An Effective Method for Fast Determination of Susceptibility of Coal to Spontaneous Combustion

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ABSTRACT

Mathematical modeling of the effect of pressure on low-temperature oxidation of coal indicates that, high partial pressure of oxygen significantly accelerates the physical and chemical interaction between coal and oxygen. Based on these findings, this paper develops a new test method for ranking the susceptibility of coal to spontaneous combustion, using a high-pressure technique to shorten the testing period. By combining an isothermal high-pressure fixed-bed flow reactor with appropriate diagnostic instrumentation, an experimental facility is designed to determine the rate of coal oxidation, the concentration of oxygenated products, as well as the rate of heat release during oxidation. It is expected that, when the facility is operated at a partial pressure of oxygen of $5MPa$, the time needed to carry out an experiment will be shortened by 75% in comparison to the data reported in the literature at atmospheric pressure.

Keywords: coal oxidation, spontaneous combustion, Thiele modulus, test method, industrial and process safety, self-heating, self-ignition

Nomenclature

a	half thickness of coal particle (m)
C_{O2}	oxygen concentration in the pores of coal particles $(kmole\ O_2\ m^{-3})$
$C_{O2,b}$	oxygen concentration in bulk gas phase $(kmole\ O_2\ m^{-3})$
$C_{O2,s}$	oxygen concentration at the surface of coal particles $(kmole\ O_2\ m^{-3})$
C_{pg}	heat capacity of gas mixture at constant pressure, per unit mass $(kJ\ kg^{-1}\ K^{-1})$
D_e	effective diffusion coefficient of oxygen $(m^2\ s^{-1})$
E	activity energy $(kJ\ mole^{-1})$
k	intrinsic rate coefficient on volume basis $(kmole\ O_2\ m^{-3}\ s^{-1}\ (kmole\ O_2\ m^{-3})^{-n})$

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k_g	gas phase mass transfer coefficient (m/s)
k_r	effective thermal conductivity in radial direction $(kJ\,m^{-1}\,s^{-1}\,K^{-1})$
k_x	effective thermal conductivity in axial direction $(kJ\,m^{-1}\,s^{-1}\,K^{-1})$
L	length of reactor (m)
n	reaction order
P	total pressure in the fixed-bed reactor (MPa)
P_{O2}	partial pressure of oxygen (MPa)
q	heat release rate $(kJ\,m^{-3}\,s^{-1})$
R_{O2}	oxygen consumption rate on the volume basis $(kmole\,O_2\,m^{-3}\,s^{-1})$, and on the particle-weight basis $(kmole\,O_2\,(kg\,coal)^{-1}\,s^{-1})$ (R_{O2}/ρ_a)
r_0	internal radius of the cylindrical reactor (m)
T	temperature (K)
T_∞	ambient temperature (K)
u	superficial gas flow velocity in the reactor $(m\,s^{-1})$
ε_b	bed porosity
η	effectiveness factor
η_G	global effectiveness factor
Θ	$T\text{-}T_\infty\,(K)$
ρ_a	apparent density of coal $(kg\,m^{-3})$
ρ_g	density of gas mixture $(kg\,m^{-3})$
Φ_n	Thiele modulus

Superscripts

in	indicates the inlet of reactor
out	indicates the outlet of reactor

INTRODUCTION

Spontaneous combustion of coal is a major problem in mining, transportation and coal-related industries in general[1-2]. Coal may self-heat and combust spontaneously when the amount of heat produced by low-temperature oxidation of coal is more than that dissipated through heat transfer to the surroundings. Because of safety and economic considerations, extensive studies have focused on the assessment of susceptibility of different types of coal to spontaneous combustion[2-8].

The rate of coal oxidation at low temperatures (that is below $363K$) is recognised as the key parameter for ranking the self-heating potential of coal. A number of experimental and test methods has been developed to measure rate of coal oxidation under specific conditions, for scientific research or industrial application. In the literature[2-7], these methods are classed as adiabatic (static or dynamic), isothermal (static or dynamic), oxygen adsorption (static or dynamic), and temperature differential (crossing-point measurement, basket). All these methods are very time-consuming and expensive to carry out because of slow process of coal oxidation at atmospheric pressure. Several days or weeks are usually needed to conduct a single test. Due to long testing period and small

variation of concentrations of reactants and products, the diagnostic instrumentation must display appropriate stability and sensitivity for accurate measurements.

This paper develops a fast and inexpensive test method to rank the susceptibility of coal to spontaneous combustion. Based on a theoretical analysis of the effect of pressure on low-temperature oxidation of coal in an isothermal fixed-bed reactor, a new test method is suggested, where the elevated partial pressure of oxygen serves to promote the reaction between coal and oxygen. An experimental facility has been developed and is illustrated in detail in the text.

THEORETICAL ANALYSIS

Although low-temperature oxidation of coal has been intensively studied both experimentally and theoretically[6-19], the effect of pressure on coal oxidation remains unknown. Using the published information, the present authors developed a mathematical model to examine the oxidation of coal at elevated pressures[20].

In the model development we assume that, coal particles are packed in an isothermal fixed-bed reactor, and a uniform oxidising gas mixture is passed through the bulk space among the particles[20,21]. Based on the previous findings[16,19,20], the reaction mechanism of low-temperature oxidation during steady state is suggested as

$$Coal + O_2 \rightarrow CO_2 .$$

(1)

The rate of oxidation is taken as

$$R_{O2} = kC_{O2}^n$$

(2)

where, k is the Arrhenius-type reaction constant, and n is the reaction order, which varies between 0.5 and 1, as reported in the literature[3,13,16].

The movement of oxygen from the surface of particles to the reaction sites in the pores of particles proceeds by molecular diffusion[22]. For a slab-like coal particle with thickness $2a$, the concentration gradient of oxygen at the surface of particles can be expressed as[20,21]

$$\left(\frac{dC_{O2}}{dx}\right)^2 \Big|_{x=a} = \frac{2}{n+1}\left(\frac{k}{D_e}\right) \cdot C_{O2,s}^{n+1} \cdot \left\{1 - \left[\frac{C_{O2}(0)}{C_{O2,s}}\right]^{n+1}\right\}$$

(3)

where, x is the distance from the centre plane of the particle, $C_{O2,s}$ represents the concentration of oxygen at the surface of coal particle and $C_{O2}(0)$ at the central of the particle. Since the concentration of oxygen at the centre of the particle is far less than the concentration at the surface[23], the last term on the right-hand side of Eq 3 is neglected in the calculations.

We now introduce the effectiveness factor defined in terms of the Thiele modulus Φ_n

$$\eta = \frac{D_e}{akC_{O2,s}^n} \cdot \left(\frac{dC_{O2}}{dx}\right)_{x=a} = \frac{1}{\Phi_n}\sqrt{1 - \left[\frac{C_{O2}(0)}{C_{O2,s}}\right]^{n+1}}$$ (4)

where, the Thiele modulus can be obtained from the following equation[23,24]

$$\Phi_n = a\sqrt{\frac{(n+1)kC_{O2,s}^{n-1}}{2D_e}} .$$ (5)

Considering the simultaneous concurrence of reaction and diffusion, the rate of oxidation can then be obtained from[18,19,23-25]

$$R_{O2} = \eta k C_{O2,s}^n .$$ (6)

The diffusive and convective contribution to mass transfer of oxygen from bulk phase to the surface of a coal particle is taken into account by the mass transfer coefficient k_g[20,21]. Under the steady state conditions, we may write

$$R_{O2} = k_g\left(\frac{1}{a}\right)\left(C_{O2,b} - C_{O2,s}\right) .$$ (7)

Introducing the global effectiveness factor η_G, the relation between the rate of oxygen consumption and the oxygen concentration in the bulk gas phase is given by[18,19]

$$R_{O2} = \eta_G k C_{O2,b}^n$$ (8)

where

$$\frac{1}{\eta_G} = \frac{1}{\eta}\left[1 + \left(\frac{2}{n+1}\right)\left(\frac{\eta\Phi_n^2}{k_g a / D_e}\right)\right]^n .$$ (9)

Neglecting the axial dispersion of gas flow, the gas concentration at the outlet of the tubular flow reactor is derived from the species conservation equation and leads to the following expressions[20]

$$C_{O2,b}^{out} = \left[(C_{O2,b}^{in})^{1-n} - \frac{L}{u}(1-n)\eta_G k(1-\varepsilon_b)\right]^{\frac{1}{1-n}}$$ (10)

$$C_{CO2,b}^{out} = C_{O2,b}^{in} - \left[(C_{O2,b}^{in})^{1-n} - \frac{L}{u}(1-n)\eta_G k(1-\varepsilon_b) \right]^{\frac{1}{1-n}} \tag{11}$$

where, u is the superficial gas flow velocity in the reactor, the superscript 'in' denotes the concentration at the reactor inlet and the superscript 'out' represents the concentration at the reactor outlet.

In conjunction with a correlation for mass transfer coefficient k_g, this model can be applied to determine the rate of oxidation and the concentrations of oxygenated products at high pressures. The calculation procedure for this model has been described in the previous work by the authors[20,21].

Typical calculation results are illustrated in Figures 1 to 4. The results in Figures 1 and 2 are computed at a pressure ratio P_{O2}/P of 0.21 and temperatures of 310, 330 and 350K. The results shown in Figures 3 and 4 are obtained at a constant temperature of 330K and pressure ratios P_{O2}/P of 0.21, 0.42 and 0.84. It is shown that, pressure has a significant influence on the rate of oxidation and on the concentration of CO_2 at the reactor outlet. With the increase of partial pressure of oxygen from 0.021 to 5MPa, the rate of oxidation and CO_2 concentration each increase by about 4 times. It is also found that, a relatively low total pressure results in a higher rate of oxidation, at the same partial pressure of oxygen.

EXPERIMENTAL FACILITY

As a result of the examination of the effect of pressure on coal oxidation, a high-pressure technique has been developed to provide a more effective procedure for the determination of coal susceptibility to self-heating. A schematic diagram of the experimental setup is shown in Figure 5. Compressed gases are introduced into the manifold through particulate filters using a pair of mass flow controllers. The gas mixture (oxygen/nitrogen) flows into the reactor at a very slow rate, of the order of several tens ml/min (NTP), and gradually builds up a pressure to the level pre-selected on the back-pressure valve. The reactor is placed into a custom-designed oven, which can provide a constant temperature control ranging from the ambient to 373K, with an accuracy of ±0.1K.

Figure 6 shows the schematic diagram of the reactor. The reactor is made of stainless steel tube (id 30mm, height 300mm). Crushed and sieved coal particles are packed in the reactor, where the volume and porosity of the sample can be adjusted by the movable metal mesh. Pressure drop across the bed is monitored with two pressure transducers located at either end of the reactor. Both axial and radial temperature profiles are measured with 'T-type' multi-points sheathed thermocouples inserted along the centre line of the coal bed. A data-acquisition system is applied to sample and process the temperature signal.

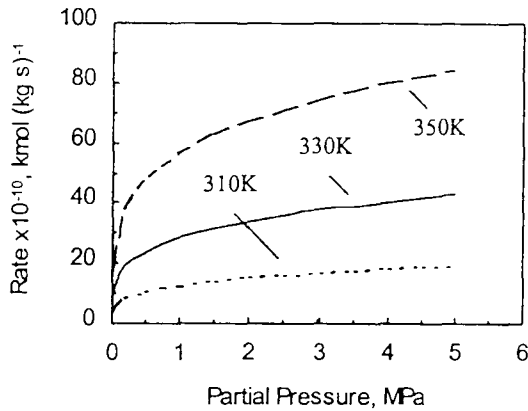The product gases exit the reactor through the annular space between the sheathed

Figure 1 The dependence of the rate of coal oxidation on partial pressure of oxygen at a constant ratio of P_{O_2}/P=0.21 and temperatures of 310, 330 and 350K.
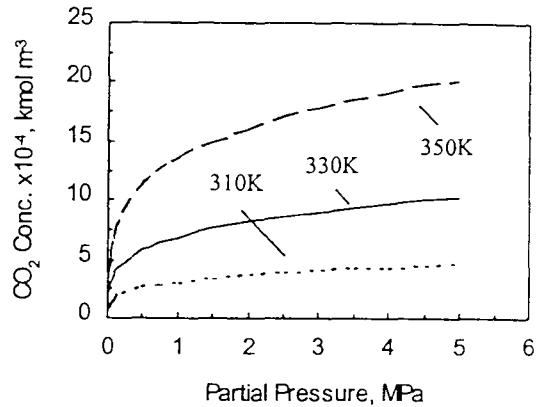
Figure 2 The variation of CO_2 concentration at the outlet of reactor with partial pressure of oxygen at a constant ratio of P_{O_2}/P=0.21 and temperatures of 310, 330 and 350K.
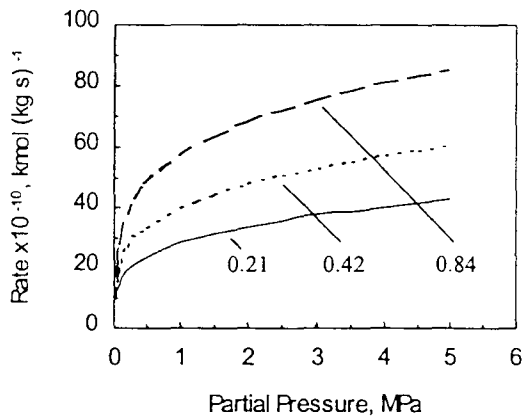
Figure 3 The dependence of the rate of coal oxidation on partial pressure of oxygen at a constant temperature 330K and the ratios P_{O_2}/P of 0.21, 0.42 and 0.84.
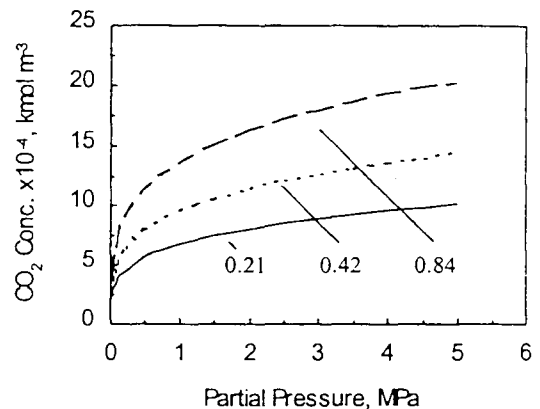
Figure 4 The variation of CO_2 concentration at the outlet of reactor with partial pressure of oxygen at a constant temperature 330K and the ratios P_{O_2}/P of 0.21, 0.42 and 0.84.

thermocouples and the reactor exit. Upon existing the back-pressure valve, the gas stream is at standard pressure, and is analysed by an on-line gas chromatograph.

The reactor will be operated in batch and continuous modes. In the batch mode, the gas mixtures will be preheated in the constant-temperature cabinet, and then flowed through

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Figure 5 Schematic diagram of the experimental setup.
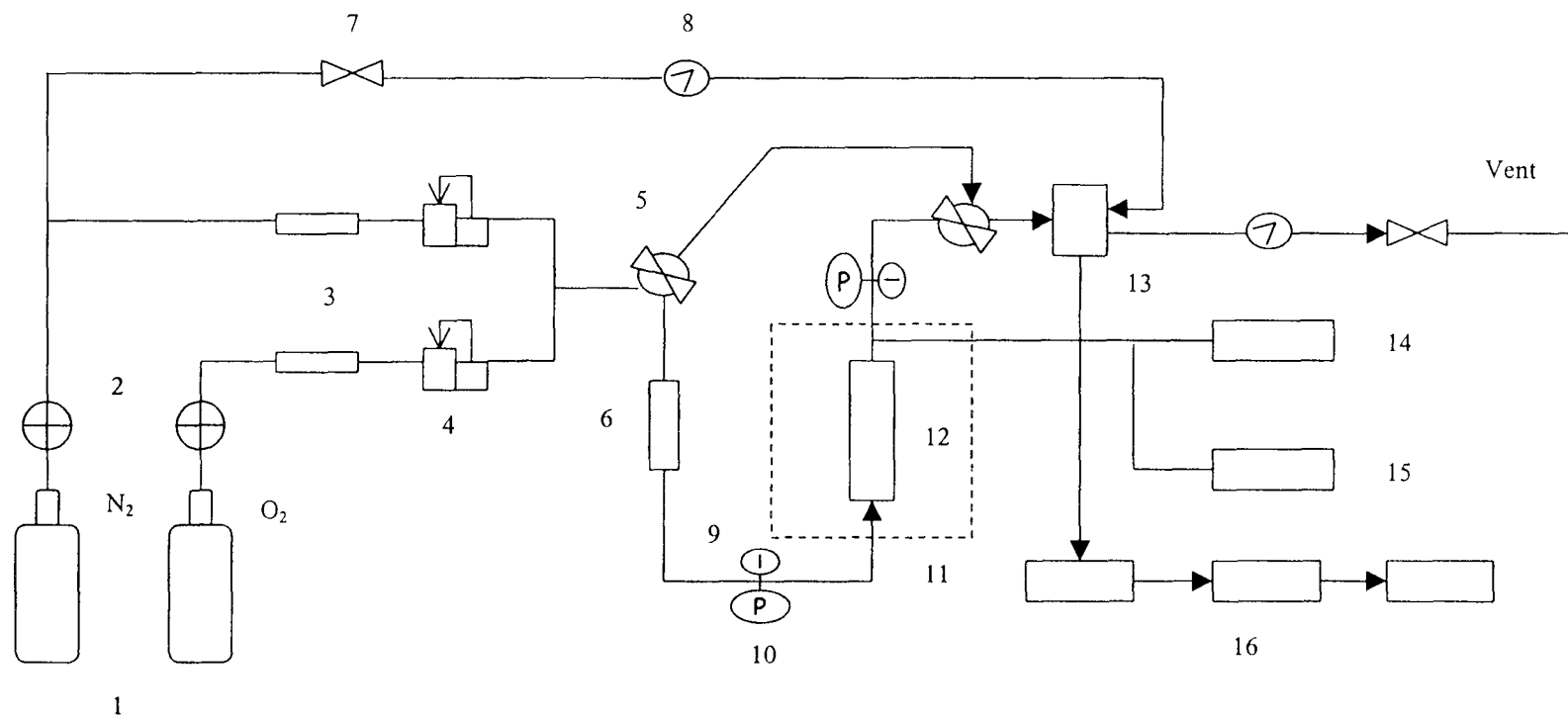
1 Compressed gases	5 Bypass valve	9 Relief valve	13 Back-pressure valve
2 Shut-off valve	6 Drying tube	10 Pressure transducer	14 Temp measurement
3 Filter	7 Needle valve	11 Cons temp enclosure	15 Calorimeter
4 Mass flow controller	8 Pressure gauge	13 Reactor	16 Gas analysers

the bed at a slow rate. When the predetermined pressure is reached, the flow will be interrupted for an "arrest" period of between 20 and 60min, depending on the reactivity of the sample. When the gas finally exits the reactor, the amount of oxygen taken up by the coal sample and the concentration of oxygenated products will be measured by gas analysers.
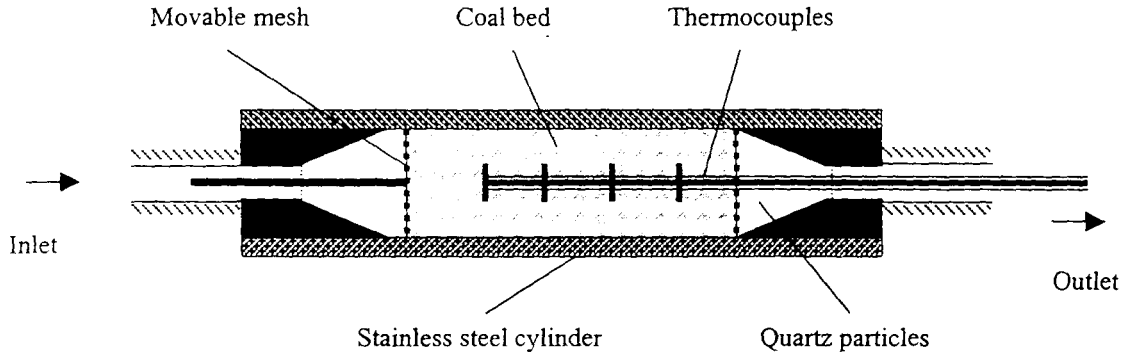

Figure 6 Schematic diagram of the reactor.

In the continuous mode, the gas mixtures pass through the reactor continuously at a flowrate of about 30±1ml/min (NTP). As in the batch mode, the thermocouples measure the variation of temperature at the different locations in the coal bed, and a gas chromatograph quantifies the concentrations of oxygen and oxygenated products at the outlet. The experimental data obtained from both batch and continuous operations will be compared for consistency.

The porosity of coal bed will be determined by weighing the coal sample (with known range of particle sizes) and adjusting the reactor volume with movable mesh. Knowing the mass flow rate at the inlet of the reactor m, the superficial gas velocity in bulk phase, u, can be obtained from the following expression

$$m = \rho_g \pi r_0^2 \cdot u .$$ (12)

The mass transfer coefficient k_g needed in Eq 9, will be computed from an empirical correlation linking k_g with the porosity of coal bed ε_b, and particle Reynolds and Schmidt numbers[20,21].

In general, not only CO_2 but also small amounts of CO and some other products are produced during the low-temperature oxidation. These products and the rate of formation can also be measured by the proposed gas analysis train. From these experimental data, and by assuming a reaction mechanism, the rate of oxidation and the kinetic parameters, k, E and n, will be determined. In continuous mode, the rate of oxygen consumption can be directly obtained from the measurements of oxygen concentration at the reactor outlet.

Usually, at the start of an experiment the rate of oxygen consumption is a little higher than the rate of oxidation due to the adsorption process. However at steady state, the rate of oxygen consumption will correspond to the rate of oxidation.
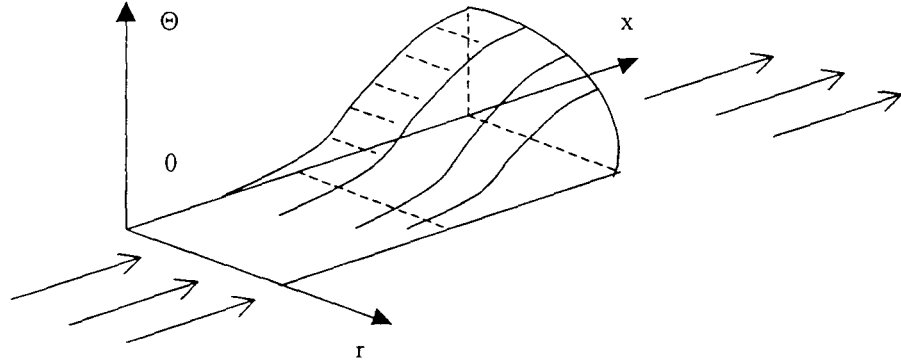

Figure 7 Expected temperature profile in the coal bed.

Figure 7 gives an expected temperature profile of the coal bed in the reactor during steady-state oxidation. We expect a temperature profile to exist in the reactor, in spite of its isothermal operation, due to heat release during coal oxidation and heat transfer limitations within the coal bed. To be able to calculate the heat release rate of coal particles, we will need to measure the temperature profile in the region adjacent to centre axial (the shadow region in the figure), with a high accuracy ($\pm 0.01K$). Assuming the uniform gas velocity in the bulk space, and uniform heat release rate of coal particles, we have the following energy conservation equation

$$\rho_g u C_{pg} \frac{d\Theta}{dx} = k_r \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial \Theta}{\partial r} \right) \right] + k_x \frac{\partial^2 \Theta}{\partial x^2} + q \tag{13}$$

where Θ represents $T-T_\infty$ and q denotes the heat release rate by oxidation of coal per unit volume; T_∞ is the ambient temperature.

The boundary conditions are given by

$$\frac{\partial \Theta}{\partial r} = 0 , \qquad\qquad r=0 \tag{14}$$

$$\Theta = 0 , \qquad\qquad r=r_0 \tag{15}$$

$$\Theta = 0 , \qquad\qquad x=0 \tag{16}$$

$$\frac{\partial \Theta}{\partial x} = 0 , \qquad\qquad x=0 . \tag{17}$$

Using a numerical method for the solution of Eq 13 with the boundary conditions 14-17 we should be able to correlate the temperature profiles with the heat release rate, q. By measuring accurately the axial temperature profile, and comparing it with the modeled data, the heat release rate will be obtained. Note that, the heat release rate can be also estimated from the oxygen consumption, and we will use this approach to confirm the value of q computed from the solution of the energy conservation equation.

In order to obtain the results of heat release rate in real time during the experiment, a software program will be developed to combine the numerical solution of the energy equation with the temperature profiles collected by thermocouples. This approach will allow us to collect the heat release data, similar to those obtained from the calorimetric techniques.

CONCLUSIONS

This paper applies a mathematical model to examine the pressure effect on low temperature oxidation of coal in an isothermal fixed-bed reactor. The calculation results show that, high partial pressure of oxygen can speed up the overall physical and chemical interaction between coal and oxygen. When the partial pressure of oxygen is increased from 0.021 to 5MPa, the rate of oxidation and the concentration of oxygenated products increase by 4 times in comparison to those obtained at atmospheric pressure.

Based on these predictions, a high-pressure method is developed for the determination of coal susceptibly to spontaneous combustion. An experimental setup, which includes an isothermal fixed bed reactor, high-pressure built-up system, data acquisition system and gas chromatograph, has been designed to determine the rate of oxidation, the concentration of oxygenated products, and the heat release rate during oxidation.

The proposed method offers a good potential to be developed into a standardised technique for the evaluation of the susceptibility to spontaneous combustion of different types of coal. However, before this method is applied to industrial applications, a database containing the rate of oxidation of typical coals at elevated pressures and a standardised procedure for the assessment of self-heating potential will need to be established.

ACKNOWLEDGEMENTS

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