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Albio Gutierrez

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Design of Oxy-Coal Reactors for Calcium Carbide Production Using CFD

Albio Gutierrez

**Dissertation submitted
to the Benjamin M. Statler College of Engineering and Mineral Resources
at West Virginia University**

in partial fulfillment of the requirements for the degree of

**Doctor of Philosophy in
Mechanical Engineering**

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Department of Mechanical and Aerospace Engineering

**Morgantown, West Virginia
2015**

**Keywords: Oxy-Coal Combustion, Calcium Carbide Production, Slag Flow Modeling,
Computational Fluid Dynamics.
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ABSTRACT

Design of Oxy-Coal Reactors for Calcium Carbide Production Using CFD

Albio Gutierrez

Oxy-coal combustion with recirculating flue gas is a promising technology in CO₂ capture. This technology is intended to reduce emissions of CO₂ and other pollutants, such as NO_x and SO₂. Since the CO₂ concentration in flue gas is higher than in conventional air operation, CO₂ capture is easier. Other unique applications of oxy-coal combustion are now possible due to the very high temperatures (circa 2000-2500°C) that can be generated with char/ O₂ /CO₂ mixtures which in turn can be used to activate chemical reactions which can lead to high valued chemical products. This for example can be an economical alternative to the energy intensive electric arc furnace process for calcium carbide (CaC₂) production. At present, research towards developing an oxy-coal combustion process for production of CaC₂ from char and calcium oxide (CaO) is being conducted by the U.S.-China Clean Energy Research Center (CERC). In this process, CaC₂ is produced in the molten slag layer flowing along the walls of an oxy-coal combustion reactor. A model capable of predicting the performance of oxy-coal reactors for CaC₂ production will be a useful tool to support this effort. Nonetheless, previous work in the field of slag modeling in coal-fired systems has been focused on analyzing its effect on the wall heat transfer and the combustion process. This alone is not sufficient to support the design of a carbide producing reactor.

In the present work, a physics-based computational model has been developed to predict the performance of oxy-coal combustion reactors for CaC₂ production. The approach is based on a computational framework that utilizes the computational fluid dynamics (CFD) method to model both the oxy-coal combustion process and the slag flow. The slag flow model (SFM) describes the slag behavior including the chemical reactions occurring during the synthesis of CaC₂, as well as the liquid and solid layer thickness, average velocity and bulk temperature of the slag layer.

The model developed was applied to the design of two different types of reactors, namely, a vertical down-fired reactor, known as very high temperature entrained flow reactor (VHTER) and a horizontal reactor referred to as CTC reactor. It was found that the minimum temperatures required to activate the CaC₂ formation in the VHTER were obtained for oxy-coal combustion cases with 35% molar oxygen concentrations; CO₂ the balance gas. The results for the slag flow model showed that although the VHTER reactor is able to attain the high temperatures required for the production of CaC₂, the viscosities obtained can be so small that the residence time of the slag is insufficient to attain a considerable formation of CaC₂ in the slag.

The simulation results for the CTC reactor indicated that the operation conditions evaluated in current tests were not suitable for CaC₂ production. Nonetheless, it was possible to obtain suitable temperatures for production of CaC₂ in the CTC reactor by modifying the operation conditions. The modifications included increasing the amount of natural gas, as well as replacing a portion of the air entering the reactor with pure O₂.

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Dedicated to

Elena

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NOMENCLATURE

A	pre-exponential factor in Arrhenius rate expression
a_{ls}	relaxation parameter in the solidification sub-model for CaO and CaC ₂ transported in the slag
C_p	specific heat under constant pressure
D	mass diffusion coefficient
E	energy
E_a	Activation energy in Arrhenius rate expression
g	gravity
g_x	gravity component along the slag flow direction
G_x	axial flux of linear momentum at the burner region of the reactor
G_ϕ	axial flux of angular momentum at the burner region of the reactor
h_{mCO}	mass transfer coefficient for carbon monoxide release from the slag
h_{env}	convection heat transfer coefficient from the reactor to the environment
H_f	heat of fusion of the slag

H_R	source term in the energy equation due to the chemical reactions of CaC_2 formation
H_l	source term in the energy equation due to the solidification of CaO and CaC_2 transported in the slag
k_r	reaction rate in the existing models for calcium carbide
k_l	thermal conductivity of the liquid slag
k_s	thermal conductivity of the solid slag
k_f	forward kinetic rate for the CaC_2 reaction
k_B	backward kinetic rate for the CaC_2 reaction
k_{f-l}	liquid-liquid forward kinetic rate for the CaC_2 reaction
k_{f-s}	solid-solid forward kinetic rate for the CaC_2 reaction
k_{B-l}	liquid-liquid backward kinetic rate for the CaC_2 reaction
k_{B-s}	solid-solid backward kinetic rate for the CaC_2 reaction
L	combustion chamber wall length
m	mass
m_p	mass flow rate of particles

n_i	number of moles of specie i
P	pressure inside the combustion chamber
R	universal gas constant
R_t	total thermal resistance including: conduction through the solid slag and insulation and convection heat transfer to the environment
S	swirl number
T_B	bulk temperature
T_{cv}	temperature of critical viscosity
T_{env}	room temperature
T_{eut}	eutectic temperature in the solid-liquid CaO-CaC ₂ equilibrium phase diagram
T_g	temperature at the interface between the combustion gases and the liquid slag
T_p	particle temperature
t	time
t_{ss}	time scale at which the slag model reaches steady state
U	velocity scale for the slag flow model
u^+	dimensionless slag velocity

u_τ	shear velocity for the slag flow problem
x	coordinate along the slag flow direction
X_i	progress variable of specie i
x_s	mass fraction of solidified material transported by the slag
x_{se}	mass fraction of solidified material transported by the slag at equilibrium conditions
x_{CaC_2}	mass fraction of CaC_2 in the solid-liquid equilibrium phase diagram for $CaO-CaC_2$
y	coordinate normal to the slag flow direction
$[y_{CO}]_l$	mass fraction of CO in the liquid slag
$[y_{CO}]_\infty$	mass fraction of CO in the combustion gas at the slag surface
y_k	mass fraction of the specie k

Greek letters

α	dimensionless coefficient in the slag velocity profile
α_p	thermal diffusivity of paraffin in the verification problem

α_r	extent of reaction in the previous models for calcium carbide
β_p	compressibility factor of paraffin in the verification problem
λ_{ls}	progress variable in the solidification sub-model for CaO and CaC ₂ transported in the slag
Δt	time step in the solution of the slag flow problem
Δx	dimension of a slag cell in the slag flow direction
ΔP	pressure change along the combustion chamber
δ_l	thickness of liquid slag
δ_{ls}	thickness of the liquid-solid interface of the slag
δ_s	thickness of the solidified slag
ε_f	ratio of the solid amount to the total amount of CaO in the slag
ε_B	ratio of the solid amount to the total amount of CaC ₂ in the slag
η	slag dimensionless coordinate in the normal direction to the slag flow
μ	dynamic viscosity
$\mu\phi$	viscous dissipation term in the slag flow
ν	kinematic viscosity

τ_{gl} shear stress at the interface of the molten slag and the combustion gas

τ_w wall shear stress

ω source term in the species transport equation

ρ density

Subscripts

$()_{Ash}$ ash

$()_{ave}$ average

$()_k$ specie k

$()_j$ particle j

$()_C$ carbon

$()_{CaO}$ calcium oxide

$[]_{cv}$ control volume

$(\)_e$ east face

$(\)_g$ generation term (source)

$(\)_l$ liquid slag

$(\)_n$ north face

$(\)_s$ south face

$(\)_w$ west face

$(\)_p$ cell center

Superscripts

$(\dot{\ })$ time rate

$[\]^o$ previous time step

Chapter 1 – Introduction

1.1. Motivation

Oxy-coal combustion with recirculating flue gas is a promising technology in the CO₂ capture and storage process. This technology is being implemented in existing air based equipment for power generation in order to reduce anthropogenic emissions of CO₂ and other pollutants such as NO_x and SO₂ into the atmosphere. Oxy-coal combustion has been recently proposed for the activation of chemical reactions due to the very high temperatures that can be obtained. (i.e., temperature gases at circa 2000-2500 °C) from char/O₂/CO₂ mixtures. This application entails an economical alternative to the traditional electric arc furnace process for production of CaC₂¹.

Calcium carbide (CaC₂) is a highly valued chemical utilized mainly for acetylene generation. In the traditional electric arc furnace process CaC₂ is obtained from the chemical reaction of coke and calcium oxide (CaO) within temperatures ranging from 1800 to 2000 °C.

The traditional process is highly energy intensive and consumes a disproportionate amount of coal in order to supply the required electrical power for the heating process. Additionally, the traditional process may also generate a significant harmful effect in the environment. This fact represents a significant limitation to his industrial expansion, consequently, affecting the availability of carbide and acetylene.

¹ See section 2.4 for a discussion on the traditional process for production of CaC₂.

These facts have motivated the pursuit of technologies intended to produce CaC_2 in a more efficient and environmentally friendly manner. An additional consideration in this pursuit is the motivation to rely on available coal reserves, especially in locations where oil resources are scarce and coal reserves plentiful.

During the 1950's, two European companies explored alternatives for an oxy-thermal process and published different number of patents. Stamicarbon [1,2,3,4,5] in Holland, and BASF in Germany [6,7,8]. Again in the 1980's, Hoechst filed additional new patents [9,10,11]. Despite all the efforts and attempts to develop an oxy-thermal process, none of these processes were ever successfully commercialized.

In 2009, Bayer Technology Services and LP Amina collaborated to develop a new and improved oxy-thermal process, and collectively filed two patents [12,13]

The uniqueness of the Bayer-LP Amina process lies in its direct coupling of an oxy-thermal carbide making process with conventional power generation. The new invention utilizes an oxy-fired cyclone burner and is highly energy efficient due to the direct coupling. This results in a step change energy efficiency gain that holds the promise of a new low-cost, low-emission supply of carbide and acetylene. A further advantage of the Bayer-LP Amina process is modularization and ease of retrofits. An individual cyclone burner can be replaced on a coal-fired power plant in way that “numbers-up” capacity without the need for all new large-scale capital investments. It is expected that this breakthrough will create new markets and open up a new industrial segment for this process and other related coal-to-liquids processes.

Research efforts intended to develop the oxy-coal combustion process for the production of CaC_2 from char and calcium oxide² (CaO) are being conducted by the U.S.-China Clean Energy Research Center (CERC). In this process, the CaC_2 will be produced in the molten slag layer flowing along the walls of an oxy-coal combustion reactor; consequently, this is a slagging reactor. In this type of reactor, the temperature is so high that coal ash will be melted down and the molten slag layer will then capture the reactants more easily. For this application, the reactants consist of char/coal and CaO particles. A model capable of predicting the performance of oxy-coal reactors for CaC_2 production will be an advantageous tool to develop this technology.

Previous work conducted in the field has been aimed at predicting the behavior of slagging in coal fired systems, mainly with the intention of analyzing its effect on the wall heat transfer and on the combustion process. Previous contributions include the work of Seggiani [14], who developed a simplified slag model coupled with a computational fluid dynamics (CFD) gasifier model. This model studied the slag accumulation and flow on the walls. The CFD model provided the inputs for the simplified slag model. In the work of Seggiani [14], the effects of changes in the gasifier operating conditions over the slag behavior were analyzed. For instance, similar effects on the slag thickness were obtained either by increasing the oxygen or by increasing the limestone amount. The transient response in the slag and gas, due to the change in operation conditions, was also assessed. The model provided solid and liquid slag thicknesses, temperature across the slag, and heat flux to the wall.

² Commonly known as quicklime or burnt lime.

Wang et al. [15] used the same approach that Seggiani used [14], i.e., the combination of the CFD combustion model with a slag model. Wang et al. [15] took into account that particles trapped in the slag can contain combustible matter that will continue burning. For this reason, the authors introduced a wall burning model. Most recently, Yong et al. [16] presented a slag model based on the work of Seggiani [14] and Wang et al. [15]. Coupled calculations between the slag model and the CFD reactor model were performed too by Yong et al. [16].

1.2. General Objective

Partially due to the more narrow focus of the production of CaC_2 in the molten slag of oxy-coal reactors, and despite of all efforts, none of the models discussed above are suitable to describe it. Therefore, the development of such a model is the purpose of this work. The proposed model will work as a tool intended to aid the design process of oxy-coal reactors for CaC_2 production.

1.3. Specific Objectives

The model developed in the present work will:

- To set the reactor operating conditions required for production of CaC_2 .
- To predict the slag behavior; including the chemical reactions within the slag, the liquid and solid thickness, average velocity and bulk temperature.
- To predict the rate of production of CaC_2 .

1.4. Methodology

The methodology consists of a CFD model for oxy-combustion combined with a slag flow model. The CFD model for oxy-combustion uses the Reynolds-Averaged Navier-Stokes (RANS)

approach for fluid flow, heat transfer, and turbulent-chemistry interactions. The multiphase character of the flow in the combustion chamber is considered using the Eulerian– Lagrangian treatment for the continuous gas phase and the particle discrete phase, respectively. The interaction between continuous and discrete phases is taken into account by using source terms in the coupling equations for mass, momentum and energy transport.

The slag model is based on an integral approach similar to the one utilized in the solution of boundary layer problems. The slag model is coupled with a chemical kinetics model for CaC_2 production. The CFD model for turbulent combustion provides the inputs for the slagging model, such as boundary conditions and source terms. This methodology was tested in the ongoing design of pilot scale reactors conducted by CERC-ACTC.

The aforementioned strategy was divided into the four following parts:

1. Application of a CFD oxy-coal combustion model suitable for the conditions required for CaC_2 production, such as high temperatures, high oxygen and CO_2 concentrations, and the presence of CaO particles. This task was done in a commercial code. This model includes a wall particle capture sub-model via a user-defined function (UDF). The CFD oxy-coal combustion model was supported by a Reduce Order Model (ROM) for chemical equilibrium calculations developed by Rowan et al. [17]. The ROM uses the NASA equilibrium

software³ along with a pre-existing coal devolatilization model, the chemical percolation and devolatilization model (CPD) HEAT developed by Grant et al. [18] and Fletcher et al. [19,20]. The ROM was used to calculate the equilibrium flame temperature under the flow conditions of interest prior to CFD modeling, thus reducing the computational time.

2. Development of a slag flow model capable of describing the conversion process of char and CaO into CaC₂ in the molten slag.
3. Integration of models and sub-models in a computational framework. The diagram depicted in Figure 1-1 illustrates the proposed computational framework.
4. Evaluation of the model in the design process of pilot scale reactors being developed by CERC-ACTC.

³ The NASA Chemical Equilibrium with Applications (CEA) code is a free web-based application (the FORTRAN source code is also available for download) available in <http://www.grc.nasa.gov/WWW/CEAWeb/>.

Figure 1-1. Computational framework for the proposed methodology

Chapter 2 – Background

2.1. Coal Technologies as an Strategic Issue for the U.S. and China

According to the U.S. Energy Information Administration (EIA) [21], world coal consumption grew by 59 percent from 2000 to 2010, due, in large extent, to China's rapidly growing energy demand. In China alone, coal consumption tripled during 2000-2010. Coal accounted for 23 percent of world energy consumption in 2000, compared to a 38 percent share for liquids. In 2010, the gap narrowed substantially, with a 28 percent for the coal share and a 34 percent for the liquids share.

According to the U.S. EIA, it is foreseen that world coal consumption will increase by an average of 1.3 percent per year from 147 Quad⁴ in 2010 to 180 Quad in 2020 (Figure 2-1a). The near-term increase reflects significant increases in coal consumption by China, India, and other non-OECD⁵ countries. It is expected that coal use in non-OECD Asia increases by 1.9% per year (Figure 2-1b).

⁴ Quadrillion BTU

⁵ Organization for Economic Co-operation and Development

Figure 2-1. a) World total energy consumption by source type, 1990-2040 (Quadrillions BTU) b) World coal consumption by leading consuming countries, 2010-2040 (Quadrillion BTU) (U.S. DOE/EIA [21])

Currently, fossil fuels make up nearly 80 percent of the total primary energy source in the United States (Figure 2-2a), with coal being about 18 percent of the total. Approximately 91 percent of the coal used for electricity generation and the remaining 8 percent used in industrial applications. Fossil fuels account for nearly 91 percent of the total primary energy usage in China (Figure 2-2b), with coal being about 69 percent of the total. Industrial applications make up 77 percent of the coal demand in China with the remainder four percent going to the commercial sector, 11 percent for the residential sector, and eight percent for transportation.

China's continued economic growth, along with the fact that the United States and China account for an important share of the recoverable coal reserves in the world (Figure 2-3), makes the development of advanced coal technologies a strategic priority for both nations.

Primary Energy Use by Source in US
Quadrillion BTU and percent of total

Source: U.S. Energy Information Administration, Monthly Energy Review, Table 1.3 (April 2013), preliminary 2012 data.

(a)

Primary Energy Use by Source in China
Quadrillion BTU and percent of total

Source: U.S. Energy Information Administration 2011 data.

(b)

Figure 2-2. a) Primary energy use by source in US (Quadrillion Btu and % of total) b) Primary energy use by source in China (Quadrillion Btu and % of total) (U.S. EIA)

Global Share of Recoverable Coal Reserves

Source: U.S. Energy Information Administration, based on the International Energy Agency (IEA) and Eurostat

Figure 2-3. Global share of recoverable coal reserves (U.S. EIA)

Although abundant and supply-secure, the future of coal will be likely constrained by greenhouse gas reduction policies. An increase in the use of high-efficiency coal-fired generation

technologies, as well as carbon capture and storage, is expected to allow a smooth transition to a low carbon power system, while reducing the risk of a shortage in the energy capacity.

2.2. U.S.-China Cooperation Agreement on Advanced Coal Technologies

The U.S.-China CERC was established in 2009 by a protocol signed by President Barack Obama and President Hu Jintao [22]. This protocol expresses the intention of the two nations to keep collaborating under the Science and Technology Cooperation Agreement of 1979 [23]. The United States and China have identified the research on advanced coal technologies as one of their three strategic areas of bilateral cooperation on clean energy innovation⁶. This joint effort is being executed through the establishment of the CERC Advance Coal Technology Consortium, collectively, the CERC-ACTC, which involves academic, governmental and industrial institutions.

In the United States, the consortium is led by West Virginia University Research Corporation, WVU, Morgantown, WV. The research conducted by the CERC-ACTC includes work in the following fields: advanced power generation, clean coal conversion technology, pre-combustion capture, post-combustion capture, oxy-combustion capture, CO₂ sequestration, CO₂ utilization, simulation and assessment, and communication and integration. This research covers the areas of oxy-combustion, clean coal conversion technology, and simulation and assessment.

⁶ The other two areas are: Building Energy Efficiency and Clean Vehicles.

2.3. Oxy-Combustion: Low Emissions Technology

Oxy-coal combustion with recirculating flue gas is a promising technology in the CO₂ capture and storage process. This technology aims at reducing the anthropogenic emissions of CO₂ and other pollutants into the atmosphere. In this process, the recycled CO₂ from the flue gases is mixed with pure oxygen to be injected later as the oxidant instead of air (Figure 2-4). As the CO₂ concentration in flue gases is higher than in the conventional air operation, the CO₂ capture is enhanced and brings about the additional advantage of a reduction in the emissions of NO_x.

Figure 2-4. Diagram of an oxy-coal combustion power plant (Alstom Group, [24])

Oxy-coal combustion with recirculating flue gas is being implemented in existing air-based equipment, such as boilers and furnaces. Nonetheless, the main drawback is the oxygen separation process, which requires a substantial amount of energy, reducing its overall efficiency. In order to overcome this issue, some technologies, such as oxygen and ion transport

membranes or chemical looping, are being developed. A review of the state of the art of oxy-coal combustion is presented in [25]⁷.

2.4 Oxy-Coal Combustion for Production of CaC₂

CaC₂ is an inorganic compound used mainly in the generation of acetylene (90–95 percent of total consumption). Other applications include production of calcium cyanamide, a nitrogen fertilizer; desulfurization reagent in the iron (foundry) and steel industries, and a slag modifier/conditioner (reducer) in the production of ductile iron and steel.

China accounts for 95 percent of the total world production and consumption of CaC₂ (Figure 2-5). This market is linked to the country's strong economic growth, large coal reserves and ever-increasing acetylene demand for the production of PVC. The CaC₂–to–PVC process, considered as an antiquated process in developed parts of the world, accounts for 94 to 97 percent of China's total PVC production. [26]. The annual production of CaC₂ has been increasing in the past decade and has reached about 17 million tons in 2011 in China alone [27].

⁷ See also: “Innovations for existing plants-Advanced Combustion,” NETL, accessed Jan 20, 2015, <http://www.netl.doe.gov/technologies/coalpower/ewr/co2/OxyCombustion.html#>

Figure 2-5. Production/consumption of CaC_2 and its link to acetylene consumption in 2007 (IHS [26])

Despite of the size of the market, traditional CaC_2 production technique has remained almost virtually the same for more than a century [28,29].

In the traditional process, a coke drier is used to remove the moisture content of coke, whereas a lime kiln is used to produce quicklime through the calcination of limestone. The fines resulting from the coke drying and the calcination of limestone may be recycled. A ground mixture of coke and quicklime is then fed into a moving-bed electric arc furnace (EAF) that uses a consumable electrode (see Figure 2-6). The electrode consists of a paste composed of coal tar pitch binder and anthracite coal fed into a steel casing that is baked by heat from the EAF before being placed into the furnace. The baked electrode exits the steel casing inside the furnace cover and is consumed in the CaC_2 production process.

There are three basic types of electric arc furnaces for CaC_2 production [30]: the open furnace, in which the CO burns to carbon dioxide (CO_2) when it contacts the air above the charge; the closed furnace, in which the gas is collected from the furnace and either used as fuel for other

processes or flared; and the semi-covered furnace, in which the mixture is fed around the openings for the electrodes in the primary furnace cover, resulting in mix seals. The molten product of the EAF is tapped, cooled, cast, and then crushed and ground to the size required for marketing.

The purity of commercial CaC_2 is measured by the percentage content of pure CaC_2 , which typically ranges between 75 to 90 percent CaC_2 . The main balance elements are lime, alumina, silica, and free carbon [31]. The percentage of CaC_2 is assessed by measuring the volume of acetylene produced when the commercial CaC_2 reacts with water, e.g., 314 liters of acetylene per kilogram of commercial CaC_2 corresponds to 90% CaC_2 purity [29].

One of the main drawbacks of the traditional EAF process is that coke and CaO particle sizes are typically in the range of 5 to 30 mm. in order to favor the release of the by-product carbon monoxide (CO). This does not allow for good surface contact of the reactants, which is large obstacle for mass and heat transfer, as well as, reaction rates. For this reason, it is necessary to obtain high reaction temperatures ($\sim 2200\text{ }^\circ\text{C}$)⁸ and long reaction times (1–2 h), resulting in high electric energy consumption ($\sim 4000\text{ kW}\cdot\text{h}$ per ton of pure CaC_2) [27].

⁸ Not practically achievable with traditional combustion processes.

Figure 2-6. Example of an EAF used in the production of CaC_2 (SMS Group [32])

Due to the elevated electric energy consumption, different options for an economical production of CaC_2 have been suggested, some including autothermal heating processes via oxy-combustion, e.g., plasma spout-fluid bed [33], rotary kiln with partial oxygen-fuel heating [34], and auto thermal processes with full oxygen-fuel heating [4,35]. These processes, however, have used ground materials with the particle size ranges as those processes, thus including the same limitations discussed above.

A work presented recently by Li et al. [36] addressed that issue and showed that it is possible to activate the CaC_2 reaction at temperatures lower than $1750\text{ }^\circ\text{C}$ if fine particles (i.e., with sizes smaller than 0.1 mm) are used. The work of Li et al. [36] is performed at these lower temperatures to understand the reaction behavior and develop a kinetic model to be applied in the scale-up of the reactor design process. A review of the state of the art of the reaction and kinetics modeling for CaC_2 is discussed in section 3.7.

Chapter 3 – Literature Review

3.1. CFD in Reactor Design

CFD has evolved as a technique that was initially used primarily for aerospace applications. However, it has been recently applied to many industrial flow problems [37]. CFD is a useful tool for designing complex flow processes and equipment. Its implementation in the power generation industry helps engineers improve equipment design, which can result in increased thermal efficiency and reduction of environmental emissions. Improvements in design can lead to lower product costs and higher product quality in the chemical industry. Current societal concerns that need to be addressed, such as environmental issues, depletion of traditionally used fossil fuels, and a competitive marketplace, require engineers to look for the aforementioned improvements constantly.

Some advantages brought about by the implementation of CFD in the reactor design process are the following [38]: i) it allows for a detailed understanding of flow distribution, weight losses, mass and heat transfer, and particulate separation; ii) it makes it possible to evaluate the effect of geometric changes in much less time and with lower costs compared to laboratory testing; iii) it answers many ‘what if’ questions in a fast manner; iv) it reduces scale-up problems because the models are based on fundamental physics and are scale independent; v) it can simulate conditions where it is not possible to take detailed measurements, such as high temperatures or dangerous environments; iv) since the implementation of the CFD in the reactor design process is a pro-active analysis and design tool, it can highlight the root cause and not just the effect when evaluating plant problems. An additional advantage of the CFD simulations over

experimental methods is that the diagnosis does not disturb the flow and normal equipment operation.

In spite of all the aforementioned advantages, the implementation of CFD in the reactor design process is a difficult task when compared to non-reacting flow applications. That is due to the additional flow complexities involved in a typical reactor design problem. Thus, turbulence as well as many different effects such as heat transfer, compressibility, multiphase flow, phase changes, combustion and other chemical reactions, and the non-linear interactions between these effects, are present. In turbulent combustion, for instance, the modeling of turbulence is one of the most critical processes because of its role in establishing the flow, mixing, and combustion processes [39]. Even though models to account for additional effects have been continuously developed and incorporated into many commercial codes, research in this area is still incomplete [40].

3.2. Turbulence Modeling

The solution of the turbulent flow field is a challenging task because flow properties change significantly in a random and chaotic fashion in space and time, even when constant boundary conditions are imposed. Similarly, flow properties reveal the existence of eddies in a wide range of different space and time scales. The presence of eddies increases the transportation of flow properties by mixing, e.g., mass, momentum, energy, entropy. Therefore, the solution methods must include the effects of the fluctuations in the flow.

Turbulent flow calculations are done using different methods: Direct Numerical Simulation (DNS), Large Eddy Simulation (LES), and RANS. In the DNS method, the Navier-Stokes equations are solved for all space scales. For this reason, spatial grids should be sufficiently fine⁹ so that the Kolmogorov length scales at which energy dissipation takes place can be resolved. Spatial grid should also allow resolving the period of the fastest fluctuations in sufficiently small time steps. DNS is then highly computationally expensive and not practical for industrial applications where the computational resources required would exceed the computer power currently available. Nonetheless, DNS is a highly valuable tool for fundamental research and model validation¹⁰.

In the LES method, the Navier-Stokes equations are solved after application of a filter process in space. The filtering process rejects the smaller eddies that should then be modeled using a sub-grid scale model. The LES solution includes the mean flow plus the effects of large eddies. LES is less computational expensive than DNS but still requires high computational resources.

Finally, the RANS method focuses on the mean flow and the effects of turbulence on the mean properties by accounting for the turbulence interaction via additional terms in the time-averaged (Reynolds Averaged) equations; therefore, no scales are solved but their effect is modeled. These additional terms are modeled with classical turbulent models, e.g., mixing length, k - ϵ , k - ω ,

⁹ Proportional to the cubic power of the Reynolds number (Re^3)

¹⁰See, for instance, “Direct Numerical Simulation”, Combustion Research Facility, Sandia National Laboratories, accessed May 25, 2013, <http://crf.sandia.gov/index.php/combustion-research-facility/reactingflow/modeling/dns/#.UaE9DpzI94M>

Spalart-Allmaras. RANS-based CFD represents a reasonable compromise between accuracy and expenses, so that it is preferred in industrial applications. In fact, it has been the mainstay of flow calculations over the past three decades [41].

3.3. Main Differences between Oxy-Coal and Air-Coal Combustion

Different aspects need to be considered when moving from air to oxy-coal combustion modeling. Chen et al. [42] provide references to the experiments and numerical studies performed in the field. The authors also present a comprehensive review to the thermodynamics, transport and chemistry processes in oxy-coal combustion. The processes and aspects to be considered in oxy-coal combustion vs. air-coal combustion are:

1. Heat Transfer
 - a. Radiative heat transfer
 - b. Convective heat transfer
 - c. Combustion temperature
2. Fuel delivery and injection
3. Heating and moisture evaporation of coal particles
4. Ignition of coal particles
 - a. Ignition delay
 - b. Burning of volatiles
5. Oxy-char combustion
 - a. Kinetics of char oxidation in oxy-fuel combustion
 - b. Effect of diffusivity

- c. Effect of gasification reactions
- d. Effect of heat capacity
- e. Effect of pressure

This section presents a discussion about the most relevant aspects to be considered in the present application. These are: radiative heat transfer and char combustion. The reader is referred to Chen et al. [42] for a more detailed discussion.

3.3.1 Radiative heat transfer

During oxy-coal combustion with flue gas recirculation, the partial pressures of CO₂ and H₂O in the burning gases are considerable higher than in normal air-fuel combustion. Gases with symmetric diatomic molecules, such as N₂, are transparent to infrared radiation and do not emit significantly. On the other hand, heteropolar gases that absorb and emit significantly, such as CO₂ and H₂O, are not transparent to infrared radiation. Therefore, absorption and radiation are considerably higher in oxy-coal combustion environment when compared with air-fuel combustion.

When a radiation beam of wavelength λ travels an infinitesimal length, ds , through a gas, a fraction of its radiation intensity, α_λ , is absorbed by the gas. In this process, the change in the spectral radiation intensity, dI_λ of the radiation beam is given by the expression [43]:

$$dI_\lambda = -k_\lambda I_\lambda ds \quad (1)$$

In this expression, k_λ is the spectral absorption coefficient, which is a function of the wavelength, gas composition, gas temperature and pressure. If equation (1) is integrated over the length, s , the spectral absorptivity and emissivity of the gas can be obtained as:

$$\alpha_\lambda = \varepsilon_\lambda = 1 - \exp[-k_\lambda s] \quad (2)$$

The effective absorptivity and emissivity of a gas mixture can be obtained by integrating equation (2) over the full spectrum. However, direct computation of the gas absorptivity is difficult. Figure 3-1 shows the spectral absorptivity, α_λ , as a function of wavenumber for water vapor, carbon dioxide and methane during a combustion process [44]. It can be observed that absorption is not continuous over the entire spectrum; instead it is concentrated in a number of moderately wide spectral bands. To overcome this difficulty more practical approaches, such as the weighted sum of grey gas model (WSGG), are used in the CFD modeling. For instance, the WSGG model has been used in the works performed by Khare et al. [45], Toporov et al. [46], Chen et al. [47], and Nikolopoulos et al [48]. This same approach has been used in the present work.

Figure 3-1. Spectral absorptivity as a function of wavenumber for water vapor, carbon dioxide and methane (Edwards [44]).

Despite of the effect of the enhanced gas radiation during oxy-fuel combustion, it has been shown by Andersson and coworkers [49,50,51] that gas radiation during oxy-fuel combustion becomes less important when compared to the particle radiation. The authors investigated the radiation intensity of lignite coal-fired oxy-fuel flames in the 100 kW test facility at Chalmers University of Technology¹¹. The authors showed that particle radiation contributes about 60 to 70% of the total radiation in both air-fired and oxy-fired cases.

This can be observed in Fig. 8 where the authors show the radiation intensity of the gas and the total radiation intensity (gas and particles) at the flame zone. The data correspond to the port located at 384 mm away from the burner inlet. It can be also observed that in lignite oxy-fuel

¹¹ This unit is described in section 5.5.

combustion with an oxygen molar fraction of 0.25 (OF25) the total radiation intensity is similar to the conventional air operation although gas radiation is enhanced. Again, the larger amount of radiation is emitted by particles, which have similar contribution in both combustion environments.

Figure 3-2. Comparison of total intensity measurements (symbols) and gas radiation modeling (lines) at 384 mm away from the burner inlet (Andersson et al. [51])

3.3.2 Char Conversion

Different works have been conducted to evaluate the differences in char conversion under oxy-fuel conditions, examples can be found in the references [52,53,54,55]. Regarding the presence of CO_2 vs N_2 , Chen et al. [42], indicate that CO_2 may affect char combustion under different mechanisms: i) the reduced oxygen mass transfer in CO_2 ; ii) the lower combustion temperature due to the higher heat capacity of CO_2 ; and iii) the char- CO_2 gasification reaction. The authors

also indicate that char oxidation may take place in three different regimes: kinetic-controlled, diffusion-controlled, or kinetics and diffusion controlled.

Based on the oxygen concentrations and nominal temperatures in char oxidation/gasification experiments conducted under air and oxy-fuel conditions, Chen et al. [42] classify the results of different investigations. Figure 3-3 shows this classification and depicts three regions (A, B, and C). Region A is characterized by low temperatures. In region A, the reactions rates are the same in both O₂/N₂ and O₂/CO₂ conditions. Region B is characterized by high oxygen levels and high temperatures. In region B, the reaction rates are lower in oxy-fuel conditions. Region C is characterized by low oxygen level and high temperatures. In region C, reaction rates are higher in oxy-fuel conditions. In Figure 3-3, the error bars are color coded to represent the change in the char consumption rate. The black color represents an unchanged char consumption rate, whereas the blue color represents a decrease, and the red color an increase in the char consumption rate.

Another important effect on char consumption is the influence of gasification reactions on char consumption. Different from char oxidation reactions, char gasification are highly endothermic, thus requiring heat transfer to the particle. An example of a gasification reaction scheme is the one utilized in the multi-surface reaction model of Smith [56]:

Gasification reactions have also much higher apparent activation energies. While the char-O₂ reaction activation energy is about 160 kJ/mol, the activation energies of the char-CO₂ are in the

range of 230-270 kJ/mol, and for char-H₂O, the activation energies are in the range of 190 to 270 kJ/mol, [149]. Therefore, gasification reactions only occur at high temperatures.

Based on the experimental work of Kajitani et al. [57], Chen et al. [42] indicate that gasification reactions can only contribute to a higher char consumption rate at high temperatures with low oxygen concentrations in CO₂-rich environments (Region C in Figure 3-3). This means that, as long as the oxygen concentration is high, the contribution of gasification reactions is relatively smaller than that of oxidation reactions¹².

Figure 3-3. Char oxidation/gasification experiments in oxy-fuel conditions (Chen et al. [42])

¹² For this reason, gasification reactions are not considered in the char combustion reaction model utilized in this work.

3.4. CFD Modeling in Oxy-Coal Combustion

When sub-models are used in connection with Reynolds-Averaged Navier-Stokes (RANS), CFD provides a relatively inexpensive and indispensable tool to perform comprehensive studies on fluid flow, heat transfer, and chemical reactions in combustion [42]. Currently, CFD modeling of oxy-coal combustion is based on approaches and sub-models that are similar to those developed under air-fired conditions.

On the other hand, significant efforts are being made in order to develop and validate new combustion sub-models that consider the differences between oxy-coal and air-coal combustion in the combustion environment. The effects of high temperatures and CO₂ concentrations in the particle combustion behavior are particularly important. For instance, it is known that high temperatures can lead to char thermal deactivation during oxy-coal combustion [58]. Furthermore, elevated levels of CO₂ may influence char consumption via the reduced diffusivity of oxygen in CO₂ [54,59,60].

Previous development of new combustion sub-models is based on those created for the air-fired conditions. Chen et al. [42] offer a review of sub-models implemented for turbulence, radiation heat transfer, char combustion and homogeneous reactions. The authors also include a selection of distinct CFD simulation studies on oxy-coal combustion where different sub-models are applied. Some of those studies are discussed next.

For instance, experiments and CFD simulations were conducted by Chui et al. [61] in the vertical combustor research facility at the Canada Centre for Mineral and Energy Technology (CANMET). The objective of that work was to improve the burner and combustor design in

order to reduce NO_x emissions. CFD proved to be an efficient and cost effective tool for this application. The new burner design showed better flame characteristics and lower NO_x and CO emissions. Moreover, the effect of the furnace size in the burner performance could be quantified, and, consequently, it was noted that enlarging the combustor to an inner diameter minimized wall effects. That becomes important when attempting to expand the flame volume so as to improve oxygen management within the flame.

Another example of a CFD application in oxy-coal combustion is presented by Toporov et al. [46]. The work was performed in a 100 kW pilot-scale furnace at the Institute of Heat and Mass Transfer, RWTH, at Aachen University. In this application, the swirl burner design and operation conditions were established in order to promote flame stabilization through CO formation, by using O₂/CO₂ mixtures with oxygen content similar to that of the air, i.e., 21 vol% O₂. Numerical model results for gas velocities, gas and particle temperatures, and gas compositions showed a good match with experiments.

Al-Abbas et al. [62] used CFD to model the combustion of pulverized dry lignite coal in air and different O₂/CO₂ atmospheres. This work was based on the experiments conducted by Hjærtstam et al. [63] at Chalmers University of Technology in a 100kWth down-fired furnace. Three different O₂/CO₂ atmospheres were evaluated: 25, 27 and 29 vol% O₂. Temperatures and species concentration profiles showed a good match with the experiments. Results for 25 percent oxygen were closer to air in terms of flame temperature distribution. On the other hand, in the 27 and 29 percent oxygen cases, the flame temperature was higher and more confined in the closest region of the burner exit plane.

Álvarez et al. [64] performed CFD based simulations of an entrained flow reactor (EFR) under oxy-coal combustion conditions. These simulations were made for different O_2/CO_2 atmospheres i.e., 21–35 vol% O_2 . The authors used three coals of different volatile matter content. These simulations were validated with experimental results in the EFR, showing a good match. The predictions of the CFD model for temperature profiles, burning rates, burnout and concentration of major species were compared with an air reference case. Their CFD model results showed that lower gas temperatures and burning rate levels observed for the 21 vol% O_2 case were lower than in the air reference case. Their results also showed a decrease in coal burnout when N_2 was replaced by CO_2 keeping the same oxygen concentration, i.e., 21 vol% O_2 , but there was an improvement when the oxygen concentration was higher than 30 vol% O_2 .

Chen and Ghoniem [39] conducted a numerical study on oxy-fuel combustion of lignite coal in a 100 kW test facility, using LES and RANS approaches. The authors evaluated the performance of different turbulence models by comparing their predictions with experimental measurements.

An example of the CFD application to the study of the particle combustion behavior under oxy-coal conditions is the work of Singer et al. [58]. CFD simulations were performed to analyze the influence of gasification reactions on char consumption of lignite coal in a pilot-scale oxy-fuel test facility with 29 percent oxygen feed. The authors considered that combusting particles experience time-dependent boundary conditions along their trajectories through different regions of the combustion chamber, i.e., through the pre-flame, flame, and post-flame regions. The

regions were obtained from CFD simulations and were used to establish representative time-dependent boundary conditions, to be applied to single particle sub-models.

Particle trajectories were divided into two different modes according to the regions where char combustion took place. Particles in mode 1 (PM1) combusted in the pre-flame and post-flame regions exposed to relatively high oxygen concentrations and lower temperatures, while particles in mode 2 (PM2) combusted in the flame and post-flame regions exposed to low oxygen concentrations and high temperatures. Singer et al. [58] concluded that the effect of gasification reactions on char conversion for PM1 particles was not significant. However, according to the authors, it can be significant for PM2 particles, depending on the particular char physical and kinetic properties.

The effect of high temperature (up to 1800 K) and CO₂ dilution (up to 36 percent O₂) have been analyzed and implemented by Chen and Ghoniem [39] in their simulations. It is also known that modifications of the char combustion behavior at high temperatures can influence the prediction of the reactor operation via loss of char reactivity. Moreover, change in the heterogeneous rate of reactions at high temperatures can be significant.

That phenomenon seems to be strongly related to thermally induced modifications of the carbon structure. Different models have been considered to account for that effect and to be implemented into CFD simulations in a practical way. Examples of those models are the CBK model by Hurt et al. [65] and in its subsequent implementations: the CBK-E model by Niksa et al. [66], the CBK-G model by Liu & Niksa [67] and the model of Senneca & Salatino [68]. This last model includes the thermal annealing effect, that is, loss of char combustion reactivity and burn off, for temperatures up to 2500 K.

3.5. Slagging Modeling in Coal Fired Combustors

Different CFD models have been used in different works with slagging models in a computational framework; their goal has been to model the slagging process in coal-fired combustors. Most of those works have studied the effect of the slag in the combustor. Particle deposition and the slag characteristics may affect the combustor conditions through modifications of the wall boundary conditions, Wang et al. [15], by changing the transfer through the wall, for instance.

The aforementioned models include sub-models for slag particle capture/rebound and for slag properties. As an example, Seggiani [14] developed a simplified slag model coupled with a CFD gasifier model. This model studied the slag accumulation and flow on the walls. The CFD model provided the inputs for the simplified slag model. The effects of changes in the gasifier operating conditions over the slag behavior were analyzed. For instance, similar effects on the slag thickness were obtained either by increasing the oxygen or by increasing the limestone amount. The transient response in the slag and gas, due to the change in operation conditions, was assessed as well. The model provided solid and liquid slag thicknesses, temperature change across the slag, and heat flux to the wall.

Wang et al. [15] used the same approach as Seggiani, [14], i.e., the combination of the CFD combustion model with a slag model. Wang et al. [15] took into account that particles trapped in the slag possibly contain combustible matter that will continue burning. For this reason, the authors introduced a wall burning model. They indicated that burning particles in the slag increase the deposition rate and, therefore, the slag thickness. Most recently, Yong et al. [16] presented a slag model based on the work of Seggiani [14] and Wang et al. [15]. Coupled

calculations between the slag model and the CFD reactor model were performed too by Yong et al. [69].

Figure 3-4 depicts the mass and heat transfer to the reactor wall and the particle/slag interaction which is typically assumed in slagging models. Figure 3-5 shows the interaction between the CFD combustor model and the slag model in the computational framework. The CFD combustor model provides the slag model inputs, i.e., particle mass flux, particle temperature, particle velocity. The slag model provides values such as average slag velocity, slag temperature profiles, slag thickness and heat transfer to the coolant. Then, the slag temperature calculated from the slag model is fed back as the boundary condition in the CFD combustor simulation.

Figure 3-4. (a) Mass and heat transfer to reactor wall. (b) Illustration of particle capture/rebound by the slag layer and wall consumption of trapped particles (Yong et al. [16]).

Figure 3-5. Slag model in CFD framework (Yong et al. [69]).

As mentioned before, particle capture/rebound and slag properties modeling are key components in the development of slagging models. Efforts oriented towards the validation and comparison of some of the models previously mentioned have been performed by Ai and Kuhlman [70]. The authors modeled ash deposition experiments conducted by Ichikawa et al. [71]. The experimental setup consisted of a 1m height and 60mm inner diameter ash-heating tube with a cooled temperature controlled surface for impinging particles. The heating tube was used for simulating a gasifier temperature history with operating temperatures between 1873 and 1573 K.

Ai and Kuhlman used a commercial CFD code and implemented a user-defined function (UDF) based on the JKR theory [72], the work of Brach and Dunn [73], and Soltani and Ahmadi [74]; their goal was to describe particle sticking/rebounding and particle detachment on the impinged wall surface. This particle sticking/rebounding model is based on a critical particle velocity. Their results for adhesion and rebound of particles showed good agreement with the experiments. Their work was the initial stage of the development and evaluation of a computer

model to be implemented in a CFD framework to study the effect of slagging and fly ash formation in the coal gasification process.

Additional work of Kuhlman and Ai [75] modeling the same experimental set up as Ichikawa et al. [71] was done to compare two models for prediction of coal ash particle deposition, i.e., the aforementioned model based on a critical velocity and the model of Walsh et al. [76], based on a critical viscosity criteria. When implementing the model of Walsh et al. [76], the model of Browning et al. [77] was used to describe the slag viscosity dependence on temperature and ash composition. The results indicated a better prediction of the experimental results of the model of Brach and Dunn [78], based on a critical velocity criteria, than the prediction of the model of Walsh et al. [76], based on critical viscosity criteria.

Krishnaswamy et al. [79] presented two analytical formulations intended to describe the fluid interactions of slag with the porous refractory linings of gasification reactors. Their first formulation considers the infiltration velocity of slag into the porous of the refractory wall. In this formulation, the capillary pressure was assumed to be the main mechanism driving the infiltration process. Their second formulation describes the thickness of the slag that flows down along the wall. In their second formulation, the slag thickness was approximated by equating the rate of slag production of the gasifier to the integration of the velocity profile with respect to the cross-sectional area of the film. The two aforementioned formulations permitted to visualize that the infiltration velocity and the slag thickness are sensitive to the slag viscosity. The authors applied their slag thickness model to predict the film thickness in a generic slagging gasifier under two different conditions. The first condition considered a constant slag volumetric flow

rate down the gasifier wall. The second condition considered a constant fly ash flux distributed uniformly along the wall of the gasifier.

3.6. Estimation of Slag Properties

Different models are described in the literature for predicting the properties of slags. Mills [80] presents a detailed review of these models. These models can be classified into the following groups: i) numerical fits, ii) neural network models, iii) partial molar models, iv) models based on structural parameters, v) thermodynamic models and vi) molecular dynamics models. Mills [80] also provides a summary of each of these models as well as references to their development and application.

One of the reasons behind such a variety of models is the difficulty to find a single model suitable for many different types of slags. This is due mainly to the great variety of slag compositions that can be found in different applications. For instance, metallurgical slags are mainly based on the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ system; non-ferrous slags are frequently based on fayalite (Fe_2SiO_4); coal slags are mainly composed of $\text{CaO+Al}_2\text{O}_3\text{+SiO}_2$ ¹³; ESR¹⁴-slags are made of oxides and significant amounts of fluorides e.g., $\text{CaF}_2\text{+CaO+Al}_2\text{O}_3$; glasses tend to have high SiO_2 contents; enamels contain significant amounts of B_2O_3 [80]. For the particular case of coal slags, it is well known that their chemical composition varies greatly between mining regions and, consequently, the properties of the slags also vary to a large extent.

¹³ In addition to the main components, elements such as: Fe_2O_3 , TiO_2 , P_2O_5 , MgO , Na_2O , K_2O and SO_3 are also part of the coal slag composition.

¹⁴ Electro-Slag Re-Melting

Another complication is the fact that these models rely on experimental measurements which are difficult to collect in most of the cases, mainly due to the high temperatures involved. Furthermore, predictive equations are based on ash analysis, but significant losses of some elements may occur as the ash is heated to the melting temperature. For example, tests results reported by Streeter et al. [81] for 18 out of 24 viscosity tests for low-rank coal showed that 80 to 100 percent of the SO_3 , if present, and all the P_2O_5 , were volatilized during melting of the ash. Although these are minor slag components, the amount of some other components such as Na_2O can be significant in some coal ashes.

Streeter et al. [81] also reported that Na_2O was devolatilized in amounts ranging from 10 to 50 percent in 11 out of 15 instances in which Na_2O was present. Additionally, reactions with the sample crucible may result in depletion or enrichment of some components; for instance, Fe_2O_3 resulted in depletion for carbon-crucible tests and depletion or enrichment for alumina crucible tests in the experiments performed by Streeter et al. [81].

Beyond all these complications, most of the models aimed at predicting the properties of slags have shown to provide satisfactory results, particularly for slag coal related processes [14,15,69,75]. In order to obtain valid predictions from the slag flow model developed in this study, it is necessary to estimate the fluid flow and thermal properties of the slag, e.g., viscosity, temperature of critical viscosity, density, heat capacity, thermal conductivity, and emissivity of the slag.

From all the fluid flow and thermal properties of the slag, viscosity is perhaps the property most related to the control and design of the process. For a Newtonian fluid, the viscosity dependence on temperature is exponential, or equivalently, the logarithm of viscosity shows linear

temperature dependence. Slag cooling experiments¹⁵ have shown that the logarithm of viscosity vs. temperature curve exhibits a linear dependence down to some point, which is designated as the temperature of critical viscosity. At this point, the viscosity starts to increase abruptly as the temperature decreases. This effect is suspected to be related to the start of precipitation of solid crystalline phases in the slag [81].

Traditionally, the straight-line portion of the logarithm of viscosity vs. temperature curve in a slag system is designated ‘Newtonian region’ of slag behavior, whereas the region below the temperature of critical viscosity is designated ‘plastic region’. Nonetheless, the slag can retain Newtonian properties below the temperature of critical viscosity [81]. It is also possible to find non-Newtonian behavior below the temperature of critical viscosity; thus, pseudoplastic and thixotropic behavior was found at the higher viscosities in almost all the slags studied by Streeter et al. [81].

Different authors have performed experimental measurements of the temperature of critical viscosity and have developed models to predict its value. Most of the models are based on empirical correlations that relate the temperature of critical viscosity to composition or, in the case of coal, on characteristic temperature values of the ASTM ash fusion test¹⁶. A detailed review of different models for prediction of the critical viscosity temperature can be found in Vargas et al. [82].

¹⁵ For instance, those performed by Streeter et al. [81]

¹⁶ ASTM standard D 1857-87.

In molten slag, viscosity is influenced primarily by temperature, composition and the structure of the slag, i.e., the degree of polymerization or de-polymerization of slag. In a simplified manner, it can be stated that elements such as SiO_2 and Al_2O_3 , known as network-formers, increase the polymerization degree which brings about and increase in viscosity. On the other hand, elements such as Na_2O , Li_2O , CaO , MgO , K_2O , SrO and BaO , known as network –breakers, decrease the degree of polymerization¹⁷, which brings about a decrease in viscosity.

All the models that have been proposed to estimate the viscosity of the slags account for the structure in some manner. Mills [80] includes a summary and classification of these models, also pointing out their uncertainties in predicting the viscosity of different slag systems. Most of the popular viscosity models are expressed in terms of Arrhenius-type or Weymann-type equations that take into account the effects of temperature, composition and structure. The parameters in these models are calculated by curve fitting experimental viscosity measurements. These models provide predictions within a 30 percent error, similarly than in experimental uncertainties in the measurements of slag viscosities [83,80]. Some selected models will be discussed below due to their applicability in coal slag systems as well as their convenience regarding their application to the development of CFD based slag flow models.

A popular viscosity model is, for instance, the model of Urbain et al. [84], which was developed for metallurgical slags by fitting experimental data from the $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO-MgO}$ system. Although, the Urbain model was developed for metallurgical slags, it has been commonly

¹⁷ The reader is referred to Mills [80] and Senior and Srinivasachar [139] for a complete discussion on the slag structure and its effect on the slag properties.

employed to estimate the viscosity of lignite slags, since the main constituents for metallurgical and lignite slags are the same.

Further modifications to the Urbain model have been developed to account for the effect of composition on the viscosity of the slag. For instance, Schobert [85] applied the Urbain model to lignite ash and derived different formulas according to the relative amount of silica in the slag, i.e., the slag was classified as high, medium or low silica. He included the effect of what Urbain categorized as the constituents of silicate melts, i.e., glass-formers (SiO_2 and P_2O_5), modifiers (CaO , MgO , Na_2O , and K_2O) and amphoteric oxides (Al_2O_3 and Fe_2O_3), which can act as glass-formers or modifiers. The effect of these elements was included by developing correlations; specifically, concluding that for high-silica slags the silica content of the slags is the dominating factor, whereas for low-silica slags the correlation term is the ratio of CaO to modifiers¹⁸.

Kalmanovitch and Frank [86] modified the model of Urbain to extend the range of composition. Unlike Schobert [85], they developed a single correlation that includes most of the major components of the slag, with exception of SO_3 . Another characteristic of this model is that all the forms of iron oxide are treated as FeO .

Browning et al. [77] developed a viscosity model by following a different procedure than the one used in the Urbain family models. Based on the observation of Nicholls and Reid [87], they assumed that the viscosity-temperature gradient profile for all coal ash slags within the Newtonian region must be consistent. Therefore, all the viscosity-temperature curves should

¹⁸ In a simplified manner, viscosity increases with the amount of SiO_2 (*glass former*) and tends to decrease with the amount of CaO (*modifier*) present in the slag.

overlay if they are shifted along the temperature axis by some quantity. By selecting a standard curve and using least squares regression, they developed a single expression that relates the temperature shift with a parameter based on the molar ratio of network-formers and network-modifiers. More particularly, the parameter is based on the ratio of former and fluxing ions. The model provided satisfactory results for British coal ash slags.

Two useful empirical models were developed during the 1960s at the British Coal Utilization Research Association (BCURA), namely, the S^2 model¹⁹ [88] and the Watt-Fereday model [89]. These models are based on regression analysis of viscosity-temperature curves for British bituminous coals. The BCURA S^2 model utilizes an Arrhenius-type equation that relates the viscosity to temperature and to a single parameter called the silica ratio. The silica ratio is defined as the relation between the mass fraction of SiO_2 to the total mass fraction of SiO_2 , Fe_2O_3 , CaO and MgO . The Watt-Fereday model is based on a linear equation that relates the logarithm of the viscosity to a single function of temperature. In this equation, the values of the slope and intercept are calculated based on the normalized weight percentages of SiO_2 , Fe_2O_3 , CaO and MgO .

Different researchers have completed studies to compare the predictions of the aforementioned viscosity models. As an example, Streeter et al. [81] conducted experimental viscosity tests and compared the predictions of different slag models. They selected 17 low-rank coal samples, ranging from lignite to bituminous, from different locations in the U.S., mostly in the western U.S., namely, North Dakota, Montana, Wyoming, Texas and Alabama. Some of the tested

¹⁹ Commonly known as the BCURA S^2 model.

models were: the aforementioned model of Urbain [84], the model of Schobert [85], the BCURA S^2 [88], and the Watt-Fereday model [89]. Their results indicate that, although the predictions for these models are satisfactory in most cases, different models perform better than others for certain types of coal slags. For instance, it was reported that the conventional Urbain model [84] provided a reasonable good fit for two thirds of the viscosity tests.

Laumb [90] compared the predictions of seven viscosity models against measured viscosities for slag produced from 19 ash samples of lignite and one cyclone slag. The author concluded that, although the broad range of composition found in lignite coals makes the prediction of slag a challenging task, many of the models provide satisfactory results for specific compositions. For instance, Laumb reported that the model of Kalmanovitch and Frank [86] worked the best for lignite slags containing high mounts of SiO_2 and lower amounts of Fe.

The work of Fernades et al. [91] is another good and comprehensive example of evaluation of different slag viscosity models. The authors tested the model of Urbain [84], the model of Kalmanovitch and Frank [86], the aforementioned model of Browning et al. [77], and the BCURA S^2 model [81]. These models were tested in a Pittsburgh No. 8 coal for different densities and particle sizes. Results indicated a high potential for the BCURA S^2 as a prediction tool.

Concerning the estimation of density, several models aimed at predicting its value for molten slags have been developed. Mills and Keene [92] proposed which is probably the most practical approach. In this model, the density of the molten slag is calculated according to an empirical expression that considers a correction from a constant value. The correction is expressed in terms of the weight percentages of FeO, Fe_2O_3 , and MnO. According to Mills and Rhine [93], this

model allows estimating density values of slag systems with a relative small error, e.g., within a five percent error for slag temperatures close to 1673 K [92].

Mills [80], points out that, since the density of liquid slags do not depend significantly on the structure, it is possible to obtain reasonably accurate density values using simple expressions; specifically, expressions involving molar weighted averages of the molar volume for every particular constituent present in the slag, even if the molar volume of every constituent in the solution is assumed to be the molar volume of the pure component. Examples of these type of density models were developed by Bottinga and Weill [94], Nelson and Carmichael [95] and Mo et al. [96]. More refined models that include the effect of the structure of the slag on the density can be found, for instance, in the works of Bottinga et al. [97] and Mills [83].

Mills [93] shows that the structure of the solid formed during the solidification of the slag depends on the cooling rate, which means that a very small cooling rate will result in the formation of a crystalline slag, whereas a rapid quench will produce a glass. Mills shows the relationship between the enthalpy change and temperature for these two conditions. The curve for the glassy phase of the slag is made of the glass phase, for temperatures between the ambient temperature and the glass-transition temperature, which is around 900 K; the supercooled liquid, for temperatures between the glass-transition temperature²⁰ and the liquid temperature, close to 1600 K; the liquid phase, for temperatures above the liquid temperature. The curve for the crystalline phase ranges from the standard temperature up to the liquid temperature.

²⁰ At this temperature, the curve of heat capacity vs. temperature for the glassy slag shows a sharp increase, similar to a step.

Both the curve for the enthalpy and the curve for the temperature of the glassy and crystalline slags show an approximately linear relation with similar slopes. The linear relation is stronger in the liquid region, which results in the usual assumption that the heat capacity is completely independent from temperature. The similarity of the slopes suggests that the heat capacity does not strongly depend on the structure of the slag, as indicated by Mills [80]. It also indicates that the value of the heat capacity for a sample in a laboratory or industrial process depends on the amount of crystallization, and thus lies between the values provided by the two curves.

Mills [93] also provides a method to estimate the constant value of the heat capacity as a function of temperature and the composition of the slag. He points out that the heat capacity can be estimated by using the partial molar heat capacities of the slag constituents. In the liquid region, the heat capacities of the slag constituents are considered independent from temperature, whereas for the crystal and glass phases, the temperature dependence of the slag constituents is taken into account by a second order polynomial relation. This method provided heat capacity values within two percent of the experimental measurements.

The work by Mills and Rhine [98] supported the observations made by Mills [93] for the heat capacity of the slags. They conducted measurements of the thermal properties of coal slags formed in a British gasifier. Slags of crystalline and glassy structures were obtained and the curves for enthalpy vs. temperature and heat capacity vs. temperature were obtained. Results for the heat capacities of the glassy and liquid slag samples were also reported.

Much work has been done in the area of thermal conductivity. Mills [80] offers a review of that previous work and includes several references. For instance, in the study conducted by Nishioka et al. [99], the thermal conductivity of $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ slags in the glassy and crystalline states

is measured. In this work, it was found that the thermal conductivity of the crystalline state is about 1.5 to 2.5 times larger than the thermal conductivity of the glassy state. According to the authors, this can be explained by the higher packing density of the crystalline state.

Mills and Rhine [98] also measured the thermal conductivity. The authors point out that the thermal conduction of a semi-transparent media such as slags is made of the contributions of the thermal conductivity²¹, the radiation conductivity, and the electronic conductivity. They also discuss experimental difficulties associated with separating each contribution, being more convenient to combine all of them in terms of an effective conductivity. Another important observation made by the authors is the convenience of obtaining the thermal conductivity using measurements of the effective thermal diffusivity.

Perhaps the most important fact about the thermal conductivity of the slag is that it strongly depends on structure. For instance, as is shown by Mills [80], it has been observed that the thermal conductivity of the slags increases with an increase in the SiO₂ content or, equivalently, with the degree of polymerization. Mills [80] considers that this is due to the fact that the resistance to phonon transportation is much smaller when passing along the chain than the resistance of moving phonons from chain to chain. He also explains that, since the thermal conductivity increases with the polymerization degree, it can be expressed as a function of the viscosity²². Mills additionally mentions that the variation of the thermal conductivity with temperature can be well represented with similar functions as those for viscosity. Examples of these relations are found in Mills [80] and Hayashi et al. [100].

²¹ Which involves the movement of phonons and it is usually referred to as ‘phonon conduction’.

²² See also Hayashi et al. [100]

Discussion and references to additional slag properties such as surface tension, electrical conductivity, absorption coefficient, and emissivity of the slag are thoroughly described in Mills [80,83], and Mills and Rhine [98].

3.7. CaC₂: Reaction Kinetics and Behavior

The reaction stoichiometry for the formation of CaC₂ from carbon and CaO is governed by the following global reaction (3/1 C to CaO):

The complete mechanism is still being researched but several authors have attempted to develop different reaction mechanisms and descriptions of the kinetic behavior. For instance, Tagawa and Sugawara [101] conducted experiments using thermo-gravimetric analysis to study the carbonization process of CaO in a solid-solid reaction, at temperatures between 1600 and 1800 °C. The kinetics of the CaC₂ formation was examined using a thermobalance at various carbon monoxide pressures, specifically, 50, 100 and 200 mmHg. The authors reported that the reaction rate curves show a parabolic behavior and that the process may be governed by the diffusion of carbon into CaO and vice versa, as well as by the diffusion of carbon monoxide through the product layer.

Brookes et al. [102] developed a model for the formation of CaC₂ in solid pellets of 2.22 cm diameter, using 3/1 mixtures of carbon and CaO between 1650 and 1720 °C and 50 mmHg. They

assumed that the heat transfer across a growing product layer controls the rate of movement of a reaction front through the solid pellet.

Müller completed a detailed study of the properties and reactions of CaO in burnt lime, including the diffusion of carbon into solid lime, as well as he included composite reactions of CaO and C in solid and liquid states [103,104,105].

El-Naas studied the kinetics using fine graphite and CaO powder ($<170\mu\text{m}$) in a semi-batch spout-fluid bed reactor with a DC plasma torch. The author suggested that chemical reaction is the controlling step with an apparent activation energy of 377 kJ mol^{-1} . [33,106].

Experiments conducted by Li et al. [107] using thermal gravimetric analysis (TGA) and mass spectrometry (MS) techniques addressed the reaction mechanisms of coke and CaO for CaC_2 production. Their results indicated that reaction of carbon with CaO has three stages. The first stage is the direct reaction of coke and lime to form CaC_2 , reaction (6), starting at 1460°C . The second stage is the reaction of CaC_2 with CaO, reaction (7), starting at 1520°C , observable only at the complete consumption of carbon. The third stage is the decomposition of CaC_2 into calcium and carbon, reaction (8), controlled by surface evaporation of Ca. The authors also propose a reaction behavior in the surface of coke and CaO particles which includes the three stages and the formation of the eutectic $\text{CaC}_2\text{--CaO}$. Finally, Li et al. [107] discuss the effect of different C/CaO feed ratios in the reaction behavior. They point out that, for instance, for a ratio of 3.6, the second stage disappears.

Additional work presented by Li et al. [27] focuses on the kinetic behavior of CaC_2 production derived from coke and CaO , including the effect of coke properties, such as crystalline structure and specific surface area, on the initial reaction temperature for CaC_2 production. The authors report a linear decrease in the dependence of the initial temperature with an increasing number of contact points between coke and CaO particles until the particle size is 0.06 mm, which corresponds to an initial temperature of 1440 °C. Furthermore, that mass transfer direction is mainly from CaO to coke, which suggests that a reduction in the coke particle size is more effective than a reduction in the CaO particle size when looking for a reduction of the initial reaction temperature.

Li et al. also suggest that the reaction proceeds in different ways for two different temperature ranges, i.e., [1550 to 1700 °C] and [1700 to 1750 °C], where the mass transfer of solid CaO toward solid coke is the rate-limiting step. There is an apparent activation energy of 456 kJ/mole in the first range and mass transfer of liquid CaO in the form of CaC_2 – CaO eutectics toward the solid coke in the second range, with a reduced apparent activation energy of 256 kJ/mole. The presence of the eutectic CaC_2 – CaO at 1700 °C was not proved but is supported by comparing the effect of a reduced activation energy found in similar systems and performing experiments where the reaction of large granular reactants was promoted by doping of fine reactants. These results

provide useful information for reactor design, especially concerning particle size and temperature ranges.

3.8. CaC₂: Kinetic Reaction Rate Models

A complete review of the kinetic reaction rate models is presented by Rowan et al. [108]. In their review, four previous reaction rate models for calcium carbide formation are explained. They also present an evaluation of these previous models and compare them with their proposed models, namely, their progress variable model (PVM) and their multistep reaction model (MRM).

From the four existing kinetic rate models for the formation of calcium carbide, the first three were predicted by considering the idea of a contracting reaction front that travels through the reacting solid whereas the fourth model was that of two reacting solids. This fourth model is based on three-dimensional diffusion of the solids. All these models are described in this section. They are also presented in greater detail by House [109]. Rowan et al. [108] also presents the comparison of these models with experimental data presented by Mu and Hard [34].

The first kinetic model for the formation of calcium carbide is based on a spherical geometry. In this model, the reaction front progresses from the surface to the center of the sphere and only along the radial direction. This model is known as the 1-D contraction model and is given by the expression:

$$1 - (1 - \alpha_r)^{2/3} = k_r t \quad (9)$$

in this expression, k_r is the reaction rate, t is time and α_r is the extent of reaction. In the case of CaC₂ formation the extent of reaction represents the fraction of CaO that is converted into CaC₂.

The second model is based on a long cylindrical solid geometry. In this model, it is assumed that the reaction does not take place on the small end surfaces but only on the long curved surfaces. Additionally, it is assumed that the reaction front progresses uniformly along the radial coordinate towards the axis of the cylinder. This model is also known as the contracting area model and is given by the following expression:

$$1 - (1 - \alpha_r)^{1/2} = k_r t \quad (10)$$

The third model is known as the contracting volume model. This model considers a more general case of a noncylindrical, nonspherical solid in which the reaction begins at each face of the solid surface and proceeds inward. This model is given by

$$1 - (1 - \alpha_r)^{1/3} = k_r t \quad (11)$$

The fourth and final existing reaction rate model is known as the two reacting solids model. This model is based upon the three-dimensional diffusion rate law. This model is typically used in cases where different solid particles are brought into contact with one another and heated in order to bring about a chemical reaction. This model is given by:

$$1 - (1 - \alpha_r)^{1/3} = k_r t \quad (12)$$

The two reacting solids model has been the typical approach to describe the kinetics of calcium carbide formation. In this model, Tagawa and Sugawara [101] assumed that k_r can be expressed as an Arrhenius rate expression having the following equation:

$$k_r = A \cdot \exp(-E_a / RT) \quad (13)$$

where A is a pre-exponential factor, E_a is the activation energy of the reaction, R is the universal gas constant, and T is the temperature at which the reaction is taking place. The values for the pre-exponential factor and the activation energy are provided by Rowan et al. [108]. However, it is important to mention that the Arrhenius rate expression is not commonly used to describe solid–solid reactions. Therefore, the value of k_r should be interpreted carefully.

From the previous four models, the two reacting solids model is the one that most accurately predicts the time-based reduction of CaO into CaC₂. Nonetheless, as pointed out by Rowan et al. [108], all the previous four models suffer from the same limitation in that they only allow for the reaction to proceed in a single direction, thus not allowing for reverse reactions to occur.

Rowan et al. [108] developed two new models for the reaction kinetics of CaC₂ from coal-derived coke and CaO that overcome the limitation of not allowing for reverse reactions to occur. The first of these new models is referred to as the progress variable model (PVM). The PVM utilizes equilibrium mass fraction data to determine the direction in which the reaction must proceed in order to reach a state of chemical equilibrium. The second model, known as the

multistep reaction model (MRM), entails modeling the kinetic rates of the CaC_2 formation and disassociation reactions.

In the progress variable model a progress variable is introduced for each of the chemical species included in the reaction. Each progress variable is defined as the ratio of the current specie mass fraction over the specie mass fraction in equilibrium conditions. Rowan et al. [108] developed this model based on the global reaction for calcium carbide, i.e., equation 6. In this formulation, the four progress variables can be expressed as:

$$\begin{aligned} X_{C(s)} &= \frac{m_{C(s)}}{m_{C(s)}^{ini}}, & X_{CaO(s)} &= \frac{m_{CaO(s)}}{m_{CaO(s)}^{ini}} \\ X_{CaC_2(s)} &= \frac{m_{CaC_2(s)}}{m_{CaC_2(s)}^{theor}}, & X_{CO(g)} &= \frac{m_{CO(g)}}{m_{CO(g)}^{theor}} \end{aligned} \quad (14)$$

where m_i and m_i^{ini} are the current and initial mass fractions of the i^{th} chemical species; and m_i^{theor} is the theoretical production or consumption of the species i , as determined from the chemical equilibrium conditions for a given reaction temperature. The progress variables lead to a system of equations that, for example, for CaO have the following form:

$$\frac{dX_{CaO(s)}}{dt} = -k_{f,1}^{eff} X_{C(s)} X_{CaO(s)} + k_{r,1}^{eff} X_{CaC_2(s)} X_{CO(g)} \quad (15)$$

where $k_{f,1}^{eff}$ and $k_{r,1}^{eff}$ are the effective chemical reaction rates in the forward and reverse directions.

Rowan et al. [108] solved this system of equations by utilizing a second order Runge–Kutta Method. In this model, the condition of chemical equilibrium is attained when the values of these progress variables approach a value of 1.0. This allows the reaction to proceed toward equilibrium in either the forward or reverse directions.

In the MRM model, the formation of calcium carbide and its subsequent disassociation into solid carbon and gaseous calcium (equations 6 and 7) are combined into a single differential equation of the form:

$$\frac{dn_i}{dt} = \nu(i,1)(k_{f1}n_Cn_{CaO} - k_{r1}n_{CaC2}n_{CO}) + \nu(i,2)(k_{f2}n_{CaC2} - k_{r2}n_Cn_{Ca}) \quad (16)$$

In this expression n denotes the number of moles of the i^{th} species, the forward and reverse reaction rates are k_{f1} , k_{r1} , k_{f2} and k_{r2} , and $\nu(i)$'s are the stoichiometric coefficients. Rowan et al. [108] also solved this equation by using a second order Runge–Kutta method. In their solution process the number of moles of each species present is updated at each time step. This allows the prediction of the instantaneous number of moles of each species present as a function of time. They also assumed that weight loss is caused by the release of gaseous calcium and carbon monoxide. This fact enables the prediction of weight loss as a function of time.

Chapter 4 – Description of the System

Different designs of oxy-coal reactor are being developed by CERC-ACTC in the U.S. and China. Those designs can be divided into two main categories according to their configuration: down-fired and horizontal.

The down-fired design is being developed at West Virginia University. This design has being named ‘very high temperature entrained flow reactor’ (VHTER). The horizontal design is being developed by LP Amina. Due to the disclosure agreement between LP Amina and West Virginia University, the results for the horizontal reactor will not be included in this document, although general description of the reactor is provided in section 4.2.

4.1 Down-Fired Reactor (VHTER)

The main design characteristics of this type of reactor are shown in Figure 4-1. The reactor is divided into several sections, each of which has several insulation layers and ports. The modular design allows the replacement of reactor lining section with significant erosion and/or thermal damage. The combustion chamber diameter is 150 mm, and the burner is composed of two concentric ports. The first port is for injection of pulverized coal by means of oxidant gas as carrier. The main amount of oxidant is injected through a second port, which is swirled with a fin angle of 45° in order to provide a swirling flame stabilization mechanism. The burner is designed

with a divergent zone and a step at the entrance of the combustion chamber diameter in order to enhance the recirculation of hot gases and further increase the flame stabilization²³ (Figure 4-2).

For injection of the chemical reactants, i.e., CaO and char, two tangential ports are provided. The tangential oxidant injection improves the flame stability via an increased swirl flow condition; it also increases the particle residence time, as well as forces the reactants to reach the wall, increasing their deposition rate in the initial section of the combustion chamber, which is desirable for slag formation.

The collection of the molten slag containing chemical products, i.e., CaC_2 and unreacted lime and char, is achieved by means of an ash collection system located at the bottom of the combustion chamber. Currently, this design has been created to be used in a batch reactor mode, and requires periodic changes of ash collector systems. The ash collector stores the liquid slag, where some chemical reactions for CaC_2 formation may be still taking place. Furthermore, the ash collector has a flue gas cleaning role, since it traps most of the fly ash. The refractory wall of the ash collector is cooled down by a water jacket. This reactor design is intended to be a simple alternative regarding maintenance and operation.

23 The design of the combustion chamber is based on the furnace described in Nikzat et al. [136] for the reactor of the Aichi Science and Technology Foundation, Cooperation Research Center for Advanced Technology, Nagoya, Japan. The burner design is based on the one described in Costa et al. [138] for the reactor facility at the Imperial College, London.

Figure 4-1. Detailed view of the sections and components of the VHTER

Figure 4-2. VHTER: (a) Combustion chamber and (b) Burner region.

4.2. Horizontal Reactor (CTC Reactor)

The main characteristic of this reactor is its horizontal design, which enhances the release of by-product gases²⁴ produced in the slag by means of buoyancy effects. The cyclonic effect is obtained by the tangential injection of a combustible gas mixture through the port SA. This flow provides the swirling flame stabilization mechanism, convects the hot gases towards the wall and provides the centrifugal effect that forces the reactants to reach the wall, thus enhancing the particle wall deposition.

A significant difference of the horizontal reactor with respect to the down-fired design is that the slag is forced to flow predominantly along the bottom wall. Additionally, the residence time of the slag is higher, since the gravitational component along the slag flow direction is much smaller. Another difference is that this design is intended to work in a continuous flow operation mode. This makes this configuration more attractive for industrial production, in exchange of additional operation and maintenance complexities.

A typical cyclone reactor for coal combustion is presented in Baumestier, T. [110]. Figure 4-3 shows the reactor inside a red box as well as their injection ports. A premixer for oxidant and natural gas can be observed in the SA port. The cooling pipe is used for exhaust gas treatment.

²⁴ By product gases in the calcium carbide (CaC_2) reaction are carbon monoxide (CO) and calcium gas (Ca_g).

Figure 4-3. Diagram of the CTC system including the methane-oxidant premixer and exhaust gas cooling pipe.

The disposition of the PA and SA ports provide the cyclonic effect. The TA port is used for injection of oxygen; the PA port is used for injection of coal and chemical reactants. The oxidant injected through the SA port consists of air plus oxygen premixed with natural gas.

Chapter 5 – Combustion Modeling

The initial stage of the combustion modeling process involved a validation study, which was presented at the 2012 International Pittsburgh Coal Conference [111]. The validation study permitted to select the most suitable combination of models and sub-models to conduct oxy-coal combustion simulations. Selected results are presented in section 5.5.

All the simulations were performed in ANSYS Fluent. In general, the combustion process was modeled using the Eulerian-Lagrangian approach for the continuous and discrete phases, respectively. This approach includes models for turbulence, multiphase flow of gas and particles, combustion reactions of coal volatiles and char, radiation heat transfer²⁵, particle motion and dispersion, heat and mass exchange between the continuous and disperse phase, and particle wall interaction, among others. A more detailed description is provided below. A summary of the models utilized is presented in Table 5-1.

5.1 Continuous Phase Modeling

The Aerodynamics of the continuous media is determined by solving the Navier-Stokes equations using the RANS Approach. In the RANS approach, the Reynolds stresses are modeled by utilizing the standard k - ϵ model of Launder and Spalding [112]. This model is used for turbulence due to its robustness, economy and reasonable accuracy for a wide range of industrial

²⁵ Due to his complexity, the radiation heat transfer equation is solved separately from the energy equation but its effect is coupled as a source term.

applications. The modeling of turbulence close to the wall region is performed by using standard wall functions developed by Launder and Spalding [113] for near-wall treatment.

Combustion and species transport for the gas phase was modeled using the species transport model, where the mixing and transport of chemical species in the continuous phase is determined from the solution of transport equations by considering convection, diffusion and reaction sources. This equation is solved for the N-1 species fractions considered in the volumetric reactions. In this model, the net rate of production of all chemical species by chemical reactions as well as additional sources²⁶ are used. The diffusion flux of species due to gradients of temperature and concentration, as well as its improved mixing effect by turbulence is taken into account too. The thermal diffusion effect, i.e., Soret Effect, is neglected, since it is just relevant for light species such as H, H₂ or He at low temperatures [114]. The turbulent Schmidt number is calculated from the turbulent viscosity and the turbulent binary diffusivity.

In ANSYS Fluent, the transport energy equation is formulated in terms of the specific energy; it includes the contribution of conduction, convection and viscous dissipation, with effective thermal and diffusive properties modified by turbulent effects. The effects of combustion, radiation heat transfer, and additional sources are also included. The enthalpy is estimated from the summation of all species mass fractions. Values for thermochemical properties are taken from the NIST-JANAF Thermochemical Tables [115].

²⁶ Additional sources can be found in domain regions of combustion systems with sinks/ sources of species, such as in the selective catalytic reaction (SCR) process for NO_x control.

Fourth order temperature dependence in combustion makes the heat transfer a dominant mode due to thermal radiation. Therefore, it is highly important to calculate the radiant heat flux inside the combustion chamber accurately. This is achieved by solving the Radiative Transfer Equation (RTE) for a participating media in which the effect of absorption, emission and scattering is considered. This equation was solved using the P-1 radiation model and the discrete ordinates (OD) radiation model (Howell, Siegel, & Pinar [43]), which can account for the effect of radiation exchange between the gas and particle phases as well as for scattering²⁷. Both models were tested for oxy coal combustion in the exploratory study completed for this project [111].

In the simulations conducted in this study, both models provided similar predictions. Although the P-1 radiation model showed more stability, it was found that the Discrete Ordinates (OD) radiation model converged for a significantly smaller amount of iterations. Therefore, further simulations were developed using the P-1 radiation model at the initial stage of the solution process of the RTE due to its stability, followed by the DO model.

For turbulent-chemistry interaction, the net reaction rate is taken as the minimum of two limits. The first limit is reached when turbulent fluctuations can be ignored, and the reaction rates are determined by Arrhenius kinetic expressions. This limit is known as the laminar finite-rate model and is true for laminar flames but it is also applied to combustion with relatively slow chemistry and small turbulence-chemistry interaction.

In the laminar finite-rate model, the source term providing each of the species in the species transport equation is determined by the sum of the generation/consumption rate over all the

²⁷ Mie Scattering is especially significant in spray and pulverized coal combustion.

reactions in which such species participates. The reaction mechanism selected provides the number of chemical species in the system and the stoichiometric coefficients for reactants and products in each reaction. The molar rate of generation/consumption of species in each of the reaction is estimated from the molar concentration of each species and the forward and backward reaction rates for such a reaction. The forward rate constant for each reaction is obtained from the Arrhenius expression formulated in terms of the pre-exponential factor, the temperature exponent, and the activation energy. The backward rate constant is obtained from equilibrium considerations, with the equilibrium constant being computed from the Gibbs free energy, which is estimated from the standard-state entropy and the heat of formation for each of the species present in the reaction.

The second limit considers that most fuels are fast burning. i.e., the chemical time scale is much shorter than the turbulent mixing time scale. Therefore, the overall rate of the reaction is controlled by turbulent mixing. This limit is known as Eddy-dissipation model. In this model, the limiting process is the rate at which turbulence transports/mixes cold reactants and hot products, as in premixed flames or fuel and oxidizer, as in non-premixed flames. In this case, the turbulent-chemistry model of Magnussen & Hjertager [116] is utilized, and the chemical reaction rate is dominated by the large eddy mixing time scale.

5.2 Discrete Phase Modeling

The evolution of a coal particle in the combustion environment is described as follows: in the initial stage, a typical particle experiences the interchange of energy with the continuous phase without change of phase or interchange of mass. In this initial stage, the particle is heated until it

reaches the point at which any existing moisture starts to evaporate. This process continues as long as the particle temperature is lower than the evaporation temperature for the liquid phases contained in the particle. In this case, the energy balance for the particle is modeled as only accounting for convection and radiation interchange with the particle environment. Once the moisture evaporation stage starts, i.e., when the particle temperature surpasses the evaporation temperature, the latent heat energy is included in the particle energy balance. After all the moisture content is consumed, the particle temperature continues increasing until the devolatilization temperature is reached.

During the devolatilization stage, a typical coal particle releases its volatiles into the continuous phase. This process continues until all the volatiles are consumed. In this work, coal devolatilization is modeled using the single kinetic rate devolatilization model of Badzioch and Hawksley [117]. This model assumes that the rate of devolatilization is first-order dependent on the amount of volatiles remaining in the particle; it also assumes that the kinetic rate is defined by empirical Arrhenius type expressions requiring the specification of the pre-exponential factor and the activation energy for the coal being modeled.

The composition of volatiles depends on the composition and properties of the coal but also on the particle evolution during the combustion process, which means that it depends on the particle temperature history, heating rate, and combusting atmosphere. Different empirical models have been developed to tackle this problem, but their generalization entails practical limitations due to the diversity in composition found in coal from one area to another. Some examples are found in Matthesiu, et al. [118], and Suuberg, et al. [119].

Unlike a more empirical approach, the Chemical Percolation and Devolatilization model (CPD) [18,19,20] characterizes the devolatilization behavior of rapidly heated coal based on the physical and chemical transformations of the coal structure. Nonetheless, the CPD model is computational expensive and it relies on coal structure parameters that must be determined experimentally.

Therefore, a more practical approach is considered, where the volatiles are defined by the following two steps reaction mechanism. In this mechanism, the specie “volatiles” is a generic hydrocarbon obtained from the proximate and ultimate analysis of coal:

The particle diameter during devolatilization is tracked by solving the equation of its evolution, whose behavior is characterized by the swelling coefficient. The effect of particle swelling is reflected in the particle trajectory via the modification in the drag coefficient and, additionally, in the oxidation rate that follows the devolatilization process, where the particle diameter has a quadratic effect.

After devolatilization, the particle is assumed to be composed of carbon in the graphite phase and ash, i.e., char. Oxidation of char is specified in terms of the stoichiometric requirement of the surface “burnout” reaction, which is defined in terms of mass of oxidant per mass of char. The oxidant and product species for char oxidation were defined with the following simple approach:

Fluid-solid reaction models are related to the particle size and the ability of the fluid to diffuse into the solid particle. Regarding the particle size, it can be assumed that particle may either change in size or remain the same with a fixed diameter during the oxidation process. Furthermore, according to the mechanism that controls the reaction, it can be considered that: (i) oxidant diffusion through a gas film controls the reaction; (ii) diffusion through the ash formed controls the reaction; (iii) chemical kinetics controls the reaction.

A detailed review can be found in Levenspiel, O. [120]. In this research, the kinetics/diffusion-limited surface reaction model of Baum and Street [78] and Field [121] was selected to model the char oxidation process. Both effects are considered in this model, which means that the reaction rate is determined either by the diffusion rate of oxygen through the particle external surface, or by the effective char reactivity.

Regarding the devolatilization process, the kinetic rate during char oxidation is given by empirical Arrhenius type expressions requiring the specification of the pre-exponential factor and the activation energy. The energy balance accounts for the rate of heat release, which is estimated from the enthalpy of reaction, from the particle mass rate of change, and from a fraction of the energy released consumed by the particle itself. This fraction is 0.3 when the char burnout product is considered to be CO_2 [122]. After the carbon in the char is consumed by combustion, the particle is composed of ash. The ash particles continue the exchange of heat with its environment without any chemical reactions taking place.

During the particle evolution through the combustion process, the trajectory of particles is calculated by integrating the momentum balance equation for the particle. This equation accounts for the effect of the drag force. The drag force is calculated from the fluid flow velocity, the particle velocity, the molecular viscosity of the fluid, the fluid density, the particle density, the particle diameter, and the relative Reynolds number. The drag coefficient is calculated assuming the spherical drag law [123]. Additional forces arising from pressure or temperature gradients such as thermophoretic forces are taken into account as well.

The turbulent dispersion of particles was modeled using the Discrete Random Walk (DRW) model [124]. Initially, the particle-wall interaction was modeled as a non-elastic spherical collision with a restitution coefficient of 0.9; once the solution showed convergence, the condition was changed to particle trap via an UDF, in order to obtain the information required for the slag model. CaO particles are treated as non-reactive particles capable of absorbing energy without change of phase.

Table 5-1. Summary of the models utilized in the oxy-coal combustion simulations.

Gas Phase	Eulerian
Particle Phase	Lagrangian
Turbulence	Standard k- ϵ model with standard wall functions
Mixing and transport of chemical species	Species transport model
Species considered	Coal Volatiles, O ₂ , N ₂ , CO ₂ , H ₂ O, CO, SO ₂
Turbulence-chemistry interaction	Eddy break-up model
Volumetric reactions	Two-step reaction mechanism
Particle combustion	Global reaction
Particle size distribution	Constant diameter 50 microns for the VHTR and the 200 Reactor; Rosin Rammler distribution for the CTC Reactor.
Turbulent dispersion of particles	Random walk model

Coal devolatilization	Single kinetic rate devolatilization model
Char oxidation	kinetics/diffusion-limited surface reaction model
CaO particles	Treated as non-reactive particles with a constant diameter 50 microns
Particle-wall interaction	Non-elastic spherical collision (Initially) UDF (for wall deposition)
Radiation heat transfer	Discrete Ordinates

5.3 Domain Discretization and Boundary Conditions

Governing equations for turbulent flow, combustion, heat and mass transfer for the continuous and discrete phase were solved using the finite volume method in structure grid systems. Although most of the simulations for the VHTR were conducted in 2D axisymmetric domains due to its symmetry, some were conducted in 3D domains. All the simulations for the horizontal reactor were done in 3D domains, due to the asymmetry brought about by the disposition of the injection ports. Grids were refined towards the center, inlet ports, and walls. Some examples are shown in Figure 5-1 and Figure 5-2. The premixer section in the horizontal reactor is not included in the model, but the assumption of a completely premixed combustion mixture was considered instead.

Regarding the down-fired design, the boundary conditions for the primary and secondary ports were set as inlet flow conditions. For the secondary port, a swirling flow component was given in order to model the 45° fins swirler. Furthermore, a tangential velocity component is set in order to model the flow conditions imposed by the tangential injection ports for chemical reactants. For the horizontal design, internal burner details are included to model the flame stabilization mechanism by swirling flow motion.

In the preliminary study, the walls were modeled assuming a constant heat transfer loss. The heat loss was considered to be 25 percent of the power plus an additional estimation for the chemical reaction of CaC_2 . This strategy was refined in the final stage, where the thin shell model available in ANSYS Fluent was utilized, along with the energy consumption from the CaC_2 reaction²⁸ estimated from the SFM. A constant emissivity of 0.8 was used to account for the presence of slag²⁹.

At the beginning of the simulation process, the particle-wall interaction was modeled as a non-elastic spherical collision with a restitution coefficient of 0.9, as recommended by Abbas et al. [62]. Once a stable combustion was attained, the particle-wall interaction was modeled as a trap condition, which is a good assumption for walls covered by molten ash [16]. The outlet condition is set as pressure outlet with standard pressure and back flow temperature close to the average outlet temperature.

The domain for the ash collector along with its cooling system is shown in Figure 5-1c. The inlet flow conditions were taken from the 2D axisymmetric model, i.e., the velocities and gas composition of the continuous phase, and the amount of particles, which are mainly fly ash and some small percentage of unburnt carbon. The top wall is set as adiabatic, and the vertical and bottom wall are considered to be at 773 K. This constant temperature condition was also utilized

28 The strategy to model the heat transfer through the wall is broader explained in chapter 7.

29 As pointed out by Mills [83], and Mills and Rhine [98], an emissivity value of 0.8 ± 0.1 can be adopted for coal and metallurgical slags in the range (1100 to 1900 K).

for the inner wall of the cooling jacket. Apart from the constant temperature condition, a constant heat transfer rate was set for the cooling modeling.

Regarding the particles, coal and CaO particles were modeled with a constant 50 microns diameter for the VHTR, since no information about the particle size distribution was available. For the horizontal reactor, the Rosin-Rammler distribution method for pulverized coal particles [125] was utilized, since the particle size distribution was provided by LP Amina. A 50 microns diameter was also used for CaO particles in the horizontal reactor.

Figure 5-1. Example of the computational domains utilized in the modeling of the VHTR.

Figure 5-2. Example of the computational domains utilized for the horizontal reactor modeling.

5.4. Solution Method for CFD Combustion

The SIMPLE scheme [41] was used for pressure-velocity coupling in conjunction with the PRESTO scheme [126] for pressure interpolation, as is recommended for strong swirling flows [127]. Turbulent flow, transport of species, and radiative heat transfer equations were solved using the first order upwind scheme [41]. Normalized residuals were set to values smaller than $1e-06$, and the energy balance was checked as recommended by ANSYS Fluent [127].

5.5. Validation Study for CFD Oxy-Coal Combustion

The validation of the CFD oxy-coal combustion models involved the study of an oxy-coal combustion process for pulverized lignite coal under an O_2/CO_2 oxidizing atmosphere, with an

oxygen molar fraction of 0.25. The simulations were based on the experimental work performed by Andersson [128] and Hjærtstam et al. [63].

The furnace modeled in this study was a 100 kW test unit located at Chalmers University of Technology. This combustor is a down-fired unit and has a cylindrical refractory-lined furnace with a height of 2.4 m and an inner diameter of 0.8 m (Figure 5-3). The combustion chamber is cooled by four water cooled tubes. The burner configuration has three concentrically separate lances. The central one (34 mm dia.) is used to feed the fuel, which is a mixture of carrier gas (air or O₂/CO₂) and pulverized coal. The primary (52 mm dia.) and secondary (92 mm dia.) registers are used to inject the oxidizer (air or O₂/CO₂). The primary and secondary registers have swirling fins oriented 45° and 15° respectively. The gas flow inlet conditions are shown in Table 5-2. The pulverized coal was injected at a mass flow rate of 3.64 e-03 kg/s. The coal utilized was German lignite. Table 5-3 shows the properties of this type of coal.

Figure 5-3. Chalmers 100 kW Combustor Unit. (Andersson [128])

Table 5-2. Flow inlet conditions for utilized in the validation study for oxy-coal combustion.

Streams	Fuel carrier gas	Primary inlet	Secondary inlet
Mass flow rate (kg/s)	1.09 e-03	1.33e-02	3.1e-02
O ₂ molar fraction	0.3	0.25	0.25
CO ₂ molar fraction	0.68	0.72	0.72
Temperature (K)	298	298	298

Table 5-3. German lignite properties.

Proximate analysis (wt% as received)			VM (%d.a.f)	Ultimate analysis (wt% d.a.f.)					LHV
Moisture	Ash	combustibles	59.4	C	H	N	S	O	(MJ/kg)
10.2	5.0	84.8		69.9	5.4	0.6	1.0	23.1	20.9

The simulations were performed using the models described in section 5.1 and 5.2. The physical parameters, such as coal size, emissivity and reaction rates, were taken from Al-Abbas et al. [62]³⁰.

Regarding the boundary conditions, different approaches were used to model the swirling fins in the primary and the secondary registers by, for instance, prescribing velocity profiles for the axial and tangential (swirl) velocity components, or by providing a solid body rotation boundary condition to describe the swirl profiles. Nonetheless, good agreement was obtained by simply prescribing constant velocity profiles with the fin angle directions. For the outlet, the usual outlet pressure boundary condition was used. The walls were modeled as constant temperature boundaries, and the emissivity values for the particles and the furnace walls were taken as 0.7 and 0.52, respectively, as suggested by Al-Abbas et al. (2011).

The simulations were performed in 2D and 3D computational domains. All the meshes were built with the furnace length, i.e., 2.4 m, and the diameter, i.e., 0.8 m. A symmetry condition was assumed in the 2D models. Examples of these domains can be observed in Figures 5-4 and 5-5.

³⁰ Al-Abbas et al. [62] also performed CFD simulations of the experimental work performed by Andersson [128] and Hjærtstam et al. [63].

Figure 5-4 . 2D Grid and boundary conditions.

Figure 5-5. (a) 3D grid (b) Closer view at the inlet region.

The results of the validation study showed that it is possible to obtain good predictions by utilizing 2D domains. Figure 5-6 shows the comparison between the experiments performed by Andersson [128], and CFD oxy-coal combustion simulations performed by the Gutierrez et al. [111] in a 2D axisymmetric domain. It can be observed that the temperatures seem to be in reasonable agreement with the experiments.

Figure 5-6. Contours and Iso-lines of temperature for (a) experiments performed by Andersson [128] and (b) CFD simulations performed by Gutierrez et al. [111].

Another comparison is shown in Figure 5-7, specifically, the comparison of CFD simulation results for the radial temperature profiles at three different port locations. The radial temperature profiles are reported in the experiments of Andersson [128]. The ports are located in the early development region of the flame. The first port is located at an axial distance of 0.215 m from the top ceiling; the second port is at a distance of 0.384 m; and the third port is located at a distance of 0.553 m. The comparison also includes the CFD simulation results reported by Al-Abbas et al. [62]. It is shown that the temperature profiles over all conform to measurements, albeit a closure look indicates differences among various investigations, as should be expected.

(a)

(b)

(c)

Figure 5-7. Comparison of temperature profiles against experiments and previous published results. (a) port 1 ($x = 0.215\text{m}$), (b) port 2 ($x = 0.384\text{m}$), (c) port 3 ($x = 0.553\text{m}$).

Chapter 6 – Slag Flow Modeling

In the model presented in this work, unsteady-state transport equations for mass, energy and species concentration were formulated in a one dimensional control volume. This was done following an integral approach, similar to that used in the boundary layer theory, where a suitable velocity profile is required. This velocity profile is derived from the solution of the momentum equation in the slag flow direction, after a simplification of such equation by conducting an order of magnitude analysis (OMA).

The boundary conditions and the particle deposition rates at the interface between the molten slag and the gaseous atmosphere of the reactor are provided by CFD results of simulations conducted in the reactor design process. Reactor dimensions and insulation materials are also included in the formulation. The source terms for the species transport equation are provided by the CaC_2 reaction and kinetics model described in Rowan et al. [108]. The formulation process leads to a set of unsteady state partial differential equations that are solved by numerical techniques. The slag model formulation and the sub-models utilized in its development are explained below in greater detail.

6.1 Conservation of Mass

Figure 6-1 shows a pictorial representation of the system. The control volume enclosed by dashed lines represents a one dimensional cell of the liquid slag layer. The size of the liquid cell

is considered to be time dependent. It is assumed that the mass flux into the slag flow direction, i.e., through the west and east faces, is due to convection only³¹.

Figure 6-1. Pictorial of the slag flow system.

³¹ The mass diffusivity of various cations and anionic species in typical silicate melts is in the order of 10^{-12} m²/s [141]. Therefore, the calculated Peclet number for mass diffusivity of these species in the slag flow direction was estimated to be in the order of 10^7 for this application. Furthermore, the Peclet number for thermal diffusivity was estimated to be in the order of 10^2 .

The north face of the cell corresponds to the moving interface between the molten slag and the gaseous atmosphere of the reactor. The south face corresponds to the interface between the liquid and molten slag. It is assumed that this interface is defined by the critical viscosity temperature.

The general expression for the conservation of mass in the control volume of Figure 6-1 can be stated as:

$$\frac{\partial}{\partial t}[m]_{cv} = \dot{m}_w - \dot{m}_e + \dot{m}_n - \dot{m}_s \quad (20)$$

The first term on the left hand side corresponds to the rate of change of the liquid mass. After special integration in the control volume, the rate of mass change inside the control volume per unit depth can be expressed as:

$$\frac{\partial}{\partial t}[m]_{cv} = \frac{\partial}{\partial t}[\rho_l \cdot \delta_l \cdot \Delta x] \quad (21)$$

The mass flow rate along the slag flow direction, e.g., for the west face, can be expressed as:

$$\dot{m}_w = [\rho_l \cdot u_{ave} \cdot \delta_l]_w \quad (22)$$

The velocity profile required to obtain the average velocity is obtained from the momentum equation. The total mass flux through the north face is given by the total particle deposition and

by-product gases of the chemical reaction such as CO and Ca_(g)³², which are released through the surface of the slag. This can be expressed as:

$$\dot{m}_n = \dot{m}_C + \dot{m}_{Ash} + \dot{m}_{CaO} - \dot{m}_{CO} \quad (23)$$

The total mass flux through the south face is given by the rate of solidification or melting at the liquid-solid slag interface. This amount is determined by using the Stefan's model [129].

Under the previous assumptions, the conservation of mass for the control volume can be expressed as:

$$\frac{\partial}{\partial t} [\rho_l \cdot \delta_l \cdot \Delta x] = [\rho_l \cdot u_{ave} \cdot \delta_l]_w - [\rho_l \cdot u_{ave} \cdot \delta_l]_e + \dot{m}_n - \dot{m}_s \quad (24)$$

6.2 Velocity Profile

The expression for the velocity profile was developed considering the main forces found in the slag flow. This was accomplished by conducting an OMA for each of the terms in the momentum equation along the slag flow direction. The general expression for the conservation of momentum in the slag flow direction can be written as:

³² However, calcium is not formed as by-product gas under the assumed chemical reaction mechanism.

$$\frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} = -\frac{1}{\rho} \frac{\partial P}{\partial x} + g_x + \frac{\partial}{\partial x} \left(\nu \frac{\partial u}{\partial x} \right) + \frac{\partial}{\partial y} \left(\nu \frac{\partial u}{\partial y} \right) \quad (25)$$

The OMA of each term is estimated according to the order of magnitude of the slag properties, the thicknesses and velocity values common to molten slag flows, and typical reactor dimensions. Table 6-1 depicts typical values for slag properties. Table 6-2 shows the order of magnitude of each term in the momentum equation.

Table 6-1. Physical properties of coal slag. Yong et al. [69].

Slag Properties	Range
Temperature of critical viscosity, T_{cv} (K)	1580-1780
Viscosity, μ (Pa s)	6.2-334.5
Density, ρ (kg/m ³)	2779.9-2887.9
Specific heat, C_p (kJ/kg K)	1.3825
Thermal conductivity, k_l (W/mK)	1.73-1.80

Table 6-2. Order of magnitude of the terms in the momentum equation.

Term	Scale as:	Order of Magnitude
$u \frac{\partial u}{\partial x}$	$\frac{U^2}{L}$	$O(10^{-6})$
$v \frac{\partial u}{\partial y}$	$V \frac{U}{\delta}$	$O(10^{-6})$
$\nu \frac{\partial^2 u}{\partial x^2}$	$\nu \frac{U}{L^2}$	$O(10^{-4})$
$\nu \frac{\partial^2 u}{\partial y^2}$	$\nu \frac{U}{\delta^2}$	$O(10^2)$

$\frac{1}{\rho} \frac{\partial P}{\partial x}$	$\frac{\Delta P}{\rho L}$	$O(10^{-2})$
$\frac{\partial u}{\partial t}$	$\frac{\Delta U}{t_{ss}}$	$O(10^{-6})$
g_x	g	$O(10)$

After the simplification, the following expression for the momentum equation in the slag flow direction x is stated:

$$0 = g_x + \nu \frac{\partial^2 u}{\partial y^2} \quad (26)$$

The previous expression is subjected to the non-slip condition at the wall and to the assumption that the shear stress is the same for the gas and the liquid at their interface:

$$u(0) = 0 \quad (27)$$

$$\tau(\delta) = \tau_{gl} \quad (28)$$

Where $\tau_{gl}(x)$ is modeled as being equal to $\tau_w(x)$, which is obtained from the CFD combustion model of the reactor. The velocity profile is given by the solution of this second order ODE and it can be expressed in dimensionless form as:

$$u^+ = \alpha[2\eta - \eta^2] + \beta\eta \quad (29)$$

Where:

$$u^+ = \frac{u}{u_\tau} \quad (30)$$

$$u_{\tau} = \left[\frac{\tau_{gl}}{\rho} \right]^{1/2} \quad (31)$$

$$\alpha = \frac{\rho g_x}{2\mu \cdot u_{\tau}} \delta_l^2 \quad (32)$$

$$\beta = \left[\frac{\tau_{gl}}{\mu \cdot u_{\tau}} \right] \delta_l \quad (33)$$

$$\eta = \frac{y}{\delta_l} \quad (34)$$

Utilizing this profile, the mass flow through a particular face normal to the slag flow direction can be expressed as:

$$\int_{\delta_s}^{\delta_l} \rho u dy = \rho u_{\tau} \delta_l \int_0^1 u^+ d\eta = \rho u_{\tau} \delta_l \left[\frac{2}{3} \alpha + \frac{1}{2} \beta \right] \quad (35)$$

And the average velocity can be determined from:

$$u_{ave} = \frac{1}{\delta_l} \int_{\delta_s}^{\delta_l} u dy = u_{\tau} \left[\frac{2}{3} \alpha + \frac{1}{2} \beta \right] \quad (36)$$

6.3 Liquid Layer Thickness Equation

Using the previous results, and after spatial integration and implicit integration in time, the expression for the conservation of mass can be written as:

$$\frac{[\rho\delta_l\Delta x]_p - [\rho\delta_l\Delta x]_p^o}{\Delta t} = [\rho u_{ave}\delta_l]_w^o - [\rho u_{ave}\delta_l]_e^o + [\dot{m}_n]^o \Delta x - [\dot{m}_s]^o \Delta x \quad (37)$$

For numerical solution purposes, this expression can be written in terms of the liquid boundary layer thickness as:

$$[\delta_l]_p = a_w^o [\delta_l]_w^o - a_e^o [\delta_l]_e^o + S_p^o \quad (38)$$

Where:

$$a_w^o = [u_{ave}]_w^o \frac{\Delta t}{\Delta x} \quad (39)$$

$$a_e^o = [u_{ave}]_e^o \frac{\Delta t}{\Delta x} \quad (40)$$

$$S_p^o = [\delta_l]_p^o + [\dot{m}_n]^o \frac{\Delta t}{\rho} - [\dot{m}_s]^o \frac{\Delta t}{\rho} \quad (41)$$

6.4 Conservation of Energy

The energy balance for the control volume of a molten slag cell can be expressed as:

$$\frac{\partial}{\partial t} [E]_{cv} = \dot{E}_w - \dot{E}_e + \dot{E}_n - \dot{E}_s + [\dot{E}_g]_{cv} \quad (42)$$

In order to determine the contribution of each term on (42), an OAM is conducted in an alternative form of the energy equation, namely, the energy equation for incompressible flow in terms of temperature, i.e., (43). The OMA is summarized in Table 6-3.³³

$$\frac{\partial}{\partial t}(\rho c_p T) = - \left[\frac{\partial}{\partial x}(\rho c_p u T) + \frac{\partial}{\partial y}(\rho c_p v T) \right] + \left[\frac{\partial}{\partial x} \left(k \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y} \left(k \frac{\partial T}{\partial y} \right) \right] + \mu \phi + \dot{H}_R + \dot{H}_{ls} \quad (43)$$

Table 6-3. Order of magnitude of the terms in the temperature energy equation.

Term	Scale as	Order of Magnitude
$\frac{\partial}{\partial x}(\rho c_p u T)$	$\frac{\rho c_p u \Delta T}{L}$	$O(10^4)$
$\frac{\partial}{\partial y}(\rho c_p v T)$	$\frac{\rho c_p v \Delta T}{\delta}$	$O(10^4)$
$\frac{\partial}{\partial x} \left(k \frac{\partial T}{\partial x} \right)$	$\frac{k \Delta T}{L^2}$	$O(1)$
$\frac{\partial}{\partial y} \left(k \frac{\partial T}{\partial y} \right)$	$\frac{k \Delta T}{\delta^2}$	$O(10^6)$
$\mu \phi = \mu \left[\frac{\partial u}{\partial y} \right]^2$	$\mu \left(\frac{U}{\delta} \right)^2$	$O(10^2)$

Neglecting the contribution of the smallest order terms, the energy equation for the slag flow model can be written as:

$$\frac{\partial}{\partial t}(\rho c_p T) = - \left[\frac{\partial}{\partial x}(\rho c_p u T) + \frac{\partial}{\partial y}(\rho c_p v T) \right] + \frac{\partial}{\partial y} \left(k \frac{\partial T}{\partial y} \right) + \dot{H}_R + \dot{H}_{ls} \quad (44)$$

³³ An alternative procedure to the OMA is show in Appendix C. In this alternative procedure the OMA for the energy equation is expressed in terms of the Peclet and Brinkman numbers.

After spatial integration and implicit integration in time, this expression can be written in terms of the slag bulk temperature T_m as:

$$\frac{[\rho c_p T_m \delta_l]_p - [\rho c_p T_m \delta_l]_p^o}{\Delta t} \Delta x = [\rho c_p u_{ave} T_m \delta_l]_w^o - [\rho c_p u_{ave} T_m \delta_l]_e^o + \dot{q}_n \Delta x - \dot{q}_s \Delta x + \sum_j (\dot{m}_p c_p T_p)_j + \dot{H}_R + \dot{H}_{ls} \quad (45)$$

For numerical solution purposes, this expression is written in terms of the slag bulk temperature as:

$$a_p [T_m]_p = F_w^o [T_m]_w^o - F_e^o [T_m]_e^o + S^o \quad (46)$$

Where:

$$a_p = [\rho c_p T_m]_p \quad (47)$$

$$F_w^o = [\rho c_p u_{ave} \delta_l]_w^o \frac{\Delta t}{\Delta x} \quad (48)$$

$$F_e^o = [\rho c_p u_{ave} \delta_l]_e^o \frac{\Delta t}{\Delta x} \quad (49)$$

$$S^o = \dot{q}_n \Delta x - \dot{q}_s \Delta x + \sum_j (\dot{m}_p c_p T_p)_j + \dot{H}_R + \dot{H}_{ls} \quad (50)$$

6.5 Species Transport Equation

The general expression for the species mass transport equation is expressed as:

$$\frac{\partial(\rho y_k)}{\partial t} + \frac{\partial(\rho u y_k)}{\partial x} = \frac{\partial}{\partial x} \left(\rho D_k \frac{\partial y_k}{\partial x} \right) + \dot{m}_n y_k - \dot{m}_s y_k + \dot{\omega}_k \quad (51)$$

Following the same integration procedure in the control volume, the species transport equation can be written for solution purposes in terms of the mass fraction of a particular specie as:

$$\begin{aligned} [\rho y_k \delta_l]_p = [y_k \delta_l u_{ave}]_w^o \frac{\Delta t}{\Delta x} - [y_k \delta_l u_{ave}]_e^o \frac{\Delta t}{\Delta x} + \\ [\dot{m}_n y_k]_p^o \Delta t - [\dot{m}_s y_k]_p^o \Delta t + [\rho y_k \delta_l]_p^o + [\dot{\omega}_k \delta_l]_p^o \Delta t \end{aligned} \quad (52)$$

Where, taking into consideration the value for the Peclet number of mass diffusivity, the diffusion term in the slag flow direction has been neglected.

The solution of the species transport equation allows estimating the species balance once some properties and variables are known at the previous time step, as, for instance, slag thickness, average velocity, and the source term for the chemical reaction of CaC_2 .

6.6 Chemical Kinetics and Reaction

Rowan et al. [108] conducted comparisons between their model predictions and experimental data found in literature for reactant consumption, CaC_2 production and weight loss. The authors showed that the second model that they developed, namely the MRM model, provides accurate predictions. Therefore, the MRM was selected as the chemical kinetics model aimed at estimating the source term in the species transport equation. Nonetheless, a simplification was

included. The simplification entailed assuming only the first reaction of their proposed mechanism.

6.7 Solidification-Melting

Two solidification mechanisms are considered in the slag flow model. The first one is the solidification that takes place inside the control volume, from which solids can be transported by the flow; the second is the solidification/melting at the solid-liquid interface. The models to account for both of these processes are discussed next.

6.7.1 Solidification sub-model for CaO and CaC₂ transported in the slag

The amount of solidified material that can be transported by the slag is considered to be a fraction λ_{ls} of the value provided by the solid-liquid equilibrium phase diagram for CaO-CaC₂.

$$x_s = \lambda_{ls} x_{se} \quad (53)$$

λ_{ls} can be considered as a progress variable that depends on the sub cooling temperature. This progress variable is modeled as:

$$\lambda_{ls} = 1 - \exp(-a_{ls} \cdot (T_{eut} - T_m)) \quad (54)$$

Where a_{ls} is a relaxation parameter.

The equilibrium diagram is shown in Figure 6-2. It can be found in the reference [130].

Figure 6-2. Solid-liquid equilibrium phase diagram for CaO-CaC₂. Taken from [130]

At this point, it should be stated that the MRM for the chemical kinetics of CaC₂ has been developed based on solid-solid reactions. Nonetheless, since a higher contact area will be brought about by the liquid, the rate of reaction will be likely to increase. In order to account for this effect, a simple model is proposed in this work. In this model, the forward and backward rate coefficients of the reaction are calculated based on a weighted average of the relative solid and liquid amounts of CaO and CaC₂. This relation can be expressed as:

$$k_f = (1 - \varepsilon_f)k_{f-l} + \varepsilon_f k_{f-s} \quad (55)$$

$$k_B = (1 - \varepsilon_B)k_{B-l} + \varepsilon_B k_{B-s} \quad (56)$$

Where the relative solid and liquid amounts of CaO and CaC₂ are expressed as:

$$\mathcal{E}_f = \frac{x_{CaO(s)}}{x_{CaO(s)} + x_{CaO(l)}} \quad (57)$$

$$\mathcal{E}_B = \frac{x_{CaC_2(s)}}{x_{CaC_2(s)} + x_{CaC_2(l)}} \quad (58)$$

And the forward and backward rate coefficients for the liquid are assumed to be multiples of the rate coefficients based on solid-solid reactions:

$$k_{f-l} = \lambda_{k-f} \cdot k_{f-s} \quad (59)$$

$$k_{B-l} = \lambda_{k-B} \cdot k_{B-s} \quad (60)$$

This simple approach allows estimating the effect a higher contact area on the rate of CaC₂ formation in terms of the parameters λ_{k-f} and λ_{k-B} .

6.7.2 Solidification sub-model for the solidified slag layer

The rate of growth or decrease of the solidified slag layer is modeled by applying the Stefan's condition [129]. This condition states that such growth or decrease depends on the difference in the amount of heat transfer to the liquid-solid interface, as shown in Figure 6-3. This condition can be expressed as:

$$k_s \frac{\partial T_s}{\partial y} \Big|_{y=\delta_s} - k_l \frac{\partial T_l}{\partial y} \Big|_{y=\delta_{ls}+\delta_s} = \rho H_f \frac{d\delta_{ls}}{dt} \quad (61)$$

Figure 6-3. Heat transfer at the solid/liquid interface

Where:

$-k_l \frac{\partial T_l}{\partial y} \Big|_{y=\delta_{ls}+\delta_s}$ is the heat transfer from the liquid to the solid-liquid interface.

$-k_s \frac{\partial T_s}{\partial y} \Big|_{y=\delta_s}$ is the heat transfer from the solid-liquid interface to the solid.

Assuming a linear temperature profile through the solid, the rate of growth or decrease of the solidified slag layer can be expressed as a function of the total thermal resistance of the solid slag and the furnace insulation materials:

$$\frac{d\delta_{ls}}{dt} = \frac{1}{\rho H_f} \left[-k_l \frac{\partial T_l}{\partial y} \Big|_{y=\delta_{ls}+\delta_s} - \frac{(T_{cv} - T_{env})}{R_t} \right] \quad (62)$$

Where $R_t = \frac{\delta_s}{k_s} + R_{ins} + \frac{1}{h_{env}}$ is the total resistance of the solid slag, insulation and the environment.

6.8 Release Model for Carbon Monoxide from the Slag

The gaseous product CO formed in the reaction is assumed to be released at the surface of the control volume, i.e., through the north face. The rate at which the CO is released is assumed to be proportional to the difference between the CO concentration in the slag and the gaseous atmosphere of the reactor in the proximity of the liquid slag layer. This can be expressed as:

$$[\dot{m}_{co}]_n = h_{mCO} \cdot \Delta x \cdot ([y_{co}]_l - [y_{co}]_\infty) \quad (63)$$

Where h_{mCO} is the CO release coefficient. This coefficient should be estimated experimentally for the slag system in this work, where the experimental value provided by Solar and Guthrie [131] in a metallurgical application has been used.

6.9 Modeling of Slag Properties

The slag properties were modeled considering the facts included in section 3.6. The models were selected to provide reliable property values at a reasonable computational cost. As was pointed out in section 3.6, viscosity is perhaps the property most related to the control and design of the process. Unfortunately, currently, there is no viscosity model available for the slag system or the temperatures involved in this application.

Figure 6-4 shows the comparison between three of the viscosity models discussed in section 3.6, namely the model of Urbain [84], the BCURA S^2 model [88], and the model of Kalmanovitch and Frank [86] (modified Urbain model). The predictions for the slag were plotted from the coal used in the design of the oxy-coal reactors developed in this work (Decker coal). Figure 6-4 (a) shows the viscosity predictions inside the temperature range of applicability for the three viscosity models, i.e., for temperatures ranging from the critical viscosity temperature up to temperatures close to 1770 K. Figure 6-4 (b) depicts the predicted viscosity for extrapolation to the temperature range of this application. It can be observed that the Urbain model predicts higher viscosity values. Moreover, the predictions of the BCURA S^2 model and the modified Urbain are similar. These two models predicted viscosity values between 0.04 and 0.1 Pa s in the range of extrapolated temperature. In this work, the BCURA S^2 model [88] was selected to predict the viscosity of the slag. Nonetheless, it is emphasized that experimental measurements

and development of viscosity models appropriate for the slag system and the temperature range of this application must be developed.

Figure 6-4. a) Predicted viscosity by the models of Urbain, BCURA S^2 and modified Urbain inside their experimental temperature range. b) Extrapolation to the temperature range of this application.

Regarding the temperature of critical viscosity, its value was estimated by using the method followed by Seggiani [132]. The estimated value for the critical viscosity temperature is close to 1485 K. The density was estimated as recommended by Mills [80], i.e., from the molar weighted average of the molar volume for every particular constituent present in the slag. As suggested by Mills [93], this same approach was used to model the heat capacity of the slag.

Regarding the thermal conductivity of the slag, it was mentioned in section 3.6 that the thermal conductivity of slag systems does not depend strongly on composition but on the structure of the slag. Nonetheless, the range of variation of the thermal conductivity is narrow, e.g., between 1.73 and 1.8 kW/m K, as reported by Yong et al. [69]. The constant value at the middle of this range was selected for the thermal conductivity.

Regarding the slag composition, only the main species were considered, which are C, CaO, CaC₂, CO, SiO₂, Al₂O₃ and Fe₂O₃. From those, the species contained in the ash were assumed as non-reacting species except for CaO. The information required for the calculations of the SFM, such as the thermo-physical properties of the slag constituents, ash composition, and reactor insulation materials, is reported in appendix B.

6.10 Solution Method for the Slag Model

The SFM transport equations were solved by using the upwind scheme for spatial integration and by using explicit integration in time. The domain was divided in 60 cells. This division provided a good compromise between accuracy and the computational time required to obtain a steady state solution. The time step was set to a value of 5 milliseconds. This value produced a conservative Courant number. The value for the courant number for a typical solution is plotted along the domain in Figure 6-5.

Figure 6-5. Courant number profile along the domain for a typical solution of the SFM (case OF35-02-B).

The steps of the solution algorithm can be summarized in the following sequence:

1. Specify parameters
 - a. Reactor dimensions.
 - b. Insulation materials.
 - c. Environment conditions.
 - d. Ash composition.
 - e. Cell size.
 - f. Solution time.
2. Specify boundary conditions in every i cell.
 - a. In the north face: gas temperature, gas velocity, shear stress, particle deposition
 - b. In the south face: critical viscosity temperature and total insulation resistance
3. Specify initial conditions in every i cell. Assume:
 - a. Solid and molten slag thicknesses.
 - b. Slag bulk temperature.
 - c. Slag average viscosity.
 - d. Initial composition.
4. Calculate liquid slag thickness in $t + dt$.
5. Calculate the velocity profile in the molten slag.
6. Calculate the source terms for the species transport equation from the chemical kinetics.
7. Solve the Species transport equation.
8. Calculate the source terms for the energy equation.
9. Solve the energy equation and calculate the bulk slag temperature.

10. Calculate the solid slag thickness in $t + dt$.
11. Update slag properties.
12. Go to step 4.
13. Finish if steady is reached.

The computational framework of the slag model is shown in Figure 6-6.

Figure 6-6. Computational framework of the slag model.

6.11. Verification of the Slag Model

Due to the lack of experimental results available for the slag system modeled in this research, a verification procedure was conducted to test the reliability of the SFM. The procedure involved the comparison of the solution provided by the slag flow model against the analytical solution for a natural convection boundary layer problem with solidification.

The problem is proposed by Bejan [133]. The author states that a vertical isothermal wall is put in contact with an isothermal pool of paraffin. Since the solidification point of the paraffin is between the wall temperature and the pool temperature, the wall becomes covered with a thin layer of solidified paraffin. The relevant properties of the paraffin are provided in the Table 6-4.

Table 6-4. Relevant properties for the natural convection boundary layer problem with solidification.

Property	Value
Thermal conductivity of the liquid paraffin, k_f	0.15 W/mK
Thermal conductivity of the solid paraffin, k_s	0.36 W/mK
Compressibility factor, β	8.5 e-04 K ⁻¹
Thermal diffusivity, α	9e-08 m ² /s
Prandtl number, Pr	55.9

The solution for the thickness of solidified paraffin is given by Bejan [133]:

$$\frac{\delta_s}{L} = \frac{k_s (T_m - T_w)}{k_f (T_\infty - T_m)} \frac{1}{0.487 Ra_L^{1/4}} \left(\frac{x}{L} \right)^{1/4} \quad (64)$$

Whereas the solution for the liquid layer thickness of the boundary layer is obtained from the integral approximate solution given by Burmeister [134]:

$$\delta_l = 4 \left(\frac{15}{16} \right)^{1/4} \frac{(1 + 20/21\text{Pr})^{1/4}}{[g\beta(T_w - T_g)\text{Pr}/\nu^2]^{1/4}} x^{1/4} \quad (65)$$

The mass flow rate deposition function along the slag flow direction, needed as an input in the SFM, was provided such that the integral of its distribution is equal to the analytical value of the mass flow rate given at that distance, x . This condition can be stated as:

$$\int_0^x \dot{m}' dx = [\rho u_{ave} \delta_l]_x \quad (66)$$

Figure 6-7 (a) shows the comparison of the liquid boundary layer thickness given by the SFM against the analytical solution given by Burmeister. It can be observed that the solution provided by the SFM matches the analytical solution.

Figure 6-7 (b) depicts the comparison of the solid layer thickness given by the slag flow model against the analytical solution given by Bejan. The solution provided by the SFM matches the order of magnitude of the analytical solution. This, taking into account that the solidification model utilized in the SFM is different than the one provided by Bejan.

In the solution provided by Bejan, the latent heat of fusion is not considered. Instead, the solidified thickness is obtained by estimating the heat transfer based on correlations for the Nusselt Number, which is a function of the Rayleigh number and the Prandtl Number.

In the SFM, the solidified slag thickness depends on the latent heat of fusion, which is a key parameter in solidification problems³⁴. As can be seen in Figure 6-7 (b), different values of the latent heat of fusion for the slag result in different solution profiles for the solidified thickness. Three different values of the latent heat of fusion were utilized, which correspond to actual values of paraffin waxes reported by Ukrainczyk et al. [135]. The selected values cover the range reported by the authors.

(a)

(b)

Figure 6-7. (a) Comparison of the liquid boundary layer thickness given by the SFM against the analytical solution. (b) Comparison of the solidified layer thickness given by the SFM against the analytical solution.

³⁴ See, for instance, the aforementioned problem of Stefan [129] and the problems found in Ozisik [140].

Chapter 7 – VHTER: Results and Discussion

7.1 VHTER: Exploratory Study

In the initial stage, a pilot study with a simplified model was conducted to analyze the down-fired design under oxy-coal conditions. Only the combustion process was studied with this simplified model. An additional simplification entailed considering only one meter length of the combustion chamber. At that point, no information regarding the type of coal to be used was known, so that the same coal used in the validation study [111], i.e. German lignite, was selected (Table 5-2). All the simulations were based on a power input of 100kW, which is equivalent to a mass flow rate of $4.78\text{e-}03$ kg/s of pulverized coal.

Two different oxidant mixtures were considered initially, including O_2 molar fractions of 0.25 and 0.50, with CO_2 as the balance gas. These cases were named OF25-E for 0.25 and OF50-E for 0.50. The heat losses through the wall were assumed to be 25 percent of the power input, which is similar to the reactor operation described in Nikzat et al. [136]. The mass flow rate of oxidant was calculated considering a fuel to oxidant stoichiometric ratio of 0.85. Approximately, 11 percent of the oxidant was injected through the primary port as carrier gas for pulverized coal, while the rest was injected through the secondary port. This value was established after different percentages were assessed in order to find a well-defined burner recirculation zone (BRZ). The oxidant mass flow rates are given in Table 7-1. Standard pressure and temperature conditions were assumed for the inlet gas and coal particles.

Table 7-1. Oxidant gas inlet conditions for the exploratory study.

CASE	Primary port		Secondary port	
	kg/s	T, K	kg/s	T, K
OF25-E	21.71	300	195.48	300
OF50-E	10.44	300	90.72	300

Figure 7-1 shows the flow pattern and temperature contours for the reacting flow of the OF25-E and OF50-E cases. A different location for the BRZ can be observed. As is depicted, the BRZ becomes narrower in the OF50 and is located downstream with respect to the OF25 case.

Figure 7-1. Velocity recirculation pattern and temperature contours in the BRZ for the OF25-E and OF50-E cases.

Figures 7-2 and 7-3 depict the temperature contours, mass fraction of volatiles, and the char burnout for the two cases. The figures show that the reactor temperatures reached values in the range of 1700 to 2000 K for the OF25 case, and 2400 to 3000 K for the OF50 case.

These contours indicate that maximum temperatures are obtained in the center of the chamber and become lower towards the wall, especially in the upper part of the chamber. This is convenient for protecting the wall from high temperatures in certain applications. However, it is not convenient for activating the formation of CaC_2 in the molten slag. This cold region towards the wall is relieved by the tangential flow injection of oxidant that works as carrier gas for feeding the coal and CaO particles.

Results for combustion of coal indicated that a complete coal devolatilization is attained for these conditions, as well as a char burnout of approximately 97 percent. An increase of the devolatilization and char burnout regions can be noted with an increase in the oxygen concentration.

Results for combustion of coal, obtained from the discrete phase model report for the OF50 case, are shown in Figure 7-4. The first arrow indicates the time spent in the combustion; the second arrow shows the mass release; the third arrow is related to the energy released by the discrete phase; the fourth arrow depicts the percentage of volatiles and char, highlighted in red, converted in the furnace; zone 20 refers to the outlet.

Figure 7-2. Contours of (a) Temperature (K), (b) Mass fraction of volatiles and (c) Char burnout (kg/s) for the OF25 case.

Figure 7-3. Contours of (a) Temperature (K), (b) Mass fraction of volatiles and (c) Char burnout (kg/s) for the OF50 case.

Arrow 1 →

Fate	Number	Elapsed Time (s)				Injection, Index			
		Min	Max	Avg	Std Dev	Min	Max		
Escaped - Zone 20	80	9.778e-02	3.619e-01	1.425e-01	4.498e-02	injection-0	72	injection-0	2
(*)- Mass Transfer Summary - (*)									
Fate	Mass Flow (kg/s)								
	Initial	Final	Change						
Escaped - Zone 20	4.780e-03	7.796e-04	-4.000e-03						
(*)- Energy Transfer Summary - (*)									
Fate	Heat Rate (W)		Change of Heat (W)						
	Initial	Final	Sensible	Latent	Reaction	Total			
Escaped - Zone 20	5.419e+04	3.846e+03	1.869e+03	-4.322e+01	-5.218e+04	-5.035e+04			
(*)- Combusting Particles - (*)									
Fate	Volatile Content (kg/s)			Char Content (kg/s)					
	Initial	Final	%Conv	Initial	Final	%Conv			
Escaped - Zone 20	2.409e-03	0.000e+00	100.00	1.644e-03	5.308e-05	96.77			

Arrow 2 →

Arrow 3 →

Arrow 4 →

Figure 7-4. Discrete phase particle (DPM) report for OF50 case (Conversion of coal is 97 percent, approximately)

The aforementioned pilot study made it possible, saving computational costs, to envisage the combustion performance in terms of combustion stability and coal conversion. The study also allowed a first glance at the temperature levels aimed at providing the required operation conditions for CaC_2 production.

The results showed that the desired conditions were obtained for oxidant mixtures with O_2 molar fractions close to 0.50. Therefore, the second stage of the exploratory study was conducted under these conditions. In this second stage, a more detailed computational model was built. This model is referred to as the OF50-E-02 case. In this model, further complexities, such as a length of 2 m for the combustion chamber, and the tangential injection of chemicals, were included. The heat losses through the wall were assumed to be 25 kW, plus an additional loss of 9.8 kW to

account for the energy consumed in the CaC_2 reaction. In this stage of the project, the type of coal was known; particularly, it was Decker's coal mine. The properties of this coal are shown in Table 7-2, and mass flow rates are depicted in Table 7-3.

Table 7-2 Decker coal properties.

Proximate analysis (wt.% as received)				Ultimate analysis (wt.% d.a.f.)					LHV
Moisture	Ash	Fixed carbon	Volatile Matter	C	H	N	S	O	(MJ/kg)
24.29	3.62	42.67	29.42	78.33	3.99	1.21	0.47	16.0	22.026

Table 7-3 Inlet mass flow rates of every reactant in kg/s through every injection port for the OF50-E-02 case.

Reactant	Primary	Secondary	Tangential
Oxidant	1.4e-03	1.62e-02	8.76e-04
Coal	4.54e-03	0	3.25e-03
CaO	0	0	2.16e-03

Figure 7-5 shows the temperature profiles for the OF50-E-02 case along with the radial distance in different axial locations and centerline. It can be noted that temperature is higher towards the wall when compared with the simplified model with no tangential flow of particle injection. This higher temperature near the wall is especially noticeable in the initial section of the combustion chamber and becomes nearly uniform after half of the combustion chamber length. Gas, particles, and wall temperature can be seen in Figure 7-6. It can be observed that all these values are within the range of temperature suggested by Li et al. [107] for CaC_2 formation, i.e., 1733 and 1973K.

Figures 7-6, 7-7 and 7-8 show the particle deposition and temperature in the wall location for each injection defined in the model, that is, coal for combustion, coal for the CaC_2 reaction, and CaO particles. These values are inputs required in the slag model. Results show that the primary coal mass deposited on the wall of the down-fired reactor is $1.68\text{e-}03 \text{ kg/m}^2\text{s}$. This value is equivalent to 34.9 percent of the total primary coal mass injected. For the tangentially injected coal, the mass deposited on the wall is $1.60\text{e-}03 \text{ kg/m}^2\text{s}$. This value is equivalent to a 46.5 percent of the total primary coal mass injected. For the tangentially injected CaO, the mass deposited on the wall is $4.27\text{e-}03 \text{ kg/m}^2\text{s}$. This value is equivalent to a 93.2 percent of the total primary CaO mass injected. Results for mass deposition are summarized in Table 7-4.

Figure 7-5. Temperature contours and profiles for the OF50E-02 case.

Figure 7-6. Particle deposition and temperature along the wall of coal injected through the primary port for the down-fired reactor (OF50-E-02 case).

Figure 7-7. Particle deposition and temperature along the wall of tangentially injected coal for the down-fired reactor (OF50 case).

Figure 7-8. Particle deposition and particle temperature along the wall of down-fired reactor for tangentially injected CaO (OF50-E-02 case).

Table 7-4 Particle wall deposition for each of the injections for the OF50-E-02 case.

Injection Type	Injected (kg/s)	Deposition (kg/s)	Deposition (kg/s m ²)	% of total injected
Primary coal	4.54e-03	1.58e-03	1.68e-03	34.9
Tangential coal	3.25e-03	1.51e-03	1.60e-03	46.5
Tangential CaO	2.16e-03	2.01e-03	4.27e-03	93.2

Regarding the ash collector, a preliminary study was conducted considering the outlet results from the OF50-E-02 case as the boundary inlet conditions, i.e., an average gas temperature of 1863 K for the incoming gases, composed mainly of 75 vol% CO₂, 21 vol% O₂ and coal volatiles three percent by volume³⁵. For the discrete phase, the percentages of the particles leaving the system were estimated considering the particle trajectory analysis. It was estimated that 28

³⁵ Remaining species were not considered.

percent of the coal particles injected for combustion, i.e., through the primary port, and 11 percent of the coal particles injected for the reaction i.e., tangentially injected, were leaving the system. Particles were considered fly ash, with a total flow of $3.5\text{e-}05$ kg/s.; for CaO, 6.8 percent were leaving the system with a total flow of $3.09\text{e-}04$ kg/s. Boundary conditions for heat transfer in the walls were specified as constant temperature in the side and bottom walls, and adiabatic in the top wall, with a value of $500\text{ }^{\circ}\text{C}$.

Results for wall deposition showed that a 91 percent of the particles were trapped in ash collection system, and the outlet average gas temperature was 1206 K. Figure 7-9a shows the gas temperature contours for the outlet gases of the combustion chamber cooled down as the gases flow through the ash collector. Figure 7-9b depicts the particles traces of fly ash. Figure 7-9c shows the temperature contours of water in the middle of the annular region of the cooling jacket. The arrows show the water flow direction in inlet and outlets. Water is considered to be entering into the system with standard conditions, with a volumetric flow rate of 2.5 US gpm. Ports A and B are the tangential water injection and ports C and D show the water outlet. Results for the cooling jacket indicated that temperatures were far below the boiling temperature, which means that maximum temperatures are about $50\text{ }^{\circ}\text{C}$. Nonetheless, it was noted that this occurs in some localized ‘dead regions’.

Figure 7-9. a) Ash collector temperature contours at planes xy and zx b) Particle flow pattern inside the ash collector c) Ash collector: temperature pattern in the middle section of the cooling jacket.

7.2 VHTR: Design for CaC_2 Production

In this section, the final results for the VHTR are included. The final set of simulations were aimed at obtaining stable combustion and estimating the required operating conditions for CaC_2 production in a more precise manner than was done in the exploratory study.

Since the insulation materials and their dimensions were known at the final stage of this project, a modification to the boundary condition for the heat transfer through the wall was added. The modification entailed utilizing the thin shell model available in ANSYS Fluent. In this approach, a one-dimensional conduction equation is used to compute the thermal resistance offered by the wall; this means that the computation of the wall heat transfer was directly included in the combustion model. This was done by calculating an equivalent resistance and wall thickness considering the insulation material and their dimensions. The relevant information for the wall insulation materials is provided in appendix B. In addition to the thin shell model, the energy

consumed by the heat of reaction Table 7-10 was included as a source term in the wall boundary condition. This required performing an iterative work between the combustion model and the SFM model.

A combustion stability study was conducted for all the simulations in order to establish the volumetric amount of oxidant injected through each port of the burner. An example of this study (for the OF50-01 case) is shown in Table 7-5. The results are tabulated based upon the volumetric gas percentage through the primary port. The volumetric flow rate through the tangential port was set to a value equal to four percent. This value provided an adequate particle deposition distribution in the initial portion of the combustion chamber.

In the combustion stability study, the swirl number was defined as recommended by Syred and Beer [137]:

$$S = \frac{2G_{\phi}}{G_x D_e} \quad (67)$$

Where G_{ϕ} is the axial flux of angular momentum given by:

$$G_{\phi} = \int_0^R (wr) \rho u 2\pi r dr \quad (68)$$

And G_x is the axial flux of linear momentum calculated as:

$$G_x = \int_0^R (u) \rho u 2\pi r dr \quad (69)$$

Costa et al. [138] suggest that, along with the swirl number, the ratio of the momentum of the secondary to the primary stream, R_m , also plays an important role in the assessment of

combustion stability. The authors describe different regions of stability performance for different types of burners. The results are presented in a diagram depicting the secondary swirl vs. the ratio of the momentum of the secondary to the primary stream. Therefore, this ratio was also monitored and is included in Table 7-5.

The results for this example show that an optimum value for combustion stability, as well as for the maximum fuel conversion efficiency, is obtained for a volumetric percentage of oxidant through the primary port between eight and nine percent. For values higher than 12 percent, the momentum of the primary stream caused the coal particles to leave the flame region with insufficient time to attain a significant amount of devolatilization, thus resulting in flame extinction. Flame extinction was also observed for values below eight percent. In this case, the lack of axial momentum of the primary stream caused most of the particles to be forced towards the wall at the initial portion of the combustion chamber, without sufficient time to attain a stable flame. The results reported in Table 7-5 match the region of stability performance for this type of burner as shown by Costa et al. [138].

Two additional effects were analyzed and are also included in Table 7-5. The first one is the effect of increasing the amount of oxidant, i.e., a fuel-to-oxidant stoichiometric ratio of 0.85 ($\phi = 0.85$). It can be observed that the char combustion increased from 93 to 99 percent at this level. This high burnout rate was already observed in the exploratory study, in which the same fuel to oxidant stoichiometric ratio was used. The second effect is a decrease in the swirl angle from 45 to 38°. It can be seen that this change caused the char burnout to decrease from 93 to 89 percent.

Table 7-5. Example of the combustion stability study for the OF50 case.

ϕ	Vol.% through primary port	Swirl vane angle	G_x primary stream (kg/ms ²)	G_x secondary stream (kg/ms ²)	$G\phi$ secondary stream (kg/m ² s ²)	R_m	S_s	Char burnout %
1	8	45	8.43	73.26	1.72	0.12	0.84	93
1	9	45	10.68	71.70	1.68	0.15	0.84	94
1	10	45	13.22	70.12	1.64	0.19	0.84	92
1	12	45	19.06	67.04	1.57	0.28	0.84	91
1	8	38	8.45	73.33	1.34	0.12	0.65	89
0.85	8	45	11.69	101.93	2.39	0.11	0.84	99

Once the optimum volumetric gas distribution was established in every case, different strategies were followed to compare the performance of the VHTEr. The first strategy involved estimating the performance of the VHTEr under different oxidant atmospheres with oxidant mixtures containing O₂ molar fractions; the O₂ molar fractions ranged from 0.25 to 0.50, i.e., OF25 to OF50, with CO₂ as the balance gas.

The initial set of calculations was based on a fuel to oxidant stoichiometric ratio equal to one ($\phi = 1$) and all the gases were injected at ambient temperature. Furthermore, this set of simulations was tagged by adding the 01 identifier at the end of the case name, e.g., OF25-01. In this set of simulations, the performance of the VHTEr was measured in terms of the gas temperature near

the wall, since this quantity provides a direct estimation of the conditions to activate the CaC_2 reaction. The inlet conditions utilized in this set of simulations are shown in Table 7-6³⁶.

The gas temperature near the wall was monitored for every condition in order to establish if the resulting temperature profile was above the recommended range suggested by Li et al. [107] for CaC_2 production, i.e., above 1973 K. Initially, the amount of coal and CaO injected through the tangential port was set to the same value, since the amounts of char and CaO deposited on the wall are not known beforehand.

Table 7-6. Inlet conditions for the VHTR simulations

Case ID	ϕ	Primary port			Secondary port		Tangential port			
		Gas		Coal	Gas		Gas		Coal	CaO
		kg/h	T, K	kg/h	kg/h	T, K	kg/h	T, K	kg/h	kg/h
OF25-01	1.0	19.04	300	16.34	116.99	300	5.44	300	11.70	11.70
OF30-01	1.0	17.20	300	16.34	94.50	300	4.47	300	11.70	11.70
OF35-01	1.0	12.83	300	16.34	81.49	300	3.77	300	11.70	11.70
OF40-01	1.0	9.75	300	16.34	71.53	300	3.25	300	11.70	11.70
OF45-01	1.0	7.47	300	16.34	63.67	300	2.85	300	11.70	11.70
OF50-01	1.0	5.67	300	16.34	57.37	300	2.52	300	11.70	11.70

Figure 7-10 shows the profiles of the gas temperature near the wall for the cases included in Table 7-6. The results indicated that just oxidant mixtures with O_2 molar fractions above 0.35

³⁶ In the final study, the values of mass flow rate are presented in kg/h, since this unit is more useful for the assessment of the calcium carbide production rate.

meet the minimum temperature required for CaC_2 production. These results allowed narrowing the range in the oxygen concentration for the next set of conditions explored.

Figure 7-10. Gas temperature profiles near the wall for the VHTR cases in Table 7-6

Table 7-7 shows the mass deposition along the wall for the oxy-coal combustion cases in Table 7-6. The values for carbon and ash contained in the char are shown in the third and fourth columns. There, the level is depicted at which the mass deposition of char along the wall decreases as a result of the higher char consumption brought about by a higher oxygen concentration in the oxidant mixture. On the other hand, the amount of deposited lime was virtually unaffected. The last column of Table 7-7 shows the molar ratio of carbon to CaO .

Table 7-7. Deposition of mass on the wall in kg/h for the VHTR cases in Table 7-6 suitable for CaC_2 production.

Case id	Char kg/h	Carbon kg/h	Ash kg/h	CaO kg/h	C/CaO molar ratio
OF35-01	6.29	5.88	0.41	11.59	2.37
OF40-01	5.51	5.10	0.41	11.49	2.07
OF45-01	5.12	4.73	0.39	11.40	1.94
OF50-01	4.75	4.37	0.38	11.33	1.80

In order to balance the amount of chemical reactants, the amount of particles injected through the tangential port was modified aimed towards obtaining a value close to the stoichiometric ratio of carbon to CaO of three. To accomplish this, the amount of coal injected through the tangential port was initially increased. Nonetheless, the increased amount of particles caused the gas temperature near the wall to decrease significantly. Therefore, a reduction in the amount of CaO was preferred. The effect of the amounts of injected reactants on the gas temperature near the wall is shown in Figure 7-11 for the OF50-01 cases. In these cases, the identifier –A indicates an increase in the amount of coal and –B a decrease in the amount of CaO.

Figure 7-11. Effect of particle injection on the gas temperature near the wall for the OF50-01 cases.

It should also be noted, by observing Figures 7-10 and 7-11, that the low temperature region at the initial part of the combustion chamber is not beneficial to promote the early activation of the CaC_2 reaction³⁷ because of the higher deposition of chemicals attained in this region. This fact motivated the idea of preheating the gas injected through the secondary and tangential streams. The preheating value was set to 600 K. This set of simulations was tagged by adding the 02 identifier at the end of the case. The letter B was kept as a remainder of the balanced condition for the chemical reactants. The conditions are provided in Table 7-8.

Figure 7-12 shows the comparison of the gas temperature profiles near the wall, with and without preheating, for the cases with the lower and higher oxygen concentrations, i.e., OF35 and OF50.

³⁷ This was already pointed out in the preliminary study.

It can be observed that the temperature increase brought about by preheating is more evident in the initial length of the combustion chamber. Particularly, the average temperature increase in the region of the combustion chamber between 0 and 0.6 m is 247 K for the OF35 case. The corresponding value for the OF50 case is 268 K. Nonetheless, the resulting temperature increase is not particularly high for the rest of the length; on the contrary, the average temperature increase for the rest of the length is 62 K for the OF35 case and decreases to 29.3 K for the OF50 case.

The results also suggest that the strategy of preheating the secondary gas stream promotes the activation of the CaC_2 formation in the initial portion of the combustion chamber. That is due to the fact that the point at which the gas temperature near the wall surpass the value recommended by Li et al. [107] is reached sooner. For instance, in the OF35 case this point is reached at a distance of 0.15 m for the preheating condition as opposed to 0.37 m for the condition without preheating. For the OF50 case, this point is reached at 0.12 m for the preheating condition as opposed to 0.25 m for the condition without preheating.

Figure 7-12. Effect of preheating on the temperature profiles near the wall for the VHTR.

This set of conditions, which is shown in Table 7-8, was selected for the study of the performance of the reactor. Figure 7-13 includes the temperature contours and the recirculation pattern in the burner region for this set of conditions.

Table 7-8. Inlet conditions for the VHTR cases with preheating and balanced amount of chemical reactants.

Case ID	ϕ	Primary port			Secondary port		Tangential port				Residence time (s)
		Gas		Coal	Gas		Gas		Coal	CaO	
		kg/h	T, K	kg/h	kg/h	T, K	kg/h	T, K	kg/h	kg/h	
OF35-02-B	1.0	12.83	300	16.34	81.49	300	3.77	600	11.70	10.49	2.17
OF40-02-B	1.0	9.75	300	16.34	71.53	300	3.25	600	11.70	10.39	2.48
OF45-02-B	1.0	7.47	300	16.34	63.67	300	2.85	600	11.70	11.06	2.79
OF50-02-B	1.0	5.67	300	16.34	57.37	300	2.52	600	11.70	10.36	3.10

Figure 7-13. Velocity recirculation pattern and temperature contours in the BRZ for the cases in Table 7-8.

Examples of the char and CaO particle distributions and temperatures are shown in Figure 7-14 and Figure 7-15 for the OF50-02-B case. The results for particle deposition are reported in Table 7-9.

Figure 7-14. a) Deposition distribution and b) Temperature for char particles (OF50-02-B case)

Figure 7-15. a) Deposition distribution and b) Temperature for CaO particles (OF50-02-B case).

Table 7-9. Particle deposition on the wall on the wall the cases in Table 7-8.

Case id	Char kg/h	Carbon kg/h	Ash kg/h	CaO kg/h	C/CaO molar ratio
OF35-02-B	6.92	6.50	0.42	12.04	3.08
OF40-02-B	7.19	6.77	0.42	10.33	3.06
OF45-02-B	7.33	6.92	0.42	10.98	2.94
OF50-02-B	6.99	6.58	0.41	10.30	2.98

7.3 VHTR: Slag Model Results

Figure 7-16 through Figure 7-22 show the results provided by the SFM for the selected cases in Table 7-8. Figure 7-16 shows the thickness of the liquid slag layer. The profiles are initially at their highest value due to most of the particle deposition occurs at the initial length of the combustion chamber. The sharp decrease is due to a significant reduction in viscosity which causes the slag to flow considerably faster. The viscosity of the slag is depicted in Figure 7-22.

Figure 7-16. Liquid slag thickness for the conditions in Table 7-8.

Figure 7-17 shows the thickness of the solidified slag layer. It can be observed that the value is higher for cases with smaller oxygen concentrations. This behavior is consistent with the gas temperature profiles near the wall, so that smaller oxygen concentrations make the gas temperature near the wall smaller, which increases the amount of solidified slag. Similar to what happens with the liquid slag layer, the maximum thickness of the solidified slag occurs at the initial length of the wall. That is due to the fact that the temperature is smaller and the residence time of the slag is higher in this region due to a higher viscosity.

Figure 7-17. Thickness of the solidified slag layer for the conditions in Table 7-8.

Figure 7-18 shows the velocity profiles for the selected cases. The profiles behave in accordance with the viscosity behavior. The significant difference in the OF35-02-B case with respect to other cases is due to the corresponding difference between the viscosity profiles shown in Figure 7-22.

Figure 7-18. Average velocity of the liquid slag for the conditions in Table 7-8.

Figure 7-19. Bulk slag temperature for the conditions in Table 7-8.

Figure 7-20 shows the formation of CaC_2 . The results are plotted in terms of the mass fraction of CaC_2 in the slag layer. The figure depicts the point at which the formation of CaC_2 starts to take place.

It can be observed that the formation of CaC_2 is small in all the cases. That is most likely due to the fact that the residence time is too small to achieve a significant amount of CaC_2 . The residence time for these conditions is in the order of two minutes, and the values are shown in

Table 7-10. Nonetheless, there is a significant difference in the level of CaC_2 formed in the slag.

In fact, it can be observed that the amount of CaC_2 in the slag is almost three times higher for the case OF50-02-B when compared to the case OF35-02-B.

Figure 7-20. Mass fraction of CaC_2 in the slag for the conditions in Table 7-8.

Figure 7-21 shows the energy consumed by the CaC_2 reaction along the slag. The values are shown in kW. The total energy consumed in the reactor by the CaC_2 reaction as well as the total energy consumed by kilogram of CaC_2 produced is reported in Table 7-10.

Figure 7-21. Energy consumed by the CaC_2 reaction for the conditions in Table 7-8.

Figure 7-22. Slag viscosity profiles along the wall of the VHTR for the conditions in Table 7-8.
a) between 0 and 0.5 m and b) for viscosities smaller than 0.5 Pa·s.

Table 7-10. Relevant information to CaC_2 production in the VHTR.

Case id →	OF35-02-B	OF40-02-B	OF45-02-B	OF50-02-B
kg/h of slag leaving the reactor	19.85	22.08	18.28	17.27
m.f. of CaC_2 in the slag leaving the reactor	0.02	0.04	0.05	0.06
kg/h of CaC_2 leaving the reactor	0.42	0.81	1.00	1.03
Residence time of the slag (min)	2.79	2.06	2.00	1.86
Energy consumed by the CaC_2 reaction (kW)	0.87	1.8	2.23	2.31
Energy consumed by the CaC_2 reaction per kg of CaC_2 (kW/ kg)	2.07	2.22	2.23	2.24

Chapter 8 – Horizontal Reactor: Results and Discussion

8.1 CTC Reactor: Combustion Results for the Experimental Conditions at WRI

Several series of simulations were conducted to support the research and development efforts of LP Amina. The results were included in the technical report developed and prepared by WRI, WVU and LP Amina this year. The results for the final set of simulations will be shown in this dissertation and will be compared with the experiments conducted at WRI. These results are shown with permission of LP Amina.

The operation conditions for these cases are shown in Table 8-1. These cases are identified by adding the month, day and year to the WRI identifier. In these simulations, the coal utilized was Decker coal, but with a moisture content decreased to 6%. In all these tests, the TA port was closed.

Table 8-1. CTC Reactor Operation conditions: WRI tests, 2015's tests. Mass flow rates in kg/h, temperatures in K.

Case id	Air (PA)	Coal (PA)	CaO (PA)	Air (SA)	O ₂ (SA)	NG (SA)	T(K) (PA)	T(K) (SA)
WRI-01-23-15	20.13	18.91	0	119.37	0	3.34	298	802
WRI-02-03-15	20.13	18.91	0	119.37	5.56	2.23	298	816
WRI-03-31-15	24.16	17.3	0.82	119.57	8.89	2.23	298	784

Figure 8-1 shows an example of the conditions registered by the instrumentation in the experiments. Those conditions correspond to the WRI-01-23-15 case. Figure 8-1 (a) shows the volumetric flow rate of primary air, secondary air, and natural gas in CFM. Conditions shown in

Figure 8-1a are registered by the meters DL_LPA.FT1, DL_LPA.FT2 and DL_LPA.FT3, respectively. Figure 8-1b shows the temperature of the thermocouple DL_LPA.TC1F, which measures the temperature of the air injected through the SA port. Figure 8-1c shows the reading of the weight gauge DL_LPA.WT1, where the coal feeder sits on. The mass flow rate of coal injected in lb/min is estimated from this reading by linear regression. Figure 8-1d shows the reading of the weight gauge DL_LPA.WT2 where the CaO feeder sits on.

Figure 8-1. Example of the registered inlet conditions for the CTC reactor

Two instruments registered the temperature inside the CTC reactor. The first one is an infrared (IR) pyrometer, identified as DL_LPA_IRT1, and is located in the third SA port. The second one is a thermocouple, identified as DL_LPA_TCR18; this thermocouple was located at the top of

the reactor, above the slag drain. The readings of these two instruments were compared to the appropriate wall and average gas temperatures from the CFD simulations. The CFD results and experimental measurements for these cases showed good agreement.

Figure 8-2 shows the comparison of simulation and experimental results for the WRI-01-23-15 case. The plot in Figure 8-2b shows the thermocouple reading, as well as it points out the location of the thermocouple in Figure 8-2a. Figure 8-2c shows the IR pyrometer reading, as well as it points out the location of the plane where the IR pyrometer is located. Figures 8-3 and 8-4 show this same comparison for the WRI-02-03-15 and WRI-03-31-15 cases, respectively.

Figure 8-2. Comparison of simulation results and experimental results for WRI-01-23-15 case.

WRI-02-03-15

Figure 8-3. Comparison of simulation results and experimental results for WRI-02-03-15 case.

WRI-03-31-15

Figure 8-4. Comparison of simulation results and experimental results for WRI-03-31-15 case.

These results showed that the CFD simulations were consistent with the measured temperatures. Nonetheless, these results also indicated that the temperatures achieved under the conditions tested at WRI were not sufficiently high for activation of the CaC_2 reaction. The temperature profiles for these conditions are shown in Figure 8-5.

Figure 8-5. CTC Reactor bottom wall temperature profiles (cases in Table 8-1).

It can also be observed that the amount of CaO injected in these tests was considerably small. This fact, along with insufficiently high temperatures, is consistent with the lack of CaC_2 formation evidenced in the tests performed at WRI.

8.2 CTC Reactor: Design for CaC₂ Production

In order to establish suitable conditions for the activation of CaC₂, additional series of simulations were performed to obtain higher wall temperatures. In these simulations, the operating conditions utilized in the WRI-03-31-15 tests were used as a reference point.

The calculated temperatures shown in Figure 8-6 illustrate that the temperature near the bottom wall of the CTC reactor can indeed be increased substantially by increasing the amount of natural gas, as well as by replacing a portion of the air entering the reactor with pure O₂. Additionally, the amount of CaO injected into the reactor was increased by approximately a factor of 10.

The operation conditions for selected cases showing significant temperature improvements are provided in Table 8-2, where the value of the varied conditions is shown in bold format. The temperatures profiles for these cases are shown in Figure 8-6. The best results were seen with the case CTC-Reactor-52, which resulted in an increase in nearly 500 K over the reference case.

Table 8-2. Reactor operating conditions for simulations to enhance CaC₂ production

Case id	Air (PA)	Coal (PA)	CaO (PA)	Air (SA)	O ₂ (SA)	NG (SA)	T(K) (PA)	T(K) (SA)
WRI-03-31-15	24.16	17.3	0.82	119.57	8.89	2.23	298	784
CTC-Reactor-48	24.16	17.3	0.82	119.57	15.56	3.9	298	784
CTC-Reactor-49	24.16	17.3	0.82	119.57	15.56	3.9	298	900
CTC-Reactor-52	24.16	17.3	7.48	104.67	22.23	6.69	298	900

Figure 8-6. Bottom wall temperature profiles for simulations detailed in Table 8-2.

8.3 CTC Reactor: Slag Model Results

The results of the CFD model for the CTC-Reactor-52 case were utilized in the SFM to analyze the rate of CaC_2 production. The deposition of chemicals is shown in Figure 8-7. These figures provide the deposition information both along the longitudinal axis of the reactor, and along the angular position with respect to the circumference of the reactor; Figure 8-8 provides a reference for how the angular positions are defined. The molar ratio of carbon to CaO in this case was balanced to a value close to 3.1.

(a)

(b)

Figure 8-7. Particle deposition of carbon and CaO as a function of (a) distance along the longitudinal axis, and (b) reactor circumference angle for the CTC-Reactor-52 case.

Figure 8-8. Reference for definition of angular deposition coordinates.

The results at steady state provided by the SFM for the CTC-Reactor-52 case are shown in Figure 8-9. In these results, the mass fraction of CaC_2 at the final portion of the reactor was close to 0.4, which is a significant increase from 0.0 for case WRI-03-31-15. This corresponds to a change in CaC_2 production of 0 kg/hr for case WRI-03-31-15 to 4.37 kg/hr for case CTC-Reactor-52.

Figure 8-9. Slag model results at steady state for the CTC-Reactor-52 case. (top left) slag pool depth (top right) average slag velocity (bottom left) bulk temperature of slag (bottom right) species mass fractions.

It is important to mention that for the case of the horizontal reactor, it was necessary to assume a small slope in order to promote the flow of slag. It was assumed that the slope was equal to 0.001° . If the slope is equal to zero, the slag flow model predicts a no flow condition in which the mass flow rate of molten ash will cause the accumulation of molten slag. In the reactors evaluated in this work, the accumulation will occur in the initial region of the combustion chamber, since this is the region where the mass is deposited. This condition is shown in Figure 8-10 for the OF50-02-B case.

Figure 8-10. Accumulation of mass predicted by the SFM for the OF50-02-B case.

Chapter 9 – Conclusions and Future Work

9.1 Conclusions

A numerical model was developed to study the process of CaC_2 production in the molten slag of oxy-coal reactors. The model was developed in a computational framework that included a CFD model for oxy-coal combustion coupled with a one dimensional CFD model for the slag flow. The model was applied to the design of pilot scale reactors.

The results for oxy-coal combustion in the VHTEr showed that it is possible to obtain high gas temperatures near the wall. These temperatures provided the minimum temperature requirements for CaC_2 production. Different O_2/CO_2 oxidant mixtures with molar oxygen concentrations ranging from 0.25 to 0.50 were evaluated. It was concluded that the minimum temperatures required to activate the CaC_2 formation were obtained for oxy-coal combustion cases with molar oxygen concentrations close to 0.35 being CO_2 the balance gas.

Regarding the design of the VHTEr, it was found that the burner design of the VHTEr allowed attaining a stable combustion with a well-defined burner recirculation zone. It was also found that the swirling flow pattern provided by the tangential flow promotes the collection of particles in the initial section of the combustion chamber. This tangential flow pattern was provided by the injection of particles by carrier gas. Additionally, it was found that the tangential injection of particles by carrier gas increases the temperature in the initial portion of the combustion chamber.

The study conducted to balance the chemical reactants showed that the particle heat absorption has a significant impact on the gas temperature near the wall of the oxy-coal reactor. It was also shown that gas preheating can be used to promote the earlier formation of CaC_2 .

The slag flow model developed in this work included different features not available in previous formulations available in the literature. The model features considered in the present work included: i) an unsteady state formulation; ii) the species transport equation; iii) the kinetic model for calcium carbide production developed by Rowen et al. [108]; iv) a new approach based on the Stefan's condition [129] for the estimation of the solidified slag thickness and, v) a model based on the CaO-CaC_2 eutectic phase diagram to estimate the amount of solids transported in the slag.

The results for the slag flow model showed that although the VHTR reactor is able to attain the high temperatures required for the production of CaC_2 , such temperatures have a downside effect on viscosity. That means that, if the typical viscosity models available in the literature are extrapolated, the viscosities obtained can be so small that the residence time of the slag is insufficient to attain a considerable formation of CaC_2 in the slag. This situation is more dramatic for the VHTR when compared to the CTC reactor.

The simulation results for the CTC reactor indicated that the operation conditions evaluated in the tests performed at WRI are not suitable for CaC_2 production. Nonetheless, it is possible to obtain suitable temperatures for production of CaC_2 in the CTC reactor by modifying the operation conditions. The modifications include increasing the amount of natural gas, as well as replacing a portion of the air entering the reactor with pure O_2 .

9.2 Future Work

The main obstacle found during the development of the present work was the lack of information related to the slag properties. This was mainly due to the more narrow focus of the production of CaC_2 in the molten slag and also to the high temperatures involved. A detailed review of the slag flow properties was considered in this work in order to select the best possible values and models available in literature. Nonetheless, is highly recommended that experimental work support the further development of the slag flow model. Due to its relevance to the control and design of the process, viscosity is perhaps the property that should be investigated with priority from all the fluid and thermal properties.

Currently, the Computational Fluid Dynamics and Applied Multi-Physics (CFD & AMP) center of West Virginia University is conducting research on the field of the reaction mechanism of CaC_2 in the slag. Once this work is concluded, such mechanism should be implemented in the slag flow model.

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APPENDIX A

Stoichiometry calculations for the combustion process

The calculations are based in the following global reaction for coal and methane:

This equation includes the possibility of using methane to provide additional heat.

For the case when no methane is used:

The mass balance is estimated using the following algebraic expressions:

$$H : m = 2y$$

$$S : p = z$$

$$C : n + ab = x$$

$$O : r + 2a + 2ab = 2x + y + 2z$$

$$2a = 2n + \frac{m}{2} + 2p - r$$

$$a = n + \frac{m}{4} + p - \frac{r}{2}$$

An example of the stoichiometric calculations is shown below, considering as example, the German lignite utilized in the exploratory study of the VHTR. The properties of German lignite are shown in Table A.1.

Table A.1. German lignite properties.

Proximate analysis (wt% as received)			VM (%d.a.f)	Ultimate analysis (wt% d.a.f.)					LHV
Moisture	Ash	Combustibles	59.4	C	H	N	S	O	(MJ/kg)
10.2	5.0	84.8		69.9	5.4	0.6	1.0	23.1	20.9

The combustibles percentage is calculated from the proximate analysis: $100 - 5 - 10.2 = 84.8\%$.

Taking 100 kg of coal as reference, the amount of each coal component is determined by multiplying its mass fraction by the percentage of combustibles, e.g., for carbon:

$$\text{kg C/ 100kg coal} = 69.9 * \text{Combustibles\%} / 100\text{kg coal} = 59.28\text{kg C/100kg coal}$$

The number of kmol/100kg is obtained by dividing the amount of each element by its molecular weight, e.g., for carbon:

$$(59.28 \text{ kg C/100kg coal}) / (12\text{kmol/kg}) = 4.94\text{kmol C/100kg coal}$$

The results for the other elements are shown in Table A.2.

Table A.2.

Element	kg/100kg coal	W(kg/kmol)	Kmol/(100kg coal)
C	59.28	12	4.94E+00
H	4.58	1	4.58E+00
O	19.59	16	1.22E+00
N	0.51	14	3.63E-02
S	0.85	32	2.65E-02
Total	84.80		

Stoichiometric calculations for the oxidant per 100 kg of coal:

From the relation:

$$a = n + \frac{m}{4} + p - \frac{r}{2}$$

The value of the stoichiometric coefficient for the oxidant is calculated:

$$a = 4.94 + \frac{4.58}{4} + 0.0265 - \frac{1.22}{2} = 5.5$$

The value of the coefficient b is modified according to the oxygen mass fraction in the oxidant, e.g., for OF25 the value of b is equal to three (b= 3):

Based on the values of the stoichiometric coefficients, the stoichiometric amount of oxidant in kmol per 100kg coal is calculated:

$$5.5 * 1\text{kmol } O_2/100\text{kg coal} = 5.5\text{kmol } O_2 /100\text{kg coal}$$

$$5.5 * 3 \text{ kmol CO}_2 / 100 \text{ kg coal} = 16.5 \text{ kmol CO}_2 / 100 \text{ kg coal}$$

The stoichiometric amount of oxidant in kg per 100kg coal is calculated as:

$$5.5 \text{ kmol O}_2 / 100 \text{ kg coal} * (32 \text{ kg/kmol}) = 176 \text{ kg O}_2 / 100 \text{ kg coal}$$

$$16.5 \text{ kmol CO}_2 / 100 \text{ kg coal} * (44 \text{ kg/kmol}) = 726 \text{ kg CO}_2 / 100 \text{ kg coal}$$

The amount of fuel and oxidant per 100kg/coal is summarized in the Table A.3.

Table A.3.

Fuel	Kmol/100kg s
C	4.94E+00
H	4.58E+00
O	1.22E+00
N	3.63E-02
S	2.65E-02
Oxidant	Kmol/100kg s
O2	5.5
CO2	16.5

The mass flow rate of coal is calculated from the power of the oxy-coal reactor (100kW):

$$\dot{m}_{coal} = \frac{power}{LHV} = \frac{100 \text{ kJ} / 2}{20900 (\text{kJ} / \text{kg})} = 4.78 \text{e} - 03 \text{ kg coal} / \text{s}$$

The molar flow rates for fuel and oxidant are calculated as:

Fuel

$$(4.94 \text{ kmol C} / 100 \text{ kg coal}) * (4.78 \text{e} - 03 \text{ kg coal} / \text{s}) = 2.36 \text{e} - 04 \text{ kmol/s}$$

$$(4.58\text{kmol H} / 100\text{kg coal}) * (4.78\text{e-}03\text{kgcoal/s}) = 2.19\text{e-}04 \text{ kmol/s}$$

$$(1.22\text{kmol O} / 100\text{kg coal}) * (4.78\text{e-}03\text{kgcoal/s}) = 5.85\text{e-}05 \text{ kmol/s}$$

$$(3.63\text{e-}02\text{kmol N} / 100\text{kg coal}) * (4.78\text{e-}03\text{kgcoal/s}) = 1.74\text{e-}06 \text{ kmol/s}$$

$$(2.65\text{E-}02\text{kmol S} / 100\text{kg coal}) * (4.78\text{e-}03\text{kgcoal/s}) = 1.27\text{e-}06 \text{ kmol/s}$$

Results in kmol/s are summarized in the Table A.4.

Table A.4.

Element	Kmol/s
C	2.36E-04
H	2.19E-04
O	5.85E-05
N	1.74E-06
S	1.27E-06

Oxidant

For OF25 b = 0.5:

The amount of stoichiometric O₂ in kg/s is in this case:

$$(5.5 \text{ kmol O}_2 / 100\text{kg coal}) * (4.78\text{e-}03\text{kgcoal/s}) = 2.63\text{e-}04 \text{ kmol/s}$$

The total amount of stoichiometric CO₂ is:

$$(16.5 \text{ kmol CO}_2 / 100\text{kg coal}) * (4.78\text{e-}03\text{kgcoal/s}) = 7.89\text{e-}04 \text{ kmol/s}$$

For other O₂/CO₂ mixtures all the values but the amount of CO₂ remains the same. i.e., the amount of CO₂ is reduced in order to increase the oxygen concentration. For example, For OF50 (b = 1), the stoichiometric equation for the combustion reaction is written as:

The stoichiometric amount of CO₂ per 100kg coal for this case is:

$$5.5 * 1\text{kmol CO}_2/100\text{kg coal} = 5.5\text{kmol CO}_2 /100\text{kg coal}$$

The total amount of stoichiometric CO₂ is:

$$(5.5 \text{ CO}_2 /100\text{kg coal})*(4.78\text{e-}03\text{kgcoal/s})=2.63\text{e-}04 \text{ kmol/s}$$

Results in kmol/s are summarized in the Table A.5.

Table A.5.

Element	Kmol/s (OF25)	Kmol/s (OF50)
O2	2.63E-04	2.63E-04
CO2	7.89E-04	2.63e-04

APPENDIX B

Property values utilized in the SFM

Table B1.

Property	Value
Convection heat transfer coefficient from the reactor surroundings (kW/m ² K)	5.57 e-03
Thermal conductivity of the slag (kW/mK)	1.76e-03
Total insulation resistance of the VHTR (mK/kW)	723.6
Silica ratio of the coal slag	0.517
Acid to basic ratio of the coal slag	1.35
Molecular weights of the species considered in the slag (kg/kmol)	
C	12.01
CaO	56.08
CaC ₂	64.10
CO	28.01
SiO ₂	60.08
Al ₂ O ₃	101.96
Fe ₂ O ₃	159.69
Enthalpy of formation of the reacting species considered in the slag (kJ/kg)	
C	0
CaO	-11340.88
CaC ₂	-934.38
CO	-3947.39
Specific heat of the species considered in the slag (kJ/kmol K)	
C	8.34
CaO	58.25
CaC ₂	74.9
CO	36.07
SiO ₂	44.57
Al ₂ O ₃	192.5

Fe_2O_3	146.8
Parameters associated with solidification/melting	
Latent heat of fusion of the slag (kJ/kg)	1200
Latent heat of fusion of the CaO (kJ/kg)	913
Latent heat of fusion of the CaC_2 (kJ/kg)	948
Relaxation parameter for solids transported in the slag (a_{ls})	0.02
Parameter to modify the forward kinetic rate (λ_{k-f})	1.5
Parameter to modify the backward kinetic rate (λ_{k-B})	1.5

Table B2. Insulation materials and dimensions for the VHTR.

Material	Thermal conductivity (kW/m ² K)	Inner radius (m)	Outer radius (m)
ZrO ₂	1.80E-03	7.50E-02	2.00E-01
Inswool	6.00E-05	2.00E-01	2.10E-01
Kol-30	6.30E-04	2.10E-01	3.46E-01
Insblock	7.00E-05	3.46E-01	3.97E-01
Steel	2.50E-02	3.97E-01	4.06E-01

Table B3. Ash composition of the Decker's coal

Component	Mass fraction %	Mole fraction %
SiO ₂	26.26	31.01
Al ₂ O ₃	17.26	12.01
MgO	3.19	5.62
P ₂ O ₅	0.95	0.24
SO ₃	21.22	18.80
TiO ₂	1.16	1.03
CaO	14.78	18.70
Na ₂ O	8.14	9.32
K ₂ O	0.48	0.36

Mn_3O_4	0.00	0.00
Fe_2O_3	6.54	2.90

APPENDIX C

This appendix considers an alternative procedure to the OMA performed over the energy equation. This OMA is intended to show that the thermal diffusion term along the slag flow direction (x direction) and the viscous dissipation term can be neglected.

Considering the energy equation in terms of temperature:

$$\frac{\partial}{\partial t}(\rho c_p T) = - \left[\frac{\partial}{\partial x}(\rho c_p u T) + \frac{\partial}{\partial y}(\rho c_p v T) \right] + \left[\frac{\partial}{\partial x} \left(k \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y} \left(k \frac{\partial T}{\partial y} \right) \right] + \mu \left[\frac{\partial u}{\partial y} \right]^2 \quad \text{C. 1}$$

Dividing this expression by ρc_p and assuming the scales relevant to the process, this expression can be written as:

$$\frac{\Delta T}{\tau} = -U_{ref} \frac{\Delta T}{L} - V_{ref} \frac{\Delta T}{\delta} + \alpha \frac{\Delta T}{L^2} + \alpha \frac{\Delta T}{\delta^2} + \frac{\mu}{\rho c_p} \frac{U_{ref}^2}{\delta^2} \quad \text{C. 2}$$

Where V_{ref} has been related to U_{ref} from the continuity equation:

$$V_{ref} = \frac{\delta}{L} U_{ref} \quad \text{C. 3}$$

The maximum temperature difference, ΔT , is assumed to be given by the difference between the temperature at the interface of the liquid slag and the and the critical viscosity temperature:

$$\Delta T = (T_g - T_{cv}) \quad \text{C. 4}$$

If the unsteady term is neglected for comparison purposes, C.2 can be written as:

$$U_{ref} \frac{\Delta T}{L} + V_{ref} \frac{\Delta T}{\delta} = \alpha \frac{\Delta T}{L^2} + \alpha \frac{\Delta T}{\delta^2} + \frac{\mu}{\rho c_p} \frac{k}{k} \frac{U_{ref}^2}{\delta^2} \quad C. 5$$

This expression can be modified as:

$$\frac{U_{ref}}{L} + \frac{U_{ref}}{L} = \frac{\alpha}{L^2} + \frac{\alpha}{\delta^2} + \frac{\alpha}{\delta^2} \frac{\mu U_{ref}^2}{k \Delta T} \quad C. 6$$

$$1 = \frac{\alpha}{L U_{ref}} + \frac{L \alpha}{U_{ref} \delta^2} + \frac{\alpha L}{U_{ref}} \frac{L^2}{L^2} \frac{1}{\delta^2} Br \quad C. 7$$

$$1 = \frac{1}{Pe_{th}} \left[1 + \frac{L^2}{\delta^2} + \frac{L^2}{\delta^2} Br \right] \quad C. 7$$

Where the Brinkman (Br) and the thermal Peclet (Pe_{th}) numbers are defined as:

$$Br = \frac{\mu U^2}{k(T_g - T_{cv})} \quad C. 8$$

$$Pe_{th} = \frac{LU}{\alpha} \quad \text{C. 9}$$

It can be recognized that the three terms inside brackets of C.7 relate to the terms of equation C.

1 in the following way:

$$\begin{aligned} 1) 1 \rightarrow \text{Relates to: } & \frac{\partial}{\partial x} \left(k \frac{\partial T}{\partial x} \right) \\ 2) \frac{L^2}{\delta^2} \rightarrow \text{Relates to: } & \frac{\partial}{\partial y} \left(k \frac{\partial T}{\partial y} \right) \\ 3) \frac{L^2}{\delta^2} Br \rightarrow \text{Relates to: } & \mu \left[\frac{\partial u}{\partial y} \right]^2 \end{aligned}$$

Clearly, the second term dominates over the first one and the third term compares to the second one depending on the value of the Brinkman number. In order to illustrate the order of magnitude of the Brinkman and Peclet numbers, their value is estimated based on the properties given in Table 6-1, the reactor dimensions and the typical slag velocity values:

$$Br = \frac{\mu U^2}{k(T_g - T_{cv})} = \frac{(6.2 Pa \cdot s)(0.002 m/s)}{(1.73e-03 kW/mK)(2200-1500K)} = 1.02e-02$$

$$Pe_{th} = \frac{LU}{\alpha} = \frac{[2m][0.002m/s]}{4.51e-07 m^2/s} = 8.86e+03$$

From the value of the Brinkman number, it can be seen that the third term is smaller than the second. Therefore, the thermal diffusion term along the slag flow direction (x direction) and the viscous dissipation term can be neglected in the energy equation.