Chapter 3. Pressurized TGA Study on the Reactivity of Canadian Lignite Coal Char under Different High Pressure Oxy-fired (HiPrOx) Environments

Paul Emanuel Cairns[a], Bruce R. Clements[a], Arturo Macchi[b], Edward J. Anthony[c]

[a]Natural Resources Canada, CanmetENERGY, 1 Haanel Dr., Ottawa, Ontario, Canada, K1M 1M1

[b]Faculty of Chemical and Biological Engineering, University of Ottawa, 161 Louis Paster St., Ottawa, Ontario, Canada, K1N 6N5

[c]School of Applied Sciences, Cranfield University, College Rd., Cranfield, Bedford MK43 0AL, United Kingdom

3.1. Abstract

High Pressure Oxy-firing of solid fuels has been proposed for direct contact steam generation (DCSG) for use in industrial applications such as *in-situ* heavy oil extraction processes like steam assisted gravity drainage (SAGD). These firing scenarios present unique operating conditions and chemical species concentrations that affect the combustion characteristics of solid fuel chars. TGA experiments were performed to study the effects of steam on a Canadian lignite coal char's reactivity in different oxy-fuel ($O_2/CO_2/H_2O$) environment as a proof-of-concept of DCSG at the bench scale. It was found that under reaction-kinetic controlled conditions at atmospheric pressure, the increased addition of steam led to a reduction in burnout time and temperature. The findings appear to have resulted from the lower heat capacity and higher thermal conductivity of steam compared to CO_2. At increased pressures CO_2 inhibited burnout due to its higher heat capacity, lower thermal conductivity, and its effect on C(O) concentrations on the particle surface. When steam was added, the inhibiting effects of CO_2 were counteracted, resulting in burning rates similar to pressurized O_2/N_2 environments. Future work using the realistic, reactive and hydrodynamic environment of an entrained flow reactor is recommended.

Keywords: Pressurized combustion, Char reactivity, Steam, Oxy-fuel, SAGD, CCS

3.2. Introduction

Recent estimates have shown that Canada has the third largest oil reserves in the world with 95% associated with the Alberta oil sands [1]. In Alberta, 80% (135 billion barrels) of the oil sands can only be accessed through *in-situ* methods such as Steam Assisted Gravity Drainage (SAGD) [2]. In 2011, total oil sands raw bitumen production was 1.74 million barrels per day (b/d) with *in-situ* techniques making up about 49% of this production. By 2025, *in-situ* production is forecast to make up 57% of a total 4.5 million b/d [3]. Although *in-situ* extraction methods such as SAGD are less invasive than mining, they will result in more greenhouse gas (GHG) emissions per barrel [4] and require large amounts of water that need to be treated and recycled with around a 10% make-up water requirement [2].

CanmetENERGY has patented [5] a pressurized oxy-fuel combustion process using direct contact steam generation (DCSG) to produce high quality steam. It is proposed that the DCSG system be applied for use in steam reforming, and of most interest for this paper, steam assisted gravity drainage (SAGD) for *in situ* bitumen extraction from the oil sands [5,6].

CanmetENERGY's DCSG system produces steam by combusting a low grade slurried fuel such as lignite coal or petroleum coke, with upwards of 95% pure oxygen at high pressure. In this case, water is used as the quench mechanism instead of the flue gas recirculation (FGR) scheme used in typical oxy-fuel applications. After the combustor, the products pass into a second vessel called the steam generator, in which additional water is injected and converted to steam via direct contact with the flue gas. The use of DCSG may make it possible to use waste water for the production of steam to reduce tailings pond pollution and simultaneously capture and store CO_2.

Another application of interest for pressurized oxy-fuel combustion is power generation. Pressurized oxy-fuel combustion systems offer better energy performance over conventional atmospheric oxy-fuel combustion power cycles [7]. Clements *et al.* [8,9],

performed process simulations of a high pressure oxy-fired (HiPrOx) system, known as the ThermoEnergy Integrated Power System (TIPS). They found that pressurized combustion at 8000 kPa lead to a 5% absolute increase in net efficiency over ambient CO_2 capture-ready oxy-fired systems (24% and 29% net efficiencies for ambient and HiPrOx systems, respectively) [8,9]. Ente Nazionale per l'Energia Electrica (ENEL) has suggested that combustion at high pressures may increase both the burning rate of coal and heat transfer rates in the convective sections of the heat transfer equipment. A series of tests on a 5 MW_{th} scale combustor, working at 400 kPa, has been undertaken to demonstrate these benefits [10-12]. Hong *et al.* performed a numerical analysis of a pressurized oxy-fuel combustion power cycle which included a flue gas purification and compression process. Compared to a base case of 110 kPa, they found that the use of pressurized combustion at 1000 kPa led to a 3% increase in net efficiency [7].

Under pressurized firing conditions, the physical properties of the bulk combustor gas are different from those for conventional air-fired and ambient oxy-fired technologies. One difference arises from the effect of total pressure, and another, from the use of a slurry-fed system as opposed to a dry fed system. The latter will result in increased steam concentrations in the combustion gas (up to 80% water for the DCSG firing mode) and varying CO_2 concentrations. These differences will affect combustion gas properties such as: heat capacity, thermal conductivity, radiation characteristics, and density. Design of DCSG systems requires a better understanding of fuel reactivity under these conditions. This study will investigate the reactivity of a Canadian lignite coal char subjected to various pressurized oxy-fired scenarios to provide insight into the effects of elevated steam concentrations and total pressures on combustion.

3.3. Factors that affect char reactivity in various atmospheres

Rathnam *et al.* [13] reported a number of factors which affect char reactivity in O_2/CO_2 atmospheres when compared to the reactivity in O_2/N_2 atmospheres. These factors are detailed below and include char particle temperature, oxygen diffusivity through the boundary layer gas, pressure, and char structure. The current paper will examine

previous studies in terms of these factors and look at the implications of employing high steam concentrations and elevated pressures.

3.3.1. Char particle temperature

The char particle temperature is an important factor, especially when burning in Regime I or Regime II conditions (chemically controlled and pore diffusion controlled, respectively). The higher molar specific heat of CO_2 compared to N_2 causes lower boundary layer gas temperatures and therefore reduced fuel particle temperatures [13]. Bejarano and Levendis [14] measured the volatile flame and char particle temperatures during single particle combustion of bituminous coal and lignite coal for various O_2 levels in N_2 and CO_2. For the bituminous coal, the flame temperatures were about 150 °C lower in systems where the combustion gases consisted of only O_2/CO_2 for various O_2 levels. They found that a higher O_2 level (30% O_2 in CO_2) for the oxy-fired combustion case was required to match the char particle temperatures in the air case, and the O_2 level required to match the char burnout time in air was 35% O_2 in CO_2. In summary, under these regimes, the higher molar heat capacity of CO_2 lowers the boundary layer gas temperature and subsequently, the char particle temperature, resulting in lower reactivity.

In $O_2/CO_2/H_2O$ fired conditions, the lower molar heat capacity of H_2O compared to CO_2 (**Figure 3.1**), leads to comparatively higher boundary layer gas temperatures. This will increase the char particle temperature resulting in increased particle temperatures. These effects are demonstrated by a recent TGA study performed by Gil *et al*. [15] in which steam (10% and 20%) was added to mixtures of O_2 (21% and 30%) and CO_2 (balance). The addition of steam led to an increase in reactivity and a decrease in burnout temperature as compared to the dry gas. The authors concluded that the lower molar heat capacity of steam led to these findings.
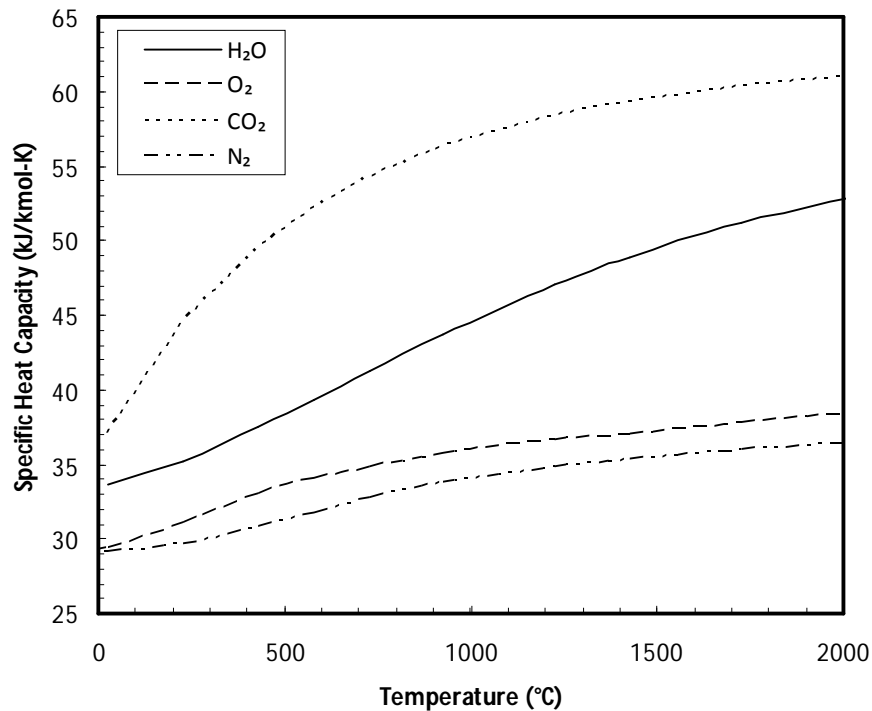
Figure 3.1 – Molar specific heat capacity for H_2O, CO_2, and N_2 at constant pressure of 100 kPa [16]

Another factor affecting particle temperature which was not discussed by Rathnam *et al.* [13] or Gil *et al.* [15] is the boundary layer gas thermal conductivity [17]. Shaddix and Molina [17] calculated the particle temperature of a spherical 100 µm coal particle in selected gas environments at 1227 °C and found that oxy-fuel environments containing steam produce higher particle temperatures than O_2/CO_2 environments (**Figure 3.2**) due to the higher thermal conductivity of H_2O than CO_2 (**Figure 3.3**). They stated that the higher heat capacities of CO_2 and H_2O will cause them to absorb heat released from the oxidation of CO in the boundary layer, reducing peak boundary layer gas temperature and therefore the heat transfer back to the particle which will reduce the burning rate. However, the higher thermal conductivity of H_2O will tend to increase heat transfer back to the particle, making the net effect of H_2O on this phenomenon unclear [17].

Therefore, the increased burnout observed by Gil *et al.* [15] may also be a result of the higher H_2O thermal conductivity. In summary, under Regime I and Regime II conditions, the higher thermal conductivity and lower molar heat capacity of H_2O

compared to CO_2 should lead to higher particle temperatures and an observed increase in burning rate. This study will perform atmospheric and pressurized TGA testing to confirm and expand upon the findings found by Gil *et al.* [15].
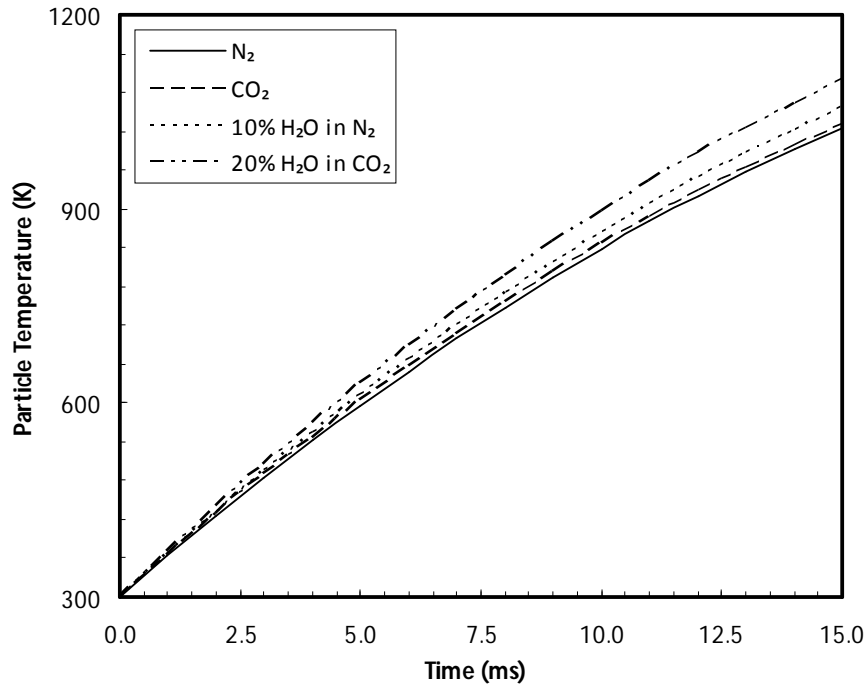
Figure 3.2 – Calculated particle temperature of a spherical 100 um coal particle in selected gas environments at 1227 °C, with radiative boundary at 1000 °C and a Nusselt number of 2.0. Gas thermal conductivities are those indicated in **Figure 3.3**, with gas mixture conductivity estimated according to simple molar mixing ratios, adapted from [17]
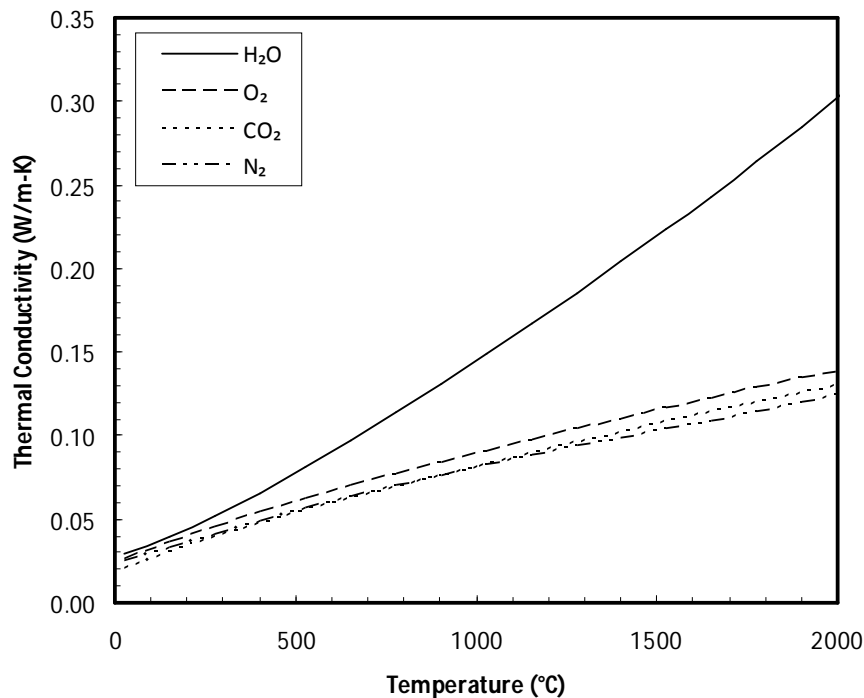
Figure 3.3 – Thermal conductivity of selected gases as a function of temperature, adapted from [17]

3.3.2. Diffusivity of O_2 through boundary layer gas

Practical combustor conditions, generally lead to char combustion being controlled by diffusion of O_2 through the gas boundary layer at very high temperatures (mass transfer limited Regime III conditions) or limited by a combination of reaction kinetics and diffusion through the porous char at moderately high temperatures (pore diffusion limited Regime II conditions) [13]. The diffusivity of O_2 is greater in H_2O than it is in N_2 and is the lowest in CO_2 (**Figure 3.4**). Rathnam *et al.* [13] reported on the findings of a study [18] that investigated the influence of CO_2 on coal char combustion kinetics in oxy-fuel conditions. The study (6 to 36 % O_2 in N_2 or CO_2) revealed that the lower observed overall burning rate in O_2/CO_2 conditions was attributed to the lower diffusivity of O_2 in CO_2 than the diffusivity of O_2 in N_2 [13].

The effect of O_2 diffusion to the char surface in CO_2 and H_2O gases was discussed by Shaddix and Molina [17]. They stated that, in all but reaction-kinetic controlled burning

conditions (Regime I), elevated H_2O concentrations may promote combustion by augmenting oxygen diffusion because the diffusivity of oxygen is 20% higher in H_2O than in N_2 at temperatures in which combustion is mass transfer limited. In summary, the higher diffusivity of O_2 in H_2O than O_2 in CO_2 should lead to increased reactivity of the char in Regime III conditions.
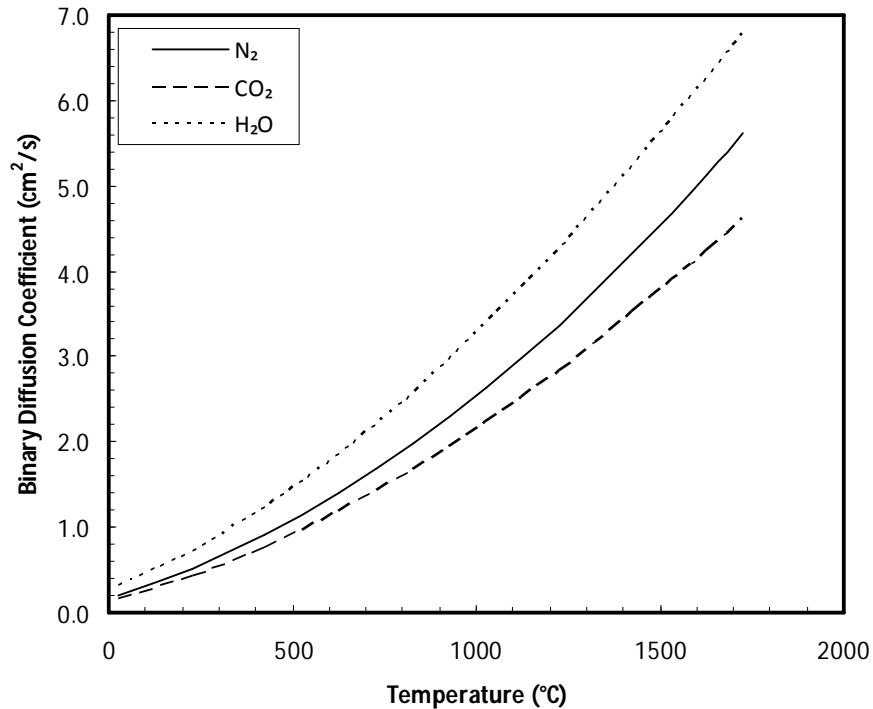

Figure 3.4 – Binary diffusion coefficient of O_2 in N_2, CO_2, and H_2O as a function of temperature, adapted from [17]

3.3.3. Pressure

The combustor pressure is another factor that affects char reactivity and more importantly the char structure [13]. Saastamoinen *et al.* [19] performed experiments in a pressurized entrained flow reactor where they varied the O_2 and CO_2 partial pressures between 25-100 kPa and 50-200 kPa, respectively. The balance gas was N_2 and the total pressure was varied between 200 kPa and 800 kPa with temperatures between 800 °C and 1200 °C. They found that at a fixed volume fraction of 10 % O_2 the reactivity increased with increase in total pressure from 200 to 500 kPa and then leveled off with further increases

in total pressure. Monson *et al.* [20] performed oxidation experiments at atmospheric and elevated pressures (100-1500 kPa) in a drop tube reactor with 5-21% oxygen and N_2 balance gas. They found that increasing total pressure from 100 to 500 kPa in an environment of constant gas composition led to a modest increase in reaction rate, whereas the reaction rate decreased with further increases in pressure. Lester *et al.* [21] performed experiments in a shock tube reactor over a particle temperature range of 1427-1927 °C, with a total pressure range of 550-1000 kPa and oxygen mole fraction of 0.1-0.5. They found that as total pressure increased from 550 to 1000 kPa, the oxidation rates for chars in air decreases. They explained the reduced rate in terms of the decreasing pore area available for reaction with oxygen with increasing total pressure. This effect may also explain the results found by Saastamoinen *et al.* [19] and Monson *et al.* [20].

The previously mentioned study by Saastamoinen et al. [19] also revealed that at high pressures and temperatures, when the combustion rate becomes increasingly controlled by diffusion of O_2 to the surface, high CO_2 concentrations may increase the char-CO_2 gasification rate resulting in a higher total combustion rate. Messenbock *et al.* [22] studied the effect of pressure on the extent of steam and CO_2 gasification in a wire mesh reactor in a pressure range of 100 to 3000 kPa. Their studies were performed in pure CO_2 environments and mixtures of 80 % steam and 20 % helium. At reaction times applicable to this study (10 seconds or less), the extent of steam gasification was about 2 to 3 times higher than those for CO_2. They also found that the reactivity of the chars decreased with increasing pressure. Deactivation of the char caused by secondary char deposition was said to have led to an un-reactive layer of re-polymerised tar. Roberts and Harris [23] measured the apparent and intrinsic reaction rate of Australian bituminous coal chars with O_2, CO_2, or H_2O in an N_2 balance at pressures up to 3000 kPa using a pressurized TGA (PTGA). It was found that the reaction order in CO_2 and H_2O was not constant over the pressure range investigated, varying from 0.5 to 0.8 at atmospheric pressure and decreasing at pressures above approximately 1000 kPa. The intrinsic reaction of oxygen was less affected by pressure over the range 100 to 1600 kPa while the apparent reaction increased with increasing pressure [23]. Changes in physical structure (shown by

apparent reaction), not chemical rates (shown by intrinsic reaction) were explained to be the cause of the observed trends.

In summary, previous studies have shown that with increasing pressure the O_2 reaction increases up to around 5 bar where it begins to level off or decreases [19-21,23]. This was attributed to physical changes in the char structure with increasing pressure [21,23]. In H_2O and CO_2 gasification studies, it was found that increasing pressure led to a decrease in reaction rate [22,23]. This was attributed to char deactivation caused by secondary char deposition of volatiles [22]. Since all of these studies were conducted with pure gases only, it is still unclear what the net effect on char reactivity will be in a mixture of these gases.

3.3.4. Char structure

Another factor that affects the coal reactivity results from the char structure formed throughout the combustion process. Rathnam *et al.* [13] performed devolatilization experiments in N_2 and CO_2 in a drop tube furnace and characterized the char formed using SEM and BET analyses. Increased swelling of the char particles and an increase in BET surface area were observed for the CO_2 chars, when compared to the N_2 chars. The char-CO_2 gasification reaction during devolatilization was suggested to be the cause of the observed results.

Using SEM Messenbock *et al.* [22] examined the effects of CO_2 and H_2O on char structure after devolatilization in a pressurized wire mesh reactor. At atmospheric pressure, the authors observed that chars from steam gasification did not agglomerate, indicating that they did not soften or melt to the same degree as their N_2 and CO_2 devolatilized counterparts, but a structure with large pore size had evolved. An increased reactivity of the char gasified in steam compared to N_2 and CO_2 was observed. It was concluded that the more reactive steam gasification reaction compared to CO_2 and N_2 led to the better observed char structure. In summary, it is expected that the char structure formed in the presence of steam should lead to a higher reactivity because it will increase pore size and cause swelling.