0.5–3 mm) and fixed bed reactors (<70 mm) and the density range obtained are characteristic of the coal batch used. Twenty-four different samples were prepared involving variation of particle size with constant densities and variation of density with constant particle size. The properties of the parent coal (Highveld seam 4 bituminous coal) is shown in Table 2 and it can be seen that it has an ash content (proximate analysis/as received) of 24.1 wt% with a 73 vol% inertinites content (of which 44 vol% are inert inertinites) which is very different to coals occurring internationally.

The original coal batch was density separated into the density fractions shown in Table 1 using the well-known sink/float techniques with a mixture of TBE (tetrabromoethane) and toluene as the separation medium. The density separated samples were dried and sieved to obtain six different size batches (Table 1). It should be noted that the results reported are bulk densities according to the densities of the separation media used.

For the combustion experiments, chars were synthesized using the coal particles prepared above followed by mechanical treatment to ensure exact particle sizes and densities shown in Table 1. To accomplish this, single particles were taken from the different coal batches (sizes and densities) and manually reduced (fine chiselling and rubbing) to produce the spherical particles. The bulk densities of single particles were determined using a mercury submerged density measurement apparatus.

Chars were prepared (Section 2.3) at 1100 °C and combustion reactivity obtained at 1000 °C which are temperatures between fluidized and fixed bed (moving) operation. After devolatilization the resulting char particles were inspected for the absence of any abnormalities including extensive cracking.

2.2. Property measurements

The proximate analyses and calorific values were done by the South African Bureau of Standards, Pretoria, South Africa, according to the standards shown in Table 2. The petrographic analyses consisting of the determination of macerals, microlithotypes, carbominerites and minerites were carried out by Petrographics South Africa, Pretoria according to procedures described in detail by Everson et al. [16]. The mineral content of the samples were determined by the QEMSCAN laboratory at the Analytical Laboratories of Eskom [12,33], South Africa. Samples for this measurement were prepared by mixing the coal particles with molten carnauba wax in