Oxy-fuel combustion of pulverized coal: Characterization, fundamentals, stabilization and CFD modeling

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Abstract

Oxy-fuel combustion has generated significant interest since it was proposed as a carbon capture technology for newly built and retrofitted coal-fired power plants. Research, development and demonstration of oxy-fuel combustion technologies has been advancing in recent years; however, there are still fundamental issues and technological challenges that must be addressed before this technology can reach its full potential, especially in the areas of combustion in oxygen-carbon dioxide environments and potentially at elevated pressures. This paper presents a technical review of oxy-coal combustion covering the most recent experimental and simulation studies, and numerical models for sub-processes are also used to examine the differences between combustion in an oxidizing stream diluted by nitrogen and carbon dioxide. The evolution of this technology from its original inception for high temperature processes to its current form for carbon capture is introduced, followed by a discussion of various oxy-fuel systems proposed for carbon capture. Of all these oxy-fuel systems, recent research has primarily focused on atmospheric air-like oxy-fuel combustion in a CO2-rich environment. Distinct heat and mass transfer, as well as reaction kinetics, have been reported in this environment because of the difference between the physical and chemical properties of CO2 and N2, which in turn changes the flame characteristics. By tracing the physical and chemical processes that coal particles experience during combustion, the characteristics of oxy-fuel combustion are reviewed in the context of heat and mass transfer, fuel delivery and injection, coal particle heating and moisture evaporation, devolatilization and ignition, char oxidation and gasification, as well as pollutants formation. Operation under elevated pressures has also been proposed for oxy-coal combustion systems in order to improve the overall energy efficiency. The potential impact of elevated pressures on oxy-fuel combustion is discussed when applicable. Narrower flammable regimes and lower laminar burning velocity under oxy-fuel combustion conditions may lead to new stability challenges in operating oxy-coal burners. Recent research on stabilization of oxy-fuel combustion is reviewed, and some guiding principles for retrofit are summarized. Distinct characteristics in oxy-coal combustion necessitate modifications of CFD sub-models because the approximations and assumptions for air-fuel combustion may no longer be valid. Advances in sub-models for turbulent flow, heat transfer and reactions in oxy-coal combustion simulations, and the results obtained using CFD are reviewed. Based on the review, research needs in this combustion technology are suggested.

Keywords:
Carbon capture
Oxy-fuel combustion
Coal
Heat transfer
Flame stabilization
CFD
Nomenclature

Symbols

A  pre-exponential factor for reaction kinetics
A  area (m²)
α  averaged absorption coefficient (1/m)
C  concentration (kmol/m³)
ci  mass diffusion-limited constant (s/K⁰.⁷5)
cp  specific heat at constant pressure (J/kgK)
Cp  molar heat capacity at constant volume (J/kmolK)
ρCp  volumetric heat capacity at constant volume (J/m³K)
D  diameter of pipe (m)
Dab  mass diffusivity (m²/s)
d  diameter of droplet or particle (m)
E  activation energy (kJ/mol)
g  gravity (9.81 m/s²)
h  convective heat transfer coefficient (W/m²K)
hg  latent heat (J/kg)
hmg  convective mass transfer coefficient (m/s)
∂h  reaction heat of char oxidation (J/kg)
l  radiation intensity (W/m² - sr)
k  thermal conductivity (W/mK)
k  reaction kinetics kg/(m²·Pa·s)
kd  turbulence kinetic energy
Mr , MW  molecular weight (g/mol)
mi  mass consumption rate (kg/s)
Nu  Nusselt number
h  mole flow rate (mol/s)
P  pressure (Pa)
Pr  Prandtl number
q  heat transfer (W)
q‘  heat flux (W/m²)
qc  heat release by combustion reaction (J/kmol)
Re  Reynolds number
r  radius (m)
s  beam length in radiation (m)
Sc  Schmidt number
Sh  Sherwood number
St  flame propagation velocity (m/s)
T  temperature (K)
u  velocity (m/s)
V  volume (m³)
v  velocity (m/s)
We  Weber number
Y  mass fraction

Subscripts

0  initial value at time 0, reference value
a  activation
air  air-fuel combustion, or O₂/N₂
airf  blowout blowout velocity
boil  boiling state
C  char
comb  combustion
conv  convection
d  diameter of particle or droplet
devolatilization
diff  diffusion
fuel  F
f  flame
g  gas
ign  i  ignition
i  gas component i
kin  kinetics
l  liquid
mix  gas mixture
oxy  oxy-fuel combustion, or O₂/CO₂
P  product
p  particle
pg  particle-gas
pu  pickup velocity
pw  particle-wall
reactant
rad  radiation
s  surface
sur  surrounding gas
unburned gas
v  wall
∞  infinity

Acronyms

AFT  adiabatic flame temperature
ANL  Argonne national laboratory
ASU  air separation unit
B&W  Babcock & Wilcox company
CANMET  Canada Center for Mineral and Energy Technology
CPU  carbon dioxide purification unit
CWS  coal water slurry
CFD  computational fluid dynamics
DAEM  distributed activation energy model
df  double/single film model
DNS  direct numerical simulation
DTF  drop tube furnace
dilution ratio
EFR  entrained flow reactor
EOR  enhanced oil recovery
EWB  exponential wide band
ESP  electrostatic precipitator

Greek letters

α  thermal diffusivity (m²/s)
α  absorptivity
ε  emissivity
ε  gas fraction contributing to atomization
ε  dissipation rate
κ  absorption coefficient (1/m)
κ  pressure absorption coefficient (1/m - atm)
λ  wavelength of radiation (μm)
ν  kinematic viscosity (m²/s)
ρ  mass ratio of oxygen-to-fuel
ν  stoichiometric coefficient of carbon in heterogeneous reactions
ρ  density (kg/m³)
1. Introduction

1.1. Carbon capture technologies for coal-fired power plants

Reliable, efficient and clean energy supply is one of the basic needs of humankind. Today, our energy supply system is undergoing a long-term transition from its conventional form to a more sustainable and low carbon style, especially addressing greenhouse gas (water, carbon dioxide, methane, nitrous oxide, chlorofluorocarbons and aerosols) emissions into the atmosphere. Strong evidence suggests that both the average global temperature and the atmospheric CO2 concentration have significantly increased since the onset of the industrial evolution, and they are well correlated [1]. Concerns over climate change have led to mounting efforts on developing technologies to reduce carbon dioxide emissions from human activities [2,3]. Technological solutions to this problem ought to include a substantial improvement in energy conversion and utilization efficiencies, carbon capture and sequestration (CCS), and expanding the use of nuclear energy and renewable sources such as biomass, hydro-, solar, wind and geothermal energy [2].

Coal has been and will continue to be one of the major energy resources in the long term because of its abundant reserves and competitively low prices, especially for the use of base-load power generation. For instance, the share of coal in world energy consumption was 29.4% in 2009, as opposed to 34.8% for oil and generation. For instance, the share of coal in world energy generation. As shown in Fig. 1(a), installed power capacity has been booming in the last two decades. As shown in the table, the reader is referred to [11–13] for more details on CLC.

In general, the technologies described above can be applied to generate energy from natural gas and coal with the exemption of some low rank coals due to unresolved engineering challenges, however, because of the important role of pulverized coal in base load electricity generation and its contribution to CO2 emission, this paper is primarily concerned with the combustion of pulverized coal, although some mention is made of other fuels as well.

These three major carbon capture technologies for coal-fired power plants have been studied in terms of power generation efficiency, capital costs and costs of electricity (COE) [14–16]. Representative energy efficiency and economic performance of these technology options are compared in Table 1. All of these estimates are based on 90% CO2 capture in rebuilt and retrofitted scenarios. The cost of CO2 indicates the cost that is incurred to capture 1 metric ton carbon dioxide without transportation and storage. Although the absolute numbers vary by few percentage points in these studies, all reports show the same trends. In general, all three capture technologies result in an efficiency penalty, while oxy-fuel capture and pre- capture or IGCC show advantages over post-combustion capture in terms of COE and cost of CO2. The IGCC technology yields a higher generation efficiency and a slightly lower cost than oxy-fuel combustion technology. However, all these technologies are in their early stages of development and still have great potential for improvement.

In particular, these studies have a common conclusion that oxy-fuel combustion is the most competitive technology option for retrofitting existing coal-fired power plants, which at the moment have the largest potential for CCS. Fig. 1(a) shows the installed power capacity of existing coal-fired power plants and their initial operation year in the U.S. Although the number of newly-built coal power generation units declined since 1990s', there is a resurgence of new coal power plants in recent years. Moreover, about 98.7 GW or 29% of all the existing coal-fired power capacity were built after 1980 [17]. This situation is even more prominent in developing countries such as China and India, where the coal power generation capacity has been booming in the last two decades. As shown in

| FGD | flue gas desulphurization |
| GLR | gas-to-liquid ratio |
| HRS | heat recovery steam generator |
| HTAC | high temperature air combustion |
| HTC | heat transfer coefficient |
| ITM | ion transport membranes |
| LSV | large eddy simulation |
| LHV | lower heating value |
| MILD | moderate or intense low-oxygen dilution |
| NETL | national energy technology laboratory |
| OEC | oxygen enriched/enhanced combustion |
| PC | pulverized coal |
| PFG | product flue gas |
| RANS | Reynolds-Averaged Navier-Stokes |
| RFG | recycled flue gas |
| RR | recycle ratio |
| SCR | selective catalytic reduction |
| SMD | Sauter mean diameter |
| SNBM | statistical narrow band model |
| TGA | thermogravimetric analysis |
| UBC | unburned carbon |
| WM | wire mesh reactor |
| WSSD | weighted-sum-of-gray-gases |
| WSR | well stirred reactor |
| ZEPP | zero emission power plants |
Fig. 1(b), the built rate of coal-fired power generation units in China is up to 80 GW per year, significantly higher than that of the U.S. This growth is driven by China’s fast economic development [18]. It can safely be assumed that a sizable reduction of CO2 emission from existing plants would come from retrofits. Oxy-fuel combustion systems have a natural advantage in retrofitting existing PC power plants because they can reuse most of the existing plant equipment.

The advantages of oxy-fuel combustion as a retrofit technology are also indicated in Table 1. The capital cost for supercritical PC retrofits with oxy-fuel is $867/kWe, which is significantly lower than the capital cost of post-combustion retrofit ($1314/kWe) and of newly-built IGCC plants ($1890/kWe).

Considering the advantages of a relatively moderate efficiency penalty and the lowest retrofit capital expenditure, atmospheric
oxy-fuel combustion systems have been widely accepted as a competitive carbon capture technology. More recently, it has been adopted to substitute the original IGCC plan in the U.S. DOE FutureGen 2.0 program [19]. Previous studies have reviewed its characteristics [6,20–22] as well as recent developments in pilot-scale and commercial-scale demonstration plants [23]. While successful, the technology still faces many challenges, such as air leakage into the flue gas system, the relatively low energy efficiency, the need for efficient air separation and better plant integration and flue gas cleanup, among others. In particular, significant challenges are expected in the combustion process itself, including stability and emissions, burner design and scaling, as well as determining of optimal operating conditions. This paper focuses on the combustion process, especially the impact of the absence of nitrogen and the reuse of flue gas as a diluent on the physics, chemistry and dynamics of oxy-combustion.

1.2. Focus and methods

The paper focuses on reviewing the fundamentals of oxy-fuel combustion of pulverized coal in a CO2-rich environment. In particular, it examines how oxy-fuel combustion differs from air-fuel combustion in areas including fuel delivery, slurry atomization, heat transfer, coal particle combustion and its interactions with the gaseous phase, flame stabilization and pollutant formation. Aside from reviewing experimental and numerical studies in the literature, qualitative modeling studies using simplified models are also carried out with the objective of determining the impact of the dilution medium on the combustion process. In these modeling studies, detailed chemical reaction kinetics and transport properties in a well stirred reactor or a plug flow reactor, as well as simplified numerical models for single coal particle combustion, are used. The implications of the simulation results on combustion design are discussed. Another focus of this review is the applications of oxy-coal combustion at elevated pressures. The potential impact of the pressure on the oxy-combustion characteristics is discussed based on previous relevant studies. These discussions will enable future developments of oxy-coal combustion over a wider range of operating conditions.

The paper outline is as follows: following an introduction on the evolution and characterization of oxy-fuel combustion and its applications in power plants for CCS in the introduction Section 1, in Section 2, some of the fundamental processes in oxy-coal combustion are discussed. The contents are organized in such a way that each subsection starts with a physical description of the process or a scaling analysis showing the difference between oxy-coal and air-coal combustion. Experimental and numerical studies on oxy-combustion of coal and at times, of gaseous fuels, are reviewed in order to compare the combustion phenomena in O2/CO2 and in O2/N2 environments. These comparisons include the impact of the environment on heat transfer, both locally and globally, transportation, demonitization, devolatilization and ignition of the coal particles, char burning, as well as combustion in the homogeneous phase, etc. Research on pollutant formation under oxy-fuel conditions is also briefly reviewed. However, the reader is referred to other literature reviews in more detail.

The distinct characteristics of oxy-coal combustion raise new challenges in flame stabilization, and this issue is addressed in Section 3. Using simplified models, the flammability limit and laminar burning velocity under oxy-fuel combustion conditions are shown to be different than in air-fuel combustion, indicating that destabilization problems may occur when using conventional coal burners. The impact of the fuel-oxygen equivalence ratio, flue gas recirculation and preheat temperature on flammability are analyzed. Based on a review of experimental studies on oxy-coal flame stabilization, the general principles for oxy-coal burners retrofitting and designing are discussed. Many of the local, meso-scale and large-scale models discussed earlier in the paper are used in computational fluid dynamics (CFD) simulations of coal combustion. The modification of sub-models and modeling results of numerical studies are depicted in Section 4. Finally, some research needs in the field are proposed in Section 5.

1.3. Brief history of oxy-fuel combustion technologies

1.3.1. Oxy-fuel combustion for high temperature processes

Even before the concern over CO2 emissions arose, forms of oxy-fuel combustion had been used in different applications. Fig. 2 shows schematically oxy-fuel combustion regimes as function of the preheat temperature and oxygen mole fraction of the oxidant stream. The following regimes have been identified:

- **Zone I**: Air combustion (diluted with N2), or air-like oxy-fuel combustion with a flue gas recycle ratio (RR) of 60–80% vol (i.e. oxygen mole fraction of about 30% in the oxidizer stream). The recycle ratio is defined as:

\[
RR = \frac{m_{\text{RFG}}}{m_{\text{RFG}} + m_{\text{PFG}}}
\]

where \(m_{\text{RFG}}\) is the recycled gas mass flow rate and \(m_{\text{PFG}}\) is the product gas mass flow rate respectively.

- **Zone II**: Oxygen-enriched or oxygen-enhanced combustion (OEC) with oxygen mole fraction significantly higher than 21%.

- **Zone III**: Full oxy-fuel combustion with pure oxygen.

- **Zone IV**: High temperature air combustion (HiTAC) and high temperature oxy-fuel combustion with greatly preheated oxidizer.

In existing utility boilers, pulverized coal is typically combusted in air which consists of 21% O2 and 79% N2, placing this combustion in Zone I. However, the flame temperature of air combustion is not high enough for some industrial processes such as the production of glass, metal and cement. Therefore, oxy-enhanced or oxy-enriched combustion (Zone II), featuring a higher flame temperature and a higher available sensible enthalpy, was proposed in the 1970s to improve the energy efficiency in these
processes [24]. At that time, oxy-fuel combustion was defined as combustion with an oxidizer stream containing oxygen mole fractions higher than 21%, in which nitrogen was retained as the dilution gas. Because of its advantages in NOx reduction and cost effectiveness in some applications, this technology was first applied in the glass and metal industries and then in the cement and incineration industries as an alternative to the High Temperature Air Combustion (HiTAC) technology (Zone IV) [25,26].

As the combustion regime moves from Zone II toward the right in Fig. 3, i.e., as the oxygen mole fraction is increased, the combustion intensity rises. As the dilution is further decreased to zero, the regime achieved is called the full oxy-fuel combustion regime (Zone III). In this regime, pure oxygen is used, resulting in a very intense flame. An example of a typical full oxy-fuel combustion system is the acetylene oxy-fuel flame used for welding and cutting purposes. The adiabatic flame temperature is as high as 3343 K, which is much higher than that of the air combustion (2535 K) due to the absence of inert gases that dilute the products in air-combustion [24].

The combustion regime at the top of Fig. 2 is the high temperature air combustion (HiTAC) regime (Zone IV). High temperatures are achieved because of the use of highly preheated air. The oxygen mole fraction can be reduced significantly below 21% while still maintaining stable combustion. For instance, experimental results show stable liquefied petroleum gas (LPG) flame combustion with low oxygen concentration air (less than 5%) at air temperatures above 800 °C [26]. In recent years, a new combustion technology named MILD combustion or flameless combustion has been developed in this regime, featuring a uniform temperature distribution and low NOx emissions. This phenomenon is defined by Cavaliere and Joannon [27] as “a combustion process with the inlet temperature of the reactant mixture that is higher than mixture self-ignition temperature, whereas the maximum allowable temperature increase with respect to inlet temperature during combustion is lower than mixture self-ignition temperature”. Since no intense flame front is formed in MILD combustion, NOx emissions are significantly reduced.

Note that all the “historical” oxy-fuel and HiTAC systems discussed above are developed for high temperature processes and are not the same as the oxy-fuel combustion systems designed for CCS. Unlike the oxy-fuel combustion for CCS, nitrogen is still used as the diluent gas, therefore, the oxy-fuel combustion used for high temperature applications are different from oxy-fuel combustion for CCS, and we will limit our discussion to the characteristics of the latter.

1.3.2. Oxy-fuel combustion for CCS

When nitrogen is removed from the oxidant, a high CO2 concentration stream is generated at the end of the combustion process. Usually, recycled flue gases are used to replace nitrogen and control the combustion temperature. The idea of applying oxy-fuel processes with flue gas recycle in coal-fired plants to control the CO2 emission [28,29] and/or produce high concentration CO2 for enhanced oil recovery (EOR) was first proposed in 1982 [28,30]. As such, the main purpose of oxy-fuel combustion applications in coal-fired plants is no longer high temperatures, but the recovery of concentrated carbon dioxide in an air-like combustion environment. Following these proposals, Argonne National Laboratory (ANL) pioneered the investigation of this process in the mid and late 1980s, focusing on the system and its combustion characteristics [31–33]. Soon after, more and more researchers agreed that this system complements the two other major approaches for carbon dioxide capture, which led to a renewed interest in this technology in the 1990s. Research conducted by the International Flame Research Foundation (IFRF), CANDM, IHI, as well as other institutes and industrial parties has made considerable contributions in understanding of this process.

In the case of retrofitting existing PC power plants, the combustion temperature and heat transfer rate in the conventional air combustion system are intentionally maintained in order to utilize the existing equipment. Therefore, the operating conditions of the optimized oxy-fuel are such that an air-combustion-like environment is achieved while satisfying the economic and safety concerns. The air-like oxy-fuel combustion (categorized in Zone I of Fig. 2) system thus has been viewed not only as an appropriate technology for new units but also as an excellent retrofit strategy for existing coal-fired power plants. Similar, or higher, O2 concentrations as in air combustion systems (15–30% by volume) are used in this regime, and the oxidizer stream is not preheated. The associated combustion phenomena in this regime have been extensively studied and reviewed by Buhre et al. [21], Wall et al. [22] and most recently, by Toftegaard et al. [20] and Zheng et al. [34].

Along with the research and development on the air-like oxy-coal technology, pilot and large scale demonstration plants are being built around the world. Wall et al. [23] surveyed research on oxy-fuel technology, from pilot-scale tests, to industry-scale tests and full-scale demonstrations, and compiled the historical development of this technology worldwide, as shown in Fig. 3. The year 2008 marks an important milestone with the commissioning of the world’s first 30 MWth demonstration plant in Germany. More large-scale demonstrations in industry-scale coal-fired boilers have been planned or are already underway, as shown in Table 2, based on the work of Wall et al. [23] and Herzog [35]. Success in these demonstrations is expected to lead to wider commercial deployment.

Recent research has also focused on extending the range of operating conditions of oxy-coal combustion to improve energy efficiency, environmental performance and economics of this technology. “Full” oxy-fuel combustion was proposed by CANMET for their third generation oxy-fuel combustion system [36] with the material constraints being the main concern and challenge. Although the MILD regime is difficult to realize in coal combustion because the heat recuperator used for external heat recirculation cannot handle flue gases with fly ash, efforts have been made to apply this regime to air-fired coal combustion [37–41] and more recently, to oxy-fired coal combustion [40,42,43]. MILD oxy-coal combustion regime may be achieved by using highly preheated [42] or even oxidizer streams without preheating [40]. Internal flue gas recirculation can make MILD combustion conditions locally possible in the vicinity of the burner [45]. These proposed operating conditions for oxy-coal
combustion, however, will require major changes to the heat exchanger system, and are still at their conceptual phases.

1.4. Oxy-coal combustion systems

The concept of oxy-coal combustion involves the burning of coal in pure oxygen to obtain a carbon dioxide-rich stream that is ready for sequestration, after removing water vapor and other impurities. Various oxy-coal combustion systems have been proposed in the literature[21,42,46–48]. The first version is the atmospheric pressure oxy-coal system in which flue gases are partially recycled to moderate the flame temperatures. An alternative to using recycled flue gases is to inject steam to control the flame temperature [46]. To further increase the performance of these systems, pressurized systems have been proposed for both oxy-coal combustion with recycled flue gases [47,49–53] and oxy-syngas combustion in combination with solid fuel gasification technology [48]. These approaches are described in greater detail in the following sub-sections.

1.4.1. Atmospheric oxy-coal combustion systems with flue gas recycle

The atmospheric oxy-coal combustion system shown in Fig. 4 was first introduced as a short-term solution to retrofit existing coal-fired power plant to include the option of CCS. In most oxy-coal system studies, recycled flue gases at various RR are used to control the flame temperature in the combustor and as a result, the flue gas consists primarily of steam which is later removed through condensation, and carbon dioxide which is purified before being sent for compression and sequestration. The additional equipment required, when compared with air-fired systems, is described below:

1.4.1.1. Air Separation Unit (ASU). When retrofitting existing PC power plants, the system primarily uses existing equipment with the exception of an ASU used to produce an oxygen rich stream for combustion. Currently, the only ASU technology that can meet the volume and purity demand of a large scale coal-fired utility boiler is based on cryogenic distillation. Air is compressed, cooled and cleaned prior to being introduced into the distillation column to separate air into an oxygen-rich stream and a nitrogen-rich stream. Cryogenic air separation is energy intensive, consuming about 0.24 kWh/kg O₂ with 95% oxygen purity [15,54]. Although the oxygen purity requirement for oxy-coal combustion (85–98%) is lower than that needed in the process industry (99.5–99.6%) [55], these cryogenic separation processes can consume more than 15% of the gross power output [15,56–58].

Conventional adsorption methods and membrane separation are also commercially available, however these methods have not been applied to large volumetric gas production due to the higher cost and integration complexity. Other advanced air separation technologies are still in the inception phase or under development, such as the ion-transport membranes (ITM) and chemical looping air separation (CLAS). In an ITM, oxygen is separated by exploiting the oxygen partial pressure gradient across nonporous, mixed-conducting,

![Fig. 4. Atmospheric oxy-coal combustion system with flue gas recycle proposed for carbon capture in coal power plants, figures are revised based on the work in [20–22].](image-url)
ceramic membranes at 800–900 °C. If successfully scaled up to CCS applications such as IGCC, the overall plant efficiency is expected to increase by 1–3 percentage points with about a 6.5% reduction of the COE [59]. However, this technology may not be directly transferable to solid fuel combustion. On the other hand, the CLAS has been lately proposed for air separation, which relies on circulating metal oxide particles between an oxidation reactor and a reduction reactor, a chemical principle similar to that used in the CLC [60].

1.4.1.2. Carbon dioxide purification unit (CPU). CPU consists of gas cleanup units to remove water, particulate matter and other pollutant gases from the flue gas before being compressed for sequestration. Because oxy-combustion is compatible with retrofits, selective catalytic reduction (SCR), electrostatic precipitator (ESP) and flue gas desulphurization (FGD) are typically retained as means of NOx, particulate matter and SOx removal from the flue gases. These pollutant control devices are also suitable for use in conjunction with amine-type absorbents for post-combustion capture plants.

It has been widely accepted that the non-condensable impurities, such as O2, may cause cavitation damage and corrosion in the pipeline during transportation, and this has raised doubts about the safety of the storage sites. Therefore, after the removal of acid gases such as SOx and NOx, non-condensable N2, O2, and Ar should also be purged using a non-condensable gas purification unit. This unit is made of multi-stage compression units with inter-stage cooling in order to separate out the inert gases. Up to the time of this review, there are still no agreed upon standards regarding the required purity of CO2 for storage and sequestration. However, it should be noted that the acceptable degree of purity of the storage-ready CO2 results from a trade-off between efficiency losses and operational costs during purification and the safety demands of transportation and storage. For a detailed discussion of this topic, the reader is referred to [20].

1.4.1.3. Flue gas recycle (FGR) system. Recycled flue gas is required to replace nitrogen and moderate the combustion temperature. Considering system efficiency and operation practices, flue gases can be recycled at different locations downstream of the economizer in the form of wet or dry recycles. In the early stages of oxy-coal system studies, the requirement on CO2 purity was not stringent and the desulphurization and de-NOx equipment were regarded as unnecessary [61,62]. Therefore, all the flue gas was proposed to be extracted from a single location downstream of the ESP in wet or dry forms [61]. Later on, Dillon et al. [62] proposed flue gas recycling at different locations for the primary (used for transporting coal) and secondary streams for the sake of energy efficiency: while the primary recycle has to be dried and reheated to 250–300 °C to take up moisture from the coal feed, the secondary stream can be recycled at higher temperatures without drying to eliminate thermodynamic losses caused by cooling and re-heating [62].

Today, with a stricter requirement on CO2 purity for pipeline transportation and storage, pollution control equipment have been again taken into account in the flue gas recycle configurations. Moreover, since SO2 concentration in the flue gas may accumulate due to flue gas recycle, resulting in 2 or 3 times higher concentration than in conventional air-firing systems, the primary recycle has to be at least partially desulphurized for medium and high sulfur coal, to avoid corrosion in the coal mill and flue gas pipes.

1.4.2. Pressurized oxy-coal combustion systems

Pressurized oxy-fuel combustion systems have been proposed recently, with the objective of improving the energy efficiency by recovering the latent heat of steam in the flue gas. The flue gas volume is reduced under elevated pressure, which results in smaller components and possible reductions in capital cost for the same power output. Several studies have reported on the technical and economic feasibility of this process [47–53,63,64], all concluding that the overall process efficiency improves with increasing operating pressure. This is mainly because latent heat recovery from the flue gases becomes possible at higher temperatures. Other potential advantages of pressurized oxy-fuel systems are the reduction of the auxiliary power consumption such as the recycle fan work, and the elimination of air ingress into the system. However, there are challenges associated with combustion and heat transfer characteristics at elevated pressures, and hence the burners, steam/gas heat exchangers and condensing heat exchangers must be redesigned [65].

Fig. 5 illustrates two different pressurized oxy-coal combustion systems proposed in the literature. One of the first designs is the ThermoEnergy Integrated Power System (TIPS) proposed and studied by CANMET [49,66] and Babcock power [53]. This system (Fig. 5a) uses a pressurized combustion unit and heat exchangers, as well as a flue gas condenser (FGC). Downstream of the radiative boiler and convective heat exchangers, steam in the flue gases is condensed in the FGC, where most of the latent heat in the flue gas is recovered by the feedwater in the steam cycle. The rest of the flue gas, which is essentially CO2, is purified and compressed to the sequestration specifications. In contrast, in the pressurized system proposed by ENEL based on a combustion process patented by ITEA [67–69], and analyzed by MIT (Fig. 5b) [51,52], the hot flue gases from the pressurized combustor is quenched to about 800 °C by the recycled cold flue gas, eliminating the need for a radiant heat exchanger and thus incurring a lower capital cost. It should be noted that these pressurized oxy-coal systems coal is fed in the form of coal-water slurry (CWS). Since the pressurized system takes advantage of the latent heat recovery from the steam in the flue gas, using a coal-water slurry does not significantly decrease the overall energy efficiency.

For the pressurized oxy-fuel power plants with CO2 enriched flue gas streams, desulphurization and NOx removal solutions have been proposed with potentially lower cost and higher energy efficiency, using lead chamber chemistry and nitric acid chemistry at elevated pressures. For instance, Air Products [70,71] proposed utilizing two high pressure countercurrent reactive absorption columns (see Fig. 5(b)) while Iloeje et al. [72] combines them into a single high pressure column to remove SOx as H2SO4 and NOx as HNO3. Both solutions claim to have significantly reduced the cost of CO2 purification with the latter having an advantage in terms of reduced power consumption and capital cost.

Although the above-mentioned studies agree on the benefits of a pressurized system, they differ on the recommended operating pressure. This difference lies mainly in the design of the flue gas condenser and in disagreement on the amount of recoverable latent heat at different pressure levels. In the TIPS system studied by CANMET [66] and Babcock power [53], a temperature difference greater than 100 °C is maintained between the flue gas and the feedwater in the flue gas condenser, with the flue gas temperature at the condenser outlet being 213–262 °C. The high temperature difference ensures a sufficiently high heat flux and a relatively small heat exchanger size. The amount of recoverable latent heat and the net efficiency increase monotonically with the operating pressure. CANMET suggested that the benefit of increasing the pressure beyond 80 bar is relatively small, while the Babcock power study indicated that the benefit of latent heat recovery is most pronounced between atmospheric pressure and 20.7 bar.

Unlike the TIPS system, the system proposed by ENEL based on a combustion process patented by ITEA [67–69] uses a much smaller temperature difference of about 20 °C in the flue gas condenser, with the flue gas temperature at the condenser outlet being roughly 50 °C. In so doing, most of the latent heat can be recovered at 11 bar [52]. As shown in Fig. 6, the net efficiency for the
ENEL system reaches a maximum value at a combustor pressure of 11 bar, very close to that of the TIPS system at 90 bar. Further increasing the system pressure does not yield additional benefits in terms of net efficiency. In order to optimize the equipment size and reduce the capital cost, Gazzino et al. [63] proposed to maintain the same maximum flue gas velocity in the convective heat exchangers while increasing the system pressure. In such a case, for a fixed flue gas mass flow rate, the cross-sectional area of the heat exchanger is reduced, but the length is increased to match the total heat transfer, which entails a higher pressure drop. Therefore, increasing the operating pressure above 11 bar results in a reduction in the net efficiency. At this point, no studies have been carried out to investigate the optimal trade-off between the capital cost (equipment size) and the net power efficiency.

Another pressurized oxy-combustion concept that has been suggested involves the gasification of solid or liquid fuels to produce gaseous fuel, or syngas. The syngas is combusted in oxygen diluted by recycled CO2 and/or steam, yielding an exhaust gas consisting mainly of CO2 and/or steam, which is used as a working fluid in a gas turbine. This new configuration and working fluid properties would require adaption of the current turbomachinery components [73-76]. Anderson et al. [48] applied the oxy-fuel combustion concept to the burning of syngas, while taking advantage of a gas turbine (and a combined cycle) to further increase the efficiency, in the so called “Oxy-Fuel Zero Emission Power Plants” (O-F ZEPP). In their initial design, a GE J79 turbine was adapted to run as an intermediate pressure turbine connected to the oxy-syngas combustor exit. The overall efficiency achieved is 30–34% based on the lower heating value (LHV) after taking the ASU and CO2 compression work into account.

1.4.3. Performance of the oxy-coal combustion systems

An important question to address at this juncture is the comparative performance of the atmospheric and pressurized oxy-fuel combustion systems described above. Fig. 6 shows the capital expenditure ($/kWe) and efficiency (HHV%) of these systems for newly-built power plants, compared to the performance of supercritical pulverized coal systems without capture and with post-combustion capture. Data are summarized from independent studies carried out by NETL [15], MIT [14,47,52], CANMET [66,77], ThermoEnergy [50,78,79], and Kanniche et al. [16]. It is noteworthy that estimates in the open literature vary according to their assumptions and approximations. For instance, fuel type, size and configuration of the power plants, percentage of CO2 captured, and parameters of the steam turbine, etc. Allowing for differences in

Fig. 5. Pressurized oxy-coal combustion systems proposed for carbon capture in coal power plants, figures are revised based on the work in [52,53,66,78]. (a) Schematic of the ThermoEnergy integrated power system (TIPS), (b) System proposed by ENEL based on a combustion process patented by ITEA, and analyzed in recent studies by MIT.

![Diagram A](image1)

![Diagram B](image2)

![Figure 5](image3)

![Figure 6](image4)
System efficiency estimates showed a loss of about 10–15% percentage points when post-combustion capture is added to the base case PC power plant. On the other hand, the atmospheric oxy-fuel combustion shows an advantage of 1–5 percentage points when compared with post-combustion capture; while the pressurized system gains a further 3 percentage points efficiency. The main advantage of pressurized oxy-fuel system is the higher power enables more thermal energy recovery and the recuperation of flue gas recycle. There are significant variations in capital costs estimates in these studies due to inflation since 2004. The MIT study [14] showed lower cost estimates for the PC without capture, post-combustion, and atmospheric oxy-fuel systems, because it was based on the cost of 2000–2004; while Pomalis et al. [77] estimated higher costs. The economic studies may only be viewed as relatively comparable values, but not absolute values before they are evaluated from commercial scale deployments, especially for the pressurized oxy-fuel systems. It should be noted that these data are for newly-built power plants, in fact, the capital cost estimates for retrofitted atmospheric oxy-coal power plants are significantly lower than any of these options as discussed in Section 1.1.

2. Thermodynamics, transport and chemistry in oxy-coal combustion

This section focuses on the thermodynamics, transport and chemistry processes that take place during oxy-fuel combustion of coal. Experimental and numerical studies of single coal particles or a group of coal particles are reviewed with emphasis on the impact of a CO2-rich environment. We start with a discussion on the heat transfer characteristics in oxy-fuel combustion and how to match the heat flux with that in the conventional air-fuel combustion, followed by a description of the stages and processes that a coal particle undergoes as it is entrained into the furnace: transport, ignition and burning of the volatile matter, flame propagation, char combustion, and pollutant formation. The physical properties of N2 and CO2 relevant to oxy-fuel combustion are summarized in Table 3. The effects of these properties will be discussed in greater detail in each of the following sub-sections.

2.1. Heat transfer

Extensive studies have been conducted on retrofitting existing coal-fired power plants for oxy-fuel combustion. Most studies agree that the first priority in the retrofit effort is to maintain the same heat transfer characteristics in the furnace as in air-fired combustion. Matching the heat transfer in the furnace can lead to similar combustion stability, carbon burnout, and slagging and fouling tendencies [33]. The following subsections focus on the fundamentals of radiative and convective heat transfer in oxy-fuel combustion, and discuss methods to maintain similar heat transfer characteristics when retrofitting a PC boiler to an oxy-fired mode, based on a review of the experimental and simulation studies on temperature distribution and heat transfer in furnaces and boilers.

2.1.1. Radiative heat transfer

Radiative heat transfer plays an important role in boilers and furnaces. The characteristics of radiative heat transfer in oxy-combustion are distinct from conventional air-coal combustion because the flue gas compositions are different. A simplified scaling analysis can be used to estimate the radiative heat transfer rate from an oxy-fuel combustion flame. The entire flame is considered to be a uniform source of radiation, and its total radiative energy release rate can be approximated as:

\[ \dot{q}_{\text{rad}} = \varepsilon A_f \sigma T_f^4 \]  

(2)

where \( \varepsilon \) is the average emissivity for the flame, and \( A_f \) and \( T_f \) are the flame surface and temperature, respectively. The flame temperature is the overwhelming factor because of its 4th order dependence [80]. Therefore, to match the radiative heat flux.

### Table 3

<table>
<thead>
<tr>
<th>Physical process</th>
<th>Physical property</th>
<th>Unit</th>
<th>CO2</th>
<th>N2</th>
<th>CO2/N2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermodynamic</td>
<td>Density</td>
<td>kg/m³</td>
<td>0.5362</td>
<td>0.3413</td>
<td>1.57</td>
</tr>
<tr>
<td></td>
<td>Specific heat capacity</td>
<td>kJ/kgK</td>
<td>1.2343</td>
<td>1.1674</td>
<td>1.06</td>
</tr>
<tr>
<td></td>
<td>Volumetric heat capacity</td>
<td>kJ/m³K</td>
<td>0.662</td>
<td>0.398</td>
<td>1.66</td>
</tr>
<tr>
<td></td>
<td>Gas-water interfacial tensiona</td>
<td>N/m</td>
<td>71.03</td>
<td>71.98</td>
<td>0.987</td>
</tr>
<tr>
<td>Momentum transfer</td>
<td>Kinematic viscosity</td>
<td>m²/s</td>
<td>7.69e-5</td>
<td>1.2e-4</td>
<td>0.631</td>
</tr>
<tr>
<td>Heat transfer</td>
<td>Thermal conductivity</td>
<td>W/mK</td>
<td>7.057e-2</td>
<td>6.599e-2</td>
<td>1.07</td>
</tr>
<tr>
<td></td>
<td>Thermal diffusivity</td>
<td>m²/s</td>
<td>1.1e-4</td>
<td>1.7e-4</td>
<td>0.644</td>
</tr>
<tr>
<td></td>
<td>Absorptivity/emissivity</td>
<td>&gt;0</td>
<td>~0</td>
<td>~0</td>
<td>~0</td>
</tr>
<tr>
<td>Mass transfer</td>
<td>Mass diffusivityb</td>
<td>m²/s</td>
<td>9.8e-5</td>
<td>1.3e-4</td>
<td>0.778</td>
</tr>
</tbody>
</table>

a Water gas interfacial tensions are evaluated for CO2/water and air/water interfaces at 298.15 K.
b Mass diffusivity refers to the binary diffusion of O2 in CO2 and nitrogen.
between air and oxy combustion, one must achieve gas temperatures in the latter that are close to those found in the former. On the other hand, for the same flame temperature, radiation heat transfer is enhanced when the emissivity is higher. Unlike symmetric diatomic gases such as N₂, triatomic gases such as CO₂ and H₂O are not transparent to radiation. Their partial pressures are significantly higher in oxy-fuel combustion flue gas than those in air-fuel combustion, and correspondingly, the absorptivity and emissivity of the flue gas substantially increases.

When a radiation beam of specific wavelength \( \lambda \) travels through a gas, a portion of the radiation intensity, \( dI_l \), is absorbed by the gas. The change in the spectral radiation intensity, \( dl_l \) within an infinitesimal beam length \( ds \) is:

\[
dl_l = -k_l dl_l ds
\]

where \( k_l \) is the spectral absorption coefficient, which is a function of the wavelength, gas composition, gas temperature and pressure [81]. The spectral absorptivity and emissivity can be derived by integrating the above Eq. (3) over the beam length, \( s \):

\[
\alpha_l = \epsilon_l = 1 - \exp(-k_l s)
\]

Fig. 8 shows the spectral absorptivity, \( \alpha_l \), of the different gas components produced in a combustion process [82]. Since triatomic gases (CO₂ and H₂O) have much higher partial pressures when flue gases are used as the diluent instead of nitrogen, the absorption and radiation in oxy-combustion are stronger than in conventional air-fuel combustion with identical gas temperatures.

A close look at Fig. 8 shows that absorption is not continuous over the entire spectrum; instead it is concentrated in a number of moderately wide spectral bands. The effective absorptivity and emissivity of a gas mixture can be obtained by integrating the above equation over the full spectrum. However, direct computation of the gas absorptivity is difficult, and gray gas or band models are widely used in the CFD modeling, which will be discussed in Section 4.3.

Soot and particle (coal, char and fly ash) radiative emission and absorption play as important a role as the triatomic gases in coal combustion [83,84]. Experimental studies in oxyfuel combustion have confirmed this trend. Andersson and coworkers [85–88] investigated the radiation intensity of propane-fired and lignite coal-fired oxy-fuel flames in the Chalmers’100 kW test facility. The total radiation intensity was measured using a narrow angle radiometer, and the gas radiation was estimated using Malkmus Statistical Narrow Band Model (SNBM). Results of the calculated gas and the measured total radiation intensities at the flame zone are shown in Fig. 9. It can be seen that the portion of the gas radiation in the total radiation intensities under OF25 condition (OF25 denotes oxy-fuel combustion with O₂ concentration of 25% in the burner gas) is significantly higher than in air-combustion. Measurements show that the temperature distribution in the flame zone under OF25 condition is very close to that under the air-firing condition (see Section 2.1.3 for greater detail), and that the H₂O partial pressure increases only slightly from air to OF25 condition, therefore, the higher gas radiation in oxy-fuel combustion is attributed to its 5 times higher partial pressures of CO₂. However, the effect of the enhanced gas radiation during oxy-fuel combustion becomes less important when comparing to the particle radiation; the particle radiation contributes about 60–70% of the total radiation in both air-fired and oxy-fired cases. This study suggests that in lignite oxy-fuel combustion, if the gas temperature is maintained the same as in air combustion by increasing the O₂ concentration to 25% (OF25), the measured total radiation intensities are similar (OF25-total and Air-total) although gas radiation is enhanced. This is because a large fraction of radiation is emitted by particles, which have similar contribution in both combustion environments.

2.1.2. Convective heat transfer

The convective heat flux of the flue gas, \( q_{conv} \), can be approximated as follows:

\[
q_{conv} = h \Delta T
\]

where \( h \) is the convective heat transfer coefficient, and \( \Delta T \) is the temperature difference between the bulk gas and the heated object. The convective heat transfer coefficient is influenced by the flow velocity and gas properties such as viscosity, thermal conductivity, heat capacity and density, which are also functions of temperature. The ratio of convective heat transfer coefficients of the flue gas in oxy-fuel combustion (\( h_{oxy} \)) to that in air-fuel combustion (\( h_{air} \)) can be expressed in terms of dimensionless numbers - the Reynolds number and the Prandtl number - and the fluid thermal conductivity [33]:

\[
\frac{h_{oxy}}{h_{air}} = \left( \frac{Re_{oxy}}{Re_{air}} \right)^m \left( \frac{Pr_{oxy}}{Pr_{air}} \right)^n \left( \frac{k_{oxy}}{k_{air}} \right)
\]

where \( m \) and \( n \) are empirical factors that vary for different geometries. The slightly higher thermal conductivity of CO₂ does
not significantly change the conductive heat transfer when compared with air-combustion. However, for convective heat transfer at identical velocity, its lower kinematic viscosity results in a larger Reynolds number and thus a higher convective heat transfer coefficient.

Woycenko et al. [89,90] studied convective heat transfer coefficients in oxy-coal and air-coal combustion. The ratio $h_{\text{oxy}}/h_{\text{air}}$ is shown in Fig. 10. This ratio increases with increasing recycle ratio because of the changes in the thermal properties of the flue gas and the increase in the gas velocity. This figure also shows that, for the recycle ratios reviewed in this paper, the convective heat transfer coefficient ratio is slightly above unity in most of the cases. For instance, this value is ~1.15 when the wet recycle ratio is 70%, at which the adiabatic flame temperatures are approximately the same.

Recall that in Eq. (5), the convective heat flux is a function of the temperature difference ($\Delta T$), which on average decreases with increasing recycle ratio. Therefore, an acceptable operational range of the flue gas recycle ratio exists in which one can approximately match the convective heat transfer in oxy-coal combustion to that of air combustion [20,91]. Thus the existing coal-fired power plant can be retrofitted to function as an oxy-coal plant without replacing the boiler or heat exchangers.

### 2.1.3. Matching of combustion temperature

There are several constraints that need to be considered when retrofitting a conventional air-fired power plant to oxyfuel combustion, including the combustion temperature, the furnace outlet temperature, and the heat transfer in radiative and convective heat exchangers. Based on the above analyses, it appears that matching the gas temperature profiles in the boiler is a starting point in the effort to maintain similar heat transfer characteristics in oxy-coal combustion. A good indication that the temperature profiles are matched is when a similar adiabatic flame temperature (AFT) is achieved. Wall et al. [22] calculated the theoretical O$_2$ mole fraction (or flue gas recycle ratio) necessary to maintain the same AFT under air-coal and oxy-coal combustion conditions using the equilibrium approximation. Approximately 20% excess air in air-coal combustion and 3–5% excess O$_2$ in oxy-coal combustion are used to ensure that all the calculations are done on the same basis of about 3.3% (v/v) residual O$_2$ in the flue gas. Fig. 11 shows the computational results of the AFT in air-fired and oxy-fired conditions with increasing oxygen fractions for both wet and dry flue gas recycle. The results suggest a temperature drop of about 400 K and 800 K, respectively, in wet and dry recycling oxy-fuel combustion with oxygen concentration of 21% by volume when compared with that of the air-fired condition. The authors did not indicate the coal type in their calculation; it should be noted that the results are depend on the approximate and ultimate analysis of coal.

Table 3 summarizes selected physical properties of CO$_2$ and N$_2$ and their ratios at 1000 K and 1 atm in four categories: thermodynamic properties, momentum transfer properties, heat transfer properties and mass transfer properties. From the data shown in Table 3, although the specific heats of CO$_2$ and N$_2$ are similar on mass basis, the CO$_2$ heat capacity on mole basis is 1.66 times higher than that of N$_2$ because of its larger molecular weight. Since the N$_2$ is replaced with CO$_2$ and H$_2$O under wet recycle oxy-fired conditions, and with CO$_2$ in dry recycle oxy-fired conditions, there is a significant reduction in the combustion temperature. In order to match the AFT with that of air-fired combustion, the overall oxygen mole fraction in the burner inlet should be increased to about 28% or 35% for wet and dry recycle, respectively, to compensate for the effects of the higher molar heat capacities of H$_2$O and CO$_2$. It is also noteworthy that in practice, the combustion temperature cannot be as high as predicted by the equilibrium calculations carried out by Wall et al. [22] because of the heat absorbed by the radiative heat exchangers.

The gas phase temperature profiles in the furnace have also been measured experimentally to investigate the influence of the flue gas recycle ratios on the gas temperature and heat transfer in the furnace under oxy-coal combustion conditions, with the objective of maintaining a heat flux similar to that observed in air combustion. Selected researches are listed in Table 4. Most of these pilot scale facilities have refractory walls lined with water jackets to simulate the combustion conditions in utility boilers. However, the heat transfer characteristics of these test facilities may vary due to facility setup and operating conditions. The measured temperature profiles are given at limited locations (usually in the centerlines of the furnaces), and are subject to measurement errors from radiation effects, and finite response times. Therefore, they can only be used as general estimates of the gas temperature distribution in the combustion zones.

![Fig. 10. Effect of recycle ratio on convective heat transfer coefficient [89]. Primary O$_2$ is the oxygen mole fraction in the primary stream.](image-url)

![Fig. 11. The O$_2$ partial pressure (fraction) required at burner inlet (to achieve similar adiabatic flame temperature as the air-fired case) for wet and dry flue gas recycle (residual O$_2$ mole fraction in the flue gas fixed at 3.3%) [22]. The symbol ▼ indicates the AFT of air-coal combustion, the red solid line --- and blue dash line --- indicate the AFT of oxy-coal combustion with wet and dry flue gas recycle, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)](image-url)
Table 4
Bench and pilot scale experimental studies on gas temperature and heat transfer in atmospheric oxy-coal combustion.

<table>
<thead>
<tr>
<th>Organization</th>
<th>Fuel</th>
<th>Facility</th>
<th>Recycle mode</th>
<th>Experiment findings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Argonne National Lab/EERC* [31,33]</td>
<td>Black Thunder Sub-bituminous Coal from Wyoming</td>
<td>3 MWth, vertical tower furnace</td>
<td>Wet/Dry FGR</td>
<td>Flue gas recycle ratios ((CO₂+H₂O)/O₂ in the oxidant) of 3.25 and 2.6, in wet and dry recycle respectively, matches the overall heat transfer of the air-fired furnace.</td>
</tr>
<tr>
<td>Argonne National Lab/BCL [32,33,250]</td>
<td>Wage coal from Colorado</td>
<td>117 kWth, bench scale furnace, i.d. 0.6 m</td>
<td>CO₂/O₂ mixture</td>
<td>Dry recycling with a CO₂/O₂ molar ratio of 2.23 yields a furnace temperature distribution similar to that of air combustion.</td>
</tr>
<tr>
<td>IFRF [89,90]</td>
<td>Coal</td>
<td>2.5 MW, 2*2 m internal square cross-section</td>
<td>Wet FGR</td>
<td>58–61% of the flue gas is recycled for stable combustion and matched convective heat transfer coefficient and radiative heat flux.</td>
</tr>
<tr>
<td>University of Leeds [182,183]</td>
<td>Bituminous coals from UK and international sources</td>
<td>Down-fired 20 kWth combustor</td>
<td>CO₂/O₂ mixture</td>
<td>When air is used as the primary stream, an O₂ concentration of 30% in the secondary stream produces matching gas temperature profiles. When an oxygen concentration of 30% is used in both primary and secondary streams, the resulting gas temperature is higher than air-coal combustion.</td>
</tr>
<tr>
<td>Chalmers University of Technology [85–88]</td>
<td>Propane and lignite coal</td>
<td>100 kWth</td>
<td>Dry FGR</td>
<td>Oxy-Propane combustion: With an O₂ mole fraction of 25%, the temperature profiles in the furnace can be matched with that of air-propane combustion. Soot formation also plays an important role in the radiation intensity in air and oxy-combustion of propane. Calculated gas radiation is higher in oxy-combustion than in air combustion, but contributes only 30%–50% of the total radiation intensity.</td>
</tr>
<tr>
<td>IHI [95]</td>
<td>Low- and medium-volatile bituminous Coal</td>
<td>1.2 MWth horizontal combustion test facility</td>
<td>Wet/Dry FGR</td>
<td>Oxy-Lignite coal combustion: With an O₂ mole fraction of 25%, the temperature distribution can be matched with that of air-fuel combustion; the flue gas temperatures at the furnace outlet are lower in all the oxy-fuel cases than in air-fuel case. When using a secondary gas stream with an oxygen mole fraction of 30%, and dry recycled flue gas as the primary gas, the gas temperature near the burner is lower in oxy-fuel combustion; the gas temperature is greatly increased with direct oxygen injection; drying the primary gas increases the gas temperature by 150 °C near the burner.</td>
</tr>
<tr>
<td>RWEn power [91]</td>
<td>Russian and South African coals</td>
<td>0.5 MWth, RWEn combustion test facility</td>
<td>Simulated Dry FGR</td>
<td>Peak radiative heat flux values are inversely related to the recycle ratio. Conversely, the convective heat transfer values increase with increasing recycle ratio. A matched radiative heat transfer is established at recycle ratio between 68% and 72% for Russian coal, and between 72% and 75% for South African coal, respectively. The experimental data show that matched heat transfer characteristics can be established with about 74% dry recycle ratio for Russian coal.</td>
</tr>
<tr>
<td>CCSD/IHI [22]</td>
<td>Three Australian coals</td>
<td>1.2 MWth pilot scale vertical test facility</td>
<td>Wet FGR</td>
<td>Gas temperatures of the oxy-fuel flame with a dry recycle ratio of 76% (21.3% O₂ in the burner gas) are lower than the temperatures in air-fuel flame. The gas temperatures downstream of the burner are almost matched with that of air-fuel combustion.</td>
</tr>
<tr>
<td>E.ON UK/Hitachi [189]</td>
<td>Tselelitis coal</td>
<td>1 MWth, horizontal firing</td>
<td>Dry FGR</td>
<td>Gas temperatures of the oxy-fuel flame with a wet recycle ratio of 53% (39.3% O₂ in the burner gas) are lower before the level 3 measurement port, and higher at all following levels.</td>
</tr>
<tr>
<td>IVD/Hitachi [189]</td>
<td>Lauszit lignite coal from Germany</td>
<td>500 kWth, down-shot firing</td>
<td>Wet FGR</td>
<td>Gas temperatures of the oxy-fuel flame with a wet recycle ratio of 53% (39.3% O₂ in the burner gas) are lower before the level 3 measurement port, and higher at all following levels.</td>
</tr>
<tr>
<td>CANMET [92,94]</td>
<td>Bituminous, sub-bituminous, and lignite coals</td>
<td>0.3 MWth, vertical combustor research facility (VCRF), cylinder down-flow, 0.6 m inner diameter</td>
<td>CO₂/O₂ mixture, or Partial FGR with make-up CO₂</td>
<td>With an O₂ mole fraction of 28%–35%, the gas temperatures and heat fluxes can be matched with those of the air-coal combustion.</td>
</tr>
</tbody>
</table>

* Energy and Environment Research Corporation in Irvine, CA.
A wide range of oxygen mole fractions (about 23.5–35%) needed to achieve gas temperatures and heat transfer performances similar to those in air-coal combustion have been reported. For instance, CANMET [92–94] conducted a series of experiments in a 0.3 MW vertical combustor research facility (VCRF) to investigate the influence of oxygen mole fraction on the combustion temperature and heat transfer in the furnace. A broad range of oxygen concentrations, from 21% to 42%, was tested in O2/CO2 modes with bottle CO2 as well as in air-fired conditions [92]. The gas temperatures and heat fluxes were found to match air-combustion with O2 mole fraction between 28% and 35% in oxy-fired conditions for bituminous and sub-bituminous coals. Similar results were obtained when using partial flue gas recycle [94]. Andersson et al. [86] and Hjartstam et al. [88] needed a relatively lower oxygen mole fraction (about 25% in the feed gas) to achieve a gas temperature equivalent to that of air-lignite coal combustion (see Fig. 12). When operating with higher oxygen mole fractions of 27% and 29%, they found that combustion temperatures are 50 °C and 100 °C higher than that of air-coal combustion, respectively.

One of the most important factors for determining the oxygen level needed to match the temperature field is whether the recycled flue gas is wet or dry. This is because of the higher volumetric heat capacity of CO2 as compared with H2O. Compared with Wall’s calculation [22] in which O2 mole fractions of 28% and 35% are required, respectively, to maintain the theoretical AFT in wet and dry recycle conditions, experimental results in the literature, listed in Table 4, indicate a slightly lower mole fraction: 23.5%–27% for wet recycle, and 25%–35% for dry recycle. This may be because of the lower combustion temperatures encountered in the practical furnaces. Moreover, no explicit relation between the oxygen mole fraction and the scale of the tested furnace thermal capacity has been found in the experimental studies shown in Table 4.

An exception to the conclusions stated above is reported in the experimental findings of Nozaki et al. [95], who performed oxy-coal combustion experiments on the IHI 1.2 MW horizontal combustion test facility using a low- and a medium-volatile bituminous coal. When using wet flue gas in the primary stream and an oxygen mole fraction of 30% in the secondary stream, the combustion gas temperature near the burner was significantly lower than that of air-coal combustion. Drying the flue gas in the primary stream was found to be beneficial to the combustion temperature. Fig. 13 shows that drying the primary gas helps to increase the combustion temperature by about 150 °C. However, the paper did not explicitly state whether the recycled flue gas volumetric flow rate was fixed in the case with dry flue gas. If the recycled flue gas volumetric rate was fixed, the recycled stream flow rate to the burner would have become lower because water vapor was removed, and the flame temperature could have been higher because of the lower total recycled gas volume.

The optimal oxygen fraction for a matched temperature is also dependent on the fuel, and this dependence needs further investigations. Fig. 14 shows the measured temperature profiles in the CANMET bench scale vertical combustor research facility [92]. It can be seen that the gas temperature of the Canadian western sub-bituminous coal (Highvale) oxy-combustion with an oxygen mole fraction of 35% is 80 °C higher than in air-coal combustion, whereas the temperature difference between the two combustion environments with the same oxygen mole fraction is much smaller for the higher rank US Eastern bituminous coal. In other words, the required oxygen mole fraction for the higher rank Eastern bituminous coal was higher. To the contrary, Smart et al. [91] conducted radiative flux measurements in the RWEn 0.5 MWth combustion test facility firing two different coals under oxy-fuel conditions and observed the opposite trend. Their results, shown in Fig. 15, compare the radiative flux in the furnace when firing Russian and South African coals. It can be seen that a recycle ratio between 68% and 72% produces a heat flux profile similar to air firing for the
Russian coal, while the ratio is between 72% and 75% for the higher rank South African coal. This difference in recycle ratios indicates that the required oxygen mole fraction for the higher rank South African coal is lower. Based on these limited findings, no conclusions can be drawn concerning the dependence of oxygen mole fraction, or recycle ratio, on the coal type (such as its rank, moisture content, etc.), and further investigations are required to address this topic.

2.1.4. Matching of radiative and convective heat transfer distribution

Considering that the radiative and convective heat transfer characteristics in oxy-fuel combustion are rather different from those in air-fuel combustion, a matched gas temperature might be close to, but not precisely, the optimum operating condition in order to obtain a matched distribution of heat fluxes in different heat exchanger components. Hence, studies have also been conducted in order to find the optimum recycle ratios for a matched heat transfer distribution in the furnace (radiative section) and in the convective section. Based on the discussion in Section 2.1.1, radiation dominates the heat transfer process in the furnace. Radiation intensifies with increasing flame temperature and decreasing flue gas recycle ratio. Therefore, to match the heat transfer distribution between radiative heat exchangers for phase change and convective heat exchangers for superheat, there is an optimal flue gas recycle ratio. Lower recycle ratios result in higher combustion temperatures and excess heat extraction in the radiative section, especially in the water-cooling membrane section. In this case, the required superheat and reheat temperatures of the steam cannot be attained. Conversely, higher recycle ratios result in a lower combustion temperature and a reduced steam mass flow rate that is overheated. In this case, considerable attemperation (a measure controlling the overheated steam temperature) with feedwater injection is required to reduce the steam superheat temperature, and this would reduce the boiler efficiency [33].

In experiments conducted by Payne et al. [33] on a 3 MWth pilot scale test furnace, heat extraction in various boiler sections was measured under oxy-coal combustion for a range of recycle ratios, in both wet and dry flue gas recycle modes. As shown in Fig. 16, the optimal oxygen mole fractions at which the radiative heat exchangers reach heat extractions similar to those of air-fired condition are 23.5% and 27.8% (corresponding to (CO₂ + H₂O)/O₂ mole ratios of approximately 3.25 and 2.6) for wet and dry recycle, respectively. Under such conditions, the furnace temperatures for both the wet and dry recycle processes were slightly lower than the case of air-coal combustion and this is compensated by the enhanced radiation and convective heat transfer in oxy-combustion.

Moreover, the same study [33] showed that the recycle ratio and oxygen mole fraction needed to match the heat transfer distribution of the corresponding air-fired system are also dependent on the scale of the combustion facility. Fig. 17 shows that the optimal CO₂/O₂ ratios in dry recycle needed to match the heat transfer distribution are 2.45, 2.6 and 2.7 for 117 kWth bench scale furnace, 3 MWth pilot scale furnace and 44 MWhe utility boiler, respectively. This scale-dependence is closely tied to the radiative heat transfer characteristics: the gas emissivity increases with increasing beam length in larger scale boilers, hence lower flame temperatures are required to maintain a similar radiative heat flux, which are attained by a higher recycle ratio.

Similarly, a recent experimental study on a 0.5 MWth RWEn combustion test facility conducted by Smart et al. [91,96] showed the effects of varying the recycle ratio on the radiative and convective heat flux under simulated dry recycle conditions. Fig. 18 shows...
a similar trend as described above, that the radiative heat flux decreases with increasing recycle ratio, and that the matching radiative heat flux is attained at a recycle ratio of about 74% with an adiabatic flame temperature that is lower than that in the air-fired condition. The authors suggested that the higher flame emissivity, due to soot and possibly a higher concentration of CO2, compensates for the lower combustion temperature in oxygen-fuel combustion. On the other hand, as shown in Fig. 18, the convective heat transfer coefficient (HTC) rises with increasing recycle ratio within the range of operating conditions analyzed in the study, and reaches a value that matches the HTC under air-fired condition at a recycle ratio of 74%. This trend, caused by the increased mass flow over the convective tube at higher recycle ratios, agrees with the results of the experiments conducted by Woycenko et al. [89] discussed in Fig. 10.

It should be noted that although the HTC matches that observed under air-fired condition at the same recycle ratio in which the radiative heat flux is also matched (74%), the corresponding convective heat flux may not match because of the lower flue gas temperature (also see Eq. (5)). Therefore, measures for modifying the heat exchangers, such as the refractory lining and/or convective heat exchanger cluster adjustment, might be necessary when retrofitting existing PC boiler to operate under oxy-combustion conditions.

2.2. Fuel delivery and injection

2.2.1. Pulverized coal transport

Pulverized coal is delivered to coal boilers using a carrier fluid. In conventional atmospheric pressure PC boilers, pulverized coal is transported by preheated primary air [97]. In an air-like oxy-coal system, recycled flue gases (primarily CO2) are used to transport pulverized coal into the boiler. The lower oxygen concentration in the carrier gas reduces the risk of coal-dust explosions. While the pneumatic transport of pulverized coal by air was extensively investigated in the past, similar studies using CO2 as the carrier fluid have yet to be performed. This is worth mentioning because the physical properties, for instance the density and the viscosity, of air and CO2 are different.

To maintain a similar transport performance, the solid-gas mass fraction, the carrier gas velocity, and the pressure drop will have to change. The pick-up velocity, \( v_{pu} \), is defined as the mean velocity of a gas stream required to transport solid particles in suspension through a horizontal pipeline without allowing them to settle on the bottom of the pipe, and it is the minimum conveying velocity in the design of pneumatic transport systems. Cabrejos and Klinzing [98] carried out experiments to determine the pick-up velocity and found that the pick-up velocity is roughly inversely proportional to square root of the gas density:

\[
 v_{pu} \alpha \sqrt{\rho_g} \quad (7)
\]

Based on dimensional analysis and experimental data, they further suggested the following correlation for the pick-up velocity, \( v_{pu} \), to convey particles that are larger than 100 \( \mu \)m in a horizontal duct:

\[
 v_{pu} = \left( \frac{0.0428 \Re_p^{0.175}}{D} \right)^{0.25} \left( \frac{\rho_g}{\rho_p} \right)^{0.75}
\]

where \( g \) is gravity, \( d_p \) is the particle diameter, \( D \) is the pipe diameter, and \( \rho, \rho_p \) are the density of the gas and particle. \( \Re_p = \rho v_{pu} d_p / \mu_g \) is the particle Reynolds number using mean gas velocity. This correlation is valid for \( 25 < \Re_p < 5000; \ 8 < D / d_p < 1340; \) and \( 700 < \rho_p / \rho_g < 4240 \). Assuming the primary stream temperature is 90 \( ^\circ \)C and using the physical properties referred from the NIST database [99], the estimated pick-up velocities for 1000 \( \mu \)m coal particle in a 0.2 m diameter horizontal duct are 9.6 m/s and 7.4 m/s in air and CO2, respectively.

Therefore, when a dry recycle flue gas composed mainly of CO2 is used for the pneumatic transport of pulverized coal instead of air, the pick-up velocity is smaller. The fact that the flow velocity required to entrain the coal powder is reduced has been observed experimentally by Cabrejos and Klinzing [98], and Villareal and Klinzing [100]. In a conventional air-fired system, it is typical to choose an air velocity higher than 20 m/s to avoid the saltation and settling of solids in horizontal pipelines. Hence, from the above argument in Eq. (7), roughly a CO2 velocity of at least 16.3 m/s should be chosen. However, pneumatic conveying technology is heavily based on engineering experience and experimental studies [101], and more work is needed to determine the guidelines, such as the minimum carrier gas velocity and pressure drop, when using recycled flue gas as the transport fluid.

2.2.2. Coal-water slurry

At higher operating pressures, pulverized coal is typically transported to the burner/combustor in the form of dry coal by lock hoppers, or in the form of slurry (coal-water slurry (CWS) or coal-liquid CO2 slurry). The dry feed lock hopper system discharges coal particles into the combustor via staged opening and closing of valves on the top and bottom of the pressure vessel. The system can work under pressures of up to about 40–50 bar [102]. CWS is prepared by wet grinding the coal in a rod mill, which is then stored and pumped into the combustor [103]. The CWS system can be operated under pressures of up to 70 bar, thus it provides a broader operating range for pressurized oxy-coal system. Later studies have shown that coal-liquid CO2 slurries have advantages over coal-water slurries, leading to higher cold gas efficiencies in gasification applications [104,105]. Since both the TPIS and ENEL pressurized oxy-coal systems use the CWS as the fuel delivery method, we confine our discussion to this form of coal delivery and review its atomization characteristics.

The coal-water slurry is atomized into small droplets during injection to maximize the reaction surface of the fuel and to facilitate its mixing with the oxidizer streams before combustion. Several types of atomizers have been developed for this purpose,
such as pressure nozzles, rotary atomizers, twin-fluid atomizers, air-assist atomizers and effervescent atomizers. A review of the operating principles of these atomizers and their application in combustion systems was given by Beer and Chigier [106].

Sojka and Lefebvre [107] conducted experiments on a CWS effervescent atomizer, and developed an empirical correlation to estimate the Sauter mean diameter (SMD) as function of the coal particle size, the atomization pressure, and the GLR. For the atomizer geometry and coal particle size in their study, they found the following correlation:

\[
\text{SMD} = \frac{12\sigma}{\rho_l \left(v_f - v_g\right) \left(1 + \frac{1}{\varepsilon \text{GLR}}\right)}
\]  

Eq. (9) and Eq. (10) indicate that the SMD is a function of GLR, \(\varepsilon\) and Weber number. \(W_e\) is the ratio of the kinetic energy of a droplet issuing from the jet relative to its surface energy. A large \(W_e\) indicates that the injected slurry liquid sheet has a relatively higher kinetic energy, which breaks up the liquid sheet to form many smaller droplets. Since the coal-water droplets contain 35–40% water by weight, the gas-water interfacial surface tension is used to calculate the \(W_e\) of the droplets.

It is interesting to compare the atomization phenomena of coal-water slurry issuing into a gaseous environment dominated by nitrogen, as in air-fuel combustion, with one dominated by CO\(_2\), as in oxy-fuel combustion. Fig. 19 shows that the \(W_e\) in a high CO\(_2\) concentration stream does not differ much from the \(W_e\) in pure N\(_2\). However, the difference is markedly obvious at elevated pressures (>5 MPa) where the \(W_e\) in the high CO\(_2\) concentration stream is significantly larger. This is mainly because of the smaller interfacial tension of CO\(_2\)-water that is observed in experiments [108]. Higher \(W_e\) corresponds to smaller atomization droplet size, indicating that CWS atomization can be better in pressurized oxy-coal combustion.

### 2.3 Heating and moisture evaporation of coal particles

Grinded pulverized coal particles are heated up and partially dried by the primary air or recycled flue gas in the coal mill in order to avoid blockage of the primary pipe. To ensure drying capacity, the primary air or recycled flue gas should be reheated to above 250 \(^\circ\)C, and maintained around 60–90 \(^\circ\)C at the mill exit [62]. The remaining moisture content of the coal particle, or the water content in the case of CWS fuel, is evaporated in the furnace before heating, devolatilization and burning take place. Considering the different heat transfer characteristics in oxy-fuel combustion, heating and moisture evaporation processes of a single coal particle might be different, which in turn may influence the heating rate, devolatilization rate and yield, as well as the standoff distance of the flame (also denoted as lift-off distance, which is defined as the distance between the burner tip and the visible ignition of the flame).

In this work, the impact of the gas composition on single coal particle drying and heating processes is analyzed using a simplified heat transfer model, and the evaporation time and heating rate in air-fuel and oxy-fuel conditions are estimated. Fig. 20 shows an illustration of a quasi-steady model that considers heat transfer between a single coal particle, the surrounding gases and the luminous flame. The energy conservation of a coal particle can be expressed as the balance of the particle internal energy and convective/radiative heat transfer:

\[
\frac{4}{3} \pi r_p^3 \rho_p c_p \frac{dT_p}{dt} = 4\pi r_p^2 \sigma (T_\text{fl}^4 - T_p^4) + 4\pi r_p^2 \sigma (e_f T_\text{fl}^4 - e_p T_p^4)
\]  

where \(T_\text{fl}\) is the temperature of the surrounding hot gas, and \(T_p\) is the flame temperature. The heating rate is strongly determined by the temperatures of the gas and the flame. If the oxygen concentration is kept the same, the flame temperature for oxy-combustion is comparatively lower than that of the air-fuel combustion (also see 2.1.3), resulting in a lower heating rate. This effect is considered in the estimation by assigning different surrounding gas temperatures. On the other hand, the convective heat transfer coefficient of the flue gas, \(h\), may be different, which also may result in a different heating rate and evaporation time in oxy-fuel combustion.

Water evaporation from the coal particle is a process that couples heat and mass transfer. Using the quasi-steady model of
droplet evaporation [109] and the model of coal-water slurry evaporation proposed by Cen et al. [110], evaporation times for different particle sizes under both air and CO₂ conditions are calculated, with the following assumptions:

1. Coal particles have a spherical shape with a fixed radius during vaporization; only the density decreases until it reaches the dry coal particle density.

2. The relative velocity between the coal particle and the surrounding gas is the terminal velocity, \( v_t \), given by
   \[
   v_t = \frac{d^2 (\rho_p - \rho_g) g}{18 \mu_g}
   \]
   when \( \text{Re}_p < 2 \) [111].

3. The evaporation rate is controlled by heat transfer rather than mass transfer in the mill and in combustion [109].

4. The contribution of convective and radiative heat transfer is considered [110,112]. Research has found that for small particles in PC combustion, convective heat transfer is more dominant over radiative heat transfer during heating and evaporation processes [110]. This is because of the small surface area of the coal particle which limits the contribution of radiative heat transfer. Therefore, in the following analysis, the same flame emissivity is used to estimate radiative heat transfer, neglecting the difference between flame emissivity in air-fired and oxy-fired conditions.

Using the above assumptions, the evaporation rate (\( m, \text{kg/s} \)) can be derived as:

\[
\frac{m}{4\pi d^2} = \frac{k_g Nu}{2c_{pg}^f \ln(1 + B_q)} \tag{12}
\]

where

\[
B_q = \frac{c_{pg}(T_e - T_{boil})}{4\pi d^2 \alpha \left( \epsilon_f T_f^4 - \epsilon_p T_p^4 \right)} / m
\]

and the Nusselt number is given by Ranz and Marshall [113] as:

\[
Nu = 2 + 0.6R_{p}^{1/2} \rho_{fl}^{1/3} \tag{14}
\]

The evaporation time is obtained by integrating Eq. (12):

\[
T_{boil} = \frac{2(\rho_0 - \rho_{coal})c_{pg}^f d^2}{3k_g N_u \ln(1 + B_q)} \tag{15}
\]

The drying process in the mill and the furnace, and the heating process after evaporation under both air- and oxy-combustion conditions are investigated using the model, and the parameters and properties used in the calculation are summarized in Table 5.

Fig. 21 shows the required time for drying a coal particle under typical conditions in the mill and the furnace. The drying time of a 100 \( \mu \text{m} \) coal particles is about 1 s in the primary gas stream, and about 2.5 ms in the furnace, respectively, and it grows with increasing particle diameter. An interesting observation is that the drying times are similar in both air and CO₂ environment. For the typical size of a pulverized coal particle, the Reynolds number is small at the terminal velocity, such that the Nusselt number is close to 2, and the convective heat transfer is similar to conductive heat transfer under stagnant condition. Therefore, the thermal conductivity dominates the heat transfer rate. Given identical primary stream and combustion temperatures, the evaporation time is only slightly longer in the mill, and shorter in the furnace under CO₂-rich environment than in air. The reason is that the thermal conductivity of CO₂ is slightly lower than air at the mill temperature, and slightly higher than air at the furnace temperature. However, the difference is negligible if the primary stream temperature in the mill, or surrounding gas and flame temperature in the furnace are identical in the two environments. Similarly, Fig. 22 shows that the particle heating rate under CO₂-rich condition is only slightly higher than that in air.

The gas temperature and flame temperature are generally lower in oxy-coal combustion with similar oxygen concentrations (see Section 2.1.3). In order to investigate the impact of the potentially lower temperatures on the evaporation time, additional calculations were performed in which the temperatures in the CO₂ gas were reduced by 100 and 200 degrees from their original values, corresponding to \( T_e = 900 \text{ °C} \) and \( T_f = 1700 \text{ °C} \), and \( T_e = 800 \text{ °C} \) and \( T_f = 1600 \text{ °C} \), respectively. The results of the new calculation are also shown in Fig. 22. The heating rate of a 100 \( \mu \text{m} \) coal particle decreases in the cases where the gas and flame temperatures are 100 and 200 K lower than their original values. These results indicate that the particle heating rate is more significantly influenced by combustion temperatures than by gas compositions.

The analysis in this section indicates that employing a similar reheated recycled flue gas temperature will result in similar coal particle drying performance to that of air-combustion, and the

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Gas properties</th>
<th>Coal properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_e )</td>
<td>( T_f )</td>
<td>( T_{boil} )</td>
</tr>
<tr>
<td>Drying in mill</td>
<td>105</td>
<td>–</td>
</tr>
<tr>
<td>Drying in furnace</td>
<td>1000</td>
<td>1800</td>
</tr>
<tr>
<td>Heating in furnace</td>
<td>1000, 900, 800</td>
<td>1800, 1700, 1600</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 21. Predicted coal particle drying time as a function of particle size in air and CO₂ gas atmospheres. Drying processes in the primary duct during fuel transportation and in the furnace before combustion are estimated. The primary gas stream is set at 105 °C, and the gas and flame temperatures in the furnace are set to 1000 °C and 1800 °C, respectively.
such as N₂ and helium, to avoid the interaction with ambient gases. The utilization kinetics and yields are usually investigated in inert gases, temperatures under oxyfuel condition. Rathnam et al. [123] comparing the weight loss curves of a pulverized bituminous coal and others observe similar volatile yields. For example, when the temperature is set to 1000 °C and attributed this to the char-CO₂ gasification reaction. They also measured the volatile yields of four coals in a DTF with N₂ and CO₂ atmospheres at a nominal wall temperature of 1673 K. Once again, the volatile yields in CO₂ are about 5–25% higher than those in the N₂ atmosphere.

Al-Makhadmeh et al. [124] have reached the same conclusion in their pyrolysis experiments on a medium volatile bituminous coal and a lignite coal using an entrained flow reactor in CO₂ and N₂ environments. Fig. 24 shows the mass release (or volatile yield) as a function of the wall temperature for both coals at 700–1150 °C. The volatile yield is almost identical in both environments at low temperatures, while higher mass releases are observed in CO₂ at temperatures above 850 °C. At higher temperatures, the volatile yields are 10% and 11–14% higher in the CO₂ environment than in the N₂ environment for bituminous coal and lignite, respectively. The higher deviation for the lower rank coal might be due to its relatively higher reactivity with CO₂. More repeats of the experimental results would gain a higher confidence. Measurements of the pyrolysis gas speciation of the lignite coal have also been carried out at the end of the reactor in order to confirm the reason for the higher mass release in CO₂. As shown in Fig. 25, CO₂ concentration is indeed significantly higher, while H₂ concentration is considerably lower in a CO₂ pyrolysis atmosphere. This may be explained by water-gas shift reaction occurring at the higher CO₂ partial pressure.

To the contrary, Borrego and Alvarez [125] conducted coal pyrolysis experiments using a drop tube reactor at 1300 °C, and reported a lower mass release in a CO₂ pyrolysis environment for both Colombian vitrinite-rich high volatile bituminous coal and Western Canadian low volatile bituminous coal. The authors suggested that CO₂ could be involved in the process of cross-linking at the char surface of the resolidifying chars, which reduces the swelling of the particles and inhibits the volatile release.

Recently, Brix et al. [126] carried out pyrolysis experiments on a South American bituminous coal using an electrically heated entrained flow reactor in N₂ and CO₂ environments. In contrast to the observations reported in the previous paragraph, they found no difference in char morphology, char N₂-BET surface area, or volatile yields in the N₂ and CO₂ environments. The authors reviewed the discrepancies from the previous experiments and suggested that the operating conditions used during these experiments, such as the mixing between cold and hot gas streams, the particle heating rate and the total particle residence times as summarized in Table 6, inevitably affected the results. These factors must be taken into consideration when the data are compared. They concluded that the char-CO₂ gasification reaction does increase the volatile yield during devolatilization at high gas temperature and with long residence times (0.62 s and 1 s) as reported by Rathnam et al. [123] and Al-Makhadmeh et al. [124], respectively; whereas the lower mass release in CO₂ environment reported by Borrego et al. [125] might be due to the high amount of cold entrainment gas (~1/3) and short residence time (0.3 s).

### Table 6

<table>
<thead>
<tr>
<th>Author</th>
<th>Facility</th>
<th>Coal sample</th>
<th>Coal mass flow rate (g/h)</th>
<th>Size (μm)</th>
<th>Carrier gas flow rate (L/h)</th>
<th>Main gas flow rate (L/h)</th>
<th>Nominal temperature (°C)</th>
<th>Residence time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rathnam [22,123]</td>
<td>TGA</td>
<td>Coal A, B, C and D</td>
<td>NA</td>
<td>63–90</td>
<td>NA</td>
<td>NA</td>
<td>&lt;1200</td>
<td>2400</td>
</tr>
<tr>
<td>Borrego et al. [125]</td>
<td>Drop tube reactor</td>
<td>High/Low volatile bituminous</td>
<td>4–5</td>
<td>63–90</td>
<td>48</td>
<td>312</td>
<td>1400</td>
<td>0.65</td>
</tr>
<tr>
<td>Al-Makhadmeh et al. [124]</td>
<td>Entrained flow reactor</td>
<td>Bituminous (KK) and lignite (LA)</td>
<td>500–2500</td>
<td>–</td>
<td>400</td>
<td>9200</td>
<td>700–1150</td>
<td>1</td>
</tr>
<tr>
<td>Brix et al. [126]</td>
<td>Entrained flow reactor</td>
<td>South American bituminous</td>
<td>50</td>
<td>90–106</td>
<td>18</td>
<td>82%</td>
<td>900–1400</td>
<td>0.15–0.297</td>
</tr>
</tbody>
</table>
Correspondingly, the char morphology and specific surface area measurements (BET) showed different trends in these above mentioned experiments. Larger surface areas were observed for coals pyrolyzed under CO₂ devolatilization conditions in [123] and [124] to different extents. This was attributed to the char-CO₂ gasification reaction and, as mentioned before, no significant differences were detected in the char sample in [126].

2.5. Ignition of coal particles

Ignition and combustion behaviors of pulverized coal particle depend on the coal rank, particle size, heating rate and oxygen concentration in the environment. In general, two types of ignition mechanism have been observed for pulverized coal combustion: homogeneous ignition and heterogeneous ignition [127–129]. Homogeneous ignition is usually observed during high volatile bituminous coal combustion when volatile matter and O₂ are heated to the mixture auto-ignition temperature. The high surface flux of volatile products forces the reaction zone away from the solid surface, thereby preventing the solid material from oxygen attack [128]. On the other hand, sub-bituminous coal and lignite may experience heterogeneous ignition, in which ignition occurs via the oxidation of the coal surface [130], with or without fragmentation [131]. In this section, the different ignition behaviors are discussed in the presence of N₂ or CO₂ as diluent gas.

2.5.1. Theoretical analysis of homogenous ignition delay

For combustion of pulverized coal with high volatile contents, homogenous ignition of the volatiles and oxidizer mixture occurs first, followed by secondary ignition and burning of the char particle. Therefore, it is instructive to investigate the factors governing ignition delay of a mixture of gaseous volatiles and oxygen in a well-defined environment. Assuming that volatile combustion reaction can be simplified to a one-step global reaction rate in Arrhenius form:

\[
\frac{dc_F}{dt} = c_F A \exp \left( -\frac{E_a}{T} \right)
\]  

where \(c_F\) is the molar concentration of the fuel and \(T_a\) is the activation temperature. Following the derivation of Law [132], the ignition delay can be related to the thermal properties of the reactant gas as follows:

\[
\tau_i = \frac{c_F \left( T_0^2 / T_a \right)}{q_c Y_F \exp \left( -\frac{T_a}{T_0} \right)}
\]  

The Eq. (17) indicates that the homogeneous ignition delay depends on the molar heat capacity of the mixture, \(c_F\), the reaction heat release, \(q_c\), the reactivity of the fuel, as well as other operating conditions (the initial temperature, \(T_0\), and the initial mass fraction of fuel, \(Y_F\)). In the homogeneous ignition of coal volatiles, ignition delay is influenced by the following:

- **Temperature of the surrounding gas**: Ignition delay of the volatiles is shorter at higher surrounding temperature, mainly due to its exponential dependence on the temperature in the Arrhenius reaction rate term [132].
- **Heating and devolatilization rate**: Unlike gaseous fuels, volatiles are released through coal devolatilization before homogeneous ignition takes place. Therefore, the heating rate of coal particles and correspondingly, the devolatilization rate, strongly influence coal ignition delay.
- **Oxygen concentrations**: That ignition delay decreases with increasing oxygen concentration has been observed in studies.

Fig. 23. Normalized mass loss of a coal sample during pyrolysis in N₂ and CO₂ atmospheres in TGA, indicating an increased reactivity in CO₂ at high temperatures, cited from [123].

Fig. 24. Mass release for a bituminous coal (KK) and a lignite coal (LA) during pyrolysis in both N₂ and CO₂ environments [124].

Fig. 25. H₂, CO and CH₄ concentrations during a lignite coal pyrolysis in N₂ and CO₂ environments [124].
for both fine coal particles [133,134] and coal pellets [130] in O2/N2, and in an O2/CO2 environment in recent experimental studies [133,135,136] which will be discussed below.

• Coal volatile content: Similar to the trend of oxygen concentration, a higher volatile content also facilitates ignition. For instance, lignite and sub-bituminous coals have shorter ignition delays than bituminous coals because of their higher volatile yields during devolatilization [136,137].

• Molar heat capacity of the surrounding gas: Eq. (17) indicates that ignition delay is linearly proportional to the molar heat capacity of the gas mixture. This is because the temperature rise during ignition is inversely proportional to the heat capacity of the surrounding gas, and a higher heat capacity slows down the temperature rise and chemical reactions. Since CO2 has a molar heat capacity that is 1.66 times larger than that of N2 (see Table 3), the ignition delay time is expected to be longer. Single coal particle experiments have also confirmed this trend when replacing N2 with CO2, which will be discussed below in greater detail.

To examine these arguments qualitatively in a more idealized environment, the ignition process of stoichiometric CH4-21% O2/79% N2 and CH4-21% O2/79% CO2 mixtures are investigated using the closed homogenous reactor model of CHEMKIN [138] with GRI-Mech 3.0 reaction mechanism [139]. In order to simplify the problem, methane is used to be a substitute for the volatiles, and it is assumed to be well mixed with the surrounding gases in the coal particle boundary layer and at atmospheric pressure. Another simplification is that reaction kinetics is much faster than heat loss to the reactor wall, and the reactor system is assumed to be adiabatic. Reaction kinetics and the energy equation are solved in the transient problem, and the results show different trends for ignition delay in N2 and CO2 diluents. These assumptions may over- or under-estimate the ignition delay. For instance, simplifying the volatile composition and ignoring the presence of hydrogen may overestimate, while ignoring heat and mass transfer may underestimate the ignition delay. Therefore, the results are only qualitative.

Fig. 26 shows the temperature profiles of the gas mixtures in the closed homogenous reactor. Ignition delay is significantly longer in the CO2 diluent gas than in the N2: the temperature rises take place at 8 ms and 10.5 ms in N2 and in CO2, respectively. Moreover, the final combustion temperature is about 400 K higher in the N2 diluent gas. It is worth noting that the initial conditions in this calculation are set to be close to that of Levendis’ experiments [136]. Although the time for particle heating and devolatilization are not considered in this simulation, the results in Fig. 26 shows the influence of the changing atmosphere on ignition delay qualitatively. Simulation studies with more detailed consideration of the ignition process are needed in order to develop a better understanding of the ignition delay process in oxy-coal combustion.

2.5.2. Experimental studies on coal particle ignition delay in O2/N2 and O2/CO2

For the same coal type and operating conditions, ignition delay of single coal particles in both O2/N2 and O2/CO2 environments has been experimentally studied. A series of experiments were conducted by Molina, Shaddix and coworkers in Sandia National Lab to study the ignition behavior of an individual coal particle [133,135] and of groups of particles [140] under O2/CO2 and O2/N2 conditions. The devolatilization time of Pittsburgh bituminous coal in different O2 concentrations in a laminar entrained flow reactor were measured, using CCD and interference filter technology for image capture and CH+ chemiluminescence measurements. The experimental results on volatile ignition delay are shown in Fig. 27. The figure shows that the ignition delay time (τi) is longer in an O2/CO2 environment than in an O2/N2 environment with similar bath gas temperature profiles along the reactor. It is also observed that under both conditions, the ignition delay time decreases with increasing oxygen concentration. Shaddix and Molina [133,135] analyzed the trends of longer ignition delay in O2/CO2, and discussed several possible effects at the presence of CO2, such as heating rate (heat transfer), homogeneous autoignition delay (heat capacity), CO2 thermal dissociation (equilibrium), as well as chemical effect of CO2 on the radical formation. They suggested that the longer ignition delay in O2/CO2 mixtures is mainly due to the higher heat capacity of CO2, its tendency to suppress radical formation, or a combination of both [133].

More recently, Stivers and Levendis [136] measured the ignition delay times of four North American coals, including two lignite coals, a sub-bituminous coal and a bituminous coal, in O2/N2 and O2/CO2 atmospheres. The coal particles were ground to a size between 74 and 90 μm and were injected into a transparent quartz tube in an electrically heated drop tube furnace. Gas stream of O2/N2 or O2/CO2 was introduced coaxially with the coal particles into
the furnace, and the centerline furnace gases were measured to heat up and asymptotically reach a temperature 50 K below the furnace wall set-point temperature of 1400 K, within a few centimeters below the injector tip. As seen in Fig. 28, the experimental results showed longer coal particle ignition delay in the O2/CO2 environment than in the O2/N2 environment with identical O2 concentrations for all the coals tested. Moreover, the ignition delay time tended to be shorter with increasing oxygen mole fraction in the bulk gas under O2/CO2 conditions, but had no significant effect under the O2/N2 conditions. The insignificant effect of oxygen concentration under O2/N2 conditions may be because of the short ignition delay, and the differences are too small to be resolved experimentally. Further experiment measurements showed that the O2/CO2 mixtures were slower to heat-up than O2/N2 mixtures, therefore, the authors have attributed the longer ignition delay in O2/CO2 partly to the effect of volumetric heat capacity of the gas mixtures as described in 2.5.1, and partly to the slower heating rate of the background gas in the drop tube furnace which affects the convective and conductive heat transfer to coal particles [141].

The effect of CO2 on heterogeneous coal particle ignition has also been investigated using wire-mesh reactor (WMR) by Qiao et al. [142]. The ignition temperatures of a Loy Yang brown coal and a Datong bituminous coal were measured in both O2/N2 and O2/CO2 environments with the objective of studying the ignition of coal particles without the interference of volatiles burning. Since all the volatiles produced by the coal particles are swept away by the carrier gas flowing past the coal samples between the wire-mesh, the effects of volatile burning on the coal particle heterogeneous ignition temperature are effectively eliminated. When air was replaced with a mixture of 21% O2/79% CO2, the average particle ignition temperatures increased by 21°C and 7°C for the brown coal and bituminous coal, respectively. In order to confirm the effect of the different diluent gases on the heterogeneous ignition temperature, the experiments were repeated using argon and helium. As shown in Fig. 29, the experimental results show that the ignition temperature with helium is significantly higher than with other gases, and ignition only occurs when increasing the sample mass to 4 mg. In general, the heterogeneous ignition temperature increases in the following order: Ar < N2 < CO2 << He. The author suggested that the significantly higher ignition temperature in helium is because of its substantially higher thermal conductivity, which effectively cools down the char particle (see Table 7). Furthermore, a closer look at the experimental conditions shows that the convective heat transfer coefficient of CO2 in the experiments is slightly higher than that of N2 due to its larger Reynolds number, which may better explain the order of ignition temperatures in N2 and CO2 as observed in the experiment.

It should be noted that there are many differences between the experiments conducted in the wire-mesh reactor by Qiao et al. [142] and the experiments conducted in the drop tubes by Levendis et al. [136] and Shaddix et al. [133,135]. In the drop tube experiments, coal particles were heated by the hot gas and the ignition was initiated via the homogenous/heterogeneous ignition of the volatile matter and coal particles. In contrast, in the wire-mesh reactor, the volatiles were not involved in the ignition of the coal particles, and the particles were heated by conductive heat transfer from the electrically heated wire-mesh, with the low temperature carrier gas acting as a cooling medium. In the latter case, heat transfer, i.e., the enhanced convective heat loss to the cooling gas, turns out to be one of the main reasons for the higher heterogeneous ignition temperatures. Because of the distinctly different boundary conditions in WMR, the assumption of an adiabatic explosion model described in Section 2.5.1 does not hold. Therefore, the significantly higher volumetric heat capacity of N2 as compared to Ar and He are not reflected by the coal particle ignition temperatures. It was also argued that the slightly higher ignition temperature in CO2 than N2 is because of the endothermic char-CO2 gasification reaction [142].

Fig. 28. Measured ignition delay times, \( \tau \) (ms), of four North American coals in O2/N2 and O2/CO2 atmospheres with increasing O2 concentrations [136]. Data are averaged from single particle images, with statistical error bar.
2.5.3. Burning of volatiles

The burning characteristics of coal vary significantly depending on its rank, size and the operating conditions. For instance, Shaddix and Molina [133] found distinct volatile burning behaviors of two different rank coals in their entrained flow reactor (EFR) experiments. During the ignition of a Pittsburgh high volatile bituminous coal particle, a large hot volatile-burning soot cloud was observed, while lower radiation intensity was observed for the sootless Black Thunder subbituminous coal particle. Likewise, Levendis and coworkers [136,143] also observed different volatile burning behaviors in their drop tube furnace experiments: the combustion of bituminous coal was initiated by the ignition of released volatile matter which was sooty and bright, whereas lignite coals experienced extensive fragmentation during pyrolysis and combustion without clearly distinguishable volatile and char combustion stages. The different volatile burning phenomena are related to coal rank because soot is produced from the burning of long hydrocarbon chains in bituminous coal tar, while tar yields are much lower in lignite and anthracite devolutilization. Since it is difficult to measure the volatile burning behavior of lignite and subbituminous coals, the volatile burning characteristics were only reported for bituminous coals.

Lower combustion temperatures and longer burning times have been reported during the combustion of bituminous coal volatiles under CO2-rich conditions. Shaddix and Molina [133,135] investigated the combustion of Pittsburgh coal particles. As shown in Fig. 30, when replacing N2 with CO2, there appeared to be a trend toward a slightly larger soot cloud size and a lower soot cloud temperature. The same trends are confirmed by Bejarano and Levendis [143]: Fig. 31 shows that the measured burning temperature of the bituminous coal volatiles was lower, and burnout time was longer in O2/CO2 environments over an oxygen mole fraction range of 20%–80%. Moreover, based on the higher volatile burning temperature and the lower particle temperature, it is believed that the volatiles burn in a diffusion flame surrounding the devolutilizing coal particle [133]. Lower burning temperatures and longer burnout times in the CO2 diluted environment are likely to be caused by the lower volatiles and/or oxygen diffusion rate (similar to the argument of the lower char combustion rate, which will be discussed in detail in Section 2.6.2).

2.6. Oxy-char combustion

The effects of CO2 on char combustion/gasification have been extensively discussed for air-fired coal combustion [144–147], and more recently, for oxy-fired coal combustion [123,143,148,149]. CO2 is not an inert diluent in combustion; thus, it may influence char combustion via several possible mechanisms: (a) the reduced oxygen mass transfer in CO2, (b) the lower temperature due to the higher heat capacity of CO2, and (c) the char-CO2 gasification reaction [148].

Many experimental studies have been performed in recent years to investigate the effect of a CO2-rich environment on the combustion rate of coal char. Care should be taken when interpreting these studies because experimental results are strongly dependent on the operating conditions. For instance, char oxidation may take place in different regimes, either kinetic-controlled (Zone I), diffusion-controlled (Zone III), or controlled by both (Zone II), depending on the experimental temperature range, the coal rank and particle size used in the experiments, as well as the oxygen level in the ambient gas, among other factors. As a result, the char conversion rate under oxy-fuel conditions may become higher or lower than that in air-fuel mixtures.

With careful investigation of the experimental conditions used in the studies, the results can be classified into three regions, as illustrated in Fig. 32, based on the oxygen concentrations and nominal temperatures in these experiments. Note that the nominal temperatures of the WMR experiments are the measured particle temperature; while in TGA, DTF and EFR experiments, because the char particle temperatures are not available in some of the studies,

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>He</th>
<th>Ar</th>
<th>N2</th>
<th>CO2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal conductivity k</td>
<td>W/mK</td>
<td>0.2811</td>
<td>0.03596</td>
<td>0.04961</td>
<td>0.04930</td>
</tr>
<tr>
<td>Volumetric heat capacity $\rho C_p$</td>
<td>kJ/m$^3$K</td>
<td>0.3618</td>
<td>0.3619</td>
<td>0.5353</td>
<td>0.8634</td>
</tr>
<tr>
<td>Thermal diffusivity $a$</td>
<td>m$^2$/s</td>
<td>7.768e-4</td>
<td>9.3832e-5</td>
<td>9.2666e-5</td>
<td>5.7092e-5</td>
</tr>
</tbody>
</table>
the nominal temperatures are the gas temperatures, which are hundred degrees lower than the burning char particle temperature, depending on the oxygen mole fraction and coal rank. For instance, the temperature difference between the char particle and the gas is 1000 K in the Sandia EFR with an oxygen mole fraction between 12% and 36% [148], and is 400 K in the Northeastern University DTF with an oxygen mole fraction between 20% and 100% [143].

- **Region A- Low temperatures at any oxygen concentration:** The char oxidation reaction dominates the char consumption, which is kinetically controlled at these low operating temperatures. Most TGA experiments fall in this region, and the experimental results show similar reaction rates in O2/N2 and O2/CO2 environments. Clearly, when the oxygen concentration approaches 100%, the difference between the two environments becomes negligible and the char consumption rate is the same even at high temperatures, as shown in the small narrow region in the top right of Fig. 32.

- **Region B- High oxygen concentrations, high temperatures:** The char oxidation reaction dominates the char consumption, but char consumption is either in Zone II (internal diffusion controlled) or Zone III (external diffusion controlled). DTF and EFR experiments are typically conducted in this region, and the results show lower char consumption rates in O2/CO2 conditions because of the lower oxygen diffusion rate in CO2.

- **Region C- Low oxygen concentrations, high temperatures:** Char gasification reactions become significant at high temperatures and low oxygen concentrations. Experiments and numerical studies have shown higher char consumption rates due to the gasification reactions. Similar to the exemption in Region A, the gasification reactions may also become dominant at low temperatures when the oxygen concentration approaches zero, as shown in the bottom left of Fig. 32.

The partitioning in Fig. 32 is only qualitative and the boundaries of different regions may differ due to the differences in apparent char combustion behavior and reactor architecture. The dominant mechanisms in Regions A, B and C will be discussed in greater detail in the following sub-sections.

2.6.1. **Kinetics of char oxidation in oxy-fuel combustion**

The kinetics of the char oxidation reactions are usually measured at relatively low temperatures (conditions in Region A) to ensure that the reaction is kinetically controlled. TGA experiments have been used to measure the char consumption rate in CO2-rich environments, and the results have shown that the intrinsic char oxidation kinetics is not affected. For example, Varhegyi and co-workers [150,151] conducted TGA experiment in O2/CO2 and O2/Ar mixtures at atmospheric and elevated pressures and did not observe any specific effect when replacing Ar by CO2 under their experimental conditions (5% O2, 400-900 °C, 1 bar and 6 bar), except that the thermal decomposition of a mineral (calcium carbonate) component shifted to a much higher temperature in the O2/CO2 bath gas.

Liu observed the same trend in TGA experiments with a high-volatile U.K. bituminous coal and an anthracite coal in non-isothermal heating processes (2.5-12.5 K/min) [152]. Fig. 33 compares the normalized reaction rates with increasing char conversion at a heating rate of 2.5 K/s in 10% O2/90% CO2 and 10%

---

Fig. 31. Average temperature (a) and burnout time (b) for bituminous coal volatiles burning in O2/N2 and O2/CO2 at T_{furnace} = 1400 K, error bars show one standard experimental deviation [143]. Broken lines — correspond to burning in oxygen-nitrogen mixtures while continuous lines — correspond to burning in oxygen-carbon dioxide mixtures.

Fig. 32. Char oxidation/gasiﬁcation experiments in oxy-fuel conditions. The diagram shows three regions where the experiments were conducted. A: At low temperatures, reactions rates are the same in both O2/N2 and O2/CO2 conditions; B: At high oxygen level and high temperatures, reaction rates are lower in oxy-fuel conditions; and C: At low oxygen level and high temperatures, reaction rates are higher in oxy-fuel conditions. The error bars show the range of operating conditions, colors show unchanged (black), decreased (blue), or increased (red) char consumption rate. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 33. Comparison of the reaction rates versus conversion between the combustion in 10% O2/90% CO2 and the combustion in 10% O2/90% N2 (heating rate = 2.5 K/min): (a) U.K. Anthracite char and (b) U.K. Bituminous char [152].
O2/90% N2 environment. Results show that replacing the inert nitrogen gas with CO2 has very little influence on the measured combustion rates of coal chars at all char conversion levels. The same conclusion was reached in TGA measurements in the temperature range of 723–1163 K for anthracite and bituminous coals [153]. The negligible effect of carbon dioxide on the char reaction rate was attributed to the much lower reaction rate of the char-CO2 reaction than that of the char-O2 at the temperature and reagent gas composition in their experiments.

To verify this explanation, Varhegyi et al. [150] measured the char consumption rate in pure CO2, and found that the char-CO2 gasification reaction rate at 900 °C has the same magnitude as that in 5–29% O2 around 450 and 500 °C. That the intrinsic kinetics of the char-O2 reaction is about three to four orders of magnitude larger than those of the char-H2O and char-CO2 reactions, whereas the char-H2O reaction is several times faster than the char-CO2 reaction, have been reported previously [144,146,147]. Considering the substantially different intrinsic rates between the oxidation and gasification reactions, the gasification reactions only affect the char consumption rate in O2-deficient environments, which will be discussed in 2.6.3.

2.6.2. Effect of diffusivity

When approaching higher combustion temperatures while maintaining a high oxygen concentration in oxy-fuel combustion, the operating conditions transit from region A to region B in Fig. 32, in which DTF and EFR experiments are typically conducted. In this region, the char-O2 oxidation reaction still dominates, similar to the case in region A. However, char oxidation (char + O2) becomes progressively more diffusion controlled with increasing char particle temperatures, and for larger particle sizes. Therefore, oxygen diffusion turns out to be the controlling process in determining the char consumption rate in this region.

Measurements of temperatures and burnout times of single char particles have been conducted in both N2 and CO2 diluent gases. Bejarano and Levendis [143] investigated the burning of bituminous coal, lignite coal, and a spherical synthetic char at increasing oxygen concentrations in both N2 and CO2 diluent gases. They conducted particle temperature and burnout time measurements in a 4.2 kW electrically heated laminar flow DTF using a three-color pyrometer at relatively high oxygen concentrations (20%–100%) and high temperatures (1400 K and 1600 K). The experimental results showed that the coal particle temperatures are lower, and the burnout times are longer, in O2/CO2 than in O2/N2. For example, when operating the furnace wall temperature at 1400 K, the differences in char temperature between the two conditions, for bituminous coal and lignite coal, were on the order of 200 K and 120 K, respectively. Similarly, Shaddix and Molina [133,148] measured the char particle temperature of a Pittsburgh high-volatile bituminous coal and a Powder River Basin subbituminous coal in Sandia’s EFR at a gas temperature of 1700 K over an oxygen concentration range of 12–36% in N2 and CO2 diluent gases. Lower char particle temperatures and burnout times were observed for both coals in the O2/CO2 environment. After accounting for the diffusion limitation of oxygen through the particle’s boundary layer, the deduced intrinsic kinetics of the char oxidation reactions were found to be the same for O2/N2 and O2/CO2 conditions.

The carbon conversions of sampled char particles during oxy-char combustion in entrained flow reactors also show the same trend. Brix et al. [126] measured the char conversion profiles in an EFR under O2/N2 and O2/CO2 conditions with a coal feeding rate of 50 g/h. At the lower temperature range of 1173–1373 K and with an oxygen concentration of about 6%–28%, they observed no significant difference in the char conversion rate between the two environments, which confirms the trends in region A. When increasing the wall temperatures to 1673 K, where char oxidation is controlled by diffusion, the char conversion rates in CO2 were lower. Likewise, Al-Makhadmeh et al. [124] studied char combustion in a once-through 20 kW EFR at 1300 °C with an oxygen concentration of 5%–15% under O2/N2 and O2/CO2 conditions. The chars used for the combustion studies were produced in N2 and CO2 devolatilization environment, respectively. Similarly, a comparison between the two conditions shows that the char conversion and oxygen consumption are indeed slower in the CO2 balance gas. Moreover, they found that the difference between the two combustion environments is less significant at lower oxygen concentrations, which indicates that the diffusion effect becomes less dominant when the oxygen levels decrease (approaching region C).

In this paper, a simplified model for char particle combustion is used to investigate the impact of mass transfer on char oxidation in both air-fired and oxy-fired environments. Studies on carbon or coal char combustion are voluminous, and various models, such as the Single Film Model (SFM) and Double Film Model (DFM), have been proposed to describe the mass and heat transfer in the boundary layer surrounding a combusting char particle. The difference between these models is mainly the approximation of CO burning locations [154]. Mitchell et al. [155] modeled the CO oxidation process in coal boundary layers and suggested that little CO2 is formed in the boundary layer when the char diameter is smaller than 100 μm, which warrants the applicability of SFM for the size range of pulverized coal combustion. Therefore, SFM is applied in this study to examine the fundamentals of single char particle combustion in O2/N2 and O2/CO2, and the experimental results in [143] are used to verify the calculations from this model.

The char particle is described as a shrinking homogeneous sphere particle surrounded by a chemically frozen boundary layer [156], and the burning process is considered to be quasi-steady in a stagnant gas environment (O2/N2 or O2/CO2 with increasing O2 mole fractions). Oxygen diffuses toward the char particle through the dilution gas (either N2 or CO2) and reacts at a finite rate with the char surface to produce CO and CO2. Based on their experimental findings, Tognotti et al. [157] suggested that the CO2/CO ratio formed by the heterogeneous reaction on the char surface is less than 0.1 at normal combustion temperatures. Therefore, the simulation only considers CO as the combustion product, which diffuses away from the char surface. Diffusion and reactions inside the char particle are neglected.

Following the derivation in [109], the reaction heat release from char surface is balanced by thermal conductive and radiative heat transfer to the surrounding gas:

\[ \dot{m}_c \Delta h = -k_\text{g} 4\pi r_s^2 \frac{dT}{dr_s} + \varepsilon_s 4\pi r_s^2 \sigma (T_s^4 - T_{\text{sur}}^4) \]  \hspace{1cm} (18)

where the temperature gradient at the particle surface is given by:

\[ \frac{dT}{dr_s} = \frac{\dot{m}_c \text{Cpg}}{4\pi \text{k}_{\text{g}} r_s^2 \rho} \left[ \frac{(T_s - T_c) \exp \left( \frac{\dot{m}_c \text{Cpg}}{4\pi \text{k}_{\text{g}} r_s^2 \rho} \right) - 1}{\exp \left( \frac{\dot{m}_c \text{Cpg}}{4\pi \text{k}_{\text{g}} r_s^2 \rho} \right) \frac{\dot{m}_c \text{Cpg}}{4\pi \text{k}_{\text{g}} r_s^2 \rho}} \right] \]  \hspace{1cm} (19)

The O2 mass transfer in the particle boundary layer follows Fick’s Law:

\[ \dot{m}_c = \frac{4\pi r_s^2 \rho D}{(1 + Y_{O_2})/Y_{O_2}} \frac{d(Y_{O_2}/r_{O_2})}{dr} \]  \hspace{1cm} (20)

where \( r_{O_2} \) is the oxygen to fuel mass ratio. Char consumption rate is estimated using a first order surface reaction:

\[ \dot{m}_C = 4\pi r_s^2 k_C P_{O_2} \]  \hspace{1cm} (21)
where the partial pressure of oxygen at the particle surface is \( P_{O_2,s} = P_Y_{O_2} \frac{MW_{\text{mix}}}{MW_{O_2}} \), and the kinetics of char-O\(2\) surface reaction rate, \( k_C \), is taken from the experimental results of Field [158]:

\[
k_C = 0.8596 \exp \left[ -\frac{17967}{T_s} \right]
\]  

(22)

Note that the pre-exponential factor in \( k_C \) is different from the original reference due to unit conversion. The diffusivities used in the mass diffusion equations are for the binary diffusion of \( O_2 \) in the \( N_2 \) or \( CO_2 \) bath gases (see Table 3).

The differential Eqs. (18), (20), and (21) with appropriate boundary conditions are solved simultaneously to find the char consumption rate, \( \dot{m}_C \), char surface temperature, \( T_s \), and the char surface oxygen mass fraction, \( Y_{O_2,s} \), for a fixed radius, \( r_s \), in quasi-steady state.

Fig. 34 to Fig. 37 shows the experimental and simulation results using the SFM model, from which the effect of diffusivity in \( N_2/O_2 \) and \( O_2/CO_2 \) combustion can be seen. Fig. 34 illustrates the simulation results for species mole fraction profiles under both environments with an \( O_2 \) concentration of 21%. Oxygen diffuses toward the particle in the bath gas (\( N_2 \) or \( CO_2 \)), as shown in the figure. Recalling that the \( O_2 \) diffusivity in \( CO_2 \) is 0.78 times that in \( N_2 \) (see Table 3), the oxygen diffusion flux, and thus the carbon consumption rate is correspondingly lower in the \( CO_2 \)-rich environment.

Fig. 35 shows the predicted temperature profile in the boundary layer of the particle. Lower temperatures, especially at the particle surface \( (R/r_p = 1) \), is observed under oxy-fuel combustion condition when compared with the temperatures in air combustion. The char surface temperature in 21% \( O_2/CO_2 \) is about 190 \( K \) lower than that in air-fired combustion. The temperature profile results from a balance between the reaction heat release and the conductive and radiation heat transfer at the particle surface during char burning process, and it reflects the extent of the char burning intensity. A lower \( O_2 \) diffusion rate in oxy-fuel combustion translates into a lower char consumption and heat release rate. Therefore, the particle surface temperatures are lower than in air combustion.

Fig. 36 and Fig. 37 show the measured and predicted particle surface temperatures and burnout times, respectively, under \( O_2/N_2 \) and \( O_2/CO_2 \) conditions with increasing \( O_2 \) mole fraction. Both the experimental results from Bejarano and Levendis [143] and the modeling results show lower particle temperatures and longer burnout times under \( O_2/CO_2 \) conditions. Similar trends have been reported by Shaddix and Molina [148] in their entrained flow reactor (EFR) experiments: the combusting char temperature is lower in \( CO_2 \) than in \( N_2 \) at the same gas temperature (1500—1750 \( K \)) and \( O_2 \) concentrations (12%, 24% and 36%). The predicted particle surface temperatures under \( O_2/N_2 \) conditions match well with the experimental data. However, the predictions overestimate the particle surface temperatures by about 200—400 \( K \) under \( O_2 \) enriched conditions (\( O_2 \) mole fraction higher than 0.8). This discrepancy may be because the simulation did not consider the dissociation reactions and equilibrium at very high combustion temperatures. Moreover, the assumptions such as \( CO \) as the sole heterogeneous reaction product and ignoring its oxidation in the boundary layer may not be valid at high particle temperatures and high \( O_2 \) mole fractions [155,157]. The gasification reactions may also become important at high char temperatures [149,159]. A more comprehensive consideration of the physics and chemistry fundamentals in \( O_2/CO_2 \) conditions is needed.
and lower O2 concentrations has been observed in air-
expected in region B.

CO2-rich environments than in N2-rich environments, as would be
of oxidation reactions, and the char consumption rate is lower in
contribution of gasification reactions. The authors attributed the higher
reactions to the char-CO2 gasification reaction. To verify this
effect, the reactivity of coal-A char formed in N2 at 1673 K in the DTF
was measured at different O2 levels with N2 and CO2 balance gases.
It can be observed in the TGA experiment shown in Fig. 40 that the
carbondioxidereaction rate only becomes noticeably higher at temperatures
above 760 °C with a very low O2 concentration of 2%. Likewise, the
char-H2O gasification reaction’s effect on char consumption was
also noticed in the char yield of Loy Yang brown coal at a very low
oxygen concentration and high temperature of 800 °C, in the
experiments conducted by Guo et al. [160] using a wire-mesh reactor. They observed that the char consumption rate in
a mixture of 2000 ppm oxygen and 15% steam with Ar diluent gas
was higher than in 2000 ppm oxygen with Ar diluent gas.

Considering that CO2 partial pressure in oxy-coal combustion is
much higher than in the air-fired case, gasification should become
more prominent at the late stages of oxy-fuel combustion processes. Rathnam et al. [123] compared the burnout of four coals (coal A, B, C and D) at oxygen concentrations of about 3–21% in a DTF at 1673 K, and the results are shown in Fig. 39. They observed that two coals (A and B) have higher once-through conversions in the O2/CO2 environment. The authors attributed the higher conversions to the char-CO2 gasification reaction. To verify this effect, the reactivity of coal-A char formed in N2 at 1673 K in the DTF was measured at different O2 levels with N2 and CO2 balance gases. It can be observed in the TGA experiment shown in Fig. 40 that the char reaction rate only becomes noticeably higher at temperatures above 760 °C with a very low O2 concentration of 2%. Likewise, the char-H2O gasification reaction’s effect on char consumption was
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experiments conducted by Guo et al. [160] using a wire-mesh reactor. They observed that the char consumption rate in
a mixture of 2000 ppm oxygen and 15% steam with Ar diluent gas
was higher than in 2000 ppm oxygen with Ar diluent gas.

It is worth noting that the previously discussed observations in
Rathnam et al.’s experiments (across region B and C of Fig. 32) [123]
and in Brix et al.’s experiments (in region B of Fig. 32, also see
Section 2.6.2) [126] seem contradictory, although both experiments were conducted in a suspension fired condition at a high temperature (1673 K) and low oxygen concentrations (around 3%–6%). This may be because of the different residence times, or the different definitions of nominal oxygen concentration in their experiments. Brix et al. [126] used the measured local oxygen concentration after volatile consumption and before char oxidation, whereas in Rathnam et al.’s experiments [123], the measurement location of the oxygen concentration and stoichiometry are not stated [123]. If the measurements of oxygen concentration were done before volatile combustion, the actual oxygen concentrations for char combustion may be lower than the reported values, and
therefore, the contribution of the gasification reactions becomes more significant.

A simplified multi-surface reaction model is used to estimate the contribution of gasification reactions to char consumption in air-fuel and oxy-fuel combustion. The char is assumed to be a 50-\(\mu\)m diameter solid sphere with heterogeneous reactions taking place on its external surface. The reactions are simplified to be 1st order following Smith’s approach [161], but three global char oxidation and gasification reactions are considered:

Reaction (I): \(2\text{C(s) + O}_2 \rightarrow 2\text{CO}\)  \(\text{(23)}\)

Reaction (II): \(\text{C(s) + H}_2\text{O} \rightarrow \text{CO} + \text{H}_2\)  \(\text{(24)}\)

Reaction (III): \(\text{C(s) + CO}_2 \rightarrow 2\text{CO}\)  \(\text{(25)}\)

The overall char consumption rate is the summation of these individual surface reaction rates:

\[
\dot{m}_C = \sum_{i=1}^{n} \dot{m}_{C,i} \quad \text{(26)}
\]

The char reaction rate for reaction \(i\) (\(\dot{m}_{C,i}\)) depends on the rate of reactant transport by external diffusion and the surface reaction kinetics

\[
\dot{m}_{C,i} = 4\pi r_p^2 P_{i,s} \frac{k_{\text{diff},i} k_{\text{kin},i}}{k_{\text{diff},i} + k_{\text{kin},i}} \quad \text{(27)}
\]

where kinetic rate constants of the char surface reactions are in Arrhenius form:

\[
k_{\text{kin},i} = A_i T_p^b \exp \left(\frac{-E_i}{K_u T_p}\right) \quad \text{(28)}
\]

The kinetics parameters for external surface reactions that are used in this estimation are taken from references [158,162,163], see Table 8. The orders of particle temperature, \(\beta_i\), are all zeros for these reactions.

Diffusion often controls the char-O\(_2\) reaction rate at high temperatures. Following the approach described in [161], the corresponding mass transfer limited reaction rate constant \(k_{\text{diff},i}\) can be expressed as:

\[
k_{\text{diff},i} = C_i \left(\frac{T_p + T_e}{2}\right)^{0.75} d_p \quad \text{(29)}
\]

where \(C_i\) is the overall mass diffusion-limited constant:

\[
C_i = \sqrt{\frac{MW_c}{MW_i}} \frac{MW_i}{Ru_T^{0.75}} \text{Sh} \cdot D_{i,0} \left(\frac{P_0}{P}\right) \quad \text{(30)}
\]

where \(e_i\) is the stoichiometric coefficient of carbon in reaction I, II and III (Eqs. (23)–(25)), \(MW\) is the average molecular weight of the gas mixture in boundary layer, the various \(D_{i,0}\) are taken from...
Table 8
Char surface reaction parameters.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$A_i$ (kg/(m$^2$Pa))</th>
<th>$E_i$ (kJ/mol)</th>
<th>Ref</th>
<th>$C_i$ (S/A^{0.75})</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.0005</td>
<td>74</td>
<td>[158, 162]</td>
<td>4.13E-12, 5.32E-12 $^a$</td>
</tr>
<tr>
<td>II</td>
<td>0.00192</td>
<td>147</td>
<td>[162, 163]</td>
<td>4.12E-12, 5.77E-12 $^b$</td>
</tr>
<tr>
<td>III</td>
<td>0.00635</td>
<td>162</td>
<td>[162, 163]</td>
<td>1.69E-12, 1.72E-12 $^b$</td>
</tr>
</tbody>
</table>

$^a$ for oxy-fired condition.
$^b$ for air-fired condition.

[164]. Note that $C_i$ is different for air-combustion and oxy-combustion because of the different diffusivities in the N$_2$-rich or CO$_2$-rich environment.

The contribution of the gasification reactions to the total carbon consumption was estimated under O$_2$-rich and O$_2$-deficient conditions, in air-fuel and oxy-fuel combustion, as shown in Table 9. Fig. 41 shows the contribution of gasification reactions to the overall carbon consumption with increasing particle surface temperatures. At the same particle burning temperatures, the contribution of the gasification reactions is increased in oxy-fuel combustion because of the higher CO$_2$ partial pressure. Moreover, the gasification reactions become more significant in O$_2$-deficient conditions. For example, the contribution of gasification reactions at 2000 K increases to approximately 40% for the oxy-fuel O$_2$-deficient condition, compared with ~10% for the air-fired O$_2$-deficient condition.

Recall that since the char-O$_2$ reaction becomes slower due to the lower O$_2$ diffusion in CO$_2$, as discussed in 2.6.2, the effects of having CO$_2$ as a bath gas are two-fold. In the early stages of char consumption in oxy-fuel combustion, the char-O$_2$ oxidation reaction dominates and the reaction rate is lowered due to the effect of diffusion inhibition. However, in the late stages of char consumption, the carbon consumption rate increases as the char-CO$_2$ and char-H$_2$O gasification reactions become significant. Note that since the understandings on char gasification kinetics and its interactions with oxidation reactions are still limited, the estimate above should be only considered as qualitative and coal-type dependent.

2.6.4. Effect of heat capacity

To identify the impact of the higher molar heat capacity of CO$_2$ on the reduced surface temperature and consumption rate during oxy-char combustion, Shaddix and Molina [148] simulated the steady-state char burning process using a detailed computational program SKIPPY (Surface Kinetics in Porous Particles, developed at the University of Sydney) in which the mass and energy conservation, the multi-component diffusion, and the reaction within the char pores are considered. When all the thermal properties of CO$_2$ except the diffusivity are artificially assumed to be identical to those of N$_2$, the temperature profiles under oxy-fuel conditions do not differ significantly from the full simulation. This indicates that the thermal properties have only a minor impact on the surface temperature and consumption rate for the combustion of a single char particle.

However, it is noteworthy that the conclusion above is made with the assumption of fixed gas stream temperature in a diluted coal burning environment in the EFR. In practice, the higher heat capacity of CO$_2$ does reduce the combustion temperature in oxy-fuel combustion (see Section 2.1.3). Without a fixed bulk gas temperature, the lower surrounding gas temperature will result in a lower particle surface temperature, and hence a lower burning rate [165].

2.6.5. Effect of pressure

Studies of the effect of pressure on char oxidation in oxy-fuel combustion are still scarce because the focus so far has been on atmospheric oxy-fuel systems. However, qualitative trends regarding the impacts of pressure on char oxidation and gasification can be obtained using observations made in previous coal gasification studies, such as that of Niksa et al. [165] and Liu et al. [166] which reviewed char oxidation and gasification characteristics under elevated pressures from selected coal reaction databases.

The char-O$_2$ reaction rate rises with increasing the oxidizer concentrations at a constant total pressure. Experiments conducted in a drop-tube reactor [167] showed significantly higher burnout with increasing O$_2$ levels for Westerholt coal at a total pressure of 1.5 MPa and a reactor temperature of 1200 °C. This is because increasing the O$_2$ level at a constant total pressure raises the oxidizer bulk diffusion flux. On the other hand, the consumption rate does not change much with increasing the total pressure at constant O$_2$ mole fraction under diffusion controlled conditions. Fig. 42 shows the burnout history of a high volatile bituminous coal at higher total pressures (0.1–1.5 MPa) and at a constant O$_2$ mole fraction of 21%. The reported degree of burnout increases only slightly while the total pressure increases from atmospheric pressure to 1.5 MPa. This is because the diffusion rate is independent of total pressure at a constant O$_2$ mole fraction: the effect of the rise in the bulk partial pressure is canceled by the drop in the mass diffusion-limited constant (also see Eq. (30)).

The pressure dependence of the char-H$_2$O and char-CO$_2$ reaction is more straightforward. As shown in Fig. 38, gasification are kinetically controlled up to about 1200–1400 °C, therefore their reaction rates increase with increasing partial pressure of H$_2$O and CO$_2$ at moderately high temperature during coal combustion and gasification. Fig. 43 shows the effect of pressure on the gasification reactions at 1000–1300 °C. Since the partial pressure is the product of the total pressure and the mole fraction, the reaction rates increase by either raising the total pressure at a constant mole fraction (in Fig. 43(a)), or increasing the mole fraction at a constant
total pressure (in Fig. 43(b)). Conversely, maintaining the same partial pressure of H2O or CO2 while raising the total pressure does not affect the reaction rates much (in Fig. 43(c)) [166]. Diffusion effects will become important at high temperatures, above about 1400 °C [147].

Comparing Fig. 42 and Fig. 43(a), the effects of the total pressure at a constant reagent mole fraction are distinctly different for char oxidation and gasification reactions, although the char conversion rates are much slower for the gasification reactions. The impacts of pressure on the char oxidation and gasification reactions are different because of the nature of their reaction regimes. As discussed in Section 2.6.3, for pulverized coal combustion conditions, char oxidation reactions are in the bulk diffusion controlled regime (Zone III) or internal diffusion controlled regime (Zone II), while char gasification reactions fall in the kinetically controlled regime (Zone I) or the internal diffusion controlled regime (Zone II), depending on the char particle size, reactivity and operating conditions. Therefore increasing the total pressure alone would not increase the coal particle-burning rate significantly in the near-burner zone in oxy-fuel combustion. It is more effective to increase the O2 level by adjusting the FGR in the burner stream or oxygen injection. Moreover, raising the total pressure may facilitate the gasification reactions and thus increase the char conversion in the late stages of oxy-fuel combustion.

2.6.6. Summary

Section 2.6 provides a review of the characteristics of oxy-fuel char combustion in a CO2-rich environment. In pulverized coal combustion, coal particles are burned mostly in Region B and Region C, where the effects of the physical properties and gasification reactions on char conversion rates are important. The main conclusions in this section are:

- TGA Experimental results for the char oxidation at low temperatures (as shown in Zone I of Fig. 38) do not show any differences between O2/N2 and O2/CO2 environments, which indicates that the intrinsic kinetics of the char-O2 reaction are the same in the O2/CO2 or O2/N2 environments.
- The char-O2 reaction rate becomes lower in a CO2 diluent under diffusion controlled conditions (as shown in Zone II and III of Fig. 38) due to the lower O2 diffusivity in CO2. Experimental measurements and predictions at high temperatures with high oxygen concentrations have confirmed this trend.
- The higher molar heat capacity of CO2 lowers the adiabatic flame temperature in O2/CO2 condition (with similar oxygen mole fractions), and hence the reaction rates. However, given identical surrounding gas temperatures (by decreasing flue gas
recycle ratio), higher heat capacity alone does not result in lower char temperature or oxidation rate.

- Since gasification reactions are much slower than the char-O\textsubscript{2} reaction, they are kinetically controlled at typical combustion temperatures. The contribution of gasification reactions becomes significant in the late stages of oxy-fuel combustion where the O\textsubscript{2} concentration is low and the surrounding gas temperature is high.
- Raising the total pressure while maintaining the oxygen mole fraction in the oxidizer stream does not increase the char oxidation reactions; however, doing so increases the gasification reaction rates under oxy-fuel conditions.

It should be noted that the above conclusions are based on analysis using simplified models. Other mechanisms might also affect oxy-char combustion, such as the interactions of the heterogeneous and homogeneous reactions, the multi-component diffusion within and around the porous char particle, as well as the catalytic effects of coal ash minerals. Comprehensive models are needed for a better understanding.

2.7. Pollutants formation

Coal combustion in air results in the formation of a number of regulated pollutants, such as NO\textsubscript{x}, SO\textsubscript{2}, mercury, and particulate matter including fly ash and soot. The formation of these pollutants under oxy-fired conditions has also been studied recently, and the essential findings in the literature are summarized with a focus on the impact of replacing nitrogen with carbon dioxide.

2.7.1. Fly ash formation

The transformation of the mineral matters during coal combustion depends on the char temperature and gas composition within and around the coal particle. The mineral transformation and particle formation mechanisms during combustion are schematically shown in Fig. 44. Coarse fly ash particles are formed through coalescence and fragmentation of the non-volatile mineral content. Fine fly ash particles of submicrometer sizes are produced through two mechanisms [168]:

(a) Vaporization and condensation of heavy metals and organically associated cations. The volatile species such as sodium (Na), lead (Pb), cadmium (Cd), and mercury (Hg) may undergo gas-phase chemical reactions and subsequently nucleate to form new particles or condense on the surface of existing particles.

(b) Chemical transformation via reduction and oxidation reactions. Nonvolatile species, such as silica, with high melting temperatures are released from the burning char particle in the form of suboxides via a reduction reaction at the inner surface of the particle. These metals or mineral suboxides, which are more volatile than the corresponding refractory oxides, diffuse away from the parent coal particle, reoxidize, become supersaturated and form particles by nucleation, followed by growth by condensation and collision mechanisms.

Stam et al. [169] investigated the thermodynamic equilibrium composition of fly ash and slag in oxy-coal combustion and found similar fly ash compositions in both air-fuel and oxy-fuel combustion. Calculations indicated no significant change in the speciation of trace element such as Hg, Se, Cr and As, even when considering their higher concentrations due to flue gas recycle. Sheng et al. [170] experimentally studied the crystalline phase of fly ash from a DTF using the X-ray diffractometer (XRD) approach. They observed similar main crystalline phases in the fly ash formed in O\textsubscript{2}/N\textsubscript{2} and O\textsubscript{2}/CO\textsubscript{2} combustion atmospheres, except that more iron melts into the glass silicates and less is oxidized, because of the lower char temperature and the high CO concentration within the char particles. The authors expected an increased slagging propensity of the fly ash under oxy-fuel combustion conditions.

Although the compositions of fly ash are similar in air-fired and oxy-fired conditions, two factors may affect the fine fly ash particle size distributions [171] (also see Fig. 44). First, the lower particle temperature in oxy-fuel combustion with an air-like O\textsubscript{2} level may slow down the vaporization of volatile species, and thus inhibit the formation of submicrometer ash particles. The second factor is the higher CO\textsubscript{2} partial pressure, which may slow down the chemical transformation rate of mineral oxides to mineral suboxides, and results in a slower particle formation rate. Suiriyawong and coworkers [168] measured the number distribution of submicrometer fly ash.
particles generated from PRB coal and observed a smaller total mass of submicrometer ash particles, as well as a smaller geometric mean size in oxy-fuel combustion. The distribution approaches that of air combustion with progressively increasing O\textsubscript{2} mole fractions. Similarly, smaller PM2.5 and submicrometer particle yields were also observed by Sheng et al. [171] in their oxy-coal combustion experiment conducted in a DTF with oxygen concentration of 20%.

In short, the fly ash particle formation pathways are complicated. In addition to the dependence on bulk gas composition when changing from N\textsubscript{2} to CO\textsubscript{2} dilution, it is also influenced by the coal type, the coal particle size distribution, the sulfur content, as well as the operating conditions [172]. Particulate matter formation and their control strategies in oxy-fuel combustion require further investigations.

2.7.2. Ash deposit/slag formation

Fouling and slagging problems caused by coal ash impedes the heat transfer in heat exchangers and may harm the operation safety. Up to the date of this review, very few studies have been published for ash deposit and slag formation propensity in oxy-coal combustion. In this subsection, the fundamentals of ash deposition in coal combustion are reviewed, followed by a speculative analysis of possible trends under oxy-fired conditions.

The deposition rate of fly ash onto the combustor walls, in both fouling and slagging, depends on the stickiness of the ash particles as well as the walls. Richards [173] defined a sticky ash particle as a particle with a viscosity that is lower than the ash melting viscosity. Thus, the melting temperature of the fly ash particles determines whether the condition for stickiness is satisfied. The melting temperature is in turn determined by the ash composition. However, though necessary, a high particle temperature is not sufficient because the molten minerals might not be exposed to the particle surface. Li et al. [174] have found that there is a critical coal conversion of about 88% at which the molten ash is exposed to the surface, which makes a particle sticky. This is consistent with the drop tube experimental findings of Fryda et al. [175] who observed a higher deposition propensity of coal particles with a longer exposure to high temperatures in oxy-coal combustion with 30% oxygen concentration, when compared with air combustion.

On the other hand, a wall is considered sticky when a layer of molten slag exists [176] as shown in Fig. 45. This is only possible if the wall temperature is higher than the melting temperature of the depositing ash which is dependent on the coal type and ash composition.

Since the dominant mechanism in deposition is inertial impaction [177], based on the experimental data in Senda et al. [178], Yong et al. [176] further proposed that the capture efficiency is also dependent on the particle’s Weber number, besides either or both of the particle and wall being sticky. This dimensionless number compares the kinetic energy of the particles and the interfacial surface tension energy between the particles and the wall and is given by:

\[
We = \frac{\text{Particle Kinetic Energy}}{\text{Surface Tension Energy}} = \frac{\rho_p v^2_d p}{\sigma_{wp}} \tag{11}
\]

where \(\rho_p\) is the particle density, \(v_d\) the normal component of particle velocity, \(d_p\) the particle diameter and \(\sigma_{wp}\) the wall-particle surface tension. The wall-particle surface tension is determined by the surface tension of the sticky wall or of the sticky particle if only one of them is sticky. However, if both the particle and the wall are sticky, the sticky particle is always captured and if both the particle and the wall are non-sticky, the particle is always reflected [176]. Therefore, in these cases, the wall-particle surface tension is immaterial.

Based on the above considerations, the fouling or slagging propensity of an ash particle is dependent on the ash particle composition and conversion, as well as the particle’s Weber number. The differences in ash deposition propensity between an oxy-coal and an air-coal combustion environment can thus be summarized as follows:

- As described in the previous section, a higher percentage of iron species have been found in ash formed in oxy-coal combustion than in air combustion [170]. According to the authors, a higher iron concentration leads to a lower ash melting temperature and an increased fouling/slagging propensity for the fly ash.
- Based on the discussions in Sections 2.1.3 and 2.5.1, with similar oxygen mole fractions, the combustion temperature is lower in an oxy-coal combustion environment and ignition is delayed. Therefore, carbon conversion of particles impacting the wall tends to be lower. Thus, the capture efficiency is affected and depending on the combustor design, ash particles may be deposited further downstream from the burner inlet.
- Given the same momentum of the primary stream flow in the burner (which will be discussed in Section 3.3.3.1), the velocity of the particles that impact the combustor wall is reduced in the oxy-coal environment. This results in a lower Weber number for the particles and a higher capture efficiency, which once again agrees with the observations of Fryda et al. [175] in an oxy-coal combustion environment. However, this effect varies with combustor design and is not expected to have a significant impact.

2.7.3. NO\textsubscript{x} formation

Comprehensive literature reviews on NO\textsubscript{x} emission and its control in oxy-fuel combustion have been written by Normann et al. [179] and Toftegaard et al. [20]. Therefore, this paper only focuses on the fundamentals of nitrogen chemistry and the mechanisms and factors that impact in NO\textsubscript{x} formation in oxy-fuel combustion.

2.7.3.1. Nitrogen chemistry. Fig. 46 illustrates the fundamentals of nitrogen chemistry in combustion processes [179]. Since NO is the most important nitrogen-oxygen product of combustion, making up most NO\textsubscript{x} emissions, and this paper confines the discussion to NO formation, NO is formed through three pathways: thermal and prompt NO from N\textsubscript{2}, and oxidation of fuel-bound nitrogen. The formation of thermal NO is described by the extended Zeldovich mechanism:
initiate it. Prompt NO is initiated by the reaction between N$_2$ and hydrocarbon radicals forming a volatile-N species (an intermediate gaseous compound), which is either oxidized to become NO or reduced back to form N$_2$ again. Prompt NO is typically of minor importance and occurs predominantly under fuel-rich conditions. On the other hand, the conversion of fuel-bound nitrogen contributes to most of the NO formed during the combustion of coal. Fuel-N is split into volatile-N and char-N during devolatilization. The volatile-N transforms into either NO or N$_2$, while char-N reacts through a set of heterogeneous reactions along with the oxidation of char. NO can also be reduced to N$_2$. Similar to the prompt formation, NO can be reduced by hydrocarbons to volatile-N under fuel-rich conditions (known as reburning). Furthermore, if present in sufficient quantities, char could act as an important catalyst for the reduction of NO, either directly or by reaction with carbon monoxide or hydrogen [179].

2.7.3.2. Lower NO$_x$ emission intensities in oxy-coal combustion. Emissions of NO$_x$ have been extensively investigated in lab scale and pilot scale studies in both air-coal and oxy-coal combustion environments, as summarized in Table 10. Almost all the studies show lower NO$_x$ emission intensities (emission per unit thermal energy) in oxy-coal combustion than in air-coal combustion. For the sake of comparison, the observations in Table 10 are compiled in Fig. 47. This figure indicates that all data points lie below the dashed line which marks the case where emission intensities are identical in oxy-coal combustion and air-coal combustion.

![Fig. 46. Mechanisms of NO formation and reduction [179].](image)

![Diagram of NO formation and reduction](image)

### Table 10
Research on NO$_x$ and SO$_2$ emissions of air-coal and oxy-coal combustion.

<table>
<thead>
<tr>
<th>Facility</th>
<th>Scale</th>
<th>NO recycle</th>
<th>Emission in mg/MJ (conversion ratio)</th>
<th>Experiment findings</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>NO$_x$</td>
<td>SO$_2$</td>
</tr>
<tr>
<td>IHI horizontal combustion test facility [95,191]</td>
<td>1.2 MW</td>
<td>Wet/Dry FGR</td>
<td>342</td>
<td>57</td>
</tr>
<tr>
<td>IHI vertical pilot scale test facility [22]</td>
<td>1.2 MW</td>
<td>Wet FGR</td>
<td>~220–420</td>
<td>~75–120</td>
</tr>
<tr>
<td>Tokyo Institute of Technology One dimensional premixed reactor [181]</td>
<td>Lab scale</td>
<td>Doped NO</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Nagoya University Entrained flow reactor [180,184]</td>
<td>Lab scale</td>
<td>O$_2$/CO$_2$</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Doped NO</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

(continued on next page)
A reduction in NOx emissions is most pronounced in experiments with FGR, with the slope of a least-square-fitted trend line being 0.22, which is substantially smaller than 1. Note that the CANMET results do not show as much NOx mitigation as the other experiments with FGR, and the lower NOx mitigation is mainly because their tests were performed under partial flue gas recycle (37%–45% of the flue gas by mass is recycled, and the remaining gas was made up with supplied CO2), hence less NO was recycled and reburned. The reasons for the lower NOx emission intensities in oxy-coal combustion are discussed in greater detail in the following sub-section.

### 2.7.3.3. Reasons for lower NOx emission intensities

The lower NOx emission intensities under oxy-fuel conditions are due to the following reasons:

1. The lower N2 partial pressure in oxy-fuel combustion inhibits the formation of thermal and prompt NO.
2. CO2 concentrations in oxy-fuel combustion are substantially higher than in conventional air combustion, which change the radical and gas compositions within and around the char particles and thus influences the NO formation.
3. The NO in the recycled flue gas is reburned in the combustion zone.
These reasons are discussed in greater detail as follows:

To better examine the influence of the lower N₂ partial pressure on the formation of NO, Normann et al. [179] calculated the chemical equilibrium concentration of NO under both fuel-rich (λ = 0.9) and fuel-lean (λ = 1.1) conditions with increasing N₂ concentrations (between 0 and 10%). The results show that the equilibrium NO concentration is reduced dramatically at lower N₂ partial pressures, above 1500 °C in fuel-lean condition and above 1700 °C in fuel-rich condition. This has implications for oxy-fuel combustion, because the N₂ impurity in the oxygen stream contributes to NO formation. It also shows that fuel-rich conditions are favorable for NO reduction in oxy-fuel combustion, and that staging technologies are still beneficial under oxy-coal conditions.

By conducting oxy-fuel combustion experiments without flue gas recycle, the impact of replacing N₂ with CO₂ could be examined without the interfering effect of NO reburning. Studies without flue gas recycle show that, similar to NO formation in air-fuel combustion, the fuel-N conversion ratio in oxy-fuel combustion is a function of temperature, O₂ concentration and equivalence ratio. For instance, Hu et al. [180] conducted NO emission tests using a lab scale entrained flow reactor and observed that the fuel-N conversion decreases with temperature, whereas it increases with fuel-rich conditions in all the NO concentrations (between 0 and 10%). The results show that the fuel-N conversion ratio decreases with increasing CO₂ concentration. Likewise, Liu et al. [183] found the same trend in both air-fired and oxy-fired coal combustion. Like that in the air combustion, the conversion ratio decreases with combustion staging [182].

Lower fuel-bound nitrogen conversions in oxy-fuel combustion were reported in all of these studies. The lower fuel-N conversion ratio is suspected to be due to the different CO concentration. Higher CO is expected to be higher in oxy-fuel combustion because of the higher CO₂ partial pressure at the same temperature. Hence, CO concentration is expected to be higher in oxy-fuel combustion because of the higher CO₂ partial pressure at the same temperature.

Zheng and Furimsky [187] calculated the CO mole fraction in the equilibrium state in oxy-coal combustion and found that the CO concentration is 316 ppm at 1700 K when burning with 10% excess oxygen. This is substantially higher than that of air combustion, which has an equilibrium CO concentration of about 64 ppm at the same stoichiometric ratio. Garborg and Bentzen [188] experimentally investigated CO concentrations during methane combustion in highly diluted environments with either N₂ or CO₂ as the diluent, in a plug-flow reactor with well-defined temperature profiles. As shown in Fig. 48 shows the CO concentration in the product gas at the exit of the reactor under lean, stoichiometric and rich conditions in O₂/N₂ and O₂/CO₂ atmospheres. Substantially higher CO concentrations in the CO₂ diluted environment than in the N₂ diluted environment were observed in all cases. Moreover, that the CO concentration increases from fuel-lean to fuel-rich conditions in both diluent gases agrees with the trends of the equilibrium calculations in [187]. An accurate prediction of the CO concentration in the flame zone in oxy-fuel combustion becomes challenging and will be discussed in greater detail in Section 4.5.

Higher CO concentrations in the furnace have also been reported under oxy-coal conditions. Hjartstam et al. [88] observed that CO concentrations in the combustion zone near the burner, where the gas temperature is high and fuel-rich conditions prevail, are higher under the OF27 (OF27 means 27% O₂/73% CO₂) and OF29 oxy-fuel conditions than under air-fired condition. Higher CO concentrations in the furnace were also reported in CANMET's tests at similar or higher combustion temperatures [92,94]. Likewise, Rehfelt et al. [189] found a significantly higher CO concentration in the oxygen lean flame region of oxy-Lausitz lignite combustion using a 0.5 MW pilot scale test facility.
of the triatomic gases, which results in different radiative heat transfer characteristics. Convective heat transfer coefficients are also changed due to the different flue gas compositions. Flue gas recycle ratio is varied in the pilot scale oxy-combustion facilities to obtain matched gas temperature profiles and/or heat fluxes. The optimized recycle ratio is dependent on the wet/dry recycle strategy, the fuel type and the heat exchanger arrangement. A matched distribution of the radiative and convective heat transfer can be achieved at a slightly lower flame temperature in oxy-coal combustion than in air-coal combustion.

- **Fuel Injection:** The larger density of CO₂ increases the drag force during the pneumatic conveying of coal particles if a dry recycle flue gas consisted mainly of CO₂ is used as a carrier gas for pulverized coal. The smaller interfacial tension facilitates the atomization of the coal-water slurry, but only at high pressures.

- **Particle heating and moisture evaporation:** Calculations using a heat transfer model show that the heating and moisture evaporation rates in CO₂-rich atmosphere in the mill and combustion zone are similar to those in air-coal combustion, given similar surrounding gases and flame temperatures. Considering the possibly lower combustion temperature in oxy-coal combustion, the heating time may be longer and ignition can be delayed.

- **Coal devolatilization:** Lab scale TGA and drop tube furnace tests under different operating conditions indicate that the weight loss might be higher or lower in a CO₂ environment than those under the N₂ conditions, depending on the gas temperature and residence time. It is believed that the higher weight loss at temperatures above 1000 K in CO₂ is due to the contribution of gasification reactions, however, there is no evident influence of the oxy-fuel environment on the devolatilization process.

- **Ignition delay:** Lab scale experiments show that ignition delay is longer in O₂/CO₂ environments than in O₂/N₂ environments for several coal types. Results from a simplified simulation on methane ignition delay with detailed reaction mechanism indicated that the high volumetric heat capacity of CO₂ is the main cause of the homogeneous ignition delay.

- **Oxy-char combustion:** The effects of CO₂ on char consumption rate are two-fold. At high temperatures and sufficiently high O₂ mole fractions where reactions are diffusion controlled, the char consumption rate is lower due to the lower binary diffusivity of O₂ in CO₂; whereas at high temperatures and deficient O₂ mole fractions, the char-CO₂ gasification reaction can increase the char consumption rate. The effect of pressure on the oxidation and gasification reactions are discussed based on the knowledge acquired in coal gasification studies.

- **Pollutant formation:** Experimental studies showed less sub-micron particulate matter in the fly ash distribution under oxy-coal combustion conditions when burning coal with an air-like oxygen mole fraction. Significantly lower NOₓ emission per unit energy was reported in the literature, although NOₓ concentrations in the flue gas may be comparable with [88,189,190], or 2 times higher than in the air-coal combustion due to flue gas recycle [93,94]. The lower NOₓ emission intensity is a result of the NOₓ reduction during flue gas recycle, the lower rate of thermal and prompt NO formation, as well as the higher CO concentrations. Given similar combustion temperatures, CO concentration is significantly higher in oxy-coal combustion than in air-coal combustion due to the thermal dissociation of CO₂.

It should be noted that there are a few studies on pressurized oxy-coal combustion. However, the fundamentals derived from studies on atmospheric oxy-coal combustion can help bridge the knowledge gap and aid in the development of pressurized systems.
3. Stabilization of oxy-coal combustion

The challenges to maintaining oxy-coal combustion stability have been reported in early pilot scale experimental studies [95,191]. These challenges stem from the lower adiabatic flame temperature, the delayed ignition and the lower burning rate of coal particles in a CO2 diluted environment, among other fundamental issues discussed above.

Muñiz and Mungal [192] measured the standoff distance and velocity of lifted methane and ethylene turbulent diffusion flames and suggested two criteria for flame stabilization: (1) the composition of the fuel/oxidizer mixture must be within the flammability limits; (2) the local flow velocity must be near the premixed laminar burning velocity \(S_L\). In this section, the flammability constraints as measured by the preheat temperature and dilution ratio under \(N_2\) and \(CO_2\) diluted combustion conditions are investigated using a simplified WSR model. Possible region of stable combustion in \(O_2/CO_2\) combustion are calculated and compared with that under \(O_2/N_2\) conditions. Regarding the second criterion of stability, the characteristics of laminar burning velocity in oxy-fuel combustion is also reviewed, as well as its implications on practical operations. Recent studies and measures taken to improve the stabilization of oxy-coal combustion are introduced.

3.1. Flammability under oxy-fuel conditions

Prior to discussing oxy-fuel combustion stabilization, it is useful to quantitatively sketch out the flammability domain in terms of the operating conditions. In conventional air-fuel combustion, flammability limits are frequently defined as the lower and upper bounds of fuel percentage by volume in the mixture, between which steady flame propagation occurs [109]. The use of almost pure oxygen and a fraction of recycled flue gases adds one extra degree of freedom to the problem, i.e., the dilution ratio. Therefore, three key factors are considered in the investigation of oxy-fuel flammable domains: the equivalence ratio, \(\phi\), the reactant preheat temperature, \(T_0\), and the dilution ratio, \(DR\). The DR is defined as the ratio of molar flow rate of the dilution gas to the molar flow rate of oxygen in the oxidizer gas stream:

\[
DR = \frac{n_{\text{Diluent gas}}}{n_{\text{Oxygen}}}
\]  

To gain some insight into flammability under oxy-combustion conditions, the flammable region of methane in \(O_2/N_2\) and \(O_2/CO_2\) is calculated using the well-stirred reactor (WSR) model and the detailed reaction mechanism GRI-Mech 3.0 [139] with an adiabatic thermal boundary condition in CHEMKIN [138]. The residence time of the reacting methane-oxygen-dilution gas (\(N_2\) or recycled dry \(CO_2\)) mixture is fixed at 0.1 s. Blow out occurs when \(\phi\) is outside the flammability limits at a given \(T_0\) and \(DR\), or when \(DR\) is too high given \(T_0\) and \(\phi\).

Fig. 49 shows the critical dilution ratios at various preheat temperatures and equivalence ratios under \(O_2/N_2\) and \(O_2/CO_2\) conditions. The curves shown are boundaries of the flammable region indicating the maximum dilution ratio that corresponds to a specific preheat temperature and equivalence ratio. Flammability is assured for any operating conditions under the curve in the WSR with a residence time of 0.1 s. The maximum dilution ratio is attained at an equivalence ratio close to stoichiometric methane/oxygen conditions (\(\phi = 1\)) for all initial temperatures, and the flammable region expands when increasing the preheat temperature. For the same \(T_0\), blow out occurs at lower dilution ratios for oxy-fuel combustion, resulting in a smaller flammable region when compared with combustion under \(O_2/N_2\) conditions. The smaller flammable region is caused by the lower combustion temperature resulting from the higher molar heat capacity of \(CO_2\) (also see 2.1.3) and the lower reaction rate caused by the chemical effect of \(CO_2\) (also see 3.2.1).

Based on the results of Fig. 49, the flammable regions with dilution gases of \(N_2\) or \(CO_2\) are illustrated schematically in a \(\phi - T_0\) space as shown in Fig. 50. This flammable region is extended to a higher dilution ratio when the reactants are preheated and when the equivalence ratio is closer to stoichiometric. The envelope of the flammable region indicates the critical operating conditions beyond which blowout occurs. Combustion becomes less stable as the operating conditions approach the flammable surface. The most interesting finding is that the flammable region shrinks significantly when changing the dilution gas from \(N_2\) to \(CO_2\), exhibiting a tendency toward destabilization in oxy-fuel combustion.

3.2. Laminar flame propagation

Pulverized coal volatiles are burned under conditions of partial premixed or nonpremixed (when the primary stream is a recycled flue gas) turbulent flames in vicinity of the burner. The rule for anchoring a flame in both laminar and turbulent flow, at conditions away from blowout, is to match the local flame speed with the local unburned stream velocity [109]. Studies on conventional air-fuel
combustion have shown that the laminar burning velocity is an important factor in determining the blow off/blow out velocity under premixed [193] and nonpremixed flame conditions [192,194,195]. Kalghatgi [195] suggested the following correlation to estimate blow out flow velocity, \( \dot{v}_{\text{blowout}} \), for jet flames:

\[
\dot{v}_{\text{blowout}} = \frac{\rho_{u}}{\rho_{F}} \left( \frac{\rho_{u}}{\rho_{F}} \right)^{1.5} \cdot 0.017 \cdot R_{H} \left( 1 - 3.5 \cdot 10^{-6} \cdot R_{H} \right)
\]

where \( S_{L, \text{max}} \) is the maximum laminar burning velocity near stoichiometric ratios for hydrocarbons. The Reynolds number, \( R_{H} \), is given by

\[
R_{H} = \frac{\rho_{u} S_{L, \text{max}} H}{\mu_{u}}
\]

The characteristic length, \( H \), is the distance along the burner axis where the mean fuel concentration has fallen to its stoichiometric value and can be estimated by

\[
H = 4 \left[ \frac{Y_{F,u}}{Y_{F,\text{stoc}}} \left( \frac{\rho_{u}}{\rho_{F}} \right)^{1/2} \cdot 5.8 \right] d_{j}
\]

where \( d_{j} \) is the diameter of the jet. This correlation was also shown to be valid for methane and propane jet combustion with partial CO2 dilution up to 60% in the fuel stream. As discussed above, the laminar burning velocity, \( S_{L} \), characterizes the stability in practical combustion facilities, and hence it is worth reviewing the impact of high CO2 concentration on it.

The laminar premixed burning velocity of coal/O2/diluent gas can be measured experimentally. Fig. 51 shows a schematic diagram for flame propagation in a coal particle suspension proposed by Taniguchi et al. [137]. A smaller number of particles are first ignited at \( t = t_{0} \), and their volatile flame heats up the surrounding coal particles at \( t = t_{1} \). Next, these heated particles are devolatilized, followed by the ignition of these particles when the volatiles reach a certain concentration after an elapsed time of \( \Delta t \). These processes repeat themselves and the spread of this chain reaction is the so-called flame propagation in coal suspension. It is expected that the flame propagation process is strongly influenced by heat transfer, coal devolatilization kinetics and reaction kinetics of the volatiles. To get a better understanding of the flame propagation velocity, these factors are examined in the following subsections.

### 3.2.1. Effect of physical properties and chemical kinetics

When replacing N\(_{2}\) with CO\(_{2}\) as a diluent gas, a change in the laminar burning velocity is expected. To study the factors governing burning velocity in an idealized environment, a simplified one dimensional scaling analysis proposed by Spalding [109,196] for gaseous fuel combustion is used, which couples the essential physics of heat transfer, mass transfer, chemical kinetics and thermodynamics:

\[ S_{L} = \left[ \frac{-2(\nu + 1)}{\mu_{F}} \frac{m_{F}}{\rho_{F}} \right]^{1/2} \]

where \( \alpha \) is the thermal diffusivity, \( \nu \) is the mass ratio of oxidizer to fuel, \( \rho_{u} \) is the density of unburned gas, and \( m_{F} \) is the fuel consumption rate per unit volume. Eq. (40) captures the dependence of the laminar burning velocity (\( S_{L} \)) on the thermodynamic and transport properties of the gas mixture, and can be used to gain qualitative insight into the process shown in Fig. 51. These factors are summarized as follows, followed by a discussion in greater detail:

- **Thermal diffusivity**: The thermal diffusivity is the thermal conductivity, \( k \), divided by the volumetric heat capacity, \( \rho c_{p} \). CO\(_{2}\) has a thermal diffusivity that is 0.64 times lower than N\(_{2}\) (see Table 3). Therefore, the temperature of CO\(_{2}\) responds less rapidly to a change in temperature boundary conditions [81], resulting in a lower burning velocity. The dependence on thermal diffusivity reflects the impact of heat transfer on the flame propagation process. The fact that a higher flame propagation velocity is expected in a diluent gas with higher thermal diffusivity has also been observed in gaseous fuel combustion. Law [132] has shown that the laminar burning fluxes of the methane-O\(_{2}\)-diluent flame follow the same order as the diluent gas thermal diffusivity (He > Ar > N\(_{2}\)) (see Table 7).

Though the laminar burning velocity is dependent on thermal diffusivity, Shaddix and Molina [34] suggested that stability is eventually independent of the thermal diffusivity. They performed a dimensionless analysis on the extinction theory, and showed that the extinction process is characterized by the inverse of the chemical timescale \( \tau_{ch} = \frac{a}{S_{L}^{2}} \), and \( \alpha \) is canceled because \( S_{L} \) is proportional to the square root of the thermal diffusivity (see Eq. (40)).

- **Heat capacity**: A higher heat capacity per unit volume, \( \rho c_{p} \), decreases the fuel consumption rate, \( m_{F} \), because of the lower reaction temperature. The dependence on \( \rho c_{p} \) reflects the influence of longer ignition delay and lower reaction rate on

![Fig. 51. Model of flame propagation in pulverized coal air mixture, proposed by Taniguchi et al. [137].](image-url)
the flame propagation process. It should be noted that the effect of higher heat capacity on $S_1$ is much larger than thermal diffusivity, because it reduces the reaction temperature that has exponential dependence on reaction rate $m_0$ through the Arrhenius law. The effect of higher volumetric heat capacity on longer ignition delay has been previously discussed in Section 2.5.1. Likewise, other factors that influence the ignition delay discussed in 2.5.1 have similar impacts on the flame propagation velocity, and will not be repeated here.

- **Chemical kinetics**: In addition to its distinct physical properties, CO$_2$ is also active chemically and can change the radical concentration and hence the burning velocity.

The lower flame propagation velocity of pulverized coal combustion in CO$_2$ has been reported by Kiga et al. [185] and Suda et al. [197] using the microgravity drop shaft facility in the Japan Microgravity Center (JAMIC). The experiment on flame propagation velocity within a coal-dust cloud was carried out in a microgravity environment to obtain a spatially homogenous distribution of coal particles and to minimize the effect of natural convection and buoyancy. In this experimental set-up, a spherical flame front was observed, from which the flame propagation velocities were measured. Fig. 52 shows snap shots of the flame propagation process in a coal-O$_2$-diluent mixture: (a) for a higher volatile coal A in an O$_2$/N$_2$ environment; and (b) and (c) for a lower volatile coal C in O$_2$/N$_2$ and O$_2$/CO$_2$ environments, respectively. It can be seen that the flame propagation velocity depends on both coal devolatilization and the diluent used. The fact that the coal flame propagation velocity increases with higher volatile contents is consistent with the experiments reported in [197]. Furthermore, a comparison between Fig. 52 and Fig. 53(c) shows that the flame propagation velocity is significantly slower, and the brightness is also substantially lower, in CO$_2$ with the same coal and oxygen concentrations.

The measured flame propagation velocities as a function of coal concentration in the suspension are shown in Fig. 53 for three different coals burning with the same oxygen concentration. The propagation velocity attains a maximum value at a moderate coal concentration, where the maximum is found by balancing the opposing effects of the reaction heat release and the volume of coal.

![Fig. 52. Flame propagation in pulverized coal clouds suspension. Coal particle diameter: 53–63 μm, O$_2$: 40%, dilution gas: 60% [197].](image)

![Fig. 53. Flame propagation velocity in different atmospheres and coal concentrations, the O$_2$ concentration is 40% [197].](image)

![Fig. 54. Impact of dilution gas and O$_2$ concentration on coal flame propagation velocity (additional heat capacity) that has to be heated. As observed in the snap shots, both the higher volatile coal (A) and the lower volatile coal (C) have much slower flame speeds in an oxy-fuel combustion environment.](image)

To determine the effect of the diluent gas physical properties, the flame propagation velocities in three diluent gases (nitrogen, argon and carbon dioxide) were further investigated in [197] and the results are shown in Fig. 54. The flame propagation velocities follow the following order: $S_1$(Ar) > $S_1$(N$_2$) > $S_1$(CO$_2$). This is a result of the thermal diffusivities, $\alpha$, of the diluent gases being in the same order of $\alpha_{Ar}$ > $\alpha_{N_2}$ > $\alpha_{CO_2}$, and the heat capacities (per mole) in the inverse order $c_{p,Ar}$ < $c_{p,N_2}$ < $c_{p,CO_2}$ (see Table 7). Based on the scaling analysis discussed above, both the increase in thermal diffusivity and the decrease in heat capacity result in increasing the burning velocity.

The last factor, chemical effect of CO$_2$, also plays a role but not as big as the physical properties. Liu et al. [198] numerically investigated the burning velocities of methane and hydrogen under air-fired and oxy-fired conditions using a CHEMKIN-based model and GRI-Mech 3.0 mechanism. In their study, the kinetic effect of CO$_2$ was isolated by implementing a fictitious specious FCO$_2$ that had identical thermal and transport properties as CO$_2$ but was not chemical active. The results for the laminar burning velocities of CH$_4$ and H$_2$ with diluent gases of N$_2$, CO$_2$ and FCO$_2$ are shown in Fig. 55. Burning velocities in three cases were calculated: fuel/O$_2$/CH$_4$ and H$_2$ with diluent gases of N$_2$, CO$_2$ and FCO$_2$. The measured burning velocities were categorized the burning velocities of methane and hydrogen under air-fired and oxy-fired conditions using a CHEMKIN-based model and GRI-Mech 3.0 mechanism. In their study, the kinetic effect of CO$_2$ was isolated by implementing a fictitious specious FCO$_2$ that had identical thermal and transport properties as CO$_2$ but was not chemical active. The results for the laminar burning velocities of CH$_4$ and H$_2$ with diluent gases of N$_2$, CO$_2$ and FCO$_2$ are shown in Fig. 55. Burning velocities in three cases were calculated: fuel/O$_2$/
N₂, fuel/O₂/CO₂ and fuel/O₂/N₂/CO₂ in which 30% N₂ in air was replaced by CO₂. Since the FCO₂ is “inert” chemically, the difference between fuel/air and fuel/O₂/FCO₂ shows the effect of the physical properties on the burning velocity, while the difference between fuel/O₂/FCO₂ and fuel/O₂/CO₂ indicates the chemical effect of CO₂. Further analysis found that the dominant reaction pathway for the chemical role of CO₂ is as follows:

\[
\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}
\]  

(41)

CO₂ competes for the H radicals through the reverse reaction in Eq. (41) with the most important chain branching reaction:

\[
\text{H} + \text{O}_2 \rightarrow \text{O} + \text{OH}
\]  

(42)

Thus, the presence of CO₂ significantly reduces the concentrations of important radicals, i.e. O and H radicals, leading to a reduction of the fuel burning rate [198]. Fig. 55 indicates that CO₂’s chemical effects play some role in reducing the burning velocity when replacing N₂ with CO₂. However, its physical properties have a more significant contribution.

### 3.2.2. Impact of operating conditions

Since the lower flame propagation velocity in oxy-coal combustion may result in a lower blow out velocity, maintaining the same operating conditions as in air-fuel combustion may weaken the flame stability. In this section, the laminar burning velocities in fuel-oxygen-diluent gas combustion with nitrogen and carbon dioxide as diluent gases are calculated to investigate the effects of operating conditions. To simplify the computation, methane is once again used as a surrogate for the volatiles, and the devolatilization process is neglected. The simulation is performed using the PREMIX package of CHEMKIN [138] while employing the GRI-Mech 3.0 detailed reaction mechanism [139].

Fig. 56 shows the predicted \( S_L \) in methane-O₂-N₂ and methane-O₂-CO₂ mixture with an oxygen concentration of 21 vol%. Experimental results at room temperature [199,200] are also shown for comparison. Similar to the results obtained by Liu et al. [198] in Fig. 55, the laminar burning velocities in oxy-fuel conditions are significantly lower than in air combustion: the maximum \( S_L \) is about 37 cm/s in the CH₄-O₂-N₂ mixture near the stoichiometry condition, as opposed to an \( S_L \) of about 3–4 cm/s in the CH₄-O₂-CO₂ mixture, both with initial temperatures of \( T_0 = 300 \text{ K} \). The simulation also predicts the trends for a broader range of operating conditions, in particular with higher initial temperatures. Preheating the reactants results in faster reaction kinetics and generally improves the flame propagation (higher \( S_L \)). One way to achieve a higher preheat temperature is by mixing with hot exhaust gas. However, this also results in a higher dilution of the oxidizer stream.

Fig. 57 shows the impact of the dilution ratio on the calculated \( S_L \) at \( \phi = 1 \) (also shown as a function of oxygen concentration in the

![Fig. 55](image)

**Fig. 55.** Burning velocities of methane and hydrogen mixtures at increasing equivalence ratios. Oxygen mole fraction in the oxidizer is kept at 21% in all cases. Also plotted are the experimental data of Zhu et al. [247] in methane mixture and Westbrook [248] in hydrogen mixtures as filled symbols [198]. The symbol -CO₂- indicates results using CO₂. -Δ- indicates results using FCO₂.

![Fig. 56](image)

**Fig. 56.** The laminar burning velocity (SL) of methane combustions in O₂/N₂ and O₂/CO₂ conditions at different equivalence ratios (ϕ) and elevated initial temperatures, experimental data are cited from [199,200]. Unburned gas are at 300 K, 600 K, 900 K and 1200 K, 1 atm.
oxidizer stream on the top axis) for methane–O\textsubscript{2}–N\textsubscript{2} and methane–O\textsubscript{2}–CO\textsubscript{2} mixtures. \(S_l\) decreases with increasing dilution ratio for both dilution gases, and as expected, the curves for the two dilution gases meet at an oxygen mole fraction of 100%, where they both reach the full oxy-fuel combustion regime. The results indicate that, given the same initial temperature, a higher oxygen concentration is required in oxy-fuel combustion to match the laminar burning velocity of air combustion; or a higher initial temperature is necessary for a fixed dilution ratio.

Results in this section have practical implications on the stabilization of oxy-fuel combustion. Flame stability can be improved by matching the primary stream velocity with local turbulent burning velocity. This may be achieved by enriching oxygen locally, enhancing hot burned gas recirculation, and increasing the combustion temperature at lower FGR, and these measures will be discussed in greater detail in the following section.

3.3. Stabilizing oxy-coal combustion

As discussed in Section 3.1 and 3.2, narrower flammability limits and lower laminar burning velocity may cause combustion destabilization in oxy-coal combustion. However, operating in the oxy-fuel regime provides more flexibility because the oxygen concentrations in the oxidizing streams are not restricted to 21%. This opens up opportunities for advanced oxy-coal burner design including the following variables:

- **Flue gas recycle ratio (overall oxygen mole fraction):** A lower recycle ratio or dilution ratio favors a higher flame temperature, broader flammability limits, and laminar burning velocity as discussed in Section 3.1 and 3.2, but its lower bound is limited by material constraints in the heat exchangers.

- **Oxygen concentrations in the primary, secondary and tertiary streams:** Coal burners employ a primary stream in which coal is delivered with a carrier gas, a secondary, and at times a tertiary, stream in which oxidizer is delivered. The oxygen concentration in different streams can be independent of one another. Dry or wet flue gas is usually used as the primary (carrier) gas in oxy-fuel combustion, but the choice should be based on an optimization for flame stabilization. Different oxygen concentrations can be used in different streams in a staged combustion scenario for stabilization and \(\text{NO}_x\) control, sometimes partial pure oxygen can also be injected.

- **The distribution of gas volumes in the different streams and their momenta:** Since the overall volumetric flow rate is lower in oxy-fuel combustion, the dimensions of the burner should be carefully designed to achieve an optimal flowfield for mixing.

- **The preheat temperature of different streams:** As shown in the previous section, preheating the reactant streams can improve flammability. Preheating the primary and secondary gas streams in conventional air-fired PC boilers using an air-preheater is widely applied for energy saving purposes. The same strategy can be utilized in oxy-coal combustion to improve combustion stability.

In recent years, studies have been conducted to investigate burner retrofit and new burner design in oxy-fuel combustion in order to achieve better mixing of the fuel, oxidizer and hot flue gases. Some of these efforts are summarized in Table 11, with a selection of typical burner configurations shown in Fig. 58. Flame stabilization and burner modifications will be discussed in detail in this section.

### 3.3.1. Optimized flue gas recycle ratios

From the discussion in previous sections, it can be concluded that combustion characteristics, such as ignition, flame temperature, burning velocity and char consumption, are improved at higher O\textsubscript{2} fraction. Therefore, reducing the flue gas recycle ratio and thereby increasing the oxygen concentrations in the primary, secondary and tertiary streams will lead to stabilization of oxy-coal combustion.

Liu et al. [182] reported an unstable oxy-coal combustion in a 20 kW down-fired furnace when operating the burner streams at 21% O\textsubscript{2}/79% CO\textsubscript{2}. A dark volatile flame was observed downstream of the burner, while coal particle ignition and peak temperature were both delayed. According to that study, the O\textsubscript{2} mole fraction in the mixture of O\textsubscript{2}/CO\textsubscript{2} has to be raised to 30% or higher to match the gas temperature profile of oxy-coal combustion to that of air-coal combustion. Under this 30% O\textsubscript{2}/70% CO\textsubscript{2} condition, the measured residual carbon in the ash was also reduced, which indicates higher burnout efficiency than in air-fuel combustion. Likewise, in the oxy-coal combustion experiments performed using a German lignite coal in the Chalmers 100 kW test unit by Hjartstam et al. and Andersson et al. [127,128] (see Fig. 58-c for the burner structure), improved combustion stabilities were achieved when maintaining a stoichiometric fuel-oxygen ratio and increasing the oxygen concentration in the staging streams from 25% to 29% (a recycled dry flue gas with 30 vol% oxygen was used as carrier gas for all cases). It was found that stable combustion could not be established with O\textsubscript{2} mole fractions lower than 25% in the feed gas streams. In contrast, the cases with oxygen fractions of 27% and 29% have the most stable flames and are least sensitive to reduced stoichiometric ratios.

### 3.3.2. Oxygen feeding strategies

There is more flexibility in supplying oxygen to the combustion zone in oxy-coal combustion than in air-coal combustion. Given an overall fixed stoichiometric ratio (SR) and flue gas recycle ratio (FGR), the oxygen feed can be split and mixed with different streams at arbitrary concentrations, or injected independently through oxygen nozzles. However, not all permutations of oxygen feeding strategies lead to a stable attached flame with low pollutant emission, or to safe burner operation. Different partitioning strategies for feeding oxygen are discussed in this section.

#### 3.3.2.1. Pure oxygen injection

Pure O\textsubscript{2} injection has been introduced in several new designs and retrofits of oxy-coal burners to stabilize combustion at a favorable location in the furnace and to...
Table 11
Oxy-coal burner design: experiments and CFD modeling in the literatures.

<table>
<thead>
<tr>
<th>Institution (Burner name)</th>
<th>Retrofit/New</th>
<th>Burner configuration (Diameter in mm)</th>
<th>O₂ nozzle</th>
<th>Primary, secondary and tertiary stream</th>
<th>Combustion performance</th>
</tr>
</thead>
<tbody>
<tr>
<td>IHI (IHI horizontal combustion test facility) [95,185,191]</td>
<td>Retrofit</td>
<td>1.2 MW, swirl burner, primary outlet D77, secondary outlet D135, w/O₂ nozzle D50</td>
<td>Up to 15% of the overall fed O₂</td>
<td>1st: Pf coal, RFG</td>
<td>Unstable flame and higher UBC w/o pure O₂ injection</td>
</tr>
<tr>
<td>CCSD and IHI (IHI vertical pilot scale test facility) [207]</td>
<td>Retrofit</td>
<td>1.2 MW, swirl burner, simplification on burner structure w/o quarl or oil gun</td>
<td>N/A</td>
<td>2nd: Swirling (S = 0.59–0.65), RFG/O₂, O₂ content 25%–30%</td>
<td>Ignition delay due to higher momentum ratio of primary and secondary stream, as well as less swirl flow effect</td>
</tr>
<tr>
<td>CANMET (Burner A, B and C) [201,249]</td>
<td>New design</td>
<td>0.3 MW, swirl burner, primary, secondary, and tertiary stream, w/pure O₂ nozzle</td>
<td>Up to 57% of the overall O₂</td>
<td>1st: Pf coal, RFG</td>
<td>Swirl number and configuration effects were studied using a CFD modeling</td>
</tr>
<tr>
<td>Graz University (over-stoichiometric and under-stoichiometric burner) [202,203]</td>
<td>New design</td>
<td>3 MW, Swirl burner, w/quarl</td>
<td>In the form of tertiary stream</td>
<td>2nd: Swirling (S = 0.2), RFG/O₂, O₂ content 23%–27%</td>
<td>Combined over- and under-stoichiometric burners to reduce FGR ratio to 50%</td>
</tr>
<tr>
<td>Hitachi modeling (Low NOₓ DS burner) [208,209]</td>
<td>Retrofit</td>
<td>1 MW, swirl burner</td>
<td>N/A</td>
<td>1st: Axial vane swirling, retain volume flow rate as air combustion, Swirling, RFG/O₂, O₂ content ~ 30%</td>
<td>With 75.1% wet FGR ratio, a similar flame shape (Temp and velocity) was observed using CFD modeling</td>
</tr>
<tr>
<td>Chalmers University of Technology [85–88]</td>
<td>New design</td>
<td>100 kW, swirl burner, fuel lance, primary/secondary stream w/pure O₂ lance, Concentric O₂ lance, but not used for the published studies.</td>
<td>Fuel lance: Pf coal, RFG/O₂, O₂ content 30%–35%, 1st: Swirling (S = 0.79), Pf coal, 30% dry RFG and O₂, O₂ content 23, 27 and 29%</td>
<td>3rd: same as secondary stream</td>
<td>Flame cannot be established at OF21, while it is stable at OF27 and OF29 conditions; Similar temperature distributions in OF25 and air combustion; OF29 may cause ash melting problem</td>
</tr>
<tr>
<td>University of Leeds [182,183]</td>
<td>Retrofit</td>
<td>20 kW, swirl burner, quarl D140</td>
<td>N/A</td>
<td>1st: Non-swirling, Pf coal, air or O₂/O₂, O₂ content 21%–30%</td>
<td>Unstable flame with OF21; O₂ has to be increased to 30% or higher to match the air-fired gas temperature profile</td>
</tr>
<tr>
<td>Siemens-REI [206]</td>
<td>New design</td>
<td>0.3 MW, swirl burner, w/quarl,</td>
<td>N/A</td>
<td>2nd: Swirling, O₂/O₂, O₂ contents 21–35%</td>
<td>Tested different retrofit strategies for primary stream; stable combustion achieved w/low O₂ content in primary</td>
</tr>
<tr>
<td>RWTH Aachen University (Burner A, Oxy-1 and Oxy-2) [162,210]</td>
<td>New design</td>
<td>40 kW, swirl burner, w/quarl, three different configurations</td>
<td>N/A</td>
<td>1st: Pf coal, CO₂/O₂, O₂ content 19%</td>
<td>Stable swirl flames at low O₂ content were achieved in Burner Oxy-1 and Oxy-2 because of well designed flow field</td>
</tr>
</tbody>
</table>
produce compact flames. Kimura et al. [191] conducted oxy-coal combustion experiments with a 1.2 MWth horizontal IHI swirl burner. In the experimental set-up, recycled flue gas was used in the primary stream for coal transport, while a mixture of recycled flue gas and oxygen was used as a secondary stream. The authors reported an unstable, dark combustion zone with high unburned carbon (UBC) when the O2 concentration in the secondary stream was less than 30%. However, when a central oxygen nozzle, as illustrated in Fig. 58(a), was used to directly inject O2 in the centerline axial direction of the burner, the flame was stabilized. Moreover, the UBC in oxy-coal combustion was reduced to the air-coal combustion level when up to 15% of the overall O2 was injected through the oxygen nozzle and maintaining the O2 concentration in the secondary stream at 30%. Likewise, further studies on the same facility by Nozaki et al. [95] showed that direct O2 injection improved combustion stability and coal ignition when compared with that under operating condition with the same O2 content in the combustion gas but without O2 injection (see Fig. 59).

In another burner designed by CANMET [201], as illustrated in Fig. 58(b), 57% of the overall O2 was injected through the O2 stream arranged inside or between the primary and secondary streams to ensure combustion stability. Likewise, a pure O2 stream was also used as a tertiary stream aside from the primary and O2/RFG secondary stream to enable a stable ignition in the over-stoichiometric burner developed by Graz University of Technology [202,203].

Recently, Praxair [204] reviewed their development of various oxygen nozzle prototypes for flame stabilization and NOx control in oxygen-enhanced combustion, and proposed the applications of these nozzles to oxy-fuel combustion for CCS as well. The idea is to deliver oxygen to the volatile combustion zone, and in doing so, the flame stability and char burnout will be improved. Injecting a suitable amount of oxygen at the fuel-rich region in a staged low NOx burner also reduces NOx emissions, whereas oxygen injection above the designed amount may result in oxygen “punching through” the fuel-rich zone and thus increasing NOx emissions. Fig. 60 shows schematics of different oxygen nozzle designs with axial, radial, combination and reverse injections. Some of the injection strategies produce mild mixing, such as the axial, radial and combination injection, while other designs (reverse injection) are more aggressive in mixing the oxidizer and fuel near the burner.

The performances of different injection directions were assessed based on the gas temperature profiles and NOx emissions. Fig. 61 shows the flame temperature profiles when various oxygen nozzles are used in the 1.2 MWth industrial scale burner facility of Alstom Power. The results show the performance of oxygen nozzles with 5% and 10% oxygen “replacement”, which is defined as the fraction of oxygen delivered directly to the furnace through the nozzle over the stoichiometric oxygen supply. The peak

![Fig. 58. Schematics of various burner design/retrofit concepts for flame stabilization in oxy-coal combustion. (a) IHI 1.2 MW swirl burner with central oxygen nozzle [191]. (b) CANMET swirl burner with oxygen nozzle inside or between the primary and secondary streams [249]. (c) Chalmers swirl burner [86,88]. (d) Hitachi low NOx DS burner [208,209]. (e) RWTH Oxy-2 burner [162,210].](image)

![Fig. 59. The gas temperature peak rises and moves toward the burner when injecting pure oxygen through the oxygen nozzle in IHI 1.2 MW swirl burner under oxy-coal combustion conditions. The excess O2 injection improved the ignition and stabilization [95].](image)
temperature moves closer to the burner when using an aggressive mixing strategy (reverse nozzle). However, this strategy should be used with caution because excessive overheating of the burner front may occur if too much oxygen is delivered. On the other hand, a mild mixing strategy (combination, radial, and 45° angle toward flame) allows a broader range of oxygen injection while still enhancing flame stability, reducing NOx, and improving the carbon burnout. From a comparison of the two oxygen replacements strategies, the flame temperature is observed to be significantly higher when the replacement rate is raised.

3.3.2.2. Oxygen partitioning in different streams. In typical PC burners, pulverized coal is delivered to the combustion zone by the primary stream, while the secondary and tertiary streams provide the remaining oxidizer needed for further combustion reactions. In conventional air-coal combustion, the oxygen content in the primary air provides oxidant for volatiles burning and stabilizes the flame downstream of the burner flow. The secondary and tertiary streams are usually injected co-axially with the primary stream, at increasing radii and with swirl, to add more oxygen to burn the char downstream of the primary combustion zone. When retrofitted to operate under oxy-coal combustion, mixtures of recycled flue gas and oxygen with various concentrations are used in the primary and secondary streams. From a safety point of view, the use of dry recycled flue gas in the primary stream can avoid auto-ignition when transporting the coal to the burner. However, a low oxygen mole fraction in the primary stream may cause destabilization [88]. Adding an appropriate amount of O2 in the primary stream with a concentration below that of air is beneficial to flame stability without compromising safety.

Some recent experimental studies have investigated the effect of oxygen partitioning and shifting in primary and secondary streams on flame stabilization. Zhang et al. [205] studied the standoff distances of co-axial turbulent diffusion oxy-coal flames with a 40 kW non-swirl burner at the University of Utah. When pure CO2 is used as the carrier gas in the primary stream (oxygen partial pressure is zero), an attached flame cannot be achieved at an oxygen/fuel ratio near stoichiometry. Increasing the oxygen-feed rate (i.e. the oxygen concentration) in the secondary stream above a stoichiometric ratio decreased the standoff distance and enhanced flame stability. As shown in Fig. 62(a), the transition point for an attached stable flame is 52% oxygen concentration in the secondary stream (and 43% in the overall feeding gas). It is worth noting that the stoichiometric ratio has to be much larger than unity to obtain attached stable flames when using pure CO2 as the primary stream. However, when shifting the oxygen supply from secondary stream to the primary stream while maintaining the overall oxygen concentration at 40% (i.e. a constant λ = 1.15), it is possible to stabilize the flame near the burner. Fig. 62(b) shows that for oxy-coal combustion, detached flames were observed at primary oxygen concentrations up to 14.4%, while the flame begins to attach to the burner at an oxygen concentration of 20.7%. The primary stream oxygen concentration required for flame stability increases with increasing primary oxygen concentration.

![Fig. 60. Schematic of nozzles used for direct oxygen injection [204].](image)

![Fig. 61. Effect of oxygen nozzle designs (combination, radial, reverse, and 45° angle toward flame) on flame temperature profile. (a) With 5% oxygen replacement, and (b) with 10% oxygen replacement [204]. Air indicates the baseline flame temperature without oxygen nozzle.](image)

![Fig. 62. (a) The effect of secondary oxygen mole fraction on the stand off distance (with pure CO2 primary stream). (b) The effect of primary oxygen mole fraction on the stand off distance (with fixed stoichiometric ratio) under O2/CO2 and O2/N2 conditions, two preheat temperatures were tested (489 K and 544 K) in the oxy-coal mode. Cited from [205].](image)
attachment, however, is much higher than that under O\textsubscript{2}/N\textsubscript{2} conditions with the matched stream momenta, indicating the challenge of flame stabilization in oxy-coal combustion. Moreover, preheating the secondary stream from 216 °C to 271 °C makes the flame more stable.

The attached flame is more likely to be achieved with swirl burners, in which stable combustion is possible while introducing no oxygen into the primary stream. Fry et al. [206] performed oxy-coal combustion experiments with a 0.3 MW Siemens-REI swirl burner using western bituminous coal from the Skyline mine. They found that when the overall oxygen concentration is 27%, an attached flame can be maintained while decreasing the primary stream oxygen concentration to as low as 2.7%, which is the typical residual oxygen concentration in the dry recycled flue gas (meanwhile the oxygen concentration in the secondary stream had to be increased to 34.5% in order to match the overall oxygen/RFG ratio). The discrepancy in the experiments of Zhang et al. and Fry et al. are caused by the different burner characteristics. More hot gas can be recirculated internally using swirl burners, and hence it is possible to achieve better flame stability with low oxygen concentrations in the primary stream.

3.3.3. Fluid dynamics considerations

The stability of oxy-coal combustion is dependent to a large extent on the flowfield in vicinity of the burners. Since the overall gas volume flow rate is reduced in oxy-coal combustion, the momenta of different streams, the swirl effects and the corresponding mixing of fuel, oxidizer and recirculated hot gas may be changed accordingly. Therefore, the geometry of the oxy-burners should be carefully redesigned in order to ensure stable combustion.

3.3.3.1. Matched mass flow rate, momentum or velocity. Khare et al. [207] numerically studied the combustion aerodynamics of an IHI 1.2 MW burner. Given the same burner geometry, the authors pointed out that if the same gas velocity of the primary stream is maintained in order to keep coal particles in suspension, the mass flow rate of the recycled flue gas fed to the secondary stream has to be reduced because the total gas volume in oxy-coal combustion is reduced to 70%–80% of that in air combustion. Therefore, the momentum ratio of the primary to the secondary burner streams may change. For instance, they found that the primary to secondary stream momentum ratio was increased from 0.13 for the air-coal case to 0.73 for the oxy-coal case when maintaining the same primary velocity. This in turn decreases the swirl effect and changes the flow regime. Consequently, a greater ignition delay is predicted with a longer flame stand-off distance in the oxy-fuel case. A similar phenomenon was reported by Rehfeldt et al. [189] when investigating the flow patterns of air-fired and oxy-fired combustion modes in the IVD (Institute of Process Engineering and Power Plant Technology, University of Stuttgart) combustion test facility. The reduced volumetric flow rate results in a significantly lower secondary/primary stream momentum ratio and an altered flow pattern. Fig. 63 shows that a type-2 flame (with internal recirculation) in air-coal combustion changed to a type-0 flame (without internal recirculation) in oxy-coal combustion due to the weaker swirl effect of the secondary stream. The measured O\textsubscript{2} and CO\textsubscript{2} concentrations also indicate weak internal recirculation and a different flame shape in oxy-coal combustion.

On the other hand, it is possible to stabilize combustion by maintaining the burner flow momenta when retrofitting. Tigges et al. [208,209] simulated the combustion field of the Hitachi Low NO\textsubscript{x} DS burner shown in Fig. 58(d) under air-fired and oxy-fired conditions. The O\textsubscript{2} mole fractions in the secondary and tertiary streams were increased to match the flame temperature with that of air-coal combustion. When keeping a similar volumetric flow rate for the primary stream and maintaining the momenta for all other streams, similar flowfields and temperature distributions were obtained.

In the investigation of oxy-fuel burner retrofit strategies performed by Fry et al. [206], the main concern was the influence of the primary stream flow characteristics on flame stability. For this

---

**Fig. 63.** Axial velocity distribution under air-fired and oxy-fired operating conditions in the IVD combustion test facility. The white areas indicate negative axial velocity values (internal and external recirculation zone) [189].
purpose, they fixed the stoichiometric ratio, i.e. the overall O2 concentration, and the ratio of the secondary to tertiary stream flow rates, and tested three cases of primary stream flow configurations: matching the mass flow rate (m), matching the momentum (p), or matching the velocity (v) with that of the primary air in air-fuel combustion. The primary stream velocities under these cases were in the following order: \( v_m < v_p < v_v \). They observed that by matching the primary gas-to-fuel mass flow ratio and primary stream momentum to that of air-coal conditions, a stable and attached flame that closely resembled the air-fired flame was attained. Conversely, when oxy-coal combustion was operated with a matched primary stream velocity, the flame was detached from the burner quarl. Recalling the discussion in Section 2.2.1, it is unnecessary to maintain the primary stream velocity for coal particle transport. Therefore, the primary stream velocity can be optimized while improving the flame stabilization.

The findings in these studies suggest that flame stability is dependent on the flow characteristics, which in turn are determined by the design and operation of the burner. The primary stream velocity should be optimized for delivering the pulverized coal, while considering its influence on the mass balance and corresponding momentum ratios of different burner streams in oxy-coal combustion. The combined effect of the burner streams on flame stabilization should be taken into account when designing the burner. More research is needed to better determine the design principles.

3.3.3.2. Advanced burner design. Combustion stability can also be attained manipulating the combustor flowfield through advanced burner design. The use of swirling flow, bluff body, and quarl geometry can create a central recirculation zone, while the inlet streams are heated by recycled hot flue gas [106]. Most studies so far have focused on retrofitting air-fired burners and optimizing the operating conditions. One of the few research studies on new oxy-burner designs, carried out by Toporov and coworkers [162,210], improved the design of the Oxy-1 and the Oxy-2 burners (also see Fig. 58(e)) by using in-flame measurements and CFD modeling. As shown in Fig. 64, the quarl geometry was changed in Burner Oxy-1 and further improvement was made in Burner Oxy-2 which features a bluff body. These geometry improvements increased the internal hot product recirculation, forced the ignition point closer to the quarl and made a stable oxy-coal flame possible at O2 concentrations as low as 18%.

3.3.4. Gas stream preheating

Another method to stabilize oxy-fuel combustion is through preheating the burner streams. This method provides another degree of freedom when operating oxy-coal burners. While preheating an oxygen-carrying primary stream may raise safety concerns, other streams could be preheated by means of heat recycle through gas–gas heat exchangers or flue gas recycle at higher temperatures. As discussed previously, preheating the secondary stream improved the flame stability in Zhang’s experiment [205] (see Section 3.3.2.2). Preheating the inlet gas streams is not new to air-fired PC combustion. Combustion of pulverized coal with highly preheated air, exceeding 1000 K, has been demonstrated [37,211]. This experience could be utilized when applying the gas stream preheating technology to oxy-coal combustion [40,42,212].

4. CFD modeling of oxy-coal combustion

CFD techniques have become the third dimension in fluid dynamics and combustion studies alongside analytical modeling and experimental diagnostics [213]. CFD provides a relatively inexpensive (when submodels are used in connection with Reynolds-averaged Navier–Stokes (RANS) or when using coarse grain large-eddy simulation (LES) models) and indispensable tool to perform comprehensive studies on the fluid flow, heat transfer and chemical reactions in combustion. Currently, CFD modeling of oxy-coal combustion utilize approaches and sub-models that are similar to those developed under air-fired conditions. With the accumulated knowledge on the fundamental differences between air-fuel and oxy-fuel combustion, some effort has gone into developing and validating sub-models for the new combustion environment.

A selection of the CFD simulation studies on oxy-fuel combustion is summarized in Table 12, which includes the sub-models used for turbulence, radiation heat transfer, char combustion and homogenous reactions. Since the existing sub-models were developed for conventional air-coal combustion, their assumptions and approximations may not be valid in the CO2-rich environment. In the following sections, the development of CFD sub-model for an accurate prediction in oxy-coal combustion is reviewed, and the findings of these recent numerical studies are summarized.

4.1. Governing equations and physical properties

Coal combustion is typically modeled as a dilute two-phase (solid-gas) reacting flow using an Eulerian-Lagrangian approach. The mass, momentum and energy interactions between the gas phase and the solid particles are calculated using the “particle-source-in-cell” method [214] while updating the particle state along a set of particle trajectories. For the gas phase, the equations governing mass, momentum, species and energy are written in conservative form:

\[
\frac{\partial (\rho \Phi)}{\partial t} + \frac{\partial (\rho u_j \Phi)}{\partial x_j} = \frac{\partial}{\partial x_j} \left( \Gamma_\Phi \frac{\partial \Phi}{\partial x_j} \right) + S_\Phi
\]  

with \( \Phi \), t, u, \( \Gamma_\Phi \) and \( S_\Phi \) denoting Favre-averaged variables, time, velocity, diffusion coefficient, and source term, respectively [215]. These equations are the same in both air-coal combustion and oxy-coal combustion. However, the thermodynamics and the transport properties of the gas mixture are different.

In turbulent flows, the effects of turbulence on the transport properties, such as the turbulent viscosity, turbulent mass diffusivity, and turbulent thermal conductivity, generally dominate the

![Fig. 64. Schematics of burner A, Burner Oxy-1 and Burner Oxy-2 [210].](image-url)
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<td>Standard k − ε</td>
<td>Standard k − ε</td>
<td>DO</td>
<td>EDC</td>
</tr>
<tr>
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<td>Standard k − ε</td>
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<td>EDC</td>
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laminar transport properties, resulting in a relatively insignificant contribution from the laminar properties. On the other hand, thermodynamic properties such as density and heat capacity are always important, regardless of whether it is a laminar or a turbulent flow.

Chen et al. [80] have shown that the gas phase specific heat distributions in oxy-fuel and air-fuel conditions are substantially different using a CFD simulation of a pilot-scale combustor at elevated pressure. In their study, a slightly higher O2 mole fraction was used in the oxy-fired oxidizer stream (22.2%). The same swirl number was used for both cases, guaranteeing a similar overall flowfield (shown in the Fig. 65(b)) under oxy-fuel and air-fuel conditions. Fig. 65(a) shows that the specific heat distribution for the oxy-fuel environment is in the range of 1300–1800 J/kg-K, significantly higher than for the air-fuel environment (1100–1400 J/kg-K), because of the higher concentration of CO2 and H2O in the former. The higher specific heat under oxy-fuel conditions results in significantly lower combustion temperatures (shown in the Fig. 65(b)). Devolatilization and char burning are delayed in the oxy-fired case as a result of the lower temperature.

4.2. Turbulent flow

Some of the most important phenomena in a practical combustion process are dominated by turbulence, a fact that complicates the effort to predict their characteristics. Although direct numerical simulations (DNS) can resolve all the scalars of the Navier–Stokes (NS) equations directly, because of its computational complexity, DNS can only be applied to simple and small geometries and at lower Reynolds number. In situations where DNS is not feasible, turbulence models are used for approximating turbulent fluxes, turbulent dispersion and turbulent-combustion interactions. Several turbulence models have been developed; they are either based on the RANS or the LES approximations. In RANS-based models, dependent variables are decomposed into space-time averaged components and fluctuations. The resulting Reynolds fluxes are modeled by solving transport equations for the turbulent quantities, such as turbulent viscosity, turbulent kinetic energy, turbulent dissipation rate, etc., at all scales. On the other hand, LES resolves the large eddies directly, while the impact of the small eddies are modeled. In terms of the fraction of the resolved scales, LES falls between DNS and RANS [216]. CFD modeling of
turbulent combustion, especially of coal or other solid fuels, is still largely based on RANS.

As can be seen in Table 12, the two-equation $k - \varepsilon$ model is widely used in oxy-coal combustion CFD simulations. These RANS simulations are reported to yield acceptable accuracy when compared with experimental data. Recently, Edge et al. [217] compared the performances of LES and RANS (RNG $k - \varepsilon$) models in their simulation of air- and oxy-fired pulverized coal combustion in a 0.5 MWth combustion test facility. Fig. 66 shows the comparison between the predicted velocity and temperature fields using these two approaches under both air-fired (top) and oxy-fired (bottom) conditions. The contour maps show that LES predicts stronger recirculation zones than RANS simulations in all cases. It also yields a hotter flame edge because of its ability to resolve the large eddies of hot gas. In general, similar improvements are observed when using LES instead of RANS under air-fired and oxy-fired conditions. The study also showed that simulations using a combination of LES and a gray gas radiation sub-model overpredicts the incident radiation while the combination of RANS and a spectral gas radiation sub-model yields better comparisons. This finding further accentuates the importance of other physical sub-models.

4.3. Radiation heat transfer

4.3.1. Models for radiative properties

Radiation heat transfer is typically computed in CFD by solving the radiative transfer equation (RTE). The RTE at position $\tilde{r}$ in the direction $\tilde{s}$ is given by [218]:

$$\frac{dl_{ij}(\tilde{r}, \tilde{s})}{ds} = \kappa_j n^2 l_{b, \lambda} - \left( \kappa_j + \sigma_{s, \lambda} \right) I_j(\tilde{r}, \tilde{s}) + \frac{\sigma_{s, \lambda}}{4\pi} \int_0^{2\pi} I_j(\tilde{r}, \tilde{s}') \Phi(\tilde{s} - \tilde{s}') d\Omega' \quad (44)$$

where $s$ is the path length, $\kappa$ is the absorption coefficient, $\sigma_s$ is the scattering coefficient, $n$ is the refractive index, and $I$ is the radiation intensity which is dependent on position $\tilde{r}$ and direction $\tilde{s}$. In this section, only the gaseous radiative heat transfer will be discussed. The gas mixture is considered to be an absorbing and emitting medium without scattering. In this case, the RTE is simplified to:

$$\frac{dl_{ij}(\tilde{r}, \tilde{s})}{ds} = \kappa_j n^2 l_{b, \lambda} - \kappa_j I_j(\tilde{r}, \tilde{s}) \quad (45)$$

Integrating the radiation intensity over the whole radiation spectrum yields:

$$\frac{dl_{ij}(\tilde{r}, \tilde{s})}{ds} = n\pi a^d - \tau_{\text{incident}} I(\tilde{r}, \tilde{s}) \quad (46)$$

The Planck-mean absorption coefficient, $\tau$, and the incident mean absorption coefficient, $\tau_{\text{incident}}$, are absorption coefficients averaged over the whole spectrum weighted by radiation intensity. Therefore, these properties are functions of gas composition, temperature and pressure; additionally, the incident mean absorption coefficient, $\tau_{\text{incident}}$, also depends on the incident radiation. An accurate calculation of the gas radiation property must consider the spectral absorption of CO2 and H2O, and also the overlap between these radiating gas components. As discussed in Section 2.1.1, since direct prediction of the absorption coefficient is computationally complex, models for absorption properties, such as the gray gas or the band models, will have to be employed in the radiation heat transfer model.

The most commonly used gray gas model in CFD is the weighted sum of gray gases (WSGG) model proposed by Smith et al. [219]. In this model, the gas is assumed to consist of a transparent gas and several gray gases without any wavelength dependence, and the model parameters are based on the radiation properties of air-fired flue gases. In contrast, when using the band models, spectral calculations are performed by dividing the entire wavelength spectrum into several bands and assuming that the absorption characteristics of each species remain either uniform or change smoothly according to a given functional form over these bands [220]. One example of this type of radiation models is the Exponential Wide Band model (EWBM) proposed by Edwards and

![Fig. 66](image-url) (a) Axial velocity distribution from LES and RANS. Individual axial velocity legends are shown in m/s. (b) Velocity vectors are superimposed over temperature distribution from LES and RANS. Temperature legend is shown in K. [217].
Menard [221], which assumes exponential functions of the line intensity around a band center. Band models are believed to be applicable in oxy-fuel combustion because of their theoretical soundness in non-gray radiation. However the use of band models is usually computational expensive, and the model is typically used to calibrate the gray gases model [222,223].

4.3.2. Modification of the gray-gas model

In the WSGG model, the Planck-mean absorption coefficient of the gas mixture over a path length, s, is determined by:

\[ \bar{\alpha} = -\ln(1 - e)/s \]  

(47)

where \( s \) is the radiation beam length, and \( e \), the gas emissivity. The latter is calculated from:

\[ e = \sum_i a_{i,j}(T)(1 - \exp(-\kappa_i p_i s)) \]  

(48)

where \( a_{i,j} \) is the emissivity weighting factor for gray gas \( i \), \( \kappa_i \) and \( p_i \) are the pressure absorption coefficient \( (1/m\text{ atm}) \) and partial pressure \( (\text{atm}) \) of the absorbing gas \( i \), respectively.

The emissivity weighting factors used in the previous Eq. (48) are polynomial correlations that can be given as a function of the gas temperature:

\[ a_{i,j} = \sum_j b_{i,j} T^{-1} \]

(49)

The coefficients of the polynomial correlations, \( b_{i,j} \), and the absorption coefficients of the gray gas, \( \kappa_i \), are derived from experimental data of oil and methane stoichiometric combustion, in which the \( \text{CO}_2 \) partial pressure is around 0.1 atm, and the partial pressure ratio of \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) is in the range of 1–2, with a path length of less than 10 m [223]. It is worth noting that the \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) partial pressures and their relative ratio in oxy-coal combustion are not within the applicable range.

Rehfelt et al. [223] compared the predicted emissivity of the flue gases in both air-fuel and oxy-fuel combustion conditions at 1000 K and 1500 K using both the WSGG model and EWBM, and the results are shown in Fig. 67. Both models predict similar gas emissivities for the air-fuel conditions. However, the agreement between the two models is poor for oxy-fuel combustion conditions, especially at high \( \text{CO}_2/\text{H}_2\text{O} \) ratios.

Therefore, when using the WSGG model, the coefficients of the polynomial correlations should be modified to reflect the conditions found in oxy-fuel combustion. Direct use of the gray gases model for the radiative properties in oxy-fuel combustion may cause errors and should be avoided [218]. In order to adapt the WSGG model to oxy-fuel conditions, Johansson et al. [222] modified its parameters by fitting the emissivity to a Statistical Narrow Band (SNB) model. The absorption coefficients are constant for each gas, while the weights are calculated from temperature-dependent relations. The two new parameter sets are applicable in oxy-fuel conditions with dry or wet recycle, in a temperature range of 500–2500 K and for path lengths between 0.01 and 60 m.

Likewise, Rehfelt et al. [223] developed a four gray gases plus one clear gas approach. Instead of providing different parameters for specified \( \text{H}_2\text{O} \) mole fractions as done in reference [222], the molar ratio of \( \text{H}_2\text{O} \) to \( \text{CO}_2 \) was considered as a variable in the emissivity weighting factor correlations:

\[ a_{i,j} = \sum_j \left[ \sum_m c_{i,j,m} \theta^{m-1} \right] T^{-1} \]

(50)

where \( c_{i,j,m} \) is the coefficient of the correlation which is derived by curve fitting with the EWBM predictions in the range of 600 K–2400 K and molar fractions of carbon dioxide in the range of 0.3–0.9. A comparison between the predictions of radiative heat flux in a furnace using both the WSGG model with these new parameters and the EWBM shows good agreement.

4.4. Heterogeneous reactions

Oxy-char combustion characteristics have been reviewed in Section 2.6, which showed that the kinetics of char oxidation and gasification reactions are not significantly different from those in air-combustion. However, the mathematical model used in CFD simulations should reflect the effects of the slower oxygen diffusion and the contributions of gasification reactions in a \( \text{CO}_2 \)-rich atmosphere.

Chui et al. [201] modeled the char burning rate as being governed by chemical kinetics and the external diffusion rate of oxygen to the char surface, in a CFD simulation of oxy-coal combustion in the CANMET vertical combustor research facility. The work only considered the char–\( \text{O}_2 \) oxidation reaction which is implemented as a global carbon oxidation reaction:

\[ \text{C}(s) + \text{O}_2 \rightarrow \text{CO}_2 \]

(51)

A similar model was used by Khare et al. [207] in a CFD simulation of oxy-coal combustion in the IHI vertical pilot-scale facility. Different mass diffusion-limited rate constants and kinetic-limited rate parameters for air-coal and oxy-coal combustion derived from DTF experimental results were used.

Taking the gasification reactions into account improves the prediction of char consumption rate, especially during the later stages of oxy-combustion (also see 2.6.3). Therefore, in some CFD simulations [189,224], the Boudouard reaction (Reaction III in Eq. (23)) was considered. In these studies, the product of carbon oxidation reaction is \( \text{CO} \) rather than \( \text{CO}_2 \) (Reaction I in Eq. (23)) which is reasonable for the combustion temperature range of pulverized coal flames, as shown by Arthur’s experiments [225]. Kuhr et al. [226] simulated char combustion in both \( \text{O}_2/\text{N}_2 \) and \( \text{O}_2/\text{CO}_2 \) atmospheres in a vertical once-through 20 kW furnace at the Institute of Combustion and Power Plant Technology (IFK). The CFD study compared the performance of an intrinsic model based on Smith’s approach [161] against a surface reaction model. Fig. 68 shows the experimental and numerical simulation results of the
O2 and CO mole fraction profiles along the reactor. It should be noted that the operating condition shown in Fig. 68 is 5% O2 with a wall temperature of 1300 °C, which falls between Region B and C of Fig. 32 where the Boudouard reaction contributes to the char consumption rate. As seen in Fig. 68(a), the intrinsic char oxidation model, which only considers the oxidation reaction, can predict the gas species distribution well for the O2/N2 condition. However, when a surface reaction model that consists of only the oxidation reaction is used for the O2/CO2 condition, it underpredicts the char consumption rate and overpredicts the O2 mole fraction as shown in Fig. 68(b). Adding the Boudouard reaction increases the char consumption rate and improves the O2 profile prediction. Additionally, since the partial pressure of H2O is substantially higher under wet recycle conditions, most other CFD simulation studies [80,95,162,215,227] implemented both the char-CO2 and char-H2O gasification reactions (Reaction II in Eq. (24)) in the char consumption model, where the char-H2O gasification reaction is considered to take place in parallel with the oxidation reaction and Boudouard reaction.

The reaction rates of the three heterogeneous reactions discussed above are determined by both surface reaction kinetics and external oxidizer diffusion. Based on the assumption that the global reaction kinetics do not change in oxy-fuel combustion [148], the kinetic parameters are usually taken from air-coal combustion kinetics for similar ranks. On the other hand, in order to capture the effect of slower diffusion rate under oxy-coal combustion conditions, the diffusion rates of the oxidizers in the boundary layer of the coal particles have to be modified based on the diffusion theory [161]. Doing so yields a lower diffusion rate constant under oxy-coal combustion conditions, the diffusion rates of the oxidizers in the boundary layer of the coal particles have to be modified based on the diffusion theory [161].

For computational simplicity, oxy-char combustion sub-models are usually simplified in CFD simulations. Important processes such as the internal diffusion and reactions within the porous char particles, the CO flame sheet around the char particles and the interactions of gas species diffusion in the boundary layer are usually ignored. Therefore, advanced sub-models that are accurate and yet computationally inexpensive need to be developed for the oxy-char combustion.

4.5. Gas phase reactions

Gas phase reactions play an important role in coal combustion and gasification. Light gases, hydrocarbon gases (alkenes and alkyls) and tar are produced alongside CO2 and pyrolysis H2O during coal devolatilization [121]. CO and H2 produced from the char particle gasification reactions are also burned in the free stream outside the char particle boundary layer for typical pulverized coal particle sizes [228]. In a CO2–rich environment, the global reaction rates might be different from the conventional air-fuel combustion due to the chemical effects of CO2. Therefore, the modeling of gas phase reactions should be modified as well. This includes both the reaction mechanism and the turbulence-chemistry interaction model.

4.5.1. Reduced reaction mechanisms

Detailed reaction mechanisms for hydrocarbon combustion such as the detailed chemical kinetic model (DCKM) presented by Glarborg and Bentzen [188], and the GRI-Mech 3.0 used previously in this work have been shown to be valid under oxy-fuel combustion conditions. However, it is computationally expensive to apply these detailed reaction mechanisms in CFD modeling of coal combustion. Alternatively, reduced hydrocarbon combustion mechanisms have been proposed.

Reduced reaction mechanisms and models used in CFD studies of oxy-fuel combustion are summarized in Table 12. In early numerical simulations of oxy-coal combustion, volatile matter combustion was simplified to a one-step global reaction. For instance, Wang et al. [32] simulated the oxy-coal combustion in the Battelle Columbus Laboratory subscale combustor using an infinitely fast reaction rate and local chemical equilibrium. The simulation results showed similar trends to the experimental data for the temperature and major composition distributions. On the other hand, the model failed to predict the CO concentration because of the assumptions of one-dimensional well-mixing and infinitely fast reactions.

Toporov et al. [162] proposed a simplified reaction mechanism for volatile combustion in the CFD simulation of oxy-coal combustion, which consists of volatile decomposition and irreversible combustion of CO and H2:

\[ C_{x}H_{y}O_{z}N_{m} + \left( \frac{x}{2} + \frac{y}{2} - \frac{z}{2} \right) O_{2} \rightarrow xCO + \frac{y}{2}H_{2} + nSO_{2} + \frac{m}{2}N_{2} \]  \hspace{1cm} (52)

\[ CO + 0.5O_{2} \rightarrow CO_{2} \]  \hspace{1cm} (53)

\[ H_{2} + 0.5O_{2} \rightarrow H_{2}O \]  \hspace{1cm} (54)

The simulation results showed agreement with experiments for the temperature and O2 species. The CO concentration measurement was not available, and hence the accuracy of the CO prediction using this mechanism was not verified.

Multi-step reaction mechanisms, such as the two-step mechanism proposed by Westbrook and Dryer (WD) [229] and the four-step mechanism proposed by Jones and Lindstedt (JL) [230], were suggested for the homogeneous reactions under conventional air-fired conditions, and have been successfully used in CFD modeling of coal combustion and gasification [231,232]. Since the WD mechanism considers the reversible CO2 dissociation reaction, and the JL mechanism consists of the reversible water gas shift reaction, they are expected to yield a more accurate CO concentration prediction than the irreversible reaction mechanisms. However, since the kinetics of these global reactions were deduced from air-combustion experimental data, Andersen and coworkers [233] concluded that these mechanisms cannot be expected to work as well under oxy-fuel conditions as they do for conventional air-fuel combustion. Therefore, they further modified the two-step
WD and four-step JL mechanisms for methane combustion by calibrating their kinetics parameters with the ignition delay and the final product concentration results predicted by the DCKM reaction mechanism under oxy-fuel conditions. Both modified mechanisms are claimed to perform better than the original mechanisms for CO and flame temperature predictions in the CFD modeling of oxy-propane combustion.

Coal combustion involves complicated hydrocarbon species, including both tar and gases that depend on the rank and property of the fuel, resulting in a large range of gas compositions. Although the reduced mechanisms are reasonably well established for natural gas and other gas fuels, and have been applied in air-coal combustion, their accuracies in oxy-coal combustion simulation remain a subject of investigation.

4.5.2. Turbulence-chemistry interactions

For laminar flows, the reaction rates can be computed using the laminar finite-rate model. However, in the case of turbulent flames, turbulent fluctuations becomes important and chemistry-turbulence interactions must be modeled while considering the effects of turbulent fluctuations on the source term of the species equation. The description of the interaction between turbulence and chemistry, therefore, becomes another concern in accurate modeling the gas phase reaction under oxy-fuel conditions.

The eddy dissipation model (EDM) [234] was used in some numerical studies of oxy-coal combustion [95,201] in which the chemical reaction is governed by the large-eddy mixing time scale based on the eddy break-up (EBU) model proposed by Spalting [235]. As a further development, the finite rate/eddy dissipation model was proposed, in which the reaction rate is taken to be the lower of the Arrhenius reaction rate and eddy dissipation rate. In the flame zone, the eddy dissipation rate is generally smaller than the Arrhenius rate, and reactions are limited by the extent of mixing. Based on the assumption that the reaction rate is limited by both the mixing of the reactants and the heating of the reactants through the mixing with hot products, the net rate of production of species $i$ due to reaction $r$, $R_{r,i}$, is given by the smaller of the reactant mixing rate (first term) and product mixing rate (second term):

$$R_{r,i} = \min \left( v_{r,i} M_{n,i} A_B \rho / k_R, \frac{Y_k}{k_R, M_{n,i}} v_{r,i} M_{n,i} A_B \rho / k_R, \frac{\sum_p Y_p}{k_R, M_{n,i}} v_{r,i} M_{n,i} A_B \rho / k_R \right)$$

(55)

Where $A$ and $B$ are model constants $v_{r,i}$ and $v_{r,j}$ are the stoichiometric coefficient for reactant $i$ and product $j$ in reaction $r$, $M_n$ is the molecular weight, $Y_k$ and $Y_p$ are mass fraction of any reactant and product species, respectively. Note that in oxy-fuel combustion, the CO$_2$ and H$_2$O partial pressures in the burner streams are already high before mixing with hot product gases. Therefore, using the same model constants $A$ and $B$ for air-fuel combustion may overestimate the second term, and thus underestimate the reaction rate of oxy-fuel combustion.

Another drawback of eddy dissipation based models is that they cannot deal with multi-step chemical mechanisms and reversible reactions, such as CO$_2$ dissociation. The reason is that multi-step mechanisms are based on reaction rates which occur at different time scales, whereas in these models, every reaction has the same turbulent rate, and therefore, the same reaction rate [216]. CFD modeling of an oxy-natural gas flame has shown that the mixed-is-burned nature of the eddy dissipation model results in a failure to predict CO accurately [236].

The eddy dissipation concept (EDC) model was developed as an extension to the eddy dissipation model to incorporate multi-step chemical mechanisms in turbulent flows [237], where the reactions are assumed to occur in a turbulence-characterized fine-scale reactor governed by Arrhenius rates. Multi-step reaction mechanisms have been implemented in this model for air-methane combustion [238,239] as well as air-coal combustion [240], and are believed to be more accurate than the eddy dissipation based models. Recently, Vascellari and Cañ [227] applied this model with a modified JL mechanism which is taken from air-fuel combustion, to simulate oxy-coal combustion in the IFRF 2.4 MWth furnace. However they did not show a comparison with experimental data. Similarly, Muller et al. [215] also used the same approach for the gas phase reactions in their simulation of oxy-coal combustion in the IFK 0.5 MWth test facility, and the CO prediction agrees well with their experimental data.

4.6. Summary

The sub-models for turbulence, reaction and radiation in conventional air-coal combustion have been modified to take into account the different characteristics of oxy-coal combustion. The effects of the physical properties of the CO$_2$-rich stream on combustion have been investigated using CFD approaches, offering insight into oxy-coal combustion. However, the development and validation of more accurate sub-models are still needed. Extensive applications of CFD are expected in the scale up and advanced design of oxy-coal combustion facilities.

5. Research need

Oxy-coal combustion is a promising novel technology, and it is being implemented at scale. New challenges have been identified as this technology is developed, from the system level, such as system integration and optimization, to the fundamental levels, such as stabilization of oxy-fuel flames. Based on this review, future research needs are suggested below.

5.1. Oxy-coal system design

- CO$_2$ purity standard for sequestration: Up to the time of this review, there is still no consensus on the required CO$_2$ purity for sequestration. The standard should consider both safety requirements and the operating costs of capture, transportation and site monitoring. The standard will determine the efficiency and cost of electricity from oxy-coal combustion technology. An overly high cost to meet the standard may become a hindrance of its application (for instance, the stringent oxygen content required for EOR).

- System integration and optimization: Before oxy-coal combustion systems can be employed, the system components must be integrated, and the operating conditions optimized for the best energy efficiency. Thus, detailed process designs of a large-scale oxy-coal power plant are required for both retrofits and new plants. Since the operating conditions, such as the recycle ratio, are coal dependent, guidelines of system designs and operating conditions for different coal ranks are also required.

- New oxy-coal combustion processes for carbon capture: As discussed previously, most of the current studies have focused on air-like oxy-coal combustion and matching the combustion and heat transfer characteristics with those in air-combustion. Meanwhile, other oxy-combustion regimes mentioned in Section 1.2, such as full oxy-combustion and MILD oxy-combustion processes, may lead to higher efficiency and lower cost and thus, should continue to be explored. Similarly, pressurized oxy-coal systems are promising, but they are still in a nascent stage. Pilot scale tests for these concepts are essential to make them strong contenders to the more established air-like atmospheric oxy-coal system.
5.2. Fundamentals of oxy-coal combustion

Considerable knowledge of the fundamentals of heat and mass transfer, combustion processes and pollutant formation under CO2-rich conditions has been acquired through extensive experiments and modeling efforts in recent years. However, many fundamental issues remain uninvestigated:

- **Oxy-combustion characteristics of different coal types**: Due to the distinct physical properties and chemical structures, studies have shown various characteristics for coal of different ranks during devolatilization, volatile combustion, char burning, and pollutant formation. Their characteristics under oxy-fuel combustion should be further investigated as an integral part of oxy-burner design.
- **Models for sub-processes**: Models for devolatilization, char formation, agglomeration and coal group combustion under the oxy-combustion conditions are mostly based on air combustion studies. For instance devolatilization measurements are usually taken in inert medium, while in oxy-combustion, pyrolysis occurs in a CO2-rich environment in which some chemical interactions might occur. Similarly, char structure and consumption sub-models are mostly formulated for combustion in air, with a typical oxygen concentration of 21%. In oxy-combustion, char oxidation sub-models may need to be modified depending on the temperature, oxygen concentration and the presence of a higher fraction of steam.
- **Scaling characteristics of oxy-combustion**: Given the complexity of combustion processes and the number of nonlinearly interacting processes, developing similarity and scaling models is usually challenging. Extending such models acquired from experience with traditional air-combustion to oxy-combustion is necessary in order to establish design guidelines and rules for burner and combustor sizing.
- **Pressure effect**: When operating under elevated pressure, the gas phase flowfield and coal particle residence time may change significantly. The effect of pressure on the characteristics of mass and heat transfer, char and gas phase combustion kinetics and dynamics, etc., are also still relatively unknown. Research on the characteristics of oxy-combustion at elevated pressures is needed.

5.3. CFD modeling of oxy-coal combustion

Although CFD approaches have been used in some studies to better understand the flowfield and combustion processes in oxy-coal combustion, several problems remain that need to be resolved to achieve a higher predictive accuracy of combustion characteristics in a CO2-rich environment. Models of some sub-processes are not yet available or verified in oxy-coal combustion, such as:

- **Oxy-char combustion sub-models**: The models should take into account the effect of physical (heat capacity and mass transfer) and chemical (its interaction with heterogeneous and homogenous reactions) properties of CO2 and be able to predict the burning rate in the different operating condition regions (see Section 2.6).
- **Gas phase reaction mechanisms**: High-fidelity reduced gas combustion mechanism should capture the chemical effect of CO2 in oxy-combustion, and provide accurate predictions of minor species and pollutant formations.
- **Radiation models**: Radiation heat transfer plays a major role in the furnace, and it also governs the energy equation in combustion. Better turbulence-radiation and gas emittance/absorptance sub-models are needed to improve the simulation of the temperature field.
- **Turbulence models**: While swirling flows and their impact on mixing via the establishment of inner recirculation zones near burners and injectors are important in all combustors, they take on a more significant role in the case of oxy-combustion. Better predictive models for rotating and swirling flows are thus needed, especially for the more economical approaches, such as RANS.

5.4. Large scale demonstration

Pilot and industrial scale demonstration of the oxy-coal combustion is imperative to verify the observations and theories developed from lab and bench scale studies, and provide valuable operating experience for future scale-ups.

- **Transition between operating modes**: Considering the uncertainty of greenhouse gas emission regulations, future power plant may need to be designed to operate under both air- and oxy-fired conditions. The capability of operating under both modes is also one of the key advantages because the air-firing operation is needed during start up/shutdown, peak hour demands, and auxiliary equipment (such as ASU and CO2 compression units) failures. Currently, the transition between these operating modes is being tested in pilot scale facilities of Vattenfall, Alstom and Doosan Babcock and shows little difficulties [241–244]. However, the steam streams and energy flows are heavily coupled in demonstration scale oxyfuel combustion system, and issues such as the control of the subsystems coupling during start-up still need to be addressed.
- **Advanced oxy-coal burner and combustor design and performance test**: As previously discussed in Section 3, efforts are being made to understand the fundamentals of flame destabilization in oxy-coal combustion, as well as the principles of retrofitting and designing the oxy-coal burners. However much more remains to be done for advanced oxy-fuel burner design, its carbon conversion and pollutant control performance, as well as its scale-up to full-scale power plants. Following the onsite tests of single oxy-burner performance, the demonstration of larger burners and multi-burner configurations should also be carried out.
- **Material and corrosion**: Since the SO2 and NOx concentration can be higher in the oxy-fuel mode, high temperature corrosion of various alloy materials should be tested at typical locations in the flue gas path to serve as guide for choosing the material of heat exchangers. Low temperature corrosion test in the flue gas duct is also needed to set up standards for the acid gases in recycled flue gas [243].
- **Fate of ash and slag**: While the emissions of pollutants like NOx and SO2 are widely studied in oxy-coal combustion, there is a lack of literature on the behaviors of ash and slag in this environment. Little is known about the phase changes, coagulation, size distribution and element partitions of the fly ash in a high CO2 environment. Particulate matter control devices have to be adapted based on these studies. In the case of slagging oxy-fuel combustion, the mechanisms of slag layer formation and its interaction with char particles are also poorly understood.

This paper reviewed the state-of-the-art progresses of oxy-coal combustion on aspects of its regime characterization, fundamentals, stabilization and CFD modeling approaches. The discussions focus on the different characteristics between oxy-fuel combustion...
and the conventional air-fuel combustion, and reveal insight on the physical and chemical effects in different combustion media. Due to its complexity, the combustion technology is still heavily dependent on experiments and operational experience, especially in its application in coal-fired power plants. Therefore, successes in pilot- and demonstration-scale tests such as the Vattenfall project should provide practical knowledge and experience for the operation, heat transfer, combustion dynamics and stability, as well as pollutant formation and control.

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