Oxy-fuel combustion of solid fuels

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\textbf{ABSTRACT}

Oxy-fuel combustion is suggested as one of the possible, promising technologies for capturing CO\textsubscript{2} from power plants. The concept of oxy-fuel combustion is removal of nitrogen from the oxidizer to carry out the combustion process in oxygen and, in most concepts, recycled flue gas to lower the flame temperature. The flue gas produced thus consists primarily of carbon dioxide and water. Much research on the different aspects of an oxy-fuel power plant has been performed during the last decade. Focus has mainly been on retrofits of existing pulverized-coal-fired power plant units. Green-field plants which provide additional options for improvement of process economics are however likewise investigated. Of particular interest is the change of the combustion process induced by the exchange of carbon dioxide and water vapor for nitrogen as diluent. This paper reviews the published knowledge on the oxy-fuel process and focuses particularly on the combustion fundamentals, i.e. flame temperatures and heat transfer, ignition and burnout, emissions, and fly ash characteristics. Knowledge is currently available regarding both an entire oxy-fuel power plant and the combustion fundamentals. However, several questions remain unanswered and more research and pilot plant testing of heat transfer profiles, emission levels, the optimum oxygen excess and inlet oxygen concentration levels, high and low-temperature fire-side corrosion, ash quality, plant operability, and models to predict NO\textsubscript{x} and SO\textsubscript{3} formation is required.

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1. Introduction

The world, and especially the developing countries such as China and India, is facing an increasing growth in the demand for electrical power [1,2]. New power plants are thus being constructed at a considerable rate in order to keep up with this demand [1–3]. The majority of the recently constructed and planned power plants, on a world-wide basis, are coal-fired [1,2]. Coal is a cheaper and more abundant resource than other fossil fuels such as oil and natural gas while at the same time being a very reliable fuel for power production [4,5].

In the developed countries an increasing part of the energy consumption is being produced from renewable sources of energy; wind, biomass, solar, hydro power, etc. [1]. The main purpose of the shift from a fossil fuel based production to renewable energy is to decrease the emission of greenhouse gases. Especially the emission of CO₂ from the combustion of fossil fuels has gained great focus in recent years in connection with the discussions of global warming. Since the beginning of the industrialization in the late part of the 18th century the amount of CO₂ in the atmosphere has increased sharply from about 280 to 380 ppm [6], see Fig. 1.

Table 1 lists the current and projected CO₂ emissions, in Gton carbon per year, from power generation (both electricity and heat) [1]. Both the emissions and the coal share of the emissions are seen to increase toward 2030 for the world as a whole. Even though the CO₂ emissions are seen to increase within Europe the percentage increase is much less pronounced than for the rest of the world and the coal share of the emissions is expected to decrease. Despite the fact that the ultimate goal for most countries is to phase out all fossil fuels in heat and power production as well as in the transport sector, the share of renewable energy sources increases only slowly and the world will depend on fossil fuels for many years to come. A rapid move away from fossil fuels could result in great conflicts concerning water and land use between biomass for energy production, food production, and forestation [7] as well as in serious disruption to the global economy [8]. The latter is mainly caused by the long lifetime of the energy supply infrastructure. In the transitional period, technologies are sought which will enable the continuous usage of fossil fuels but at the same time eliminate the emission of CO₂.

1.1. Carbon capture and storage

Since power plants constitute large point sources of CO₂ emission the main focus is related to their operation. Currently,
several possible technologies are being investigated which will enable the so called Carbon Capture and Storage (CCS) from power plants [5,8-14]. Both researchers in universities and other research institutions, most manufacturers of boilers and other power plant related equipment, and many power companies are active. CCS will act as a complimentary technology to the ongoing work related to increasing fuel efficiency and the change toward fuels with lower fossil carbon content, e.g. natural gas and/or biomass. As indicated by the term CCS, the elimination of CO$_2$ emissions include two consecutive operations:

1. Capture of CO$_2$ from the power plant flue gas
2. Storage of the CO$_2$ (incl. transport to storage site)

The estimated cost of separation, capture, and compression of CO$_2$ (point 1) from power plants or other point sources accounts for around 75% of the total cost of a geologic sequestration process [11,15-17].

1.2. Carbon storage technologies overview

The disposal technology should ensure a complete elimination of the CO$_2$ from the earth’s carbon cycle in order to stabilize the CO$_2$ concentration in the atmosphere. Two types of disposal are defined: sequestration (permanent disposal) or storage (disposal for a significant time period) [7]. These terms are often interchanged in the sense that time periods of more than 10,000 years are considered permanent. Possible storage methods suggested include injection in e.g. depleted oil and gas reservoirs, coal beds, deep saline aquifers, etc. [7,11,17-24]. The estimated storage potential for the suggested options is given in Table 2.

When CO$_2$ is injected below the caprock in oil and gas reservoirs as well as deep saline aquifers it is first trapped by static and hydrodynamic mechanisms. Secondary trapping mechanisms begin operating over time and act to immobilize the CO$_2$ in the reservoir, thereby significantly limiting the risk of leakage [7,15,24-26]. This type of storage is considered secure even in the initial injection phase where the secondary trapping mechanisms contribute only minimally [7].

The large storage potential in deep aquifers without structural traps is only obtainable if the traps are not required for secure storage during the initial phases [19]. Even without this storage volume the remaining sites offer storage capability for potentially the next many hundreds of years [19,22], see more below. According to Table 2 the estimated retention time in the underground storage sites is 10$^5$-10$^6$ years. The retention time for storage in combination with enhanced oil recovery (EOR) differs between authors and ranges from only 10s of years [20,19] to permanent disposal [7].

Because of the limited retention times and the great risks of explosive release of CO$_2$ back into the atmosphere and/or an alteration of the ocean chemistry in the near vicinity of the disposal sites [7] ocean disposal is regarded a less attractive storage solution.

A comparison of the estimated CO$_2$ emissions from power production, Table 1, and the estimated storage capacities in EOR and saline aquifers, Table 2, yields between 75 and 6000 years of storage on a world-wide basis (2.5 Gton C/year stored). This calculation is based on the fact that due to small size and remote location of many utility plants only a limited fraction of these emissions can be captured and stored cost-effectively. Baes et al. [18] estimate this fraction to be around 50%. CCS is generally not anticipated as a permanent solution to the elimination of anthropogenic CO$_2$ emissions from electricity and heat generation. The lower limit of 75 years of storage capacity should thus be sufficient in order for the industry to change almost entirely toward renewable sources of energy.

1.3. Carbon capture technologies overview

The identified technologies for carbon capture can be divided into four main categories [5,11,12,23,27-30], described briefly below. Fig. 2 shows the main operations concerned with the post-, pre-, and oxy-fuel combustion technologies.

Post-combustion capture: CO$_2$ is separated from the flue gas of conventional pulverized-coal-fired power plants. The separation is typically performed via chemical absorption with monoethanol-amine (MEA) or a sterically hindered amine (KS-1) [23,31-35]. Amine absorption is a proven technology in the process industry [23,34,36,37]. The demonstrated scale of operation is, however, significantly smaller than the typical size of power plants [34] and serious penalties to the plant efficiency exist at the current state of development [5,8,12,16,34,38-43]. The anticipated drop in the net efficiency of the power plant is about 10-14% points [41,34]. Some current research projects investigate the possibility of developing

### Table 1

<table>
<thead>
<tr>
<th>Region</th>
<th>2005</th>
<th>2015</th>
<th>2030</th>
</tr>
</thead>
<tbody>
<tr>
<td>World</td>
<td>3.0 (72)</td>
<td>4.0 (74)</td>
<td>5.1 (74)</td>
</tr>
<tr>
<td>European Union</td>
<td>0.38 (70)</td>
<td>0.39 (66)</td>
<td>0.42 (61)</td>
</tr>
</tbody>
</table>

Estimated CO$_2$ emissions from power generation (Gton C/year). The numbers in parenthesis indicate the percentage coal share of the emissions. Data taken from [1].

### Table 2

<table>
<thead>
<tr>
<th>Sink</th>
<th>Storage capacity (Gton C)</th>
<th>Retention time (years)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Enhanced Oil Recovery (EOR)</td>
<td>20–65</td>
<td>10–10$^6$</td>
</tr>
<tr>
<td>Deep aquifers with structural traps</td>
<td>30–650</td>
<td>10$^5$–10$^6$</td>
</tr>
<tr>
<td>Deep aquifers without structural traps</td>
<td>~14,000</td>
<td>10$^5$–10$^6$</td>
</tr>
<tr>
<td>Depleted oil and gas wells</td>
<td>130–500</td>
<td>10$^5$–10$^6$</td>
</tr>
<tr>
<td>Coalbeds</td>
<td>40–260</td>
<td>10$^5$–10$^6$</td>
</tr>
<tr>
<td>Ocean disposal</td>
<td>400–1200</td>
<td>500–1000</td>
</tr>
</tbody>
</table>

Estimated storage capacities and retention times for CO$_2$ in different types of sinks on a world-wide basis. Data taken from [7,17-22].

![Fig. 2](image-url) Possible, overall plant configurations for the three main categories of carbon capture technologies. Adopted from [10].
more efficient absorbents [35]. More on the technology can be seen in [5,8,13,29,44–47].

The chilled ammonia process in which an aqueous solution of ammonia constitutes the absorbent has shown promising reductions in energy consumption in laboratory studies, up to 50%, compared to the MEA process [42]. The process benefits from low operating temperatures and precipitation of ammonium bicarbonate (NH4HCO3) yielding a higher CO2 loading of the absorbent.

Retrofit to existing plants for both process types is considered relatively simple since the capture unit can be added downstream of the boiler and flue gas cleaning systems without any significant changes to the original plant [8,45]. There are, however, strict requirements for removal of SO2 and NO2 from the flue gas prior to the CO2 capture since these components react irreversibly with the absorbent leading to its degradation.

Pre-combustion capture: Also termed fuel decarbonisation. The process is typically suggested to be used in connection with Integrated Gasification Combined Cycle (IGCC) power plants where it is termed IGCC–CCS. Coal gasification is applied to obtain a gas (syngas) containing CO, CO2, and H2. The CO is transformed into CO2 by the water-gas shift reaction and can then be separated from the remaining hydrogen containing gas before this is combusted in a gas turbine. Alternatively, H2 can be separated from the syngas and the CO combustion process is performed in an O2/CO2 atmosphere [48]. Some techno-economic calculations [11,30,36,49,50] show that IGCC has promising process economics and plant efficiency characteristics. However, high capital costs are associated with plant construction and IGCC plants are generally much more complicated systems than suspension-fired boilers [51,37]. Only few electricity producing IGCC units exist [29,50,52–54], none of which are equipped with CCS. As a consequence of the few plants and limited operating experience along with the highly integrated nature of the plants compared to the more matured, conventional pulverized-coal-fired power plants, the demonstrated availability for IGCC is significantly less (80–85% versus ~ 96%, respectively) [5,30,37,50,52,55]. IGCC–CCS is not a viable option for retrofit of existing pf plants [30,51,56,57].

Oxy-fuel combustion: By eliminating molecular nitrogen from the combustion medium the flue gas will consist mainly of CO2 and water. The plant configuration typically suggested involves flue gas recirculation to the burners to control the flame temperature to within the acceptable limits of the boiler materials. Implementation of the oxy-fuel combustion technology in existing pulverized-coal-fired power plants will induce a larger change of the plant configuration when comparing to the post-combustion absorption processes mentioned above. This is mainly due to the fact that the combustion chemistry is altered by substituting recycled flue gas (mainly CO2 and water) for nitrogen in the oxidizer. Several of the earlier techno-economic assessment studies indicate that oxy-fuel combustion should be the most energy and cost efficient of the carbon capture technologies [9,16,38,58–63]. This conclusion is mainly based on assumptions of greater boiler efficiency caused by a smaller flue gas volume and the reduced need for flue gas cleaning, i.e. deNOx and desulphurisation, including the derived decrease in capital and operating costs. It is suggested that SO2 and NOx can be stored along with CO2 in the geospheric sinks [8,12,64,65]. Typically, no experimental validation of these assumptions has been performed. Whether co-storage of SO2 and NOx is politically acceptable is, however, questionable.

The main disadvantage of the oxy-fuel combustion technology is the need for almost pure oxygen. The available large-scale technology for air separation is based on cryogenic distillation which will impose a very large energy penalty on the plant [65]. The expected efficiency drop is about 7–11 percent points, or about 15–30% of the generated electricity (net power output), depending on the initial plant efficiency [5,8,12,16,27,29,43,58,59,66–69].

Emerging technologies: Technologies such as membrane separation, chemical looping combustion, carbonation–calcination cycles, enzyme-based systems, ionic liquids, mineralization, etc. impose the possibility to drastically reduce the cost of electricity and the energy penalty concerned with carbon capture from power plants. The papers by Eide et al. [70], Abu-Khader [28], Hossain and de Lasa [71], and Figueroa et al. [14] provide broad overviews of these technologies and their current state of development.

The choice of technology will depend on several factors. First and foremost the economy and the expected development in plant efficiency is of importance. The maturity, expected availability, operating flexibility, retrofit or green-plant built, local circumstances, utilities preferences, etc. will likewise have to be taken into account. No general acceptance of superiority of one of the presented technologies over the others exists. Several techno-economic studies also indicate that with the current knowledge on the technologies no significant difference in cost within the limits of precision of the applied cost estimates can be determined between amine absorption capture, coal-based IGCC type capture, and oxy-fuel combustion capture [5,8,22,57,66,72].

Because of the large changes induced in the power plant by the implementation of oxygen-fuel combustion, more research is needed to fully clarify the impacts of the introduction of this technology. Many laboratory and scale investigations of the technology have been performed within the last two decades and it is generally accepted that it is possible to burn coal and natural gas in an O2/CO2 atmosphere. On the other hand, it is likewise recognized that much work still remains in obtaining sufficient insight into the effects on e.g. emissions, residual products such as fly ash, flue gas cleaning, heat transfer, etc.

In 2005, Wall and coworkers [4] published a literature review on the oxy-fuel combustion technology. The work was updated in the broader CCS review by Wall [5] in 2007. The reviews focused mainly on combustion fundamentals, overviews of research groups and their experimental facilities, techno-economic assessments of the technology, and research needs.

The amount of literature on the oxy-fuel technology has increased drastically over the latter years and significant new information is thus now available. The objective of the present review has been to summarize the current knowledge status on the oxy-fuel combustion technology. The current review has two focuses. (1) The possible advantages and challenges associated with retrofitting of existing pulverized-coal-fired power plants to the oxy-fuel combustion technology as well as considerations regarding green-field plants. (2) The reported results from laboratory- and semi-technical scale experiments regarding the combustion process fundamentals, including the flue gas composition and residual products.

2. The oxy-fuel combustion technology and retrofit implications

2.1. Process overview

In open literature, oxy-fuel combustion with recirculation of flue gas was proposed almost simultaneously by Horn and Steinberg [58] and Abraham et al. [60] in the early eighties. Abraham et al. proposed the process as a possible mean to produce large amounts of CO2 for Enhanced Oil Recovery (EOR) whereas Horn and Steinberg had in mind the reduction of environmental impacts from the use of fossil fuels in energy generation. As such, the technology received renewed interest in the mid-90s in connection with the re-emerging discussions of global warming caused by increased CO2 levels in the atmosphere [12].

Oxy-combustion in principle be applied to any type of fuel utilized for thermal power production. The research interests have
mainly been focused on coal and natural gas since these are the most abundant fuels. For these specific fuels the technology is typically termed oxy-coal and oxy-natural gas combustion, respectively. Application of CCS through oxy-combustion of biomass or blends of coal and biomass will result in a possible mean of extracting CO₂ from the atmosphere and thereby possibly inverting the presumed anthropogenic caused changes to the climate [11,23,30].

As indicated in Section 1.3 a shift from conventional air-firing to oxy-fuel combustion in a power plant will induce multiple changes to the plant configuration. Fig. 3 provides a sketch of a coal-fired oxy-fuel plant with indications of the major process steps and the necessary energy inputs and low-temperature-heat outputs new to the plant when retrofitting an existing coal-fired unit. The sketch covers the original state-of-the-art plant with boiler, coal mills, and flue gas cleaning equipment. The final processing of the CO₂ stream, i.e. the removal of water and the non-condensible gases like O₂, N₂, Ar, etc. to meet the requirements regarding purity of the CO₂ stream, as well as the air separation unit (ASU) and the compression step for the CO₂ stream before it is transported to the storage site are new to the plant. The discussion in the coming sections is based on the assumption that an underground geological formation, a saline aquifer, is used as storage site. The type of storage will have an impact on the oxy-fuel process, especially the flue gas purification units, through the quality criteria for the CO₂ stream.

Table 3 provides the results of our calculation on the approximate daily flows in and out of a 500 MWₑ oxy-fuel combustion power plant. The calculations are based on a state-of-the-art electrical efficiency of 46% of the conventional plant (supercritical steam parameters, LHV basis) [49] with a 10 percent point decrease due to oxy-fuel operation. The used reference coal is a high-volatile bituminous coal from Colombia see Table 4 for its properties. The oxygen is assumed to have a purity of 100%, in order to simplify the calculations. The combustion is performed in a mixture of 30% O₂ in CO₂ with an oxygen excess of 10%, corresponding to an oxygen concentration of 3% in the dry recycle stream. The recycle ratio for the dry flue gas is 0.75. As a preliminary assumption, the condenser will remove 100% of the water in the flue gas. The CO₂ capture efficiency is ~92%. The remainder of CO₂ is vented to the atmosphere together with the non-condensable gas species in the exhaust gas from the CO₂ cleaning unit. Generally, between 90 and 95% capture efficiency is expected for oxy-fuel plants [30].

The survey of the implications of retrofitting for oxy-fuel combustion in the next sections will be starting at the point of delivery of the sequestration-ready CO₂. The discussion will proceed with the auxiliary units new to the plant and end up with the original parts of the power plant. In order to limit the survey, the discussions, when relevant, will refer to plants utilizing bituminous and/or sub-bituminous coals. Specific aspects regarding lignite fired plants are excluded.

### 2.2. CO₂ purity requirements

The exact requirements to the quality of the CO₂ stream for different storage scenarios are not yet fully clarified [30,73–75].

Table 3

<table>
<thead>
<tr>
<th>Stream</th>
<th>Mass Flow (ton/day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen in</td>
<td>9700</td>
</tr>
<tr>
<td>Coal in</td>
<td>4400</td>
</tr>
<tr>
<td>Waste water (from condenser)</td>
<td>2000</td>
</tr>
<tr>
<td>Exhaust gas</td>
<td>1100</td>
</tr>
<tr>
<td>CO₂ for sequestration</td>
<td>10,300</td>
</tr>
<tr>
<td>N₂ from ASU</td>
<td>31,800</td>
</tr>
</tbody>
</table>

Table 4

<table>
<thead>
<tr>
<th>Properties for El Cerrejon bituminous coal (Colombian).</th>
</tr>
</thead>
<tbody>
<tr>
<td>LHV, as received (MJ/kg)</td>
</tr>
<tr>
<td>Moisture, as received (wt%)</td>
</tr>
<tr>
<td>Proximate analysis (wt%, dry)</td>
</tr>
<tr>
<td>Ash</td>
</tr>
<tr>
<td>Volatile</td>
</tr>
<tr>
<td>Fixed carbon (by difference)</td>
</tr>
<tr>
<td>Ultimate analysis (wt%, daf)</td>
</tr>
<tr>
<td>C</td>
</tr>
<tr>
<td>H</td>
</tr>
<tr>
<td>N</td>
</tr>
<tr>
<td>S</td>
</tr>
<tr>
<td>O (by difference)</td>
</tr>
<tr>
<td>Ash composition (wt%, dry)</td>
</tr>
<tr>
<td>Al</td>
</tr>
<tr>
<td>Ca</td>
</tr>
<tr>
<td>Fe</td>
</tr>
<tr>
<td>K</td>
</tr>
<tr>
<td>Mg</td>
</tr>
<tr>
<td>Na</td>
</tr>
<tr>
<td>P</td>
</tr>
<tr>
<td>Si</td>
</tr>
<tr>
<td>Ti</td>
</tr>
<tr>
<td>O (by difference)</td>
</tr>
</tbody>
</table>
caused by impurities in the CO2 stream. Secondly, the limitations to and the risk of structural changes within the storage formations are two general issues which should be considered. First, the purity and removal of non-condensible gas species, and how to minimize the loss of CO2 to the atmosphere during the purification process. The Suggested CO2 quality specifications from different sources. Table 5

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Modest quality, aquifer storage</th>
<th>High quality, on-shore storage</th>
<th>U.S. Specifications</th>
<th>Saline formation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Anheden et al. [76]</td>
<td></td>
<td>Lee and Miller [77]</td>
<td>Fout [78]</td>
</tr>
<tr>
<td>Pressure</td>
<td>110 bar</td>
<td>110 bar</td>
<td>–</td>
<td>150 bar</td>
</tr>
<tr>
<td>Temperature</td>
<td>50 °C</td>
<td>50 °C</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>CO2</td>
<td>&gt;96 vol%</td>
<td>&gt;96 vol%</td>
<td>–</td>
<td>Not limitedb</td>
</tr>
<tr>
<td>H2O</td>
<td>&lt;300 ppm</td>
<td>&lt;50 ppm</td>
<td>–</td>
<td>150 ppmv</td>
</tr>
<tr>
<td>N2, Ar</td>
<td>&lt;4 vol%</td>
<td>–</td>
<td>–</td>
<td>Not limitedb</td>
</tr>
<tr>
<td>SO2</td>
<td>&lt;200 mg/Nm³</td>
<td>&lt;50 mg/Nm³</td>
<td>–</td>
<td>&lt;10 ppm</td>
</tr>
<tr>
<td>H2S</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>&lt;3 vol%</td>
</tr>
<tr>
<td>NOx</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>Uncertain</td>
</tr>
<tr>
<td>NH3</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>Not limited</td>
</tr>
<tr>
<td>CO</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>Not limited</td>
</tr>
<tr>
<td>CH4</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>&lt;0.8 vol%</td>
</tr>
<tr>
<td>HC's</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>&lt;5 vol%</td>
</tr>
<tr>
<td>H2</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>Uncertain</td>
</tr>
<tr>
<td>Glycol</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>&lt;0.04 ppmv</td>
</tr>
</tbody>
</table>

a Sum of N2, O2, and Ar should be <4 vol%.

b No limit but the impacts on compression power and equipment cost need to be considered.

However, Table 5 provides a number of suggestions for purity requirements found in the literature. Some authors lay down different criteria for different storage sites [76,78], the differences mainly being associated with the content of water, oxygen and SO2. Lee and Miller [77] comment on the individual limits with respect to e.g. the minimum miscibility pressure (CO2, hydrocarbons, and N2), the risk of corrosion (O2, water), as well as materials (temperature), operations (glycol), and safety (H2S). Anheden [76] likewise identifies the aspects which should be taken into account when determining the individual limits. These aspects come down to operational issues, storage integrity, environmental aspects during the full lifetime of the capture and storage chain, health and safety aspects, legal aspects, and economic considerations. The authors state that the requirements arising from exposure limits in case of leakage to air put the strictest restrictions to the process and are, at the same time, the easiest to quantify. The exact requirements will most probably be determined for each individual case of capture and storage.

Jordal and coworkers [10,74] considered the optimum specifications with respect to technical and economical considerations. Not surprisingly, the optima differed. For economic reasons, the preferable option is to co-store as many of the impurities (SOx, NOx, non-condensible gas species, and water, as possible. This will reduce the plant investment and operating costs of the process. The disadvantage could be the requirement for more expensive materials in e.g. compressors and pipelines to withstand the potentially severely corrosive environment. There is, however, an economic optimum for the non-condensables (N2, O2, NO, CO, H2, CH4, Ar, etc.) since co-storage of these species will increase energy and reservoir size requirements as well as capital and operating expenses in the transport chain with an amount proportional to their concentrations [24,73,74]. At the same time the non-condensable gas species will entail an energy and capital penalty when removed from the CO2 stream [73,74]. Technically, there are two general issues which should be considered. First, the purity requirements for transport and storage with respect to corrosion and the risk of structural changes within the storage formations caused by impurities in the CO2 stream. Secondly, the limitations to the present best available technology for flue gas cleaning, i.e. particle removal, water condensation, dehydration, SOx removal and removal of non-condensable gas species, and how to minimize the loss of CO2 to the atmosphere during the purification process. It is obvious that the technical considerations will set both the lower and upper limits to the purity requirements.

SO2 receives the largest amount of interest with respect to the effect of contaminants on the structure of storage formations. A typical assumption regards the possibility of co-storing the SO2 together with the CO2 because of very similar physical and chemical properties at supercritical conditions [10,58,65,67,75,79]. However, even small amounts of SO2 may cause problems due to the risk of calcium sulphate formation and thus a decreasing porosity of the reservoir rock [26,75,79,80]. Oxygen could likewise lead to the formation of precipitations [74]. On the other hand, if the concerns regarding SO2 in the storage formations prove to be insignificant there would obviously be a possible economic benefit from combined capture and storage of CO2 and SO2 [80]. The current state of flue gas cleaning on modern power plants involves ~85% removal of NOx, ~98% removal of SOx, and ~99.8% removal of particulates [68,30]. The fact that only a finite percentage of the SO2 is removed with the current best available technology elucidates the importance of identifying the correct purity demands through e.g. field tests since these may have a significant impact on the plant configuration, operating conditions and operating costs [43,64]. Besides the chemical effects of impurities in the CO2 on the reservoir rock, CO2 itself has the potential to alter the mechanical properties of the rock [26,17]. Especially calcite (CaCO3) precipitation which can cement the reservoir around the injection well and render further injection impossible should be taken into consideration.

With respect to transportation the greatest concern involves the water content in the CO2 stream [27,64,73,75]. In the presence of water, CO2 can cause so called sweet corrosion [26,17]. Water vapor and CO2 in the presence of liquid water can likewise form solid ice-like crystals known as hydrates [64,73,79,80]. Concurrent presence of both water and SO2 (incl. H2S) in the CO2 stream will increase the risk of sulfuric acid corrosion. If the flue gas is dehydrated to a dew point 5 °C below the temperature required for transport conditions, the sulphur dioxide will behave almost as carbon dioxide in the supercritical state and the two gases should not cause any corrosion problems [26,79,80]. Others report no risk of corrosion at a dew point of less than ~60 °C [66]. A requirement for a very low water content in the CO2 is thus present. This can most likely not be achieved by condensation alone and drying by e.g. absorption in a recyclable dehydrant (triethylene glycol) in combination with the last compression step, see Section 2.3, will be necessary [43,65,74,79].

Some researchers believe that all the limiting factors regarding purity of the CO2 stream arise from compression and transportation requirements [67,73,74]. In this respect, the demand of dryness is crucial.
Another aspect regarding the concentrated CO₂ stream is the legislative classification. This will depend on the content of contaminants such as H₂S, sulphur oxides, NOₓ, hydrocarbons, etc. Significant quantities of these elements could mean that the stream should be regarded as a hazardous waste [71, 64, 73, 74, 80]. This could eventually lead to difficulties with respect to locating suitable storage sites or a large penalty concerned with the purification.

2.3. CO₂ processing

Assuming that CO₂ transportation should be in pipelines, the CO₂ must be conditioned to both pipeline and reservoir specifications, as described in the above section. Moreover, the stream must be compressed to a high enough pressure to overcome the frictional and static pressure drops and deliver the CO₂ at the storage site without risking flashing of gas anywhere in the process [73, 75].

The typically suggested conditions of the CO₂ stream at the delivery point includes the following ranges of pressures and temperatures; 80–200 bar and 0–50 °C [8,11,25,27,41,56,67,74, 81–84]. There is, however, a preference for 100–110 bar and a temperature above the critical value (31.1 °C), see Fig. 4. At these conditions the CO₂ is in the supercritical state, even though the presence of impurities will increase the critical pressure of the mixture compared to that of pure CO₂ [67].

2.3.1. Compression step

Compression of gases is a highly energy demanding process. This step will induce one of the larger penalties to the plant efficiency in oxy-fuel operation when comparing to conventional air-firing. Generally, ~2–3% point decreases in electrical efficiency, directly associated with the compression step, have been reported [5,16,50,66,67]. Factors such as compressor efficiency, the amount of impurities in the CO₂-rich stream, and opportunities for integration with the remaining plant will influence the power consumption [65, 85].

Since no specific new problems are expected with respect to the compression of CO₂, no demonstration programs are considered to be required [66].

2.3.2. Removal of water and non-condensable gas species

Many existing boilers were not designed to be leak tight and may be difficult to retrofit to oxy-fuel operation where air ingress should be avoided. It is generally reported very difficult to totally avoid air ingress into even small laboratory and pilot scale burners [12,16,63,86–91] and in real size plants it will be almost impossible [62, 83, 92, 93]. The amount of work put into tightening the boiler and flue gas passages will thus be a trade off with the power consumption of the compression unit. Air-fired boilers operate at negative gauge pressure for obvious safety reasons. To avoid air ingress in oxy-fuel boilers one could consider operation at positive gauge pressure. It is, however, questionable whether the avoidance of air ingress can counterbalance the enhanced risk of severe CO and CO₂ poisoning of the boiler surroundings and the necessary safety systems to avoid casualties [83]. The amount of air leaking into the boiler and flue gas ducts is believed to constitute around 3% of the flue gas mass flow (1% in boiler and 2% in ESP) [5,40,67,94] for a new-build plant. As the ingress of air typically increases over time, older boilers can have air in-leakage rates of 8–16% [65, 67]. Significant air ingress will reduce the CO₂ concentration in the flue gas and thus result in increased costs for CO₂ cleaning since the non-condensable gases most likely must be removed before (or during) compression. According to Tan et al. [12] the air ingress level should be limited to about 3% in large-scale plants to obtain CO₂ concentrations in the flue gas which will enable an economical treatment of the CO₂ stream.

This additional need for clean-up, besides air separation, is potentially a significant drawback of the oxy-fuel technology compared to e.g. post-combustion capture with amine absorption which has only one purification step [95]. When the oxy-fuel technology was first proposed purification of the CO₂ was not discussed and has most likely not been considered necessary.

The purity of the oxygen for combustion will likewise be a trade off between the ease of liquefaction of the flue gas and the power requirement for the air separation [61, 62, 67]. Nakayama et al. [61] performed an investigation regarding the combined power requirement for air separation and CO₂ liquefaction under the assumption of no air ingress into the system. Fig. 5 shows the relationship between purity of feed oxygen and power consumption for a plant with a gross capacity of 1000 MWₑ. According to the figure, an oxygen purity of 97.5% will require the lowest overall power consumption. Purities greater than this leads to a significant increase in the air separation energy consumption which the decreased consumption in the liquefaction step cannot counterbalance. Others report optimum purities of 95% [8,43,62,66,67,83,95] taking into account the effect of air ingress. At an oxygen purity of 95% obtained by cryogenic distillation, the

![Fig. 4. Phase diagram for CO₂.](image-url)

![Fig. 5. Theoretical relationship between the purity of oxygen fed to the burners and the power consumption for air separation and CO₂ liquefaction in a 1000 MWₑ (gross) plant. Data taken from [61].](image-url)
remaining impurities present will be argon (3–4 mol%) and nitrogen (1–2 mol%) [67,68]. The almost complete avoidance of nitrogen is beneficial with respect to also reducing NOx emissions.

Fig. 6 illustrates in more detail suggestions to the CO2 processing and purification steps in an oxy-fuel plant. It is possible that an initial dehydration of the flue gas is performed in combination with the flue gas cleaning step before the initial compression in order to reduce the total flue gas volume and thus costs and equipment size.

After condensation of water vapor, the CO2 stream will have a purity of about 70–95% depending on oxygen purity, oxygen excess, and air ingress into the boiler [4,8,16,40,43,67,91,92,96]. The condensation process will likewise serve to remove water-soluble gas phase components as well as other species with higher boiling points than CO2 [74]. Some CO2 will dissolve in the water and cause a loss in the capture efficiency if not regenerated [74]. If the major part of the flue gas water content is removed at relatively high temperatures and low pressures the loss of CO2 can be kept low [74].

The flue gas processing and purification systems will produce three streams as indicated in Fig. 6: The CO2 stream for compression and sequestration, an exhaust gas containing mainly the non-condensable gas species (Ar, N2, O2, CO, NOx) and some CO2 depending on technology, see more below, and a waste water stream originating from the condensed water.

The exhaust gas stream, around 10–20% of the dry flue gas by volume, is vented to the air. Its composition depends on the chosen cleaning process but is assumed to be about half CO2 and half N2, O2, and Ar. Aspelund and Jordal [73] state that the loss of CO2 to the exhaust stream for a one column system will be 1:1, i.e. 1 mol of CO2 per mole of non-condensable gas.

Depending on the plant configuration, especially whether a desulphurization plant is installed, the waste water stream could be very acidic (sulfuric acid, hydrochloric acid, etc.) and thus extremely corrosive (pH 1.5–3) [10,67,92,97]. The flue gas purification unit should thus be designed acid-proof [82,10] as well as the flue gas pathway [10] due to the risk of low-temperature acid corrosion. Additionally, a fraction of the CO2 (due to its solubility in water) and a large part of the particles remaining after the ESP will be captured in the waste water stream. This stream therefore requires further processing before disposal. This is expected to occur with methods already commercially available [10].

The gas purification unit could e.g. be a flash [40,10] or a distillation unit [27,74,92] since CO2 forms non-azeotropic mixtures with impurities such as N2, O2, and Ar [85]. The thermodynamic properties of the CO2 stream fed to the purification unit will be affected by its content of impurities (N2, O2, Ar, NOx, and SO2). Possible ranges of impurity concentrations are: Ar (0–5%), N2 (0–15%), O2 (0–7%), and SO2 (0–1.5%). The changes are mainly affecting the dew and bubble points, heat capacity as well as the enthalpy and entropy. This again will have an impact on the operating conditions, energy consumption, configuration, and separation performance of the purification system [85]. Generally, removal of SO2 in a flash or distillation system is not preferable since it has a large, negative impact on product purity and energy requirements for even small impurity levels [85] since the thermodynamic properties are very close to that of CO2.

The basic principle in the flash and distillation units is to utilize the differences in boiling point for the different species to separate them. Fig. 7 shows a comparison between the performances of the two purification systems. The figure reveals that for the same recovery rate and feed compositions the distillation process requires less energy and produces a slightly higher-purity CO2 stream than the flash process. This has likewise been reported by Aspelund and Jordal [73,74].

The typical CO2 recovery for oxy-fuel plants is reported at ~90% [12,30,40,43,67,91]. 100% capture was expected theoretically in one of the earlier studies of the technology [59], under the assumption that the entire flue gas stream could be sequestered in the ocean. A possibility exists that the initial flue gas cleaning and the CO2 processing steps can be combined in one process unit. This is interesting in the case that desulphurization is neglected within the recycle loop. Air Products Inc. has proposed a process that removes both non-condensable impurities as well as Hg, essentially all SOx.

![Fig. 6. Possible process scheme for CO2 processing and purification, i.e. removal of non-condensable gas species, in an oxy-fuel power plant. Adapted from [85].](image37x533to280x727)

![Fig. 7. Performance comparison between 2-stage flash and distillation column based on simulations. The CO2 recovery rate is 92.15% and the feed compositions (in mol%) to the purification units are CO2: 76, O2: 6, N2: 15, Ar: 2.5, and SO2: 0.5. Adopted from [85].](image344x84to510x400)
and about 90% of the NOx through the production of waste water containing sulfuric and nitric acid [98].

This compression and purification process has been initially tested in mid-2008 [98]. The tests have confirmed the potential of the process. However, further tests are necessary to gain further understanding of the chemical mechanisms and the kinetics [98]. This is expected to be performed at the Vattenfall Schwarze Pumpe pilot plant [99]. The process should likewise be evaluated against well proven denox and desulphurization technologies [67,43].

2.4. Air separation

The air separation unit provides the oxygen for the combustion. The current state of technology development necessitates the application of a cryogenic distillation unit. No other mature technologies exist which can be applied for the necessary size of operation [40,59,65,79,80,82,93,100], see Fig. 8. At the same time, because of mechanical size limitations it will be necessary to build more cryogenic air separation units to operate in parallel. The largest cryogenic ASU plant currently operating (2008) produces 4500 t/d, but design studies for a 7000 t/d have been performed [65]. As seen from Table 3 the oxygen requirement for a 500 MW<sub>e</sub> plant is between 9000 and 10,000 t/d, indicating the need for 2–3 parallel ASU plants.

Cryogenic distillation consumes high amounts of energy in the form of electricity. Preliminary calculations indicate that this operation alone requires about 60% of the power consumption for carbon capture and reduces the overall efficiency of the power plant by about 7–9 percentage points [8,10,16,40,43,50,67]. Major improvements are thus required to yield a more efficient oxygen production. It is not likely to find these improvements within the cryogenic technology [62,65,67] and thus alternative technologies like e.g. ion transport membranes (ITMs) should be investigated further. However, it is possible that some synergies can be obtained from an integration of the ASU's with the power plant, i.e. by using the low-temperature heat from the ASU intercoolers for e.g. feed water heating [93].

The availability of the oxygen plant is crucial to the power plant operation. Typical availabilities of 98-99% and only limited time for maintenance are reported from suppliers [65,67]. Another important requirement is the ability to follow the load changes of the power plant. According to Xu et al. [43] the maximum ramp rate for an ASU is 3%/min. The boiler, however, can generally be operated at a ramp of up to 6%/min. At the same time, ASU’s are only able to operate at 60–100% load [82,43] and show rather poor efficiencies below 80%. In combination, this gives rise to some operational difficulties, which should be investigated further.

The introduction of a liquid oxygen storage could provide a solution in which the difference between demand and production during positive load changes in the boiler is taken from the storage and vice versa during decreases in the boiler load [43,92,99]. The storage facility also makes it possible to shift to air-firing mode within a relatively short amount of time without risking boiler trips in case of unexpected ASU shut-down. Even without the load changing challenges, it may be beneficial to decouple the ASU and power plant by introducing oxygen storage. In that way, the liquid oxygen could provide a means of energy storage in periods with high electricity production from e.g. wind mills. The safety issues related to a liquid oxygen storage on a power plant site should be assessed thoroughly however in order to evaluate its applicability. Preliminary studies by Xu et al. [43], suggest to install a tank with a 500 tonne capacity for liquid oxygen at 2.5 bar (about –175 °C), corresponding to approximately 1.5 h of operation of their 413 MW<sub>e</sub>, net, oxy-fuel reference plant.

For economic reasons it should be considered whether the massive amount of almost pure nitrogen, ~31,800 t/d at low temperature, could be applied for a purpose in the plant or elsewhere.

2.5. Flue gas recirculation

The oxygen for combustion is mixed with recycled flue gas to moderate flame temperatures and obtain a boiler heat transfer profile similar to that of air-firing in the case of retrofit. Typically, between 60 and 80% of the flue gas is recycled to the boiler [4,5,8,10,43,66–68,79,80,101,102].

As shown in Fig. 3 two recycle streams will be necessary. The primary recycle is used for fuel transport and corresponds to the primary air in conventional units. It will be about 20% of the total amount of combustion air (RFG + O₂) [67]. The secondary stream will constitute the equivalent to the secondary, tertiary, and over-fire (if necessary) air flows when oxygen has been added.

A study performed by Kather et al. [68] determined that the temperature of the recirculated flue gas should be between 200 and 350 °C in order to take into account the operation of an ESP and flue gas fan, among others.

2.5.1. Positioning of recycle streams

2.5.1.1. Primary recycle. A general consensus exists that the primary recycle stream must be cooled, scrubbed, dried and then reheated to about 250 °C or more before entering the mills [66–68,83,101]. The obvious choice is thus as indicated in Fig. 3 to take this stream after the first condensation step during the flue gas processing.

The reheating is necessary in order for the stream to be able to dry the coal and carry the moisture at the typical mill exit temperature of 60–90 °C [67,68]. If the drying capacity of the primary recycle gas is too small the wet coals will clog the mills. Scrubbing of the flue gas ensures removal of SO<sub>2</sub> which would induce corrosion in the mills due to condensation of sulfuric acid at temperatures below 150–160 °C [103]. Xu et al. [43] suggest adding a bypass from upstream the ESP outlet to increase the temperature of the recycle streams approximately 5 K in order to avoid moisture condensation along the recycling ductwork.

2.5.1.2. Secondary recycle. Several options exist for the position where the secondary recycle stream is taken. The dashed lines in Fig. 3 indicate these possibilities. Depending on the actual position the heat and water contents along with the concentration of

![Fig. 8. Oxygen supply technologies. Selection as a function of quantity (tonnes per day) and required purity. Cylinders and Liquid: Continuous delivery from manufacturers in either cylinders or for own storage vessel. VSA: Vacuum Swing Adsorption. Future plants could be either cryogenic or based on other technologies, such as e.g. membranes. Adapted from [65].](image-url)
pollutants (NOₓ, particles, SOₓ, etc.) will vary. Even though several reports on oxy-fuel combustion conclude that both deNOₓ and desulphurization can be eliminated due to co-sequestration of the impurities with the CO₂ [60,61,67] this is not necessarily possible in practice, see Section 2.2. Most probably, the power plant should be able to run in air-firing mode without capture, at least during start-up and shut-down, and thus also needs the flue gas cleaning equipment to obey the legislation regarding emissions. There is, however, the possibility of by-passing the SCR and FGD plants during oxy-fuel operation. It will still be necessary to remove the particulates to avoid accumulation of solids in the boiler and to prevent the flue gas recirculation fan and gas passages from unnecessary wear due to erosion.

Even though oxy-fuel combustion provides the opportunity of highly reduced emissions of NOₓ [4,12,16], it is doubtful if the legislations concerning emissions can be fulfilled without some degree of NOₓ removal for all future power plants. During start-up and shut-down which most likely will occur at air-firing conditions NOₓ removal is likewise regarded necessary. It is possible that the SCR plant can be run at reduced efficiency during oxy-fuel combustion and that operating costs thus can be reduced. The SCR is typically positioned at high-dust conditions. By passing as large an amount as possible of the flue gas around the SCR it is possible to significantly enhance the catalyst lifetime. Even though ammonia is not added to the flue gas, its passage through the SCR catalyst will reduce the catalyst lifetime. It is likely that the extra cost related to the bypass will be counterbalanced by the reduced cost for change of catalyst may be even with an overall saving. An alternative option is the production of a concentrated liquid waste water stream containing both NOₓ and SOₓ [66] which can be treated to avoid pollutant emissions to the air, see Section 2.3.2.

The acid gases such as sulphur oxides, HCl, and HF are not reduced through the same mechanisms as NOₓ in the boiler. Recirculating the flue gas before desulfurization will result in up to an about 3—4 times increase of the sulphur (and chloride) levels in the boiler [4], see Table 6. Since both sulphur and chloride are potentially corrosive this significant increase can cause problems in the boiler components when firing medium to high sulphur containing coals [43]. Significantly increased levels will likewise have a negative impact on a wet desulfurization plant. The change corresponds to firing coals with excessive amounts of S, Cl, F, etc.

Sulphur retention in fly ash is another area of concern. Significantly increased retention can lead to problems utilizing the fly ash for cement and concrete production. The upper limit for sulphur in fly ash used for concrete is 3 wt% measured as SO₃ [104]. The limiting value for sulphur in fly ash used in cement production is not regulated by standards but rather determined individually between the cement manufacturer and the fly ash producer. However, the limit is usually not less strict than for concrete purposes. Utilization of fly ash from power plants is becoming increasingly important [105]. The potential risk of contaminating the fly ash with excessive amounts of sulphur is thus very critical to the configuration of an oxy-fuel power plant. In conclusion, the secondary recycle stream will most likely have to be taken downstream of some sort of desulphurization process whether it be a conventional wet FGD plant or another process.

The water content in the secondary recycle could potentially have an impact on the combustion characteristics and the general plant performance and efficiency [102]. This is mainly a consequence of the differences in thermodynamic properties, e.g. heat capacity, between CO₂ and water vapor. The effect of wet and dry recycle streams on in-furnace temperatures, ignition, emissions, etc. are discussed in more detail in Section 3. This section will focus on the plant configuration aspects of a wet versus a dry flue gas recycle.

Nakayama et al. [61] proposed five different plant configurations covering both wet and dry recycle, see Fig. 9. The configurations differ in the position of the recycle path and the oxygen preheater. Changing the position of these units will have an impact on the size of both the preheater, the electrostatic precipitator (ESP), and the flue gas cooling unit. The choice of a wet versus a dry recycle will influence the gas recirculation fan (GRF) as will the possibility of recirculating fly ash to the boiler (system A). In relation to the gas recirculation fan, a dry recycle is most favourable since it induces less wear of the fan. On the other hand, a dry recycle will require

<table>
<thead>
<tr>
<th>Fraction of total flue gas recycled</th>
<th>Sulphur concentration in flue gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.7</td>
<td>3110</td>
</tr>
<tr>
<td>0.6</td>
<td>2370</td>
</tr>
<tr>
<td>0.5</td>
<td>1920</td>
</tr>
<tr>
<td>0.4</td>
<td>1650</td>
</tr>
<tr>
<td>0.3</td>
<td>1390</td>
</tr>
<tr>
<td>0.2</td>
<td>1230</td>
</tr>
<tr>
<td>0.1</td>
<td>1080</td>
</tr>
<tr>
<td>0</td>
<td>1000</td>
</tr>
</tbody>
</table>

Fig. 9. Different, possible configurations for oxy-fuel combustion with either dry or wet recirculated flue gas. The suggested configurations do not include process units for removal of NOₓ and SOₓ. ASU: Air Separation Unit; GRF: Gas Recirculation Fan, ESP: Electrostatic Precipitator. Adopted from [61].
approximately four times larger capacities of the preheater, cooling, and drying units compared to the wet recycle case.

Nakayama et al. [61] concluded that a wet recycle taken after the ESP and oxygen preheater (system B) was the most promising configuration. The evaluation is based solely on theoretical considerations and no experiments were performed to test the effect of wet and dry recycle on the combustion process. The suggested configurations include only particle removal for flue gas cleaning, not deNOx or desulfurization since these were not considered necessary to obtain the required purity of the CO2 stream. The investigation likewise neglects the fact that some of the recycled flue gas should be used in the coal mills as transport and drying gas.

Dillon et al. [66] likewise assess different recycle arrangements considering both a primary and secondary recycle stream. All of their five arrangements did, however, have the same conditions for the primary recycle, the only difference being the type of equipment for reheating. The authors arrived at a wet, reheated secondary recycle as being the most advantageous option.

As described in Section 2.2, mixtures of CO2 and H2O are known from the oil and gas industry to cause potential corrosion problems in piping. Corrosion in the flue gas recirculation ducts in case of temperatures below the water dew point is thus an issue that should be addressed when designing an oxy-fuel plant.

For security and availability reasons, Hellfrisch et al. [82] suggest that the flue gas recirculation should consist of multiple independent paths (e.g. 4 of 25% each).

In relation to retrofit of an existing power plant the exact benefits and disadvantages concerned with each of the possible plant configurations regarding secondary recycle position and its water content should be clarified in order to choose the most optimal solution. For green-field plants it is possible that a specific concept could prove to be generally accepted.

### 2.5.2. Oxygen addition

#### 2.5.2.1. Primary stream.

Fig. 3 indicates that no oxygen is added to the primary recycle before entering the mills. This is mainly due to safety reasons [83]. The highest possible temperature in the coal mills is 120 °C. This limit is set according to materials considerations. In N2 there is no risk of explosions in the mills if the oxygen concentration is below 12%. The use of air during operation in conventional plants can thus be considered a safety risk and is handled through safety precautions. Due to a suggested, inhibitory effect of CO2 on explosions it is possible that the O2 level in the mixture sent through the mills can be raised to above 21% without inducing a risk of explosion [67]. No data are available however.

Even though it is theoretically possible to have relatively high oxygen concentrations in the primary recycle without risking an explosion, some authors advise against it [67]. In practical power plant operation, mills are continually brought in and out of operation to meet the changes in electricity demands. This provides a possibility of transient mismatches between recycle and oxygen flows and thus significant variations in the oxygen concentration. Additionally, equipment failures in control valves, recycle fans, etc. are considered severe security risks [67]. The risk of obtaining significantly higher oxygen concentrations than the safe limit in the coal mills and induce an explosion from ignition of coal dust is thus profound.

With respect to NOx formation, it is likely that limiting the oxygen concentration in the primary oxidant stream is beneficial since a fuel-rich flame core will be formed. The only concern could thus be flame stabilization. Some preliminary results obtained by IFRF [88,12] suggest, however, that satisfactory ignition and flame stabilization is obtainable when all oxygen is introduced with the secondary oxidant stream. It should be noted that oxygen corresponding to the excess amount, approximately 3 vol%, will be present in the primary recycle.

#### 2.5.2.2. Secondary stream.

If no oxygen is added to the primary recycle the entire amount should be mixed into the secondary stream. Due to the risk of spontaneous ignition of dust in the recycle stream there will most probably be an upper limit to the concentration of oxygen in this stream as well. If this limit is exceeded it will be necessary to inject oxygen either directly through the burners or the over-fire ports [83].

Mixing of the oxygen stream into the recycled flue gas cannot be considered unproblematic with the amounts relevant for a power plant. It is crucial that the resulting oxidant stream has a homogeneous composition in order to maintain stable burner operation and prevent safety hazards due to injection of large amounts of pure oxygen to the furnace. Generally, it is very important to minimize the risk of having pure oxygen present together with combustibles anywhere in the system. It is questionable if nozzle injection of one stream into the other without e.g. a static mixer will be satisfactory. In the Schwarze Pumpe pilot plant static mixers are used to ensure proper mixing of oxygen and flue gas [106,54]. Some researchers are addressing alternative equipment which will allow proper mixing in the flue gas ducts [91].

Table 7 summarizes the advantages and disadvantages associated with the different options for oxygen introduction to the boiler. Either way the oxygen addition to the boiler is performed it is most likely that new (or modified) burners will need to be developed to obtain efficient and stable combustion in an oxy-fuel plant [67,107–109].

#### 2.6. Operation of conventional flue gas cleaning equipment

In case it is necessary to include both desulphurization and deNOx in an oxy-fuel combustion power plant the operation and performance of these units in atmospheres with high CO2 concentrations should be clarified. These aspects of oxy-fuel combustion seem to be an overlooked area in the research since most investigations neglect these basic units in the plant configuration. Most of those who actually do include these units [4,10,63,80,82] assume that they can operate with exactly the same or even better settings, throughput, and economics as in a conventional plant.

#### 2.6.1. Desulphurization

The largest uncertainties regarding operation concerns the desulphurization plant. Below, the series of reactions occurring during the process in a wet plant are provided. First, SO2 is dissolved in the aqueous phase producing hydrogen sulﬁte, (1). Simultaneously, limestone (CaCO3) is dissolved releasing CO2, (2) and (3). The hydrogen sulﬁte is oxidized to sulphate in the irreversible reaction given by (4). Finally, gypsum (CaSO4·2H2O) is produced by the reaction between calcium and sulphate ions, (5).

\[
\begin{align*}
\text{SO}_2 + \text{H}_2\text{O} &\rightleftharpoons \text{HSO}_3^- + \text{H}^+ \\
\text{CaCO}_3 + 2\text{H}^+ &\rightleftharpoons \text{Ca}^{2+} + \text{HCO}_3^- + \text{H}^+ \\
\text{Ca}^{2+} + \text{HCO}_3^- + \text{H}^+ &\rightleftharpoons \text{Ca}^{2+} + \text{H}_2\text{O} + \text{CO}_2 \\
\text{HSO}_3^- + 0.5\text{O}_2 &\rightarrow \text{SO}_2^{2-} + \text{H}^+ \\
\text{SO}_4^{2-} + \text{Ca}^{2+} + 2\text{H}_2\text{O} &\rightleftharpoons \text{CaSO}_4·2\text{H}_2\text{O}
\end{align*}
\]
to the high CO₂ concentration in the flue gas. Likewise, the oxidation of HSO₃⁻ to SO₂⁻ (4), in the desulphurisation plant is performed with air in conventional units. Application of air to oxy-fuel desulphurisation would induce an undesirable dilution of the CO₂ with nitrogen [68,101,110]. Instead, a portion of the secondary oxidant stream or alternatively pure oxygen could be directed to the desulphurisation unit. The consequences of each of the three possibilities should be investigated. An other alternative could be to construct the desulphurisation plant in such a way that the SO₂ absorption and the oxidation occur in two separate units [68,76,94,110]. In that case air can be used as oxidizer without the risk of reducing the CO₂ concentration in the flue gas.

In the case of a wet recycle the flue gas entering the flue gas desulphurization unit will contain significantly higher amounts of water vapor than in a conventional plant. Even in the case of a dry recycle, the water vapor concentration will increase due to less dilution. The increase in water concentration could lead to an increase of the equilibrium temperature of the gypsum/limestone suspension and thereby influence the kinetics of the desulphurization process. A higher temperature of the suspension could thus lead to a reduction in the degree of desulphurization due to a decrease of the solubility of SO₂.

Studies performed by Air Liquide Inc. together with The Babcock & Wilcox Company in the 30 MWth test facility located in Alliance, Ohio [91,51] revealed no noticeable change in the performance of a conventional wet FGD scrubber. Similar conclusions were obtained by Oryshchyn et al. [111] from laboratory-scale experiments.

Due to the fact that only few results on desulphurization in oxy-fuel atmospheres have been published, this is an area of the oxy-fuel process which needs further attention.

The gypsum produced should likewise meet certain quality requirements, see Table 8. The high partial pressure of CO₂ in the gas phase could limit the dissolution of the limestone in the solution and thus potentially increase the amount of residual limestone in the gypsum. This could cause problems in the further utilization of the gypsum and would influence process economics negatively.

### 2.6.2. NOₓ removal

The concerns regarding removal of NOₓ from the flue gas stream are much less than for desulphurization. However, it will still be necessary to verify the performance of e.g. an SCR unit, which is the typical choice for large power plants, if the NOₓ reduction obtained during the oxy-fuel combustion is not adequate. An increase in the CO₂ concentration above the catalyst is not considered to have an effect on performance. The possibly increased levels of both SO₂ and NOₓ in the flue gas do, however, impose a risk for reduced performance. SO₂ in the flue gas is known to form sticky and corrosive ammonium bisulfate when NH₃ is added [113]. Increasing the NOₓ level will likewise increase the dew-point temperature for ammonium bisulfate. If the SCR operating temperature falls below the dew point, especially during low load operation, severe clogging of the catalyst must be expected. Additionally, the catalyst acts as an oxidizer and will convert part of the SO₂ content of the flue gas to SO₃ increasing the risk of ammonium bisulfate formation [113].

### 2.6.3. Particulate removal

As Suriyawong et al. [114] state, the collection efficiency of particulate removal devices is size dependent. Since oxy-fuel combustion shows the ability of altering the size distribution of ash particles, see Section 3.5, the performance of the electrostatic precipitator (ESP), which is the most common particulate removal system in large-scale power plants, will be subject to changes. For both ultrafine (<100 nm) and sub-micrometer (100 nm < d₉₀ < 1 µm) sized ash particles the penetration (1 − collection efficiency) depends on particle size due to different charging effects and these particles are thus not effectively captured.

A potential change in the size distribution of the fly ash from oxy-fuel combustion is not the only aspect of relevance for ESP performance. The flue gas composition could likewise impose a change in the ion production rate within the ESP and thus lead to a change in collection efficiency. Suriyawong et al. [114] have found that for ESP’s with positive coronas it is necessary to increase the applied voltage to obtain similar collection efficiencies in oxy-fuel plants as for air-fired plants. However, when negative coronas are used, there is only an insignificant effect of the ESP performance from the change in flue gas composition in the oxy-fuel plant.

Based on equilibrium calculations Schnurrer et al. [115] conclude that the increased SO₃ content in the flue gas is expected to improve the performance of the ESP. This is caused by lower ash resistivity as a result of deposition of sulphate particles on the fly ash.

### 2.6.4. Potential improvements for a green-field plant

For a green-field plant there could be an incentive for applying a hot ESP as the first flue gas cleaning unit downstream of the boiler. The hot ESP is generally considered too costly for air-blown units. Removal of the particulates as the first step will, however, yield the possibility of applying a low-dust SCR downstream of the ESP with low catalyst degradation compared to the more conventional high-dust option. The secondary recycle can then potentially be taken in between the ESP and SCR, which additionally reduces the necessary size of the SCR unit. In order to control the sulphur accumulation in the system and thus prevent

### Table 8

Selected quality requirements for gypsum produced by wet desulphurization of flue gas [112].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Purity</td>
<td>&gt;95</td>
</tr>
<tr>
<td>Residual limestone</td>
<td>&lt;4</td>
</tr>
<tr>
<td>Moisture</td>
<td>&lt;10</td>
</tr>
</tbody>
</table>

### Table 7

Advantages and disadvantages associated with the different options for oxygen addition to recirculated flue gas.

<table>
<thead>
<tr>
<th>Option</th>
<th>Advantage(s)</th>
<th>Disadvantage(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before coal mills</td>
<td>(1) Sufficient space in recirculation duct to ensure adequate mixing</td>
<td>(1) Risk of zones with very high-oxygen concentrations if mixing is inadequate and thereby increased risk of combustion/explosions in mills</td>
</tr>
<tr>
<td></td>
<td>(2) The stream to the mills will be drier than without oxygen</td>
<td>(2) Primary stream will be cooled due to the low temperature of the oxygen</td>
</tr>
<tr>
<td></td>
<td>(3) With oxygen in primary stream burner design is expected to be closer to that for conventional air burners</td>
<td>(1) Significant risks are associated with the injection of nearly pure oxygen into a high temperature stream of coal and flue gas</td>
</tr>
<tr>
<td>After mills, before burners</td>
<td>(1) No risk of explosion in mills</td>
<td>(1) Burner design has to be re-thinked</td>
</tr>
<tr>
<td></td>
<td>(2) Possible to obtain the same oxygen concentration in the burner as in the case for operation on air</td>
<td>(2) Limited capacity for coal drying in mills</td>
</tr>
<tr>
<td>Directly in burners (either pure oxygen lance or with the secondary stream)</td>
<td>(1) No risk of explosion in mills or flue gas ducts</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(2) No expenses for mixing in primary stream</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(3) Oxygen lance provides increased control of the mixing of oxygen and fuel in the near-burner zone</td>
<td></td>
</tr>
</tbody>
</table>
both corrosion and ammonium bisulfate degradation of the SCR catalyst due to high SO\textsubscript{3} levels, a desulphurization unit prior to the SCR should be installed.

The major advantage concerned with the change of sequence of the flue gas cleaning units is to reduce the size of the equipment due to the fact that the flue gas volume is reduced with about 60–80% after the secondary recycle has been taken. In the suggested configuration, the desulphurization unit will, however, not be reduced in size. A disadvantage is that if a wet FGD (the conventional choice) is installed before the SCR, additional cooling and reheating will be necessary. These operations will reduce the plant efficiency.

2.7. Boiler and steam cycle

The oxy-fuel boiler is subject to relatively extensive changes regarding chemistry compared to the case of air-firing. The two main, combustion related properties that change during oxy-fuel combustion are [5]:

- Gas radiative properties
- Gas heat capacity

Substituting CO\textsubscript{2} (plus water vapor) for N\textsubscript{2} in the oxidant results in a larger specific heat capacity compared to air, see Table 9. Firing with the same ratio between oxygen and ‘inerts’ will thus result in a lower flame temperature [118–122] and difficulties in stabilizing the flame [12,123]. In order to obtain a stable flame and the same adiabatic flame temperature in oxy-fuel experiments as in air combustion overall oxygen concentrations between 25 and 42 vol% have been reported necessary [87,97,116,118,120–122,124–126]. The span is somewhat dependent on the coal type and the typical values reported for bituminous coals are 28–35%.

CO\textsubscript{2} and water vapor are radiating species as opposed to N\textsubscript{2}. The radiative heat flux in the flame zone originating from the gas phase is thus expected to increase in oxy-fuel combustion compared to air-firing at comparable gas phase temperatures. The radiative heat flux from solid particles (soot, char, and ash) depends on a number of parameters. Radiation from ash particles depends mainly on the particle temperature whereas radiation from soot and char is influenced by the mixing characteristics of the flame, local O\textsubscript{2}, CO\textsubscript{2}, and H\textsubscript{2}O concentrations, and temperature.

In coal flames radiation from soot can dominate the heat transfer in the radiative section. The formation rate of soot can be very sensitive to the mixing of fuel and oxidizer in diffusion flames. The near-burner flow dynamics are expected to change in oxy-fuel combustion compared to air-firing due to the changes in flow rates through the burners if conventional burners for air-firing are used. Soot formation and hence the radiation intensity is thus expected to change as well.

2.7.1. Burner operation and flame stabilization

Increasing the oxygen concentration to achieve similar adiabatic flame temperatures to that of air operation is the obvious solution to obtain stable combustion. With this approach the total volumetric flow through the burners and boiler is reduced compared to air-firing because of the overall lower amount of ‘inerts’. In order to keep the coal particles in suspension, it has been suggested that the primary flow must have the same linear velocity as in air-firing [83], typically 17 m/s as minimum [116]. Since the density of CO\textsubscript{2} likewise is higher than for N\textsubscript{2}, see Table 9, the mass flow ratio of primary to secondary flows through the burner inlets is increased. This could create an imbalance in the burner aerodynamics compared to air-firing and thus have an impact on ignition, flame shape, and mixing [116]. It is possible that the minimum velocity will depend on the density of the primary stream. A lower value than used in air-firing could then prove to be adequate for oxy-fuel combustion. This would have to be tested in larger-scale setups.

Besides increasing the oxygen concentration to obtain stable combustion, other suggestions have been made:

Liu and Okazaki [127] suggested to stabilize the flame by recirculating additional heat with the flue gas while maintaining an air-like composition of the oxidant. In connection with the application of Ion Transfer Membranes (ITM) for air separation they likewise suggested heat recirculation to obtain stable combustion with oxygen concentrations down to about 15 vol% in the burner inlet. Utilization of ITM membranes will require relatively low oxygen concentrations in the oxidant in order to achieve sufficient driving force in the air separation. The authors claimed that the recirculation of heat should not affect the plant efficiency negatively. There has been no reports of experiments with this approach in larger scale.

Another alternative approach is taken by Toporov et al. [107,108] who work on changing the burner design in order to obtain stable flames at low oxygen concentrations in the O\textsubscript{2}/CO\textsubscript{2} oxidant mixture. This approach is likewise to enable the use of ITM membranes for air separation instead of a cryogenic unit and thus reduce the penalty on the plant efficiency from about 8 to between 3 and 5% [108]. In order to obtain stable operation their aim is to provide the necessary heat to compensate for the higher heat capacity of the oxidant and the heat used for the endothermic gasification reactions taking place in the near-burner region from the post-flame zone. This is done by promoting under-stoichiometric conditions near the burner region (\(\lambda = 0.6\)) and having a strong internal recirculation zone to lead hot combustion products back into the burner quarl. A burner design was obtained which allowed stable operation with just below 21% oxygen in the oxidant and an overall stoichiometry of \(\lambda = 1.3\). The drawback of this concept is an increase in the recirculation rate of flue gas. However, this is believed to be fully offset by the reduction in power demands for the air separation process [107,108].

2.7.2. Heat uptake

Existing boilers have been carefully designed to match the radiative and convective heat transfer properties of the air-fired combustion process. Especially important is the distribution of heat transfer between the furnace chamber (evaporation) and

| Properties of gases at 1123 °C and atmospheric pressure [116,117] |
|-----------------|------|------|------|------|--------------------------|
| Density (\(\rho\)) [kg/m\textsuperscript{3}] | H\textsubscript{2}O | O\textsubscript{2} | N\textsubscript{2} | CO\textsubscript{2} | Ratio CO\textsubscript{2}/N\textsubscript{2} |
| 0.157 | 0.278 | 0.244 | 0.383 | 1.6 |
| Thermal conductivity (\(k\)) [W/m K] | 0.136 | 0.087 | 0.082 | 0.097 | 1.2 |
| Specific heat capacity (\(c_p\)) [kJ/kg K] | 45.67 | 36.08 | 34.18 | 57.83 | 1.7 |
| Specific heat capacity (\(c_p\)) [kJ/kg K] | 2.53 | 1.00 | 1.22 | 1.31 | 1.1 |
| Heat sink (\(\mu_p\)) [kJ/m\textsuperscript{3} K] | 0.397 | 0.278 | 0.298 | 0.502 | 1.7 |
| Dynamic viscosity (\(\eta\)) [kg/m s] | 5.02e-05 | 5.81e-05 | 4.88e-05 | 5.02e-05 | 1.0 |
| Kinematic viscosity (\(\nu\)) [m\textsuperscript{2}/s] | 3.20e-04 | 2.09e-04 | 2.00e-04 | 1.31e-04 | 0.7 |
| Mass diffusivity of O\textsubscript{2} in X (\(D_{O_2,X}\)) [m\textsuperscript{2}/s] | — | — | 1.7e-04 | 1.3e-04 | 0.8 |
convective part (superheating) but the maximum heat flux to the furnace walls is also important.

The choice of recycle ratio, i.e. the fraction of the total flue gas flow which is recirculated to the boiler, and thus the oxygen concentration in the oxidant affects the heat transfer by controlling the flame temperature and the volume flow through the boiler [65]. The radiative heat transfer is mainly determined from the flame temperature and the gas radiative properties, whereas the convective heat transfer is determined mainly by the Reynolds and Prandtl numbers, the thermal conductivity, and the temperature of the flue gas passing the superheater banks. Fig. 10 shows the connection between the recycle ratio and the adiabatic flame temperature and flue gas volume. In this respect, the flue gas volume is a rough indicator for the convective heat transfer. It is seen that recycle ratios of either 0.61 or 0.76 yield conditions corresponding to air-firing (with \( \lambda = 1.15 \)), although only for one of the parameters. It is thus not possible to simultaneously obtain both an adiabatic flame temperature and a volumetric flue gas flow through the boiler similar to that of air combustion. Section 3.2 will assess the subject of heat transfer in more detail.

2.7.3. Oxygen excess

It is important to note that excess oxygen for oxy-fuel combustion carries a much greater penalty than in the air-firing case and that the power consumption in the ASU is directly proportional to the amount of oxygen lead to the boiler [95]. A reduction in the oxygen excess would thus benefit both the ASU and CO\(_2\) compression train power demands [66,68,81,195]. In modern power plants the air excess is typically 15–20\% (\( \lambda = 1.15–1.2 \)) [68,103,128] corresponding to about 3 vol\% O\(_2\) in the dry flue gas. The excess is predominantly determined by the uncertainty in the coal mass flow to each burner. By introducing more efficient monitoring of the coal flow to each burner and thus a better control of the oxidizer and fuel flows, it should be possible to reduce the required oxygen excess during oxy-fuel combustion to no more than 10\% [68]. At 10% excess oxygen and an oxidizer containing 30% O\(_2\) the dry flue gas O\(_2\) concentration will likewise be about 3 vol\%.

Theoretical considerations regarding the second law efficiency of gas-fired power plants equipped with either oxy-fuel combustion or post-combustion capture have been conducted by Simpson and Simon [95]. Their computations showed that oxy-fuel combustion becomes more favourable with respect to efficiency than post-combustion systems as the oxygen excess level is decreased.

2.7.4. Fire-side corrosion

The change in the composition of the combustion medium in oxy-fuel combustion could potentially give rise to increased risk of corrosion. The increased levels of CO\(_2\), H\(_2\)O, and SO\(_2\) are expected to change the corrosion potential of the flue gas. Both aspects regarding metal surface oxidation and corrosion under deposits due to changes in deposit compositions are important to investigate [129–131]. Regarding deposits, especially the co-existence of sulphates and carbonates within the deposits could be critical to the boiler tube surfaces [131]. The aspect of carburization of Cr-containing steels due to high partial pressures of CO\(_2\) could likewise constitute a challenge to materials lifetimes due to brittleness.

Pirón Abellán et al. [132] studied the oxidation of martensitic steels (Cr-containing alloys) in different CO\(_2\) and H\(_2\)O-containing atmospheres at temperatures between 550 °C and 700 °C in a laboratory setup. They found significant carburization in high CO\(_2\) containing atmospheres. They expect the carburization to be governed primarily by the permeability of the protective oxide layer toward CO\(_2\). However, the authors show that the presence of water vapor will limit the transport of CO\(_2\) through the oxide layer and thus the extent of carburization. The exposure atmospheres contained no O\(_2\) and the consequence of the presence of excess oxygen on the obtained results will need to be examined to fully clarify the effect of the change from air-firing to oxy-fuel combustion on fire-side corrosion.

2.7.5. Aspects regarding green-field plants

The above discussions are based on the case of a retrofitted conventional air-fired plant to oxy-fuel conditions. For a green-field plant it will be possible to refine the boiler design. The adoption of conditions similar to those of air-firing is not necessarily the most optimal for an oxy-fuel combustion plant. A major target will be a significant reduction or even complete elimination of the rate of external flue gas recirculation. Instead, control of the flame temperature can be obtained from internal recirculation in the boiler [10]. This will likewise have a positive impact on the residence time and thus the burnout of the char particles. The possible avoidance of the external recirculation will reduce the size of the boiler and thus the boiler capital cost significantly [10]. At the same time, efficiency loss due to thermal radiation to the environment and the electricity demand for the flue gas recirculation fans will be reduced.

Maintaining the external recycle is likewise an option. Instead of matching the flame temperature to air-like conditions it would be possible to shift heat transfer to higher temperature throughout the entire boiler, leading to less entropy loss. Higher combustion temperature may lead to more efficient combustion with better burnout at reduced oxygen excess levels. Higher oxygen concentration will at the same time require less flue gas recirculation and thus a smaller volume flow through the boiler.

2.8. Summary

The present section has discussed the effects of retrofitting a suspension-fired power plant to oxy-fuel operation. A number of new process units are necessary; an air separation facility to provide the combustion process with almost pure oxygen, ducts and fans for external recirculation of flue gas to the burners in order to control flame temperatures, and a CO\(_2\) processing facility including a flue gas condensation unit, compressors, and a purification unit to remove non-condensable species from the product stream.

The review of the literature has shown that even though the cost and efficiency penalties associated with the technology are significant, oxy-fuel combustion of pulverized coal is technically and economically feasible for retrofitting of existing power plants. At the
same time, oxy-fuel combustion for CO₂ recovery and sequestration is a competitive power generation technology in relation to post-combustion capture with amines. However, a number of critical aspects regarding the technology and plant configuration have been identified, as listed below. These are the issues which should be investigated in further detail to ensure that the technology is in fact a useful alternative to air-firing and post-combustion capture.

**Plant availability:** The risk of lowering the availability of the plant due to the introduction of the additional auxiliary equipment could be crucial to implementation.

**Plant efficiency:** With the currently available cryogenic technology for large-scale oxygen production the efficiency penalty for an oxy-fuel power plant is significant. Besides alternative air separation technologies, it is necessary to investigate additional measures that will allow the improvement of the electrical efficiency. Reduced oxygen surplus during combustion and a high steam cycle efficiency would have a positive effect on the efficiency.

**Load changes:** The relatively low gradients for load change in the air separation unit compared to those for the thermal cycle could provide a problem with respect to operation of the plant in a system with a large amount of decentralized, non-constant electricity sources, e.g. wind mills. In a world with an increasing fraction of the electricity produced by variable sources, central power plants will be required to run with frequent changes in the load to adjust to the demand for electricity. Additionally, the inability of current air separation units to run at low load without major penalties to the efficiency will require several oxygen plants running in parallel, as well as some sort of storage/buffer capacity.

**Enhanced purification:** The potential need for two purification steps, i.e. both the air separation unit and the pre-compression purification due to leakage of air into the flue gas ducts, could be a major disadvantage to the process. Post-combustion, in comparison, only requires the amine absorption step. The exact requirements for the final CO₂ quality are still to be determined and they will dictate the plant configuration with respect to the different purification units.

**Flue gas recycle:** The optimal positioning of the flue gas recycle withdrawal points has not been identified. The choice could have a large impact on both operation, economics, and plant maintenance related to corrosion issues.

**Combustion process:** The significant changes to the combustion process, including the potential effects on heat uptake, fly ash quality and fire-side corrosion likewise provide a challenge.

Several of the above aspects are difficult to examine either theoretically or during small-scale tests. The information and experience obtained from the operation of a larger-scale demonstration plant will greatly improve the knowledge of the process.

The majority of issues regarding the combustion process is, on the other hand, possible to clarify in smaller scale experiments. Much work has already been performed in this area including heat uptake and burner stability measurements as well as aspects regarding coal particle ignition, burnout, flame propagation, radiating properties of the flame, boiler efficiency, and changes in emission levels. In fact, most of the literature related to oxy-fuel combustion is concerned with the combustion chemistry and emissions.

In addition to the changes in the combustion, issues related to corrosion are also very relevant for the evaluation of the process. Because of the increased concentration of CO₂ and perhaps SO₂ in the flue gas, the risk of enhanced high temperature corrosion compared to conventional air-firing is present.

### 3. Oxy-fuel combustion fundamentals

The following subsections summarize the work performed on oxy-fuel combustion fundamentals by different researchers and reported in the open literature. The assessment will focus on chemical aspects connected to the boiler and other issues directly related to the combustion, e.g. convective and radiative heat transfer, corrosion, and emissions.

#### 3.1. Research groups and experimental facilities

Tables 10 and 11 provide an overview of the different groups active within oxy-fuel combustion research. The groups have been divided according to the scale and type of their experiments, i.e. whether they run combustion experiments with flue gas recirculation in semi-technical scale or in once-through, laboratory-scale reactors.

Included in the tables is information on the most important parameters for the experiments; maximum reactor temperature, oxygen concentration, fuel type, and oxygen excess, as well as an interpretation of the aim of the research performed by each group.

#### 3.2. Heat and mass transfer effects

The present section covers aspects of the effects of operating parameters such as oxidizer composition and oxygen excess levels on flame temperature and heat transfer in the boiler.

As described in Section 2.7 the differences in the radiative and thermo-physical properties of CO₂ and N₂, see Table 9, affect the combustion process through alterations of the temperature and mass transfer properties of the gas phase. As a consequence, the heat uptake in a boiler will likewise change compared to that of a conventional air-fired plant.

#### 3.2.1. Flame and gas phase temperatures

Croiset et al. [120] report the results of combustion of two different coals in air and different mixtures of O₂ and CO₂ in the 0.3 MW oxy-fuel combustion facility at CANMET. The coals tested were a Canadian western sub-bituminous coal (Highvale) and a US eastern bituminous coal. Temperatures along the centre-line have been measured with a suction pyrometer for air-firing and 21, 28, 35, and 42 vol\% O₂ in CO₂, see Fig. 11. The experiments have been performed with an oxygen excess between 1.46 (21% O₂) and 1.3 (35% O₂) for the Highvale coal. For the Eastern bituminous coal the oxygen excess was between 1.2 (28% O₂) and 1.1 (42% O₂), corresponding to 5% oxygen in the flue gas (dry). The data in the lower figure show that for the 21% O₂ case a direct substitution of N₂ for CO₂ in the oxidant leads to a considerably lower temperature in the flame zone, a decrease of up to about 300 °C, caused by the higher specific heat capacity of CO₂ compared to N₂. By increasing the oxygen concentration it is possible to obtain flame and gas phase temperature profiles almost similar to those obtained from conventional combustion in air. The necessary oxygen concentration is somewhat dependent on the type of coal, ~35% for the bituminous coal and ~31% for the sub-bituminous coal. Based on additional experiments the authors conclude that up to 5% nitrogen in the combustion medium has no significant effect on flame temperatures. Comparable results regarding the effect of oxygen concentration on flame temperature have been reported by Wang et al. [118], Liu et al. [121], and Tan et al. [122], among others.

Experiments in a 1.2 MW burner at Ishikawajima-Harima Heavy Industries Co. Ltd. (HI) [119] explored the effect of wet (16 wt% H₂O) and dry primary recycle (for coal transportation) on furnace temperature and flame stability, see Fig. 12. During the experiments the flow rate and composition of the secondary recycle gas was kept constant. It was found that drying the flue gas increased the gas temperature near the burner by about 150 °C for the same volumetric gas flow rate and thus helped stabilizing the flame by improving ignition stability. The heat capacity of water
Table 10
Oxy-fuel combustion research groups working in pilot scale and semi-technical scale with flue-gas recirculation.

<table>
<thead>
<tr>
<th>Group</th>
<th>Ref.</th>
<th>Test unit [MWth]</th>
<th>Unit description</th>
<th>Inlet O₂ [vol%]</th>
<th>Recycle: wet/dry</th>
<th>Coal type</th>
<th>Aim of work (interpretation of the authors)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ANL</td>
<td>[118,86]</td>
<td>3</td>
<td>Tower furnace, single swirl burner</td>
<td>22–40</td>
<td>Wet/dry</td>
<td>Bituminous</td>
<td></td>
</tr>
<tr>
<td>IVD</td>
<td>[143–148]</td>
<td>0.5</td>
<td>Vertical furnace, swirl burner</td>
<td>27–30 (dry basis)</td>
<td>Wet</td>
<td>Bituminous, Lignite</td>
<td></td>
</tr>
<tr>
<td>CANMET</td>
<td>[120,97,89,149,150, 9,151,122]</td>
<td>0.3</td>
<td>Vertical combustor, down-fired swirl burner</td>
<td>28–42</td>
<td>Wet/dry</td>
<td>Bituminous, Sub-bituminous, Lignite, NG</td>
<td></td>
</tr>
<tr>
<td>CIRCE</td>
<td>[157]</td>
<td>0.10</td>
<td>Bubbling Fluidized Bed combustor</td>
<td>20–40</td>
<td>Wet</td>
<td>2 Sub-bituminous, wood, olive residues</td>
<td></td>
</tr>
</tbody>
</table>
Table 11
Overview of oxy-fuel combustion research groups working in once-through laboratory-scale reactors.

<table>
<thead>
<tr>
<th>Group</th>
<th>Ref.</th>
<th>Test unit [kWth]</th>
<th>Unit description</th>
<th>Max T [°C]</th>
<th>Inlet O₂ [vol%]</th>
<th>λ</th>
<th>Fuel type</th>
<th>Aim of work (interpretation of the authors)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tokyo</td>
<td>[158,127,159]</td>
<td>–</td>
<td>Flat flame burner</td>
<td>1177</td>
<td>21</td>
<td>0.7–1.2</td>
<td>Anthracite/CH₄</td>
<td>Cause of NOₓ reduction. Investigate concept of heat recirculation. Influence of O₂, O₃ concentration, temperature, and type of coal with and without initial NOₓ. Verifies lab-scale results for high-oxygen concentration oxy-fuel combustion with respect to NOₓ emission and fuel burnout. Burner design.</td>
</tr>
<tr>
<td>Nagoya</td>
<td>[96,160,161]</td>
<td>–</td>
<td>Quasi-1D EFR</td>
<td>1300</td>
<td>20–100</td>
<td>0.7–3.3</td>
<td>3 Bituminous, Semi-Anthracite</td>
<td></td>
</tr>
<tr>
<td>Nagoya</td>
<td>[109]</td>
<td>145</td>
<td>Bench-scale vertical furnace</td>
<td>&gt; 3000</td>
<td>85–88</td>
<td>0.9–1.1</td>
<td>Sub-bituminous</td>
<td></td>
</tr>
<tr>
<td>Leeds</td>
<td>[162,121]</td>
<td>20</td>
<td>Down-fired vertical furnace</td>
<td>1350</td>
<td>21, 30</td>
<td>1.2</td>
<td>7 Bituminous</td>
<td>Comparison between air- and oxy-firing. Sensitivity to different fuels.</td>
</tr>
<tr>
<td>Sandia</td>
<td>[166,167,168]</td>
<td>–</td>
<td>Optical EFR facility</td>
<td>1730</td>
<td>6–36</td>
<td>–</td>
<td>Bituminous, Sub-bituminous</td>
<td></td>
</tr>
<tr>
<td>DTU</td>
<td>[172–174]</td>
<td>–</td>
<td>Laminar Flow Reactor</td>
<td>1527</td>
<td>0.05–0.4</td>
<td>0.25–8</td>
<td>CH₄</td>
<td></td>
</tr>
<tr>
<td>BYU</td>
<td>[124,175,176]</td>
<td>–</td>
<td>Multi-fuel Flow Reactor (MFR), laminar Gas Combustion Chamber</td>
<td>1627</td>
<td>21–37</td>
<td>0.75–1.05</td>
<td>2 Bituminous, Sub-bituminous</td>
<td></td>
</tr>
<tr>
<td>TU Aachen</td>
<td>[107,108,178,179]</td>
<td>100</td>
<td>Lab Scale Oxy-coal Test Rig</td>
<td>1250</td>
<td>19–30</td>
<td>1.3</td>
<td>2 Lignite, 3 Bituminous</td>
<td>Burner design for stable oxy-fuel combustion at low O₂ concentrations. NOₓ emissions comparison between flameless and flame combustion.</td>
</tr>
<tr>
<td>Utah (UU)</td>
<td>[185]</td>
<td>29</td>
<td>U Furnace</td>
<td>1550</td>
<td>21</td>
<td>1.15</td>
<td>3 Bituminous, Sub-bituminous, Lignite</td>
<td></td>
</tr>
<tr>
<td>Utah (UU)</td>
<td>[186]</td>
<td>100</td>
<td>Oxy-Fuel Combustor</td>
<td>1088</td>
<td>21–30</td>
<td>1.15</td>
<td>Bituminous</td>
<td></td>
</tr>
<tr>
<td>Washington Uni. in St. Louis</td>
<td>[117,114]</td>
<td>–</td>
<td>Tubular furnace</td>
<td>1200</td>
<td>20–50</td>
<td>–</td>
<td>Sub-bituminous</td>
<td></td>
</tr>
</tbody>
</table>
vapor is significantly lower than that of CO₂, see Table 9. Taking only this factor into account, the presence of water vapor in the recycle would act to increase the flame temperature, i.e. the opposite effect of what was observed. These findings thus suggest that factors such as radiation and endothermic radical formation (O, OH, H, etc.) dominate the temperature effect of water vapor in the recycle.

Injection of pure oxygen through the centre of the burner likewise increased the gas temperature in the near-burner area compared to a similar experiment with the same O₂/CO₂ ratio in the oxidant but without separate oxygen injection.

3.2.2. Radiative and convective heat transfer

As mentioned in Section 2.7, it is essential to match the flame and heat transfer characteristics for oxy-fuel combustion to those for air-firing in case of a boiler retrofit. In order not to reduce plant efficiency or induce operational difficulties, the ratio between radiative and convective heat transfer should be maintained similar to that of air-firing as well [12].

3.2.2.1. Overall heat transfer. Experiments performed by IFRF [88,12] have shown that a recycle ratio of 0.58 (26 vol% O₂) yields radiative and convective heat transfer rates similar to those of air-firing in their experimental setup. The observed, optimum recycle rate is marginally lower than the theoretically determined value, see Fig. 10, which is caused by some degree of air leaking into the boiler and the fact that pure CO₂ was used for fuel transportation [88].

Investigations of the possible differences between wet and dry recycle has been performed by the Argonne National Laboratory [86], see Fig. 13. The experiments showed that the optimal (CO₂ + H₂O)/O₂ molar ratio is different in each case. The ratio yielding the same overall heat uptake changed from 3.25 (equal to a recycle ratio of 0.68 or 23.8 vol% O₂ at the burner inlet) for the wet case to 2.6 (recycle ratio of 0.63 or 27 vol% O₂ at the burner inlet) for the dry case. The optimum recycle ratios were likewise validated at reduced load and with a bituminous coal. Wall et al. [128] saw a similar difference between wet and dry recycle. Their values were 28% and 35% for wet and dry recycle, respectively. The difference suggests that the absolute concentration of water vapor in the boiler has a significant effect on overall heat transfer efficiency. The exact reason for this influence is not clear and modelling could provide indications to the influence from different factors such as radiation, thermo-chemical properties of the gases, etc.

3.2.2.2. Radiative heat transfer. The main contributor to the heat transfer from a flame from conventional fuels is thermal radiation [4,5]. The radiating species considered for pulverized-coal-fired systems are H₂O, CO₂, CO, SO₂, soot, char, and ash particles [65,86,128,188].

The presence of higher concentrations of CO₂, H₂O, and SO₂ in oxy-fuel combustion will increase the non-luminous radiation [65]. Payne et al. [86] and Khare et al. [116] estimated gas emissivities in both air- and oxy-fuel atmospheres. Even though their estimates are not in exact agreement, they generally find a difference of 0.1 between the two types of environments, e.g. from 0.45 in air to 0.55 in oxy-fuel [116,128].

Because of the higher concentrations of H₂O and CO₂ in the furnace and their higher gas emissivities compared to nitrogen, the radiative heat transfer in the boiler will exceed that of conventional air-firing for the same adiabatic flame temperature [4,5,128,155]. In order to obtain the required heat transfer profile in both the radiative and convective passes a slightly lower oxygen concentration than required to reach a comparable adiabatic flame temperature should thus be chosen [4,5,128]. Typical results suggests a decrease of the oxygen concentration of 2–3 vol%. The use of the adiabatic
flame temperature as a rough indicator of radiative heat transfer characteristics is thus altered compared to air-firing [88,12].

Fig. 14 shows the radiative heat transfer profiles for three different coal flames; the air-firing case, as well as oxy-fuel flames with overall oxygen concentrations in the oxidant of 22 and 26 vol %. The experiments are performed in the IFRF 2.5 MWth furnace. It is seen that 26% O2 in the oxidant yields a profile very similar to that of air-firing, as expected. At the same time, the inlet oxygen concentration of 26% was reported to yield in-flame gas composition trends, combustion performance, flame length, and flame stability comparable to normal air operation.

Experiments on oxy-fuel combustion of propane [153,155] have revealed an up to 30–60% increase in the flame radiation intensity (27% O2) at peak levels compared to air-firing. At the same time, the gas temperature levels are generally slightly lower for the oxy-fuel case. The authors observed that the increased gas emissivity due to enhanced CO2 concentrations could not account for the entire difference. Further investigations showed that the in-flame soot volume fraction increased when shifting to oxy-fuel conditions [153]. Due to the lower volumetric flow rates and higher fuel concentration compared to oxidant in the oxy-fuel combustion the concentration and residence time of soot precursors in the near-burner region are increased. The formation of soot will thus be promoted [155]. These mechanisms for a gaseous fuel most probably also apply to volatiles combustion in coal-fired operation. The relative effect of an enhanced soot formation from volatiles on overall radiation from a solid-fuel flame is not known and could thus be the subject of future research.

Shaddix and Molina [168] measured the soot cloud size for a bituminous and a sub-bituminous coal in both N2 and CO2-based combustion media. Fig. 15 show the results for the bituminous coal. Generally, oxy-fuel combustion leads to larger soot cloud formation compared to the nitrogen based experiments at equivalent oxygen concentrations, confirming the results from Andersson et al. [153,155]. For increasing oxygen partial pressure the soot cloud size decreases for both types of combustion atmospheres.

The effect of in-flame particulates on flame radiative properties is mainly a function of their total mass and temperature. The absolute amount of ash does not change between air- and oxy-firing operation for equal fuel input. The amount of soot in the flame can, on the other hand, change drastically with changes in the near-burner flow dynamics. Changes in the burnout rate of char can likewise affect the location of heat transfer by radiation in the flame zone.

Besides experiments on propane, Andersson et al. [188] conducted radiation intensity measurements in air- and oxy-fuel flames burning lignite. They found that the shift in combustion medium resulted in only a negligible increase in the total radiation intensity at comparable gas phase temperatures. Due to gas-particle overlaps and the fact that particle radiation dominates in solid-fuel flames the effect of increased gas emissivity is limited. Regarding the gas phase, the authors concluded, however, that operating with a wet flue gas recycle would have a much larger impact on radiation intensity in large-scale boilers than the increase in CO2 partial pressure. This observation is in line with that of Nozaki et al. [119].
flue gas. All of the above will change with the change in flue gas composition and the flue gas temperature associated with the shift from air-firing to oxy-fuel combustion. Whether the resulting heat transfer rate in the convective section will match that of the air-firing case is dependent on the specific case. Simulations would be a valuable tool in the evaluation.

3.3. The combustion process

3.3.1. Devolatilization and ignition

Volatiles constitute a major fraction of the combustible matter of most coals used for power generation. The combustion of volatiles releases heat which is important for ignition, local stoichiometries, and pollutant emissions [172]. The differences in properties for N2 and CO2 presented in Table 9 suggest that devolatilization and ignition in oxy-fuel combustion will occur at different rates than for combustion in air if CO2 is substituted directly for N2.

Shaddix and Molina [126,168] studied the effects of the presence of CO2 and enhanced oxygen concentrations on the devolatilization and ignition of pulverized Pittsburgh (high-volatile bituminous) and Black Thunder (sub-bituminous) coals in a laminar flow reactor. Fig. 16 shows estimated values of particle devolatilization and ignition times for the Pittsburgh coal at 1700 K in different gas mixtures. From the data it is concluded that the exchange of CO2 for N2 does not significantly affect the devolatilization time for this particular type of experiment. From a consideration of heating an inert particle, the authors reason that for a fixed gas phase temperature the only factor that influences the initial heating of a particle is the thermal conductivity [126,168]. As seen from Table 9 the ratio between the thermal conductivity of CO2 and that of N2 is close to one at 1400 K. Hence, the initial heating profile of particles in each atmosphere will effectively be similar. Since coal devolatilization is an endothermic process with a rate that is strongly dependent on particle temperature and heating rate the specific conditions of the reported experiments suggest that there should be no difference between the different atmospheres, as observed. The result is, however, only valid for the case of equal gas phase temperatures, regardless of the gas phase environment. For a practical boiler this assumption is not necessarily satisfied.

As the oxygen concentration increases the devolatilization as well as the ignition occur more rapidly. In earlier work on air combustion Murphy and Shaddix [166] proposed the increase in the devolatilization rate with increasing oxygen concentration to be the result of (1) a closer proximity of the volatiles flame to the coal particle, and (2) a higher temperature of the volatile flame. Furthermore, modelling considerations suggested increasing kinetic control for increasing oxygen concentrations. At a low oxygen partial pressure and high temperature, oxygen transport through the gas film surrounding the particles will be rate limiting. At increasing oxygen partial pressures and constant temperature the kinetic rate will remain almost constant whereas the rate of gas film transport will increase linearly with the pressure.

The differences in particle ignition times observed in Fig. 16 is a consequence of the differences in transport properties of the surrounding gas, the combustion heat release, and the reactivity of the local fuel-oxidizer mixture [126,168]. Generally, increasing the mixture reactivity and heat release will decrease the ignition time, whereas an increase in the product of density and heat capacity (the heat sink, $\rho C_p$) leads to an increase in the ignition time. The heat sink for CO2 is substantially larger than for N2, see Table 9, leading to an increase in ignition time for similar oxygen levels. Kiga et al. [136], Kimura et al. [87], and Liu et al. [121] have observed similar delays in the ignition of coal particles when burning in an atmosphere of 21% O2 in CO2. Increasing the oxygen concentration will increase the characteristic reaction rate of the local mixture and thus decrease the ignition time [126,168,189]. Changing from 24 to 36% O2 is seen to have a large, absolute effect on the oxy-fuel mixture. Comparing the results for air- and oxy-fuel combustion reveals that it should be possible to obtain similar devolatilization and ignition properties for oxy-fuel combustion as for conventional air-firing.

Suda et al. [190] measured the flame propagation velocity with respect to different coal concentrations, coal types, and ambient gas compositions in a microgravity facility. Fig. 17 shows the observed
particle diameters: 53
coals differ in their volatile matter contents. Coal A has the highest amount (46.0 wt%), followed by coal B (36.2 wt%) and then C (32.9 wt%), all on an “as received basis”. Coal particle diameters: 53–63 μm, O2 concentration: 40% by volume. Data taken from [190].

The effect of each parameter: The coal type is seen to have a significant effect on the flame propagation speed in both enriched air- and oxy-fuel environments. Each case operates with 40 vol% O2 in the oxidizer. The difference in coal type is mainly a matter of the volatile content of each coal. The speed is seen to increase with increasing volatile matter content. For a given coal in a given environment an optimum in the propagation speed exists with respect to the coal concentration. The optimum concentration is seen to be approximately similar for all data series. According to the authors, this particle concentration corresponds to an inter-particle distance roughly equal to the flame radius of a single, burning particle [190].

3.3.2. Volatile and char burnout

Besides the impact from exchanging N2 with CO2 on the devolatilization and ignition of coal particles the burnout of both char and volatiles is expected to be affected.

The coal burning process is typically limited by both chemical kinetics and external diffusion (Zone II conditions). At 1400 K the diffusivity of O2 in CO2 is only about 75% of that in N2. The lower diffusivity will thus reduce both the burning and heat generation rates for the coal particles [169]. At the same time, the diffusivity is a strong function of temperature. Hence, the effect of the enhanced heat capacity of CO2 and the associated decrease in flame temperature for similar oxygen concentration in oxy-fuel and air combustion will further reduce the burning rate. Fig. 18 shows trends in ambient gas phase as well as soot cloud and char combustion temperatures for different combustion media obtained by Shaddix and Molina [168] in their EFR facility. At equal oxygen concentrations and gas phase temperatures combustion in O2/N2 mixtures generally yield higher temperatures of both soot clouds and char than in O2/CO2 mixtures.

The consumption rate of volatiles in oxy-fuel combustion is likewise expected to be slower than in air due to the lower diffusivity of small hydrocarbons in CO2 compared to N2 [122,126,168]. This is because of the higher oxygen partial pressure experienced by the burning fuel, possible gasification by CO2 (and H2O), and longer residence times due to the lower gas volumetric flows [5,128]. Other researchers claim that excess CO2 in the vicinity of the burning particle could alter the reaction equilibrium and slow down the burning rate [117]. However, that conclusion is based on a simplified analysis.

3.3.2.1. Burnout times. Bejarano and Levendis [181] have conducted a series of experiments with non-intrusive optical multi-colour pyrometry measurements of volatile flame and char burning phenomena in single particle environments. Fig. 19 illustrates average temperatures and burnout times measured for a high-volatile bituminous coal. The data indicate an effect of exchanging N2 for CO2 and the effect of varying the O2 concentration in the oxidizer. The lower diffusivity of O2 in CO2 compared to N2 is the major cause of reducing the burning rate during char combustion [167]. Generally, it is seen that an oxygen mole fraction of 0.3–0.35 yields similar temperature and burnout data for oxy-fuel combustion compared to combustion in air. By comparing the measured and calculated burnout times shown in the figure, Bejarano and Levendis [181] conclude that the char combustion for both air- and oxy-fuel combustion occurs in Zone II.

Wang et al. [118] have shown a significant increase in char burnout rate when increasing the oxygen concentration in O2/CO2 combustion from 21 to 29%. Similar results were found by Naredi and Pisupati [187] from drop-tube experiments on bituminous coals with 21% and 30% oxygen in the oxidant. Tan et al. [12] refer to studies performed by Takano and coworkers in the IHI 1.2 MW swirl burner which gave similar results. Moreover, a marked reduction in unburned carbon in the fly ash with increasing oxygen level was observed.

In general, the reported investigations have shown that increasing the oxygen concentration in the oxidant for oxy-fuel combustion can compensate for the larger specific heat of CO2 compared to N2. Comparable burnout times are thus achievable.

3.3.2.2. Gasification reactions. Both CO2 and H2O may contribute to the burnout of char particles through gasification reactions, (6) and (7), when these species are present in high concentrations at high temperature [191,166] and the oxygen excess, λ, is significantly lower than 1.

\[
\begin{align*}
C + CO_2 & \rightarrow 2CO \quad (6) \\
C + H_2O & \rightarrow CO + H_2 \quad (7)
\end{align*}
\]
In low-temperature regions (400–900 °C) gasification does not play a role. This is due to a much lower rate of reaction for gasification with CO\textsubscript{2} compared to O\textsubscript{2}-combustion at these conditions [192].

Results presented by Wall et al. [139,128] indicate that the volatile yield is higher during oxy-fuel combustion than in air. They attribute it to gasification. However, Borrego and Alvarez [193] found the opposite trend during their experiments.

Due to the conflicting results, the possible influence of gasification reactions during oxy-fuel combustion is an area which needs further investigations.

3.3.2.3. Effect of coal properties. Liu et al. [162] investigated the burnout efficiency compared to combustion in air for a range of bituminous coals in their 20 kW swirl burner, see Fig. 20. Even though the burnout efficiency differs between the samples it is always higher for combustion in 30% O\textsubscript{2}/70% CO\textsubscript{2} than in air. Generally, the increase in burnout efficiency is between 0.5 and 2%.

An examination of the coal characteristics has not revealed any obvious correlation between the burnout efficiency and the proximate or ultimate analysis. The reason for the differences within each coal type is suggested to be the higher oxygen concentration combined with similar temperatures for the oxy-fuel tests. The authors stress that gasification and longer residence times of the burning particles in the combustion chamber could also contribute to the higher burnout efficiency observed [162].

Fig. 21 shows the results of the work performed on burnout characteristics of different coals by Arias et al. [180]. The burnout of both coals show similar trends with changes in the stoichiometry. At fuel-lean conditions the burnout asymptotically approach a value of 100%. It is seen that the burnout of the high-volatile coal generally is a little lower than for the low-volatile coal. This is contrary to what was expected since the high-volatile coal should be more reactive. However, there may be significant uncertainties in the experimentally determined burnout, particularly because of alkali metal volatilization and possible ash carbonization from CO\textsubscript{2}. For both coals the overall lowest burnout is, as expected, observed for oxy-fuel combustion with a low oxygen content.
3.3.2.4. Particle size effects. An investigation of the effect of particle size (45–53 and 75–90 μm) on volatiles and char temperatures has been performed by Bejarano and Levendis [181]. Given that the actual data and the measurement uncertainty has not been stated, the results given in Fig. 22 show only small or insignificant differences between the investigated particle size ranges.

The burnout times for the char particles are seen to depend on the particle size. As expected, the larger the particles the longer the burnout times. The effect of particle size is seen to be more significant in an oxy-fuel environment. A plausible explanation could be the lower diffusivity in CO2 compared to N2. Comparable results have been obtained by Huang et al. [189] from experiments in a TG thermal analyser.

3.3.2.5. CO. At high partial pressure and high temperature CO2 can dissociate into CO and O2 through the strongly endothermic reaction, (8), [172].

\[ \text{CO}_2 \rightarrow \text{CO} + 0.5 \text{O}_2 \]  

(8)

In the flame zone in oxy-fuel combustion both of the above conditions are present. Gasification of carbon, reaction (6) and (7), could likewise contribute to increase in the production of CO during oxy-fuel combustion. However, among researchers there is a difference in opinion on whether it is the thermal dissociation, [175], or the gasification reactions, [149], that play the dominant role in the significant increase in CO concentration in the flame compared to air-firing.

An even more important pathway to the increase in CO concentrations in the flame zone of oxy-fuel flames could be the reaction between CO2 and H radicals, see reaction (9). The increased level of CO2 induces a possible alteration of the composition of the O/H radical pool during oxy-fuel combustion due to the competition between O2 and CO2 for H radicals, (9) and (10) [172,194].
H + CO₂ ⇌ CO + OH  

H + O₂ ⇌ O + OH  

Due to the high partial pressure of CO₂ in oxy-fuel combustion the ratio of OH to both O and H will increase and the total amount of radicals is expected to decrease compared to air-blown combustion. Besides the reaction with H radicals, reaction of CO₂ with CH₃ radicals will likewise contribute to enhance the concentration of CO in the flame zone [172,194–196].

Whether the emission of CO from oxy-fuel combustion is larger than from air-firing has been subject to investigation. Because of its severe toxicity it is important that oxy-fuel combustion does not lead to an increased CO emission. Wang et al. [118] report no significant difference in the CO concentration levels both within the latter part of the flame zone and in the exhaust from a 3 MWₘ₉ horizontal furnace for both air- and oxy-fuel combustion experiments with comparable flame temperatures. A five time increase in the CO level within the flame was expected however based on a modelling study. For an oxy-fuel experiment with an air-like composition of the oxidant the CO concentration in the flame zone was expected to be slightly larger than for air combustion based on modelling. The observed values for the oxy-fuel experiment were lower than calculated. All experiments yielded full burnout of CO before the exhaust.

Experiments performed in the IFRF 2.5 MWₘ₉ furnace by Woycenko et al. [88] show significantly increased CO levels within the flame zone. Still, the combustion of CO has completed before the furnace exit and no significant CO emission is observed. Similar results were obtained by Scheffknecht and coworkers [164,148] and Liu et al. [121] even when the excess oxygen level was slightly higher for the latter oxy-fuel test. Changing the oxygen concentration from 30 to 21% increased the CO emission from 34 to 200 ppmv, due to delayed ignition and lower peak temperature.

Experiments on natural gas combustion performed by Glarborg and coworkers [172–174] indicate that the high levels of CO₂ in oxy-fuel atmospheres prevent complete oxidation of fuel (CO) to CO₂ at high temperatures even when excess oxygen is present. However, the effect is most pronounced at fuel-rich or stoichiometric conditions. There is no indication that high CO₂ levels influence CO oxidation at low temperatures when oxygen is in excess and hence there should be no increased risk of high CO emissions from a gas-fired oxy-fuel plant if mixing of fuel and oxidant is adequate.

### 3.3.2.6. Summary

The difference in the thermo-chemical properties of N₂ and CO₂ affects the combustion process. At 21% O₂ in CO₂ devolatilization, ignition, and burnout proceeds at a lower rate than in air. However, increasing the oxygen concentration in the oxy-fuel environment to about 30% to obtain the same adiabatic flame temperature as in air yields similar devolatilization, ignition, and combustion rates as seen in air combustion. At comparable adiabatic flame temperatures oxy-fuel combustion is reported to yield improved burnout of char. This is most likely due to longer residence times and higher partial pressures of oxygen in the vicinity of the burning particles. Even though contribution of gasification by CO₂ and/or H₂O to the increased burnout is suggested several times in literature, it is questionable if this effect is of significant importance for the conversion of the fuel.

CO levels in the flame zone are generally reported to increase significantly in oxy-fuel combustion compared to air-firing. Even though the high CO₂ levels prevent CO from being oxidized at high temperatures complete conversion is expected when excess oxygen is present during cool-down of the flue gas.

### 3.4. Gaseous pollutants emissions

The following subsections discuss the reported knowledge on the most important gaseous emissions besides CO from oxy-fuel combustion: NOₓ, SOₓ, and NO. Trace elements in the gaseous phase, e.g. Hg, Cd, As, and Se, are likewise treated. No results have been published regarding emissions of HCl and HF.

#### 3.4.1. NOₓ

##### 3.4.1.1. NOₓ formation

In conventional air combustion the generally accepted pathways for NOₓ formation are the following three mechanisms [197–199], see e.g. Fig. 23:

**Thermal:** Thermal NO formation results from N₂ and O₂ reacting at high temperatures (above 1500 °C) to form NO. The mechanism involves three reactions, known as the extended Zeldovich mechanism.

\[
N₂ + O ⇌ NO + N \tag{11} 
\]

\[
O₂ + N ⇌ NO + O \tag{12} 
\]

\[
N + OH ⇌ NO + H \tag{13} 
\]

**Prompt:** Prompt NO is formed when hydrocarbon radicals in fuel-rich zones attack molecular nitrogen to form cyanide species, which subsequently form NO when oxidized. These reactions can take place at temperatures lower than is required for thermal NO formation.

**Fuel:** Fuel NO is derived from nitrogen in the fuel reacting through either volatile-N or char-N. Nitrogen released with the volatiles further decomposes into cyanide and amine species. These intermediate species may react to produce N₂ or NO, depending on the conditions. Char-N reacts through heterogeneous reactions and intermediate CN species to eventually produce NO or N₂. Detailed understanding of the reaction pathways for the conversion of char-N has not been established and is still an area of active research. The split between NO and N₂ on an overall level depends on factors such as the nitrogen content of the coal, its rank and volatility, as well as the stoichiometry.

It is generally assumed that up to 20% of the total NOₓ formed from pulverized coal combustion in air is due to thermal NOₓ and about 80–100% is derived from fuel-N while the prompt NOₓ mechanism is negligible, depending on the quantity of fuel-bound nitrogen species [199]. The low level of molecular nitrogen in oxy-fuel combustion will...
suppress the formation of thermal and prompt NOx and hence potentially lower the overall NOx emission rate.

The general conclusion in published literature is that the amount of NOx emitted from an oxy-fuel plant can be reduced to somewhere between one-third and half of that from combustion in air [51,63,87,88,91,97,119,120,128,162]. However, the application of an oxygen concentration higher than 21% to obtain adequate flame temperatures could result in an enhancement of fuel-NOx formation [122].

The potential for reducing the NOx emissions from a power plant considerably compared to air-firing [4,200] has been one of the key drivers in oxy-fuel combustion research, particularly in USA [5] and thus, NOx chemistry has been one of the most heavily investigated areas within the oxy-fuel combustion technology. Normann et al. [201] have recently published a review on emission control of nitrogen oxides from oxy-fuel combustion.

The potential for a significant decrease in NOx formation is mainly important for oxy-fuel power plants with a configuration of the flue gas clean-up train which releases the impurities, including NOx, to the atmosphere. If instead a CO2 cleaning process is chosen which captures NOx and produces e.g. nitric acid the NOx formation rate is of less importance although it will affect process economics. In any case, if NOx formation can be reduced without significant negative consequence to the remaining combustion process it is desirable.

3.4.1.2. Mechanism for the reduction of NOx during oxy-fuel combustion. The majority of homogeneous NOx chemistry is taking place in the devolatilization and near-flame zone. The implications of oxy-fuel combustion on the homogeneous NOx formation and destruction are therefore likely to be alterations in equilibria and reaction pathways caused by higher concentrations of CO2 and NOx in this part of the furnace. If the recycled flue gas is wet the higher partial pressure of H2O will likewise interfere through its influence on radical formation and destruction. The enhanced levels of CO2 and NOx are also expected to affect the heterogeneous formation and reduction of NO. In addition to chemical effects, changes in the mixing patterns between fuel and oxidizer are likely to affect the nitrogen chemistry. In the following, these mechanisms for reduction of NOx in oxy-fuel combustion are discussed.

Effect of the increased NO concentrations (reburning): Recirculation of NO with the flue gas through the burner would be expected to lead to a considerable reduction of the nitrogen oxides emission through processes similar to those of reburning. Reburning is a chemically complex process in which nitric oxide is abated using fuel as reducing agent [202]. The process involves partial oxidation of the reburning fuel under fuel-rich conditions, reduction of NO by reaction with fuel fragments, and subsequent conversion of the intermediate nitrogenous species.

The reduction of NO may involve the following types of reaction:

1. NOx is reduced to cyanide and amine intermediates by reaction with hydrocarbon radicals, formed from the volatiles released from the coal particles in the early flame zone.
2. NOx is converted to N2 through reactions with other reactive nitrogen species (XN), such as cyanides and amines. The XN species may be formed either from the hydrocarbon-NO reactions or from release of N- volatiles in the early flame.
3. NO is converted to N2 by heterogeneous reactions on char or soot.

From experiments performed in a small-scale laboratory reactor, Okazaki and Ando [158] evaluated the relative impact of these mechanisms for NO reduction. They concluded that reburn type reactions, i.e. reactions of recycled NOx with hydrocarbons, is the dominant mechanism in reducing NOx emissions and that it accounts for 50–80% of the decrease in NO observed in oxy-fuel combustion. Reactions of NOx with N- volatiles were estimated to contribute 10–50% to the NO reduction. The reduction of NO on char in oxy-fuel combustion was found to be of minor importance, but their results may be biased by the choice of a char with a low reactivity (formed from anthracite).

Effect of the low N2 concentration: At a very low concentration of N2 in the oxidizer, the thermal NOx formation mechanism can be disregarded since the oxy-fuel combustion atmosphere will be oversaturated with NO at all times [123,156]. For this reason the Zeldovich reactions will be reversed and serve to convert NO to N2.

A modelling study using detailed chemical kinetics on oxy-fuel combustion of lignite performed by Andersson et al. [90] indicates that while the formation of NO from fuel-N is the same or even slightly higher for oxy-fuel combustion compared to combustion in air, the destruction mechanisms at oxy-fuel conditions are enhanced compared to air conditions, leading to an overall reduction in the NO emission. At high temperatures (>1500 °C), the near-elimination of molecular nitrogen in oxy-fuel combustion facilitates reduction of NO by the Zeldovich mechanism. In order to obtain an effective reduction of NO by the reverse Zeldovich mechanism a sub-stoichiometric reaction during can insignificantly amount of air ingress into the furnace is required (air-staging to promote long enough residence time) [156]. At the same time, applying a wet flue gas recycle will increase the NOx reduction potential [156].

Effect of the increased CO2 concentration: Only few studies have been reported on the impact of high CO2 concentrations on the nitrogen chemistry in oxy-fuel combustion. Mendiara and Glarborg [174,173] investigated the implications of the alterations to the radical pool as described in Section 3.3.2 on NO formation and destruction. They considered oxidation of methane doped with either NH3 (used to simulate volatile-N) [174] or NO [173] in a laminar flow reactor. According to their results, CO2 acts to promote NO formation from volatile-N under fuel-rich conditions whereas it inhibits NO at both stoichiometric and fuel-lean conditions. At low oxygen concentrations formation of NO is favoured by the increase in OH-concentration. At conditions with oxygen excess, the reduced formation of NO is caused by the limitation of the O/H radical pool, particularly O. In reburning, a high concentration of CO2 had only a small impact on the NO reduction efficiency under reducing conditions, while at stoichiometric conditions CO2 slightly enhanced removal of NO.

Okazaki and Ando [158] pointed to the increased importance of reduction of NOx on char surfaces due to reaction with CO. The CO levels increase because of the high CO2 concentration as described in Section 3.3.2. The promoting effect of CO on NOx reduction on char is well documented [199,203–206], but this mechanism is mostly important at fluidized bed conditions [198], i.e. at temperatures well below those characteristic of pulverized fuel combustion.

A change in selectivity of the release of char-N to NO has been suggested by Park et al. [207]. They investigated nitrogen release from pulverized bituminous coal char during the reaction with O2, CO2, and H2O using Ar as carrier gas in a fixed bed flow reactor. Their experiments showed that increasing the concentration of CO2 in an H2O and O2 free environment reduced the char-N to NO release ratio. In contrast to gasification with H2O, no HCN or NH3 were measured when CO2 was the reactant. These experiments thus suggest that the increased levels of CO2 during oxy-fuel char combustion may suppress the formation of NO and its precursors.

Effect of changes to the flame and fuel/oxidizer mixing pattern: Implementation of oxy-fuel combustion may bring about changes in the flame structure and the fuel/oxidizer mixing pattern. These
changes will depend on the burner geometry and the degree of recirculation and the composition of the flue gas.

Mackrory et al. [124,175] identify the following mechanisms that may enhance NO\textsubscript{x} reduction in oxy-fuel combustion:

- Less secondary oxidizer entrainment into the burner’s recirculation zone due to a more detached flame, i.e. reduced oxygen availability and limited initial NO formation.
- Temperature increase in the fuel-rich zone will increase the rate of NO\textsubscript{x} destruction. At higher temperatures the conversion of volatile-N proceeds faster toward N\textsubscript{2} than NO\textsubscript{x}.
- Reduced NO\textsubscript{x} formation from char since more fuel-N is released with the volatiles.
- Indirect effects through changes in reaction rates (combustion) and temperatures from the enhanced importance of gasification reactions.

Their overall conclusion is that faster NO\textsubscript{x} destruction in oxy-fuel combustion appears to be at least partially due to the higher CO and NO concentrations.

3.4.1.3. Summary of reported, experimental results. Table 12 provides a summary of the reported results on NO\textsubscript{x} emission from oxy-fuel combustion in setups with flue gas recirculation compared with that from air-firing. Most of the experiments yield a decrease in the NO\textsubscript{x} emission rate during oxy-fuel combustion. However, some experiments show an increase which is suggested to be caused by the fact that the mechanism of fuel-NO\textsubscript{x} formation is very sensitive to the method with which oxygen and fuel is mixed in the flame [122,124,151]. As oxy-fuel burners are typically adopted from air-firing principles the resulting fluid dynamics of the flame can be disadvantageous with respect to NO\textsubscript{x} emissions even though the flames are stable.

In the following sections the reported results on NO\textsubscript{x} emissions from oxy-fuel combustion are divided according to the effects of different operating conditions and design aspects. Results from both once-through laboratory reactors and setups with flue gas recirculation are included. In each section a further subdivision is made, separating the different types of experimental setups, i.e. EFR type experiments from swirling flames. The underlying mechanisms of NO\textsubscript{x} formation and destruction do not change between setup types. However, scaling effects and the fact that mixing of fuel and oxidizer in larger burners is crucial to NO\textsubscript{x} formation will influence the absolute levels of NO\textsubscript{x} emitted. A direct comparison of small laboratory-scale setups and larger swirl burners with respect to NO\textsubscript{x} concentrations and emission rates is thus not possible. A clear example of this is the experiments performed by Hasatani et al. [161,109]. They burned a sub-bituminous Indonesian coal in an oxy-fuel environment with oxygen concentrations between 85 and 88 vol% in both an entrained-flow reactor [161] and in a 145 kW\textsubscript{th} vertical furnace [109]. They observed NO\textsubscript{x} concentrations of 4700 ppm and 1500 ppm, respectively, for otherwise similar combustion conditions.

3.4.1.4. Effects of changes in the oxygen concentration, oxygen excess, flue gas recycling ratio, and gas phase temperature. Experiments on NO\textsubscript{x} emissions from oxy-fuel combustion of a high-volatile bituminous coal in the IFRF 2.5 MW\textsubscript{th} furnace were performed in the early nineties by Woycenko et al. [88]. As shown in Fig. 24 they observed considerably higher NO\textsubscript{x} concentrations during oxy-fuel combustion with 26 vol% O\textsubscript{2} in the oxidant than in the air-firing case. However, the total mass of NO\textsubscript{x} formed per energy input of coal [mg/MJ], also termed the emission rate, was significantly lower in the oxy-fuel case which was assigned to the near-elimination of thermal NO\textsubscript{x} formation and reburning of recirculated NO\textsubscript{x}.

Further experiments showed that an increase of the concentration of oxygen in the oxidant, and thus the flame temperature, yielded an increase in both the flue gas NO\textsubscript{x} concentration and the emission rate. The increase in oxygen concentration was performed by decreasing the flue gas recycle ratio. Similar trends of reduced

<table>
<thead>
<tr>
<th>Author(s)</th>
<th>Fuel input (MW)</th>
<th>Inlet O\textsubscript{2}, Oxy (%)</th>
<th>Emission (mg/MJ)</th>
<th>Conversion ratio (%)</th>
<th>Conclusion(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Payne et al. [86]</td>
<td>3</td>
<td>Dry: 28, wet: 24</td>
<td>Air: 560&lt;br&gt;Oxy: dry: 160&lt;br&gt;Oxy: wet: 95</td>
<td>–</td>
<td>NO\textsubscript{x} formation is reduced by approximately 70% for dry recycle and 80% for wet recycle compared to air-firing.</td>
</tr>
<tr>
<td>Woycenko et al. [88]</td>
<td>2.1</td>
<td>26</td>
<td>Air: 320&lt;br&gt;Oxy: 50–150&lt;br&gt;Air: 100–175&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Air: 30&lt;br&gt;Oxy: 5–14</td>
<td>NO\textsubscript{x} formation is lower in oxy-coal combustion with flue-gas recirculation than in air case. Potential for drastic NO\textsubscript{x} reduction of up to 60–70%</td>
</tr>
<tr>
<td>Châtel-Pélage et al. [63]</td>
<td>1.5</td>
<td>25</td>
<td>Air: 25–55&lt;br&gt;Oxy: &lt;90</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Kimura and coworkers [87,119]</td>
<td>1.2</td>
<td>27</td>
<td>Air: 340&lt;br&gt;Oxy: &lt;90</td>
<td>Air: 30–33&lt;br&gt;Oxy: &lt;8</td>
<td>NO\textsubscript{x} conversion ratio in oxy-fuel combustion is significantly lower than that in normal air combustion because the recycled NO\textsubscript{x} is rapidly reduced to HCN or NH\textsubscript{3} in the combustion zone (reburning).</td>
</tr>
<tr>
<td>Scheffknecht and coworkers [144]</td>
<td>0.5</td>
<td>27–30</td>
<td>Air: 90–350&lt;sup&gt;b&lt;/sup&gt;&lt;br&gt;Oxy: 55–325</td>
<td>–</td>
<td>NO\textsubscript{x} formation is significantly lower than that in normal air combustion because the recycled NO\textsubscript{x} is rapidly reduced to HCN or NH\textsubscript{3} in the combustion zone (reburning).</td>
</tr>
<tr>
<td>Croiset and coworkers [120,97]</td>
<td>0.21</td>
<td>28, 35, 42</td>
<td>Air: 340&lt;br&gt;Oxy: 100–210&lt;br&gt;Air: 110&lt;br&gt;Oxy: 62–150</td>
<td>Air: 35&lt;sup&gt;c&lt;/sup&gt;&lt;br&gt;Oxy: 10–22&lt;br&gt;Air: 14&lt;br&gt;Oxy: 8–19</td>
<td>High NO\textsubscript{x} concentration inside the furnace but lower NO\textsubscript{x} emission rate with the flue gas than for air-firing. NO\textsubscript{x} formation is strongly dependent on burner design, i.e. the near-burner flow field. NO\textsubscript{x} emission from oxy-fuel combustion can change from lower to higher than in the air-firing case.</td>
</tr>
<tr>
<td>Chui et al. [150,151]</td>
<td>0.21</td>
<td>28</td>
<td>Air: 211–269&lt;br&gt;Oxy: 68–233</td>
<td>Air: 21–31&lt;br&gt;Oxy: 8–24</td>
<td>NO\textsubscript{x} emissions dependent on coal type. Lignite, sub-bituminous, and bituminous coals tested. Specially designed burner for oxy-firing significantly reduces the NO\textsubscript{x} emission rate.</td>
</tr>
<tr>
<td>Tan et al. [122]</td>
<td>0.21</td>
<td>35</td>
<td>Air: 150&lt;br&gt;Oxy: 40–50</td>
<td>Air: 24&lt;br&gt;Oxy: 7–8</td>
<td>The reduction in NO\textsubscript{x} emissions for oxy-fuel combustion is due to an increased destruction of formed and recycled NO compared to air-firing. The conversion of fuel-N to NO is similar or even slightly higher during oxy-fuel combustion than in air.</td>
</tr>
<tr>
<td>Andersson et al. [90]</td>
<td>0.1</td>
<td>25, 27, 29</td>
<td>Air: 150&lt;br&gt;Oxy: 40–50</td>
<td>Air: 24&lt;br&gt;Oxy: 7–8</td>
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</table>

<sup>a</sup> The interval reflects the variation between λ = 0.68 and 1.2 for the air tests and λ = 0.85–1.05 for oxy-fuel tests.
<br>
<sup>b</sup> The interval reflects the variation between ϕ\textsubscript{burner} = 0.75 and 1.15 for both the air- and oxy-fuel tests.
<br>
<sup>c</sup> Conversion made using coal HHV.
NO\textsubscript{x} emission rates during oxy-fuel combustion compared to air-firing have been reported for different fuels in laminar flow reactors [174], entrained-flow reactors [96,160,161,169], and swirling flames [72,90,97,120,121,164].

According to Hu et al. [161] there are two opposing factors influencing NO\textsubscript{x} formation and reduction in coal combustion; the oxidation of fuel-N by oxygen and other oxidizing species, and the reduction of NO\textsubscript{x} by reducing agents, such as hydrocarbons from pyrolysis and resident char. They have performed a series of experiments in their entrained-flow reactor analysing the influence of oxygen concentration, oxygen excess, and gas phase temperature to clarify the importance of each parameter on NO\textsubscript{x} formation and destruction. Fig. 25 shows, as expected, that the NO\textsubscript{x} concentration generally increases with increasing oxygen concentration, partly due to decreased dilution, and shows a peak at near stoichiometric conditions. The NO\textsubscript{x} emission rate (bottom row), however, increases approximately linearly near $\lambda = 1$ when changing from fuel-rich to fuel-lean conditions. At high oxygen excess for all oxidant compositions the NO\textsubscript{x} emission rates approach asymptotic values. Increasing the gas phase temperature results in both increasing NO\textsubscript{x} concentrations and emission rates for all stoichiometric values. As accentuated in Fig. 26 for a temperature of 1273 K, it is likewise seen that the emission rate yields a slight peak at around 50% O\textsubscript{2} in the oxidizer, however most significantly for fuel-lean conditions. Hu et al. [96] state that this phenomenon is a consequence of the concentration of reducing agents increasing proportionally to the increase in \textit{O}_2 concentration (decreasing recycle ratio). At low oxygen concentrations (<50 vol%) they thus assume oxidation to dominate and NO\textsubscript{x} emissions to increase with increasing \textit{O}_2 concentration. For \textit{O}_2 concentrations above 50%, reduction by reducing species should play the dominant role and NO\textsubscript{x} emissions decrease with increasing \textit{O}_2 concentration [96].

The concentration of reducing agents does undoubtedly contribute to the behaviour in Fig. 26 but other factors may likewise contribute. As the oxygen concentration is increased the reaction between char and oxygen proceeds faster which will result in higher particle temperatures. The fractional conversion of char-N to NO has been reported to increase initially with temperature [199] until the point where the oxygen-char reaction approaches the diffusion limited regime. A further increase in particle temperature

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig24}
\caption{NO emissions and flue gas concentrations for air-firing and oxy-fuel combustion (oxy) with and without low-NO\textsubscript{x} burner technology. The fuel, a high-volatile bituminous coal (Gottelborn), is burned in the IFRF 2.5 MW\textsubscript{th} furnace. The combustion is performed at an overall stoichiometry of $\lambda = 1.15$ and the inlet oxygen concentration in the oxy-fuel experiments is 26%, corresponding to a recirculation ratio of 0.58. The NO\textsubscript{x} concentration is in the dry flue gas and is normalized to 0% O\textsubscript{2}. Data taken from [88].}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig25}
\caption{NO\textsubscript{x} emission versus stoichiometric ratio and temperature at different \textit{O}_2 concentrations for \textit{CO}_2-based oxidizers. Experiments performed on a bituminous coal in an entrained-flow reactor with a coal flow rate of up to 180 g/h. The NO\textsubscript{x} concentrations in ppm are given as measured. Data taken from [96].}
\end{figure}
will mainly increase the rate of NO reduction by char [199], in fact what is observed from the data in the figure.

Nozaki et al. [119] showed that air- and oxy-fuel combustion of a low-volatile bituminous coal yielded similar NOx profiles in their 1.2 MW burner with flue gas recirculation, even though NOx was recirculated to the burner during oxy-fuel firing. The experiments were performed with fixed firing rate and excess oxygen conditions at the burner. Measurements of HCN and NH3 along the burner axis showed significantly increased levels of NH3 in oxy-fuel combustion compared to air-firing, see Fig. 27. The authors concluded that NOx recycled with the flue gas is reduced primarily to NH3 and N2 in the early part of the flame. Experiments with direct oxygen injection in the burner revealed a significant increase in the HCN concentration in the flame zone. Nozaki et al. [119] assume this to be caused by increased devolatilization arising from a higher flame temperature compared to the oxy-fuel case without direct oxygen injection. Air-firing and oxy-fuel combustion without oxygen injection yielded similar HCN profiles even though the flame temperatures were significantly different. Based on the described observation, oxy-fuel combustion leads to higher concentrations of the intermediate cyano and amine species in the NOx formation mechanism in the flame zone compared to air-firing. At the same time, oxy-fuel combustion yields similar concentrations of NOx in the exhaust gas compared to air-firing and thus reduced NOx emission rates due to the lower volume of flue gas.

3.4.1.5. Effect of flue gas composition. Most laboratory-scale experiments on oxy-fuel combustion are performed in once-through reactors, where the recirculated flue gas is simulated by pure CO2. It is relevant to compare the results of once-through experiments to those with flue gas recirculation to clarify whether there are significant differences which should be accounted for.

The experiments reported by Croiset and coworkers [97] yield a 40–50% decrease in NOx emission rates when flue gas is recycled, compared to once-through runs, see Fig. 28. The experiments were performed in the CANMET 0.3 MWth vertical combustor facility at a firing rate of 0.21 MW with 5 vol% excess oxygen in the dry flue gas. Comparison of air combustion as well as oxy-fuel experiments with flue gas recycle (open symbols) and once-through runs (O2/CO2, filled symbols). Oxy-fuel experiments with flue gas recycle are provided for the case with a dry recycle stream (O2, dry). The recirculation ratios are 0.63 (28% O2), 0.51 (35% O2), and 0.40 (42% O2). Data taken from [97].
a firing rate of 0.21 MW with 5 vol% excess oxygen in the dry flue gas. Oxygen concentrations in the inlet of 28, 35, and 42% were tested.

The results reported in the literature generally show that combustion in air yields the highest NOx emissions, oxy-fuel combustion based on synthetic gas mixtures (CO2 + O2) yields lower emission rates at comparable conditions, whereas oxy-fuel combustion with recirculation of flue gas yields the lowest emission rates.

**Wet versus Dry Recycle**: Payne et al. [86] observed that the reduction efficiency of NOx through reburning in a 3 MWth oxy-fuel sub-bituminous coal flame appeared to be higher when a wet instead of a dry recycle was applied. The reduction was 80% and 70%, respectively, compared to results obtained for air-blown combustion. During the experiments the flue gas oxygen concentration and the firing rate were fixed.

Nozaki et al. [119] likewise investigated the effect of wet and dry flue gas recycle for the primary flow, i.e. the flow for coal transport, in their 1.2 MWth burner. The experiments were performed with fixed firing rate and excess oxygen at the burner. Fig. 29 shows measurements of gas phase temperature as well as NOx, HCN, and NH3 concentrations along the burner axis. The NOx concentration in both experiments peaks at the same level, although the formation of NOx is shifted further down the reactor in the case of a wet, primary recycle. This can be attributed to the significant reduction in flame temperature in the first measurement point. At the same time, both the HCN and NH3 concentrations are markedly higher for the dry recycle compared to the wet. This is likewise attributable to the differences in temperature profiles and hence the effect on the homogeneous gas phase chemistry dominating NOx formation in the flame zone.

**Initial NOx Concentration**: As indicated in Section 3.4.1.2 it is likely that high NOx concentrations at the onset of both devolatilization and char combustion will limit the formation of further NO in the flame.

Liu et al. [162] determined the difference in reduction efficiency for experiments on a bituminous coal with 500 and 1000 ppmv NOx in the oxidant O2/CO2 mixture in their 20 kW swirl-stabilized once-through burner setup. They saw that the change in reduction efficiency between the two levels of NOx was less than 1% and thus within the experimental uncertainty. For their specific operating conditions, the NOx concentration in the oxidant was thus not a limiting parameter in the reduction process.

Based on experiments in air, Spinti and Pershing [185] have shown that the apparent conversion of char-N to NOx is a strong function of the initial NOx level at the onset of char combustion in the range of 0–900 ppm NOx on a dry basis. Likewise, the excess oxygen level affected the conversion rate, see Fig. 30. To remove the effect of volatile-N to NOx conversion during the experiments the authors burned premade chars in methane. The char particles were withdrawn from a pulverized-coal flame just after devolatilization was terminated. For the conditions tested, increasing the initial NOx concentration had a greater effect on the reduction of the apparent conversion of char-N to NOx than decreasing the oxygen excess level. In air combustion which is the case for the described experiments, a high initial NOx level translates to a high conversion of volatile-N to NOx. This will have a negative impact on the process through an increase of the overall NOx emission rate. In oxy-fuel combustion a high initial NOx concentration at the base of the flame will most likely almost entirely originate from the recirculated flue gas. The apparent conversion of char-N to NOx during oxy-fuel combustion could thus decrease as the concentration of NOx in the oxidant increases, e.g. due to a reduced recycle ratio.

Fig. 31 shows computations of the total NOx emission as a function of the conversion of volatile-N to NOx and the fraction of coal-N released during devolatilization in air. It is seen that the lowest overall emission rate is achieved when the volatile-N to NOx

---

**Fig. 29.** Effect of wet versus dry recycle of primary gas on gas temperature, NOx, HCN, and NH3 concentrations along the burner axis in the HFI 1.2 MW furnace. The setup is operated in oxy-fuel mode with direct O2 injection through the burner and with a low-volatile bituminous coal (Coal A). Data taken from [119].

**Fig. 30.** Comparison of the effects of excess O2 and of initial gas phase NOx concentration on the conversion of char-N to NOx for an Illinois #6 coal char combusted in air in a 29 kW furnace. Data taken from [185].
conversion is low and as much of the coal-N content as possible is released with the volatiles. The governing assumption applied in the modelling was that char-N to NOx conversion decreases with increasing initial NOx level during combustion.

Based on the observations above it seems that a high concentration of NOx in the recirculated flue gas could increase the reduction rate of NOx in the flame and thus lead to a further reduction of the emission rate.

3.4.1.6. Effect of oxygen purity and air penetration. Croiset et al. [120] have determined the NOx emission rates from air-firing and once-through oxy-fuel combustion experiments of a US eastern bituminous coal with two different oxygen purities, 90 and 100% (remaining is N2). The experiments were performed in the CANMET 0.3 MWth vertical combustor facility at a firing rate of 0.21 MW and with temperature profiles as shown in Fig. 11. As expected, the NOx emission rate increases with decreasing oxygen purity, see Fig. 32. The difference between data obtained with an oxygen purity of 90% and 100% in the experiments with an oxygen concentration of 28% versus those obtained with 35% oxygen at the inlet is quite significant. There is, however, no obvious explanation to the deviations.

The data indicate that a less clean inlet O2/CO2 mixture (increased N2 content) or air entrainment near the burners may give rise to increased NOx emission due to thermal NO formation.

3.4.1.7. Influence of oxidant staging. The use of oxidant staging in oxy-fuel combustion as a primary measure to reduce NOx emissions introduces a necessity for optimization due to the fact that the oxidant stream will contain NOx.

Liu et al. [121,162] have investigated the effect of staging on the reduction of NOx emissions from both air and oxy-fuel combustion in a once-through reactor. The authors focused on the effect of staging and NOx recycling position on the reduction of recycled NOx. Fig. 33 shows their results for the bituminous coal, Polish Blend. It is obvious that both the combustion media, air or oxy-fuel, the operating mode, with or without staging, and the NO recycling location influences the reduction efficiency. Focusing on the position where NOx is recycled there is no significant difference between the primary and secondary oxidant streams, which both are introduced through the burner. The tertiary stream constitutes the staging stream. Recycling of NOx through the tertiary stream markedly reduces the reduction efficiency, down to the range of 44–54% [162] as also shown by Scheffknecht and coworkers [144,148,164] in comparable experiments.

For a commercial oxy-fuel plant NOx would be present in all oxidant streams. The use of over-fire air would then potentially decrease the rate of reduction of NOx. On the other hand, a significant fraction of the NOx present in the recycled flue gas will be
introduced through the burners and thus experience fuel-rich conditions for a longer period of time. The optimum degree of over-fire oxidant still remains to be determined and would, at the same time, be dependent on the burner design.

3.4.1.8. Coal properties. The effect of coal properties on the formation and reduction of NOx in oxy-fuel combustion has been investigated by several researchers. In entrained-flow reactor type experiments both Hu et al. [161] and Shaddix and Molina [169] have observed increasing NOx emission with decreasing rank of the coals. The coals investigated range from semi-anthracite over high-volatile bituminous to sub-bituminous. Shaddix and Molina [169] attributed the trend to the higher volatile content, higher char combustion temperature, and the lower fuel-N content for the lower ranking coals.

Mackrory and Tree [175] have observed that the difference between the NOx emissions in air- and oxy-fuel combustion in their laminar flow reactor increases with the rank of the coal. Their observations are based on experiments performed with one sub-bituminous coal and two high-volatile bituminous coals, Illinois # 6 and Pittsburgh # 8.

Seven different bituminous coals were investigated in a 20 kW swirl-stabilized once-through burner setup by Liu et al. [162]. The authors measured the coal-N to NO conversion ratio between oxy-fuel combustion with 30% O2 in CO2 and in air. Their data showed no clear correlation between the conversion ratio and the coal rank, volatile matter, nitrogen content, etc. Instead, as shown in Fig. 34, there seems to be a dependence of the char reactivity. Increasing reactivity leads to a relatively larger conversion of coal-N to NO at oxy-fuel conditions. This could be attributed to the observation of Liu et al. [162] that reactive coals produced slightly higher temperatures in the combustion zone. According to Liu et al. this will promote NOx formation at the fuel-lean conditions at higher temperatures in the combustion zone. The effect could be caused by a greater sensitivity of coal properties on NOx. According to Liu et al. [162], the NOx concentration increases with increasing reactivity of the coal char. The effect could be caused by a greater sensitivity of the coal char to char combustion temperature of the NOx formation mechanism in an oxy-fuel environment than in air.

Fig. 34. The dependence of the ratio of coal-N to NOx conversion between coal combustion in 30% O2/70% CO2 and coal combustion in air on the coal burnout efficiency in air for seven different bituminous coals. Experiments are performed in a 20 kW swirl-stabilized once-through burner setup with an overall stoichiometric value of 1.2. SA: South African, Aus: Australian, POL: Polish Blend, COL: Colombian, UK1(2): UK Bituminous 1 (or 2), US: US Blend. Data taken from [162].

Fig. 35. Reduction ratios of recycled NO and recycled NO2 as a function of stoichiometry obtained in an entrained-flow reactor. The reduction ratio at a given stoichiometry is obtained from the difference in NOx emission between an experiment with and without recirculation of NOx. The operating conditions are: recycling ratio of 0.4; T = 1373 K; fixed residence time of 2 s; concentration of NOx in the inlet gas of 1000 ppm for recycled-NOx experiments. Prima: high-volatile bituminous Indonesian coal; Datong: medium-volatile bituminous Chinese coal. Data taken from [161].
3.4.19. Effect of burner configuration for swirling flames. Fig. 24 showed that exchanging a conventional burner for a low-NOx burner in oxy-fuel combustion yielded a 56% reduction in the NOx emission rate. Thus, NOx formation in oxy-fuel combustion depends on the burner configuration and especially the flow field in the near-burner zone, just as is the case during conventional air combustion.

Experiments performed by Chui et al. [150] in the CANMET 0.3 MW vertical combustor research facility show that NOx emissions are highly dependent on the burner swirl number, i.e. flow dynamics. Increasing the swirl number from 1 to 2 decreases the NOx formation by 34%. However, for the range of swirl numbers applied in the experiments NOx emissions during oxy-fuel combustion was higher than for air-firing, 140–150 versus 110 mg/MJ. This was true for both burner configurations tested. Because of safety limitations, the amount of oxygen mixed into the secondary oxidizer stream was restricted to 28% on a dry basis. For the same reason, the primary stream contained little or no oxygen. To obtain the necessary overall oxygen concentration during combustion a portion of the total oxygen demand was injected as pure oxygen through a special annulus in the burners. The burners provided stable burnout at the lower gas temperatures. This is not different from the case of air-firing. However, because of the changes in mass flow rates in the primary and secondary inlets, see Section 2.7.1, the optimal burner design for oxy-fuel combustion is not necessarily similar to that developed for conventional air-firing.

3.4.2. SOx

Sulphur emissions and the effect on ash properties and boiler-tube corrosion in oxy-fuel combustion from significantly increased levels of gas-phase-S in the boiler have received increasing attention in the recent years. There have been contradictory observations on the SO2 emissions from oxy-fuel combustion. Some researchers experimentally show a decrease when comparing to combustion in air [88,96,97,128,136,138] whereas others on the basis of either semi-technical and pilot scale experiments [121,113] or equilibrium calculations [149] report no differences.

Kiga et al. [136] reported oxy-fuel experiments performed in the IHI 1.2 MWth combustion facility with recirculation of dry flue gas. The investigations showed that the conversion of the coal sulphur content, measured as the amount of S in the outlet divided by the amount going in with the coal, decreased markedly in oxy-fuel combustion compared to air-firing operation. Even though the authors were not able to close the mass balance for sulphur the results indicated that the major part of the difference could be attributed to removal of S through condensation as H2SO4 in low-temperature ducts and by retention in ash particles.

Zheng and Furimsky [149] modelled the formation of SO2 and SO3 based on equilibrium considerations during both air- and oxy-fuel combustion. They found that practically all of the sulphur content in coals is released as SO2 and SO3 irrespectively of the combustion medium, as CO2 plays an insignificantly small role for the release compared to oxygen. With respect to recycle ratio and oxygen excess, their simulations yielded an increased amount of SO3 with an increase in the amount of available oxygen.

Generally, the disagreements observed between experimental findings and the computations based on equilibrium modelling are expected to be a consequence of computations reflecting conditions immediately after combustion and not accounting for changes occurring further downstream. Another plausible explanation is the fact that some of the processes could be kinetically controlled, e.g. the heterogeneous reactions controlling retention of S in ash and other deposits, a fact that is not captured in the simulations.

Table 13 provides a summary of the results on SO2 emissions from semi-technical and pilot scale experiments with flue gas recirculation.

In the following sections the reported results on SO2 emissions from oxy-fuel combustion are divided according to the effects of different operating conditions and design aspects. The subject of boiler-tube corrosion due to the presence of sulphur in the flue gas is likewise treated.
3.4.2. Effects of changes in the oxygen concentration, oxygen excess, flue gas recycling ratio, and gas phase temperature. Hu et al. [96] focus on the effect of oxidizer composition, stoichiometry, and flame temperature in their investigations of SO2 emissions in an entrained-flow reactor with a coal feed rate up to 180 g/h. They encountered the highest conversion ratios at or near stoichiometric conditions, see Fig. 37. The decrease in S conversion at fuel-rich conditions is assumed to be due to retention in unburned coal and formation of other, reduced S-containing species (e.g. H2S, COS, and CS2). These species were not measured. The reduction in SO2 emissions at fuel-lean conditions compared to stoichiometric conditions has not been explained but could partly be due to increased conversion to SO3.

According to Liu et al. [121] SO2 emissions are not significantly affected by the use of staging or changes in the combustion media.

3.4.2.2. Effect of the composition of the recirculated flue gas. Croiset and coworkers [120,97] reported experiments regarding SO2 emissions from the combustion of a US eastern bituminous and a Canadian sub-bituminous (Highvale) coal in the 0.3 MW CANMET oxy-fuel combustion facility. Fig. 38 shows SO2 emission rates for air-fired experiments, once-through experiments (synthetic flue gas denoted O2/CO2), and dry flue gas recycle (O2, dry) experiments. The data for the bituminous coal in the figure show similar emission rates for experiments with air and the synthetic O2/CO2 mixture. For the recycle experiments with 28 and 35 vol% O2, however, the emission rates were slightly lower.

Comparing gas phase concentrations instead of emission rates reveal that the measured SO2 concentrations in the burner during oxy-fuel combustion were approximately 3 times higher than for air-firing [97]. The theoretical increase in the SO2 concentration was about a factor of 4. The authors concluded that the conversion of sulphur into SO2 was independent of oxygen concentration and that retention in ash and/or further oxidation into SO3 could explain the difference. Ash analysis showed that less than 3% of the initial S-content in the coal was

### Table 13

<table>
<thead>
<tr>
<th>Author(s)</th>
<th>Fuel input (MW)</th>
<th>Inlet O2, Oxy (%)</th>
<th>Emission (mg/MJ)</th>
<th>Conversion ratio</th>
<th>Conclusion(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Woycenko et al. [88]</td>
<td>2.1</td>
<td>26</td>
<td>Air: 645</td>
<td>Air: 100%</td>
<td>The conversion ratio of fuel-S into SO2 is lower for oxy-fuel combustion than air.</td>
</tr>
<tr>
<td>Croiset and coworkers [120,97]</td>
<td>0.21</td>
<td>28, 35</td>
<td>Air: 300–320</td>
<td>Air: 91%</td>
<td>Increased SO2 concentrations increases acid dew point from ~ 133 to ~ 156 °C.</td>
</tr>
<tr>
<td>Tan et al. [122]</td>
<td>0.21</td>
<td>35</td>
<td>–</td>
<td>Air: –Oxy: 96–100%</td>
<td>SO2 emission rates slightly lower for oxy-fuel combustion than in air even though the concentration was 3–4 times higher in the oxy-fuel case.</td>
</tr>
<tr>
<td>Scheffknecht and coworkers [144,145,147]</td>
<td>0.5</td>
<td>27–30</td>
<td>–</td>
<td>–</td>
<td>Negligible reduction of SO2 in the radiative section of a boiler. Higher SO2 concentrations yields higher H2S formation in fuel-rich zones. Calcium-rich coals show greater tendency to capture S.</td>
</tr>
</tbody>
</table>

![Fig. 37. SO2 emissions versus stoichiometric ratio and temperature at different O2 concentrations for N2 and CO2-based oxidizers. Experiments are performed in an entrained-flow reactor with a coal feed rate of up to 180 g/h. The SO2 concentrations in ppm are given as measured. Data taken from [96].](image-url)
present in the ash. However, the condensed water did have a sulphate content of above 3000 mg/L and a pH between 2 and 3. The high sulphate concentration in the condensate indicates high SO2 levels in the flue gas. In the work by Mönckert et al. [147] the sulphur retention in calcium containing coals is shown to increase with increasing SO2 concentration in the recycled flue gas. This is due to the formation of CaSO4.

Experimental runs with wet flue gas recycle were likewise performed by Croiset and Thambimuthu [97] but showed no significant difference to the dry case. The authors, however, expected a lower emission rate for the latter case since some SO2 should be removed with the waste water during the flue gas condensation.

3.4.2.3. Effect of coal sulphur content. Comparing the data in Fig. 39 leads to the conclusion that the specific SO2 emissions are almost exclusively dependent on the coal type, i.e., sulphur content. The Eastern bituminous coal has a sulphur content of 0.96 wt% (dry basis) whereas the sub-bituminous coal (Highvale) contains 0.24 wt% (dry basis) [120]. The relative differences due to changes in combustion medium and oxygen concentration are thus negligible in this context.

3.4.2.4. The SO2 to SO3 conversion and sulphur-induced corrosion. In later work from CANMET, Tan et al. [122] reported further results on the conversion of SO2 to SO3 in the flue gas. They showed that the conversion was about 5% whereas it is typically between 1 and 5% in conventional air-firing systems [113,122,147] depending on the combustion conditions and the sulphur content of the coal. These values have likewise been found by Scheffknecht and coworkers [145]. Klostermann [113] and Mönckert et al. [147] report that SO3 formation is promoted by both high oxygen and high water levels in the flue gas. In the case of a flue gas recycle without prior SO2 removal the amount of SO3 in the boiler can thus reach high values (up to about 85 ppmv [147]) and thus increase the risk of sulphur corrosion in the regions of the system which operate below the acid dew point.

Because of the potentially higher SO3 concentrations in the flue gas, the acid dew point will increase accordingly [115,138,145,147,148]. Increases of about 20–40 °C from ~130 to ~160 °C have been reported [113,138,145]. Schnurrer et al. [115] found a similar trend from their thermo-chemical equilibrium calculations. An earlier formation of sulfuric acid in the flue gas ducts will increase the risk of flue gas side corrosion in the low-temperature parts considerably. Schnurrer et al. suggest using a dry flue gas recycle to decrease the concentration of water in the flue gas and thus the amount of acid that can form.

Scheffknecht and coworkers [144,145,147,148] investigated the impact of recirculation of SO2 (by doping the oxidant stream in their 20 kW EFR) on the transformation of SO2 in the radiant section of a boiler. They found only a negligible reduction in the concentration of the recycled SO2. However, high concentrations of SO2 in the furnace was found to increase the concentration of H2S in the fuel-rich regions for both air- and oxy-fuel firing conditions, see Fig. 40, inducing a higher risk of corrosion. The H2S to SO2 ratio in the oxy-fuel experiments were lower than in air even though the absolute concentration was higher.

3.4.2.5. In-boiler desulphurization. In a series of papers Liu and coworkers [127,208,209] address the ability of oxy-fuel combustion
to drastically reduce the emissions of SO₂ from combustion of coal. They suggest in-boiler desulphurization by injection of limestone. The combination of both high SO₂ and CO₂ partial pressures should ensure high reactivity of the limestone toward SO₂. The authors explain the increased reactivity by two factors: (1) high SO₂ limits CaSO₄ decomposition and (2) high CO₂ limits decarbonisation of limestone before sulphation whereby direct sulphation of limestone without decarbonisation is favoured. The direct sulphation will minimize the diffusion resistance through the solid phase (no pore clogging) and hence a larger part of each limestone particle will participate in the desulphurization reaction.

Even though the experiments show significantly increased reactivity of the limestone toward SO₂ for a sulphur containing flue gas recycle compared to conventional air-fired conditions, this strategy is not likely to be adopted in power plants which produce fly ash for cement and concrete production due to the associated mixing of gypsum and fly ash.

3.4.2.6. Summary. The substitution of N₂ by CO₂ in oxy-fuel combustion does not affect the release of sulphur from the coal during combustion. However, the increased oxygen partial pressure necessary to maintain an appropriate flame temperature increases the formation rate of SO₂. During operation with a flue gas recycle without SO₂ removal the SO₂ and thus the SO₃ levels in the boiler will participate in the desulphurization reaction.

3.4.3. Trace elements

The subject of trace element emissions during oxy-fuel combustion is generally seen to have drawn minor attention compared to other of the fundamental combustion issues investigated. Because of the scarcity of published results within this area of research none of the results described below have been confirmed by other research groups.

According to the equilibrium calculations performed by Zheng and Furimsky [149] the Hg-, Cd-, As-, and Se-containing emissions are only insignificantly affected by the combustion medium. However, in case of incomplete elimination of these species in the flue gas cleaning equipment situated before the cooler and flue gas ducts increase significantly which will enhance the risk of sulphur-induced corrosion at both high and low temperatures. High in-boiler concentrations of sulphur oxides can likewise increase retention of S in the fly ash. Increased retention will reduce the SO₂ emission rate but could at the same time yield problems with further utilization of the fly ash in cement and concrete production.

3.5. Ash and deposition chemistry

The transformations of coal mineral matter during combustion are significantly affected by the temperature and the gas phase composition surrounding the coal particles [125]. The change in combustion atmosphere and the potential change in local particle temperature between oxy-fuel combustion and air-fired combustion may thus have an effect on the ash formation mechanisms and hence the ash composition and quality.

3.5.1. Particle formation mechanisms

Fig. 42 shows the mineral transformation and particle formation pathways for both fine (sub-micrometer, mode around 0.1 μm) and coarse particles during coal combustion. There are two pathways for the formation of sub-micrometer particles: (1) direct vaporization of volatile metals, e.g. Na, Pb, Cd, and Hg, which react in the gas phase and subsequently nucleate or condense on the surface of existing particles; (2) non-volatile species like e.g. silica oxides can be reduced to sub-oxides, e.g. as in reaction (14). These sub-oxides have a lower melting point and are devolatilized and rapidly reoxidized in the gas phase causing an oversaturated mixture.

\[
\text{MeO}_x + \text{CO} = \text{MeO}_{x-1} + \text{CO}_2 \quad (14)
\]

Particle formation occurs mainly through nucleation whereas growth is dominated by condensation and collision mechanisms. The sub-micrometer particle formation mechanisms are complex functions of such factors as coal type, combustion temperature, fuel to oxidizer ratio, and residence time. This is likewise the case for the resulting particle size distributions [117].

Coarse ash particles are formed from the non-volatile mineral inclusions in the coal which are not released as sub-oxides. These inclusions can coalesce and form a glassy matrix or remain in their original state if the temperature does not exceed their melting points [117].

The main fraction of the fines will consist of spherical particles due to their origin from gas phase species. On the other hand, the shapes of the coarse particles may vary from spherical or near-spherical to irregular, depending mainly on the char particle temperatures during combustion, i.e. whether they have been melted.

3.5.2. The effects of gas composition on particle formation

Combustion at oxy-fuel conditions with an air-like composition of the oxidant will result in a lower adiabatic flame temperature and hence a reduction of the coal burning rate compared to combustion in air, see Sections 2.7, 3.2, and 3.3. The vaporization of both volatile metals and metal sub-oxides as well as the particle
formation rates will thus be significantly smaller, as observed by Suriyawong et al. [117] and Sheng and coworkers [125,182,183]. From their investigations, Suriyawong et al. found that the ratio between fine and coarse particles shifted significantly toward fewer sub-micrometer particles in this particular oxy-fuel case. The mean size of the fine particles likewise became smaller because the particles have less time to grow when ignition and combustion is delayed, see Fig. 43. The bottom part of the figure shows the amount of various elements in the fine ash. It is generally observed that a smaller amount of ash forming elements have vaporized from the coal in the case of oxy-fuel conditions causing the lower number concentration. At the same time, the ratios between the different elements have changed. Particularly calcium and iron are released to the gas phase to a much lesser extent than in air. Suriyawong et al. [117] explain this phenomenon in the way that the increased concentration of CO2 in the bulk gas will shift the sub-oxides formation equilibrium toward the oxides, see reaction (14), and thus reduce the formation of sub-micrometer particles through this pathway. The reduced particle surface temperature is, however, of significant importance. Sheng et al. [182] likewise determined the compositions of their ashes. They observed a similar shift in the ratio between volatile and less volatile species in the sub-micron ash for oxy-fuel combustion with an air-like oxidant composition. Increasing the oxygen concentration diminished the difference between air and oxy-fuel combustion. Differences in the oxygen concentration and thus the combustion temperature of the coal and char particles can alter the distribution between the main phases slightly, as more or less of the included minerals melt into a glass phase [183,125].

Increasing the O2 concentration in CO2 from 20 to 50% increases the particle surface temperature during combustion from 1772 K to 2679 K [117]. As a result, the particle size distribution of the sub-micrometer-sized fraction of ash particles is shifted toward larger sizes, see Fig. 44. Sheng et al. [183] observed the same trend for their Chinese coals. They likewise concluded that the temperature difference between air and oxy-fuel combustion with 20% O2 in CO2 might alter the particle fragmentation and coalescence mechanisms in addition to lowering the ash vaporization rate. However, the particle number concentration in the less than 50 nm range does not change.

![Fig. 42. Mineral transformation and particle formation pathways during coal combustion [117].](image1)

![Fig. 43. Top: Sub-micrometer particle size distribution from air and 20% O2/80% CO2 combustion of a sub-bituminous coal obtained in a laminar flow reactor with a fixed temperature of 1200 °C. Bottom: Measured elemental compositions in sub-micrometer-sized ash from the same experiments. Data taken from [117].](image2)
According to Suriyawong et al. [117] this is due to the fact that the nucleation and condensation mechanisms are competing. Below a critical concentration of small particles vaporized species tend to nucleate. Above this limit condensation dominates leading to growth in particle size instead of particle number concentration.

Comparing Figs. 43 and 44 leads to the conclusion that increasing the oxygen concentration in oxy-fuel combustion from 20% to between 25 and 40% will produce a particle size distribution similar to that obtained in air for the small size fraction of ash particles. Experiments reported by Wall et al. [138,128] confirm this observation.

A modelling study by Krishnamoorthy and Veranth [210] investigated the effect of particle size, bulk gas composition, and in-furnace temperature during oxy-fuel combustion on the vaporization of metal sub-oxides from the burning char due to locally reducing conditions within the particles. Fig. 45 shows the ratio between CO and CO₂ as a function of radius in a char particle burning in atmospheres of varying CO₂ concentrations.

The results indicate that increasing the CO₂ level in the bulk gas significantly decreases the CO/CO₂ ratio inside the particles even though the absolute concentration of CO increases. Based on equilibrium considerations considering reaction (14) a shift from air-blown to oxy-fuel combustion should thus impose decreased vaporization of refractory oxides from the coal mineral phase during combustion.

### 3.5.3. Ash quality

To the power plants which sell their coal fly ash for cement or concrete production the quality of the ash in this respect is crucial. Especially the sulphur content of the ash is a critical parameter, the concrete production the quality of the ash in this respect is crucial.

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Wall et al. [138] report similar compositions and melting behaviour of both fly and bottom ashes obtained from air and oxy-fuel combustion. The coal with the highest calcium content showed a slightly increased concentration of sulphur. During the experiments emphasis was reported to be on generating the same temperature and heat transfer conditions, i.e. by operating with 27% O₂ on a wet basis in the oxidizer. From their experiments Sheng and Li [125] reported a small increase in the content of limestone due to the higher partial pressure of CO₂ at oxy-fuel conditions compared to air-firing.

For a flue gas recycle without prior sulphur removal the sulphur level in the boiler could increase with a factor of up to 4–5. This significant increase will induce a risk of enhanced sulphur retention in the fly ash [12,115,128,145]. Lowering the flame temperature in the boiler will also increase the possibility of SO₂ retention in ash [12]. Maier et al. [145] state that retention of sulphur in ash does not take place in the radiant section of a boiler due to the temperature being above the 1150 °C which sulphate salts are stable. However, in the convective section the temperature will be lower and the ash will be able to capture sulphur compounds.

Experiments by Croiset et al. [97] on a US eastern bituminous coal have shown that the retention is generally low, i.e. only about 2–3% of the initial S-content in the coal is present in the ash. A later investigation showed that the retention of sulphur in the fly ash is very dependent on the alkaline and alkaline earth content of the ash [122]. For a sub-bituminous coal with a highly alkaline ash they observed that nearly 14% of the initial sulphur content of the coal
was retained in the ash. It is suggested that it is the SO$_3$ in the flue gas that is retained through sulphate salts.

Based on the above, a possible solution could be to restrict the power plants to operate on only low alkaline and/or low sulphur bituminous and sub-bituminous coals and thereby limit the changes in the sulphur content of the fly ash from oxy-fuel combustion. This is however not a desirable restriction for the plant owners as it will reduce the operability of the plants.

The question of ash quality, especially the risk of increased sulphur retention, is still a potential risk for the application of oxy-fuel combustion as a carbon capture technology. The risk is largest for the most frequently proposed process design where flue gas is recycled before the desulphurization plant.

### 3.5.4. Depositions, slagging, and fouling

Early studies on ash deposition, slagging, and fouling at the ANL 3 MWth pilot scale furnace referred by Payne et al. [86] showed that there were no identifiable differences between air-firing and oxy-fuel combustion. However, Glarborg and Bentzen [172] state that the high CO levels in the near-burner region could promote increased corrosion and slagging. Similarly, Schnurrer et al. [115] saw from their equilibrium calculations that the formation of deposits potentially could occur at furnace wall temperatures 30–60 °C higher than what is seen during conventional combustion in air. This may alter the position of deposits and thus potentially necessitate a relocation of soot blowers, etc. At the same time, they expect oxy-fuel combustion to provide a higher propensity for slagging and fouling caused by increased amounts of molten and solid alkali sulphates.

Experiments conducted by Mitsui Babcock Energy, Ltd on a 160 kWe test facility in Renfrew, UK [72], likewise included studies into the impact of oxy-fuel combustion on slagging and fouling. Inserting a deposition probe into the combustion chamber led to the observation of a slightly faster rate of deposition compared to air-firing. The temperature of the probe has not been stated by the author. At the same time the deposition rate was largely independent of the operating parameters such as recycle ratio during oxy-fuel combustion. Also, fouling occurred more rapidly during oxy-fuel than during conventional air combustion. The impact was, however, small and the deposits were easy to remove.

Wall et al. [138,128] collected ash samples from the deposits in the radiative and convective sections of the IHI 1.2 MW test facility. SEM images showed no significant difference between samples from air and oxy-fuel combustion. The furnace deposits, however, contained significantly more sulphur compared to samples collected from air combustion. The deposition rates for the different combustion conditions were different. In the convective section (fouling) the coals tested generally showed increased fouling tendency during oxy-fuel combustion compared to air-firing. The slagging propensity of the different coals tested changed from being higher to less than that in air combustion.

The composition of the deposits from both the radiative and convective sections showed no difference between air and oxy-fuel conditions, except for the SO$_3$ content which was higher (0.65 (oxy) versus 0.2 (air) wt%) during oxy-fuel combustion for the coal with the highest sulphur content (0.88 wt%, dry). This particular coal does, at the same time, have the highest content of alkali and alkali earth metals in the ash prior to combustion. This could be the explanation to the increased sulphur retention, see Section 3.5.3.

A lower conversion of the iron species in the parent coal into oxides can increase the amount of iron melting into glass silicates and thus increase the slagging propensity of the coal. Untransformed FeO-FeS phase with an eutectic temperature of 940 °C will likewise increase the slagging propensity of the ash. This effect of reduced oxidation of iron-bearing species can be seen for relatively low char combustion temperatures and high CO concentrations inside the burning particles. However, no direct comparison between air- and oxy-firing at the same heat transfer rates with respect to slagging has been found. It is thus unknown, whether incompletely oxidized iron will induce a problem in a full-scale boiler.

Deposit sampling tests performed by Mönckert et al. [147] indicate that besides sulphation, carbonization of deposit surfaces occur. The most obvious reason is that the decomposition temperature of carbonates will increase due to the high partial pressure of carbon dioxide [4]. However, the implications of this observation is not clear.

The investigations reported till now indicate that the changes to depositions in an oxy-fuel plant compared to an air-fired unit will not be of essential significance to the plant operation.

### 3.6. Oxy-fuel combustion of biomass

Carbon capture and storage from combustion of biomass has the potential to reduce the CO$_2$ emission to below zero, i.e. to extract CO$_2$ from the atmosphere and possibly limit the anticipated global warming [84,157,180,211–214]. The abbreviation BECS is used to denote the concept of Biomass Energy for Carbon Capture and Sequestration [213–215]. In principle, all CCS technologies suggested for fossil fired power systems can be applied to systems utilizing biomass fuels [216].

This section contains a survey of the very limited amount of literature available on the use of biomass in oxy-fuel combustion. The main type of biomass investigated is wood. This is a natural consequence of its abundance compared to other types of biomass, such as straw and other annual plants, olive residues, or other dedicated energy crops. Additionally, the transport and feeding of wood is easier to perform than for herbaceous energy sources.

When utilizing biomass in oxy-fuel combustion it is important to consider whether there are any special issues regarding biomass compared to coal which could have a significant impact on the combustion process and related phenomena. Of particular importance will be the volatile matter content, the ash composition, i.e. the content of Cl and alkali, and the change in fuel particle size. At the same time, in order to conclude on specific aspects related to the change of combustion atmosphere when co-firing coal and biomass it is necessary to compare the reported results with the behaviour of these types of fuel blends in conventional combustion.

#### 3.6.1. The combustion process

Arias et al. [180] have investigated the ignition behaviour of coal/biomass blends during oxy-fuel combustion and the effect of oxy-fuel conditions on burnout. Their experiments are performed in an electrically heated entrained-flow reactor (EFR) at about 500 °C for ignition tests and 1000 °C for combustion tests. Both fuels are ground and sieved to a particle size of 75–150 μm. Oxy-fuel combustion with 21, 30, and 35 vol% oxygen were compared with results obtained in air, see Fig. 46. As has previously been seen for pure coals, a delay in ignition (higher ignition temperature) is observed as the oxygen concentration in the oxy-fuel oxidizer is reduced. From these experiments the relative effect of oxygen concentration is nearly independent of the type of fuel.

In air there is a reduction in the ignition temperature when the bituminous coal is blended with the biomass, see the three most left-hand-side bars in the figure for each case. The effect is, however, much less pronounced in the case of oxy-fuel combustion regardless of the oxygen concentration. This can be attributed to the fact that even though the biomass has a high reactivity and a high volatile matter content the heating value is lower than for the coal. The heat released from the biomass during ignition is thus
not substantial to enhance the heating of the coal particles and the
ignition temperature is thus not increased significantly. As previ-
ously described, more heat is needed to increase the temperature of
the surrounding gases and hence the coal particles in the case of
oxy-fuel combustion than for combustion in air [180].

Results of burnout experiments for the same high-volatile coal
and its blends with Eucalyptus are shown in Fig. 47. An obvious
difference in burnout degree is seen for all three cases when
changing the combustion atmosphere from air to CO2-based. In
oxy-fuel combustion with an air-like oxidizer composition the
burnout degree decreases below that found in air. For oxygen
concentrations of 30 and 35% the burnout increases above that
found in air. However, the effect of blending biomass and coal is
seen to have only little impact on the burnout, i.e. there is only a
minor improvement by an increasing biomass content in the
blend.

Because of the significantly higher volatile content in biomass
compared to coal an improvement in the burnout degree of the fuel
blends could be expected. However, reported data do not confirm
this. Arias et al. [180] explain the lack of improvement in burnout for
the blends in terms of the changes in oxygen and temperature
profiles in the reactor caused by the introduction of the more reactive
biomass fuel.

Characteristics of wood chip, rice husk, and forest residues chars
obtained by pyrolysis in air and oxy-fuel atmospheres were
investigated by Borrego et al. [217]. They saw that the char char-
acteristics such as pore volume, morphology, optical texture, specific
surface area, and reactivity showed no significant difference
between air and oxy-fuel combustion. The authors thus concluded
that the application of biomass in co-fired oxy-fuel boilers (coal/biomass)
should not constitute any specific difficulties regarding the chars.

3.6.2. Emissions

In commercial-scale tests co-firing coal and biomass in air, large
decreases and moderate increases are occasionally observed for the
NOx yields [218]. Tests by Robinson et al. [218] have shown that
these changes most probably are caused by the biomass influencing
fluid dynamics as well as temperature and stoichiometry profiles
during the combustion. No fundamental synergistic chemical
effects could be observed. The coals tested were bituminous
whereas the biomass were red oak wood chips and switchgrass.

Fryda et al. [184] have found that the NOx emission rate during
oxy-fuel combustion can be decreased when coal (Russian) and
biomass in the form of cocoa residues are co-fired in a lab-scale
setup compared to tests with pure coal. Generally, using over-fire
air (OFA) reduces the emission rate. The cocoa residues have
a higher content of N compared to the pure coal (2.61 versus
0.87 wt%, dry basis) and thus has the fuel blend. The decrease in
NOx emission rate can thus be explained by the increased volatile
content and the related, lower amount of fixed carbon in the blend
compared to the pure coal.

Emissions of SOx from oxy-fuel combustion of pure biomass or
carbon and biomass blends have not been reported in open literature.

3.6.3. Ash and corrosion

Robinson et al. [218] have investigated the ash deposition rates
from both individual fuels and their blends (wood chips, coal,
switchgrass, and wheat straw) during conventional combustion in air.
They observed that the particle capture efficiency (the ash deposition
rate normalized by the fuel ash content and the size of the deposition
probe) was significantly larger for straw than for wood chips and coal
in the order: wood chips < coal < switchgrass < wheat straw. The
order is closely related to the absolute amount of alkali in the fuels.
Blending coal and biomass, especially straw, yield deposition rates
which are lower than what would be expected based on the behaviour
of the unblended fuels, see the upper part of Fig. 48. Especially in the
case of co-firing coal and straw the particle capture efficiency is
markedly reduced compared to the predicted value (about 10%).
Sulphation of alkali chlorides released from the straw with sulphur
from the coal is expected to account for part of the observed effect
[218]. The main effect is due to incorporation of mainly potassium
from the biomass into alumina-silicates in the coal ash followed by
release of HCl, see (15).

\[
\begin{align*}
(AI_2O_3)(SiO_2)_2 + 2KCl + H_2O &\rightarrow (K_2O)(AI_2O_3)(SiO_2)_2 + 2HCl \\
\end{align*}
\]

(15)

This is a recognized method for reducing corrosion in biomass
fired boilers.

In the bottom part of Fig. 48 the capture efficiency is calculated
based on the amount of available alkali in the blend. It is clearly
seen that this is a better measure of the slagging and fouling
tendency of the fuel blends.

Studies of deposition and fouling in oxy-fuel combustion per-
formed by Fryda et al. [184] have shown no significant change in

Fig. 47. Burnout of a high-volatile bituminous coal (DA) and blends of
the coal and Eucalyptus (RE) at a stoichiometric value of 1.25. Experiments are performed in air and
oxy-fuel atmospheres with different oxygen concentrations at the inlet of the
entrained-flow reactor setup used. The blending ratio is presumably given on a mass
basis. Data taken from [180].
deposition rate between pure coal and coal/biomass blends (cocoa residues and wood chips). The coal to biomass ratio in the blends is 80/20 on a mass basis. The coal/wood blends slightly increase the specific fouling factor, whereas blends with cocoa residues slightly decreases the fouling factor. This correlates well with the results obtained by Robinson et al. [218].

In relation to the aspects of corrosion and ash quality during co-combustion of coal and biomass at oxy-fuel conditions the sulphur and alkali contents of the parent fuels could induce both advantages and disadvantages. If the concentration of sulphur in the boiler during oxy-fuel combustion is enhanced there is a larger potential to convert alkali chlorides released from the biomass to sulphates before the flue gas meets the superheater banks and deposition occurs. The corrosion potential could thus be reduced. On the other hand, the higher alkali content in biomass ashes, and especially straw, will potentially increase the sulphur retention in the fly ash when co-firing with coal as described in Section 3.5.3.

3.7. Summary

Below is a short summary of the main findings presented in Section 3.

Research Groups: 26 research groups with different experimental equipment doing oxy-fuel combustion studies have been identified. The experimental setups range from 4.2 kWth to 30 MWth in size and include units both with and without flue gas recirculation.

**Heat and Mass Transfer:** The differences in thermo-chemical properties between CO₂ and N₂ cause changes in the heat and mass transfer rates within a boiler if CO₂ is substituted directly for N₂ in the oxidizer. In order to obtain an adiabatic flame temperature during combustion similar to that seen in air-firing the oxygen concentration in the oxidizer should be increased to 27–35 vol% depending on the type of fuel. Lower rank coals require lower oxygen concentrations than higher rank coals. CO₂ and H₂O are radiating gases whereas N₂ is not. The radiative heat transfer in oxy-fuel combustion is thus higher than in air combustion for the same flame temperature. In order to match the heat uptake profile in a retrofitted boiler the flame temperature should thus be kept lower than during air operation.

**Combustion Process:** Devolatilization and ignition of coal particles are affected by the change in oxidizer composition from air to oxy-fuel combustion. The rate of devolatilization is primarily determined by the surrounding gas temperature as the difference in thermal conductivity of N₂ and CO₂ is rather low. Particle ignition, on the other hand, is a strong function of both the transport properties of the gas phase surrounding the particles as well as the combustion heat release rate and the reactivity of the local fuel-oxidizer mixture. Ignition times comparable to those observed during air combustion can be obtained by increasing the oxidizer oxygen concentration to 27–35 vol% and thus the flame temperature. Burnout of volatiles and char are likewise affected by the high CO₂ and H₂O concentrations in the flame. Especially the lower diffusivity of both oxygen and small hydrocarbons in CO₂ compared to N₂ is an important factor. Generally, a slight improvement in char burnout is reported in the literature when the flame temperature matches that of air combustion. This improvement is assumed to be caused primarily by the higher oxygen partial pressure experienced by the burning particles. Gasification reactions and residence time differences are believed to be of minor influence.

Due to the high CO₂ concentration in the combustion environment high levels of CO are expected in the near-flame zone. There is thus an increased risk of CO corrosion in this zone. Because of the large oxygen partial pressure the CO is reported to oxidize before leaving the larger of the test furnaces yielding similar CO emission rates as for air combustion.

**Emissions:** NOₓ emissions from oxy-fuel combustion is probably the single most investigated area of this technology. Due to the very low levels of molecular nitrogen a potential exists to reduce the emissions rate considerably compared to combustion in air through near-elimination of both thermal and prompt NOₓ formation. Reductions by 70–80% have been reported. Different suggestions to the mechanisms responsible for the reduction have been proposed. However, it is generally accepted that reburning reactions play a major role. Experiments indicate that increasing the oxygen concentration and the oxygen excess yield higher emission rates. On the other hand, the use of oxidant staging, recycling of flue gas before drying, increasing the partial pressure of NOₓ in the oxidant, increasing the oxygen purity, and limiting the air ingress into the boiler work to decrease the emission rate.

Sulphur oxides is the other major pollutant from coal-fired combustion. The emission of these oxides is not reduced to the same degree as NOₓ. However, increased retention in ash due to the higher partial pressure of SO₂ in the boiler when flue gas is recirculated before the desulphurization unit has been reported. Increased risk of low-temperature corrosion by sulfuric acid and a higher acid dew point are some of the major concerns regarding sulphur in oxy-fuel combustion.

Limited work has been reported on the emission of trace elements from oxy-fuel combustion. The work performed has focused on Hg, Cd, As, and Se with Hg attracting the most attention.
No significant differences between air-firing and oxy-fuel combustion have been reported at this point.

Ash and Depositions: The transformations of coal mineral matter during combustion are affected by the temperature and the gas phase composition surrounding the coal particles. At low combustion temperature (for below 30% O2 in CO2) a shift in the size distribution of the sub-micrometer-sized fly ash toward smaller particles can be observed. Increasing the O2 partial pressure provides a size distribution similar to that found in air combustion. The ash quality is crucial to its application in cement and concrete production. Significantly increased sulphur retention could cause problems in this respect.

The propensity for slagging and fouling in oxy-fuel combustion is likewise subject to research. At this point, the reported results suggest that only minor changes compared to air-firing will result from the change in the combustion environment.

BECS: Utilization of renewable biomass fuels such as wood, straw, and other energy crops in thermal power plants with carbon capture and storage is attracting increased attention. The combination of CO2 neutral fuels with CCS opens a possibility of extracting CO2 from the atmosphere. Until now, only few experiments on oxy-fuel combustion of biomasses have been reported. It is expected that further work on BECS will reveal comparable changes to the combustion fundamentals as is the case when biomass is introduced during combustion of coal in air.

4. Conclusions

The reduction of CO2 emissions from power plants has become an increasing important topic in the discussions of how to prevent global warming arising from anthropogenic CO2 emissions. Three CCS (Carbon Capture and Storage) technologies have been suggested for medium term application which will reduce the emissions to near zero; Chemical absorption by amines (post-combustion capture), Integrated gasification combined cycle plants (pre-combustion capture), and oxy-fuel combustion capture. Of these, the post-combustion and oxy-fuel technologies can be applied as retrofit solutions to the existing fleet of pulverized-coal-fired power plants. Compared to post-combustion capture oxy-fuel combustion is less mature and thus requires comprehensive fundamental research as well as pilot and demonstration scale testing before commercial operation of an oxy-fuel power plant seems to be feasible. Currently, no full-scale oxy-fuel plants are in operation. The only announced large demonstration plant (250 MWt) is planned to be put into operation in 2015 by Vattenfall. Commercial operation does thus not seem to be feasible before 2020.

The current literature review describes the available knowledge on the oxy-fuel technology. The focus has been on both the changes induced to an existing, conventional air-fired plant if retrofitted to oxy-fuel combustion and the research performed on the fundamental combustion characteristics including heat transfer effects, ignition and burnout, emissions, ash quality, and deposit build-up. Both coal and the application of CO2 neutral fuels such as wood or other types of biomass are included in the review.

Retrofitting an existing pulverized-coal-fired power plant to oxy-fuel operation requires a number of new process units – an air separation facility to provide the combustion process with almost pure oxygen, ducts and fans for external recirculation of flue gas to the burners in order to control flame temperatures, and a CO2 processing facility producing a near-pure CO2 stream for storage. The retrofit to oxy-fuel operation will reduce the plant electrical efficiency by about 10 percent points depending on the initial efficiency. It is generally accepted that a 95% pure O2 stream constitutes the optimum with respect to minimizing the combined expense for air separation and CO2 cleaning. Leakage of air into the boiler necessitates removal of non-condensable species from the CO2 stream prior to storage. The capture efficiency of an oxy-fuel power plant is thus expected to be around 90%. Two flue gas recycle streams are necessary. The primary stream is used for coal drying and transportation to the burners and should preferably be desulfurized and dry. Most process configuration suggestions avoid addition of O2 to the primary stream. Instead, O2 is added either to the secondary flue gas recycle stream or directly through special lances in the burners. The overall O2 concentration at the inlet to the boiler should be between 27 and 35 vol% in order to yield comparable adiabatic flame temperatures and heat transfer profiles as seen for conventional combustion in air. The exact level depends on the type of coal and the boiler design. Even though CO2 has significantly different thermo-chemical properties compared to N2, increasing the O2 concentration in oxy-fuel combustion yields similar devolatilization and ignition behaviour in the two environments. The burnout is reported to improve in oxy-fuel combustion. The emission rate of CO is reported to be similar in air and oxy-fuel combustion even though significantly increased CO levels are seen within the flame zone in the oxy-fuel environment. SO2 emissions are likewise reported to be of similar magnitude regardless of flue gas composition. The NOx emission is, however, significantly reduced during oxy-fuel combustion compared to air-firing due to a near-elimination of thermal NO formation and to reburning of NOx passed through the burners with the recirculated flue gas. Reductions of the emission rate by 70–80% have been reported. Only minor changes to the deposit build-up are expected for oxy-fuel combustion compared to air-firing. However, the oxy-fuel environment is expected to lead to a significant increase in the SO3 concentration within the boiler increasing the risk of both high and low-temperature corrosion as well as increased retention of sulphur in the fly ash.

A significant amount of new information on the oxy-fuel technology has been published since Wall and coworkers released their literature survey in 2005. At that time the following research needs were concluded to require the most attention in order to gain a deeper fundamental understanding of the oxy-fuel technology:

- Match of heat transfer characteristics in retrofitted boilers.
- The cost of electricity and the cost of CO2 avoided.
- Combustion characteristics and emission levels (pilot plant scale).
- Requirements for gas cleaning – especially SO2.

Based on the fact that no full-scale plants are in operation, the required large-scale investigations of heat transfer characteristics still remain. Additional work on both convective and radiative heat transfer in laboratory-scale reactors has however been conducted. Several techno-economic assessments of the oxy-fuel technology exist and new are continuously being published. However, the estimated costs of electricity and CO2 avoidance costs generally suffer from large uncertainties due to the lack of construction and operation experience from full-scale plants.

Few results regarding combustion characteristics and emission levels in pilot plant scale setups (>1 MWth) have been published within the last five years. This area thus needs continued attention. Suggestions to the purity requirements for CO2 for sequestration and enhanced oil recovery have been published. No standards or legislative requirements have however been found. Clarification of the necessary extent of cleaning is very important to plant configuration and eventually the process economics.

Besides the topics discussed above, this review has revealed that a deeper understanding of the effect of a shift from air-blown combustion to oxy-fuel combustion on the following issues is necessary:
- Optimum oxygen excess and inlet oxygen concentration levels.
- Corrosion at both high and low temperatures.
- Ash quality, especially regarding the risk of enhanced sulphur retention.
- Operability, i.e. start-up and shut-down, dynamics during transients, the need for air-firing capability, etc.
- Models to predict NO₃ and SO₃ formation.

The oxy-fuel combustion process is still in the developing phase and much research is still required in order to fully clarify the consequences of its implementation in power plants.

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References


