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Combustion processes for carbon capture

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Abstract

A review of the technologies for coal-based power generation closest to commercial application involving carbon capture is presented. Carbon capture and storage (CCS) developments are primarily adaptations of conventional combustion systems, with additional unit operations such as bulk oxygen supply, CO_2 capture by sorbents, CO_2 compression, and storage. They use pulverized coal combustion in entrained flow—the dominant current technology for coal-based power, or gasification in entrained flow, although similar concepts apply to other solid–gas contacting systems such as fluidized beds. Currently, the technologies have similar generation efficiencies and are associated with efficiency penalties and electricity cost increases due to operations required for carbon capture. The R&D challenges identified for the combustion scientist and engineer, with current understanding being detailed, are those of design, optimisation and operational aspects of new combustion and gasification plant, controlling the gas quality required by CCS related units and associated emission compliance, and gas separations. Fundamental research needs include fuel reactions at pressure, and in O_2/CO_2 atmospheres, as few studies have been made in this area. Laboratory results interpreted and then included in CFD models of combustion operations are necessary. Also identified, but not detailed, are combustion issues in gas turbines for IGCC and IGCC-CCS. Fundamental studies should be a component of pilot-plant and demonstrations at practical scale being planned. Concepts for new designs of combustion equipment are also necessary for the next generation of technologies. The challenges involved with the design and operation of these integrated systems, while supplying electricity on demand, are considerable.

Keywords: Carbon capture; Gasification; Oxy-fuel; PCC; IGCC

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1. Introduction

Energy production from fossil fuel combustion results in the emission of greenhouse gases, the dominant contributor being CO_2. Public awareness and legislation have led to a policy of reduction of greenhouse gas emissions in most economically well-developed countries, with the regulations partially driven by (international) initiatives such as the Kyoto protocol and the Intergovernmental Panel on Climate Change [1]. Greenhouse gas emissions from energy production can be reduced by the use of alternative energy sources such as nuclear power and renewable energy. Renewable energy sources are increasingly used, however, until these sources can reliably produce significant amounts of energy, the immediate energy demand is likely to be met by conventional fossil fuel combustion, as indicated by energy policies and use projections [2,3].

To reduce greenhouse gas emissions from fossil fuel-fired power generation, several possibilities exist:

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- Improving efficiency of power plants.
- Introduction of combined cycles with generation by gas and steam turbines, which can achieve high thermal efficiencies.
- Replacement of hydrocarbon fuels with renewable resources.
- Substitution of coal by gas (having a lower carbon content).
- CO_2 capture and storage (called CCS).

Incremental reduction of greenhouse gas emissions can be achieved by the first four options, however, to make a step-change reduction in emissions, the CO_2 generated from combustion needs to be captured and stored (or sequestered).

Over the past decade, the role of coal as an energy source has remained due to its wide availability (geographically and as traded coal), stability of supply, and cost. However, coal emits more CO_2 than other fuels, and the lowest cost for CO_2 reduction may be a decision between gas firing (expensive fuel—cheap technology) and coal firing with CCS (inexpensive fuel—more expensive technology). Several coal technologies are therefore being progressed with CCS, and this paper reviews the status of the technologies, foreseen developments, their combustion issues, and R&D needs.

2. Carbon dioxide capture and storage (CCS) benchmarking

Technologies that are being developed for CO_2 capture and sequestration from combustion and gasification technologies include [4]:

- CO_2 capture from plants of conventional pulverized fuel (pf) technology with scrubbing of the flue gas for CO_2 removal, here called post-combustion capture (PCC).
- Integrated gasification combined cycle (IGCC) with a shift reactor to convert CO to CO_2, followed by CO_2 capture, which is often called pre-combustion capture, here called IGCC-CCS.
- Oxy-fuel (Oxyf) combustion, with combustion in oxygen rather than air, and the oxygen is diluted with an external recycle flue gas (RFG) to reduce its combustion temperature and add gas to carry the combustion energy through the heat transfer operations in the current first generation technology.
- Oxy-combustion with an internal recycle stream induced by the high momentum oxygen jets in place of external recycle. This technology is now widely used in the glass industry and, to a lesser extent, in the steel industry.
- Chemical looping which involves the oxidation of an intermediate by air and the use of the oxidized intermediate to oxidize the fuel.

This review covers the first three options, as these are the closest to commercial application involving carbon capture. All three are being developed through planned demonstrations (at 30–300 MW, some involving sequestration), with government and industry funding in the US, EU, Japan and Australia. Commercial availability is targeted from 2015 to 2020. The technologies are primarily based on pulverized coal combustion in entrained flow—the dominant current technology for coal-based power, or gasification in entrained flow, although similar concepts apply to other solid–gas contacting systems such as fluidized beds. PCC and Oxyf involve combustion, IGCC involves gasification, CO_2 capture and H_2 separation. IGCC uniquely produces H_2, which can be utilized for heat and power and also potentially as a transport fuel. All technologies include compression of the CO_2 product to a supercritical state, typically 10 MPa, prior to transport and geological storage at a depth (and thereby pressure) retaining this state.

Table 1 compares the main characteristics of the CCS options and Figs. 1–3 give flow sheets. PCC and Oxyf may be retrofitted to an existing plant, PCC and IGCC-CCS can be applied to partial capture from the flue gas. IGCC may use O_2 rather than air as the oxidant to establish higher proportions of CO_2, only Oxyf does not require CO_2 capture prior to compression. Entrained flow systems use similar combustion temperatures of 1300–1700 °C, IGCC uniquely uses high pressures of 2–8 MPa, with 2–3 MPa typical for IGCC without CCS and 7–8 MPa being proposed for IGCC-CCS.

As shown on Fig. 1, PCC can use established technology applied in chemical and natural gas processing for CO_2 and SO_2 removal, with

Table 1
Comparison of main characteristics of CCS options, with desirable characteristics indicated by X

Technology	Suitable for retrofit of existing pf plant	Can be applied on slip-stream, i.e., for partial CO_2 capture	Does not require O_2 supply	Does not require CO_2 capture prior to compression	Generates H_2 as alternative fuel
PCC	X	X	X		
IGCC-CCS		X, but unlikely			X
Oxyf	X			X	

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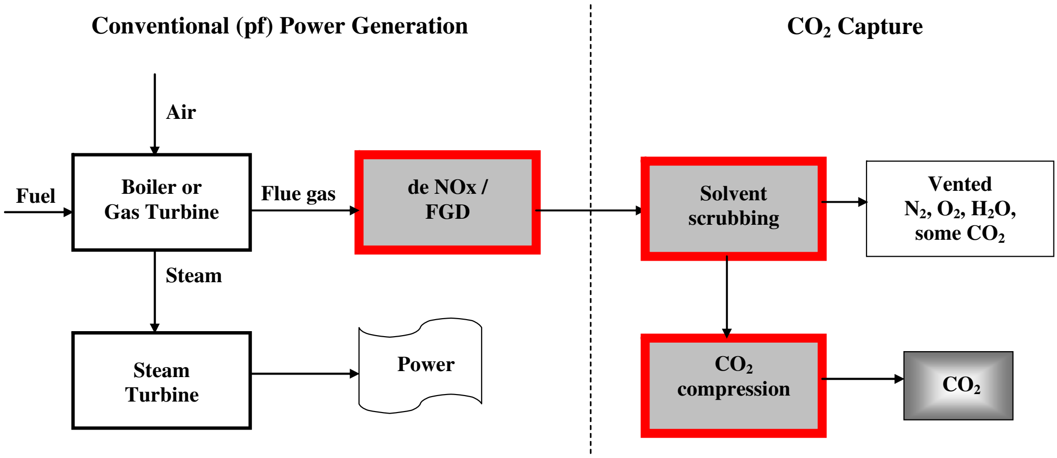

Fig. 1. Illustrative flowsheet for PCC (post-combustion capture) process, with additional unit operations for carbon capture shown bold.

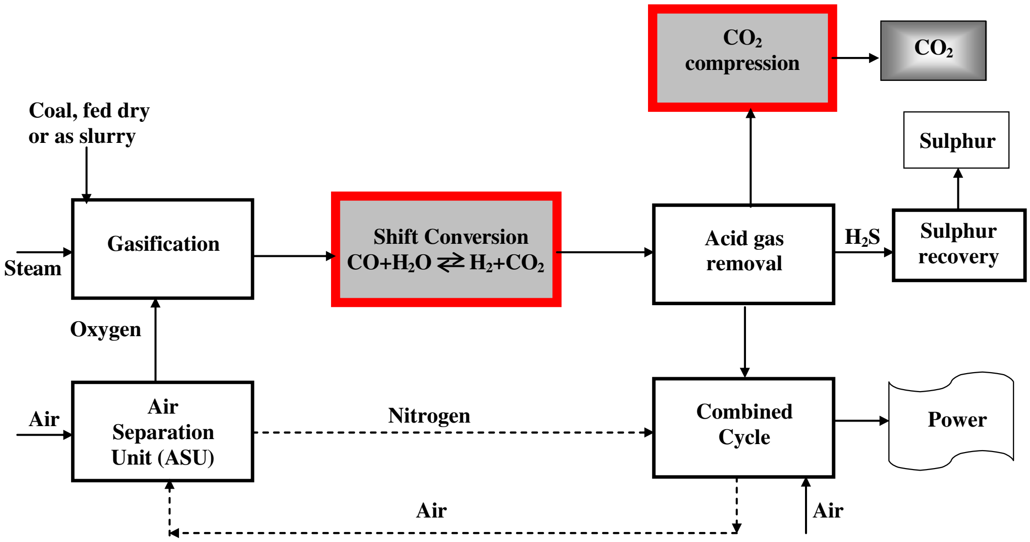

Fig. 2. Illustrative flowsheet for IGCC (pre-combustion capture) process, with additional unit operations for carbon capture shown bold.

CO_2 scrubbed using chemically active agents that are regenerated by heating to release CO_2. Amines such as monoethanolamine (MEA) and methyldiethanolamine (MDEA) are primarily considered. As shown on Fig. 2, in its CCS form the IGCC gasifier product gas is converted to additional H_2 and CO_2 using a shift reaction, with the H_2 burnt in a gas turbine with N_2 as a diluent. As shown on Fig. 3, Oxyf involves combustion in an oxygen/recycled flue gas mixture, containing about 30% O_2 to maintain similar furnace heat transfer, with the CO_2 rich gases being cooled and compressed. No CO_2 separation is required. All three technologies are associated with higher generation costs with energy penalties for CO_2 compression, for O_2 production for IGCC and Oxyf, and for CO_2 capture for PCC and IGCC.

Many recent studies [5–8] have compared the three technologies in terms of efficiency of generation with and without capture, the contributions to increased costs, and the cost of electricity (COE) with carbon capture with comparisons of COE with a CO_2 tax or penalty, as given on Figs. 4–6. Figure 4 indicates that the efficiency penalties vary from 7% to 10%, with efficiencies for technologies with carbon capture being typically 35% LHV (apart from the IGCC-CCS slurry system,

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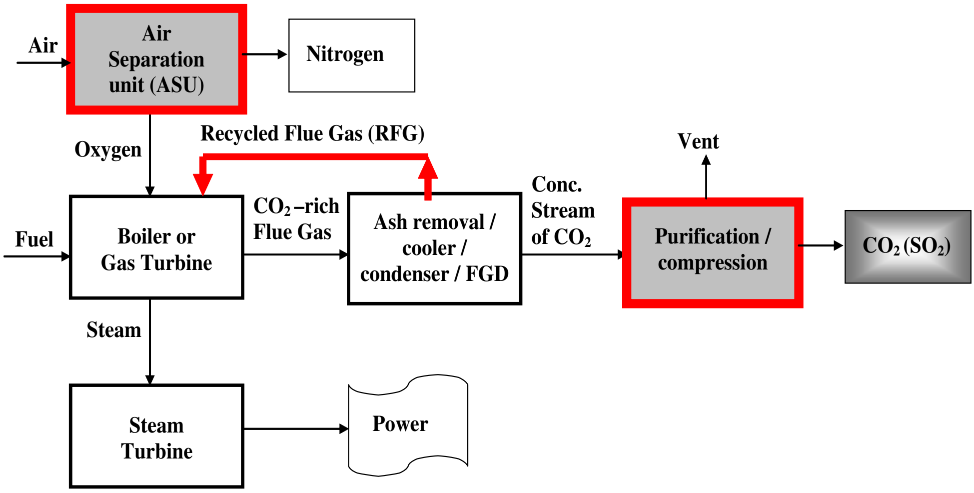

Fig. 3. Illustrative flowsheet for oxy-fuel (Oxyf) process, with additional unit operations for carbon capture shown bold.

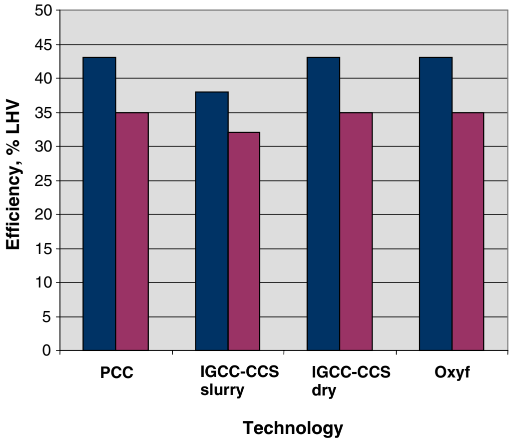

Fig. 4. Efficiency comparisons without (left) and with (right) capture, with transport and storage neglected, from IEA studies [100–102]. IGCC technologies are for dry and slurry (wet) feeding of coal.

which has a lower efficiency due to the additional water addition).

Important contributors to efficiency losses are: PCC—solvent regeneration, CO_2 compression, IGCC-CCS—oxygen production, CO_2 compression, Oxyf—oxygen production, CO_2 compression.

An implication of the comparisons given on Fig. 4 is that CCS is best applied to high efficiency plant, where the penalties are a lower proportion of the non-CCS efficiency. In addition, efficiencies of power technologies are improving, so that the energy associated with the efficiency penalty will reduce over time.

Increases of costs due to additional operations and increased fuel use (due to reduced efficiency);

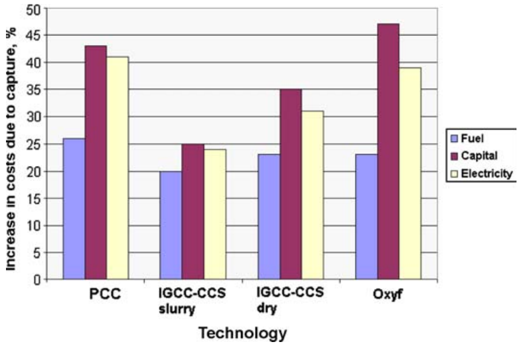

Fig. 5. Increases in costs due to additional operations and increased fuel usage relative to the same base plant without capture, from IEA studies.

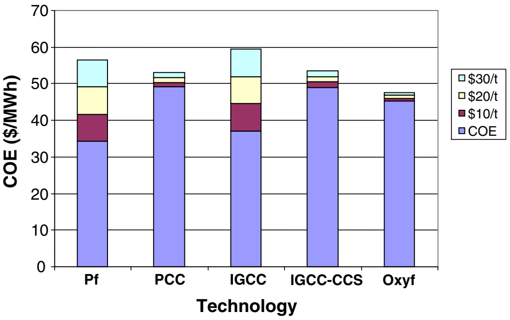

Fig. 6. Cost of electricity (COE, in US$) without capture (pf and IGCC) and with capture indicating the incremental impact of a carbon tax in \$/t CO_2, to allow estimation of the tax justifying carbon capture. Transport and storage neglected. Ten percent DCF, coal \$1.5/GJ, \$ taken as equivalent to Euro. Data adapted from IEA studies.

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given on Fig. 5, do differ with the combustion systems having greater increases, but from a lower base for non-CCS systems for capital and electricity costs. Fig. 6 compares estimates of the COE, with and without capture, including the impact of a carbon tax, at several levels of \$/t CO_2 to allow estimation of the tax justifying CCS technology implementation. For example, the COE for pf and PCC are approximately matched with a tax of \$25/t CO_2, IGCC and IGCC-CCS at \$20/t CO_2, and pf and Oxyf at \$15/t CO_2. These values, and Fig. 5, are based on a common availability. IGCC is claimed by technology providers to be a proven technology, but currently has a lower availability than pf plant, a major factor influencing COE and technology of choice.

An additional comparison basis used [5–8] is the cost of CO_2 avoided (COCA)—the difference in cost of CCS and non-CCS systems per CO_2 avoided. The comparison can be considered to apply when a CCS technology substitutes for a non-CCS system, referred to as the baseline system. COCA depends on many factors, such as the baseline system chosen, the fuel cost, efficiency of technology (or particular plant) to which CCS is applied and a commonly assumed annual operation of 75:00 h is used which, for example, is unlikely for immature technologies. For coal fired—CCS substituting for coal pf (i.e., coal baseline), the same values derived above from Fig. 6 apply, for coal-CCS and gas-baseline values exceed \$125/t CO_2, for gas-CCS and coal-baseline values are less than \$5/t CO_2, indicating the impact of fuel substitution.

Figures 4–6 provide general comparisons. Detailed assessments depend on local factors, emission standards and assumptions such as an assumed annual operation of 75%, which is unlikely for immature technologies. But the studies indicate that currently the three capture technologies do not differ greatly.

Research can be expected to reduce the energy penalty. For example, energy for O_2 production using an air separation unit (ASU) is the major factor in the penalty for Oxyf and IGCC-CCS, and requires 200 kWh/t CO_2, with 30 kWh, being the theoretical energy requirement to compress O_2 from 0.21 to 1 atm [9], a target for membrane separation. ASUs consume more than six times the theoretical energy requirement. Although the unit energy consumption to produce O_2 by cryogenic processes continues to decrease, a step change technology is needed in the long term for CO_2 sequestration applications.

The CCS technologies are continuously being developed, will improve following demonstration, and all are expected to find application in a regulatory environment with costs for CO_2 release. The review will therefore consider all three in more detail.

3. Gas quality and emission targets

Before considering the combustion implications of CCS, the gas quality aspects of CCS will be considered, as the technologies must meet emission targets and the combustion processes must provide the required gas quality. Table 2 gives suggested zero emission technology (ZET) targets from an IEA report [7], including those for CO_2. The current emissions are for "good" current plants, the ZET targets are projections based on progressive improvement in emission technology and legislative pressures. Mercury targets are also suggested. The pf + flue gas desulphurisation (FGD) emission of Table 2 may be compared with a typical natural gas combined cycle current CO_2 emission of 370 kg/kWhe, which can be matched for the coal ZET systems with ~50–60% removal. With all CO_2 sequestered, Oxyf has no stack gas and therefore zero CO_2 emissions.

Nominal CO_2 capture levels of 80% are indicated in Table 2, this being project specific and determined by the relationships between the CO_2 partial pressure, capture % and the energy for compression. For example, for Oxyf, unavoidable air leakage into the boiler is determined by the boiler itself, and reduces the CO_2 partial pressure (demonstrations planned have specified >80% CO_2 (dry), the balance being N_2, Ar and O_2), and >80% capture.

The quality of the gas provided by the technology has an impact on the CCS system. As

Table 2
Zero emission technology (ZET) targets, and stack gas concentrations at 6% O_2, dry [7]

Technology	SO_2 emissions (mg/m^3)	NO_x emissions as NO_2 (mg/m^3)	Particulates (mg/m^3)	Hg removal (%)	CO_2 (kg/kWhr)
Pf + FGD	100–400, ~90–98% removal	100–200 (with selective catalytic reduction)	10–25		710–920
IGCC	98–99% removal	<1	<1		>80% removal
PCC target ZET	<100 interim (2015) <30 eventual	<100 interim (2015) <50 eventual	<10	90%	>80% removal
IGCC target ZET	<25	<25	<1	90%	>80% removal
Oxyf target ZET	(No stack gas)	(No stack gas)	(No stack gas)	(No stack gas)	(No stack gas)

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Table 3
Gas quality and CO_2 capture impacts

CCS technology	CO_2 % v/v (dry) prior to capture	Other gases	Comments on impacts
PCC	5–20	Primarily N_2 from air, O_2 from XS air, NO_x and SO_x from converted fuel N and S	Chemical solvents for CO_2 react irreversibly with SO_x, NO_2 and O_2 with solvent loss. Equipment corrosion
IGCC-CCS	15–60, for O_2 blown gasifier	CO_2 levels from shift reactor, balance being primarily H_2, with impurities	Sulfur removed prior to shift reactor. CO_2 capture at elevated pressure prior to gas turbine, impurities influencing both.
Oxyf	80–95	N_2 from air leakage (~3% typical), O_2 from XS O_2 and air leakage, Ar from ASU supply of O_2. NO_x is reduced by 50–75% due to reactions of recycled NO_x, SO_x is typically 3 × air firing	CO_2 levels determine recovery and energy for compression, NO_x reduction a technology driver in some countries, SO_x levels associated with corrosion and may restrict to low S fuels. SO_2 remains with CO_2 on compression, and may result in avoidance of FGD if CO_2 is sequestered

given in Table 3, the CO_2 concentrations and system pressures are quite different, with PCC and IGCC-CCS therefore requiring different solvents for capture. Minor gases, also listed on Table 3, have impacts on CO_2 capture and recovery. PCC captures CO_2 at atmospheric pressure with low CO_2 partial pressures, and therefore uses a liquid solvent. IGCC-CCS captures CO_2 from a high pressure gas, allowing a physical sorbent to be used.

The state and composition of the gas following capture is determined by the storage method. Enhanced oil recovery (EOR) is a mature technology, with a specified gas quality of >95% CO_2, <10 ppm O_2 for safety requirements, with Ar and NO levels to determine a minimum miscibility pressure (MMP). Sequestration in aquifers requires compression to the supercritical state at pressures exceeding 80 atmospheres, when SO_2 is retained with CO_2. Assessments, such as those presented on Figs. 4–6, assume that SO_2 may be sequestered with the CO_2, with scrubbers for removal not included, and their cost not considered. This possibility will be determined by future regulation and community attitude.

4. Combustion processes and carbon capture technologies

The development of carbon capture technologies has been rapid in recent years, and many R&D needs have been identified, some of which are combustion related, as identified in Table 4. The technology related issues have a primary focus on cost reduction, including O_2 production and CO_2 capture. The combustion related issues depend on the technology developments, for example, the gas quality tolerance of CO_2 capture. Combustion conditions include high pressure and O_2/CO_2 environments.

4.1. Post combustion capture

PCC is based on solvents developed many years ago, technologies are commercially available and applicable to existing plants, and are proven at small scale. There are several facilities where CO_2 is recovered from flue gas [10] at rates up to 800 t/d [11].

Amines-based solvents are suited to the lean combustion CO_2 concentrations of flue gas (12–15 v/v% for coal and 4–8% for gas fired plants [12]), but require a large amount of energy to regenerate the solvent (in the solvent stripper), this being as much as 80% of the total energy of the process. A generation efficiency loss results, requiring the use of additional fuel.

The significance of the energy requirements depends on the efficiency of the plant to which PCC is attached (either new or as a retrofit), so that the development of materials to allow higher efficiency (temperature) steam cycles is significant for PCC, as it is for oxyfuel for the same reason.

There are also interactions between the CO_2 capture system and the control of other emissions such as acid gases as given on Table 4 in that SO_2 and NO_2 react with MEA to form heat-stable salts that reduce the CO_2 absorption capacity of the solvent. Gas cleaning to 10 ppm levels is desirable to avoid the loss of costly solvent [10]. As NO_x is mostly NO and typically 5% NO_2, SO_2 is the main issue. The addition of costly SO_x scrubbers are required where local emissions regulations do require these units, with more efficient gas cleaning even for operations with existing scrubbers. Combustion optimisation to reduce acid gases in flue gas will reduce operating costs, but is not a consideration in current research on PCC.

O_2 in the flue gas also causes degradation of the amines with the byproducts leading to corrosion problems, necessitating chemical inhibitors or process modification involving deoxidation of the CO_2-rich amine [13]. Combustion for lower O_2 levels reduce operation costs.

Table 4
R&D requirements for technologies

Technology	Combustion related			Technology related
	Fuel conversion	Emissions	Other	
PCC		NO_x, SO_x and Hg removal, consistent with solvent tolerance		Materials for high efficiency (temperature) steam cycles. CO_2 capture by improved chemical and physical solvents, or by membrane and absorption techniques. Reduced energy for CO_2 capture
IGCC-CCS	Improve and understand coal (particularly char) conversion	Ultra-low NOx burners for H_2 and syngas	Slag flow prediction	Oxygen production (with higher efficiency and lower cost, perhaps by ion transport and other novel systems). Longer life refractories. System design specific to local conditions and regulatory environment
			Deposition control of gas coolers Gas turbines for H_2 and capable of operating at the higher pressures of IGCC-CCS gasifiers	
Oxyf	Combustion characterisation in O_2/RFG environment	NO_x, SO_x, Hg and need for removal	Radiative heat transfer prediction	Materials for high efficiency (as for PCC)
		Burner development for ignition, avoiding external recirculation, and NO_x reduction	Corrosion and ash deposition	Oxygen production (as for IGCC)
			Operability and dynamic behaviour	Cycle optimisation and system thermal integration
			Furnace design for reduced recycle CFD modeling of furnace design	

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Amine solvents with lower solvent requirements (called sterically hindered [14]), some (KS-1 [15]) with lower regenerative temperature and heat of reaction are now being applied. The International Energy Agency (IEA) International Network for CO_2 Capture [16] has an emphasis on MEA and derivative solvents with Network proceedings detailing the current state-of-the-art and the research effort in Japan, the EU, and USA for improvement. R&D objectives [17] are indicated for the development of solvents and also thermal integration with the power plant to reduce thermal energy consumption to 2 GJ/tonne CO_2, and an efficiency loss of less than 5% at 90% recovery by 2015. Research to develop new solvents, membranes, process integration and pilot-plant development are objectives of most PCC research programs [16,17].

4.2. Integrated gasification combined cycle—with carbon capture

In pre-combustion capture the CO_2 is removed prior to dilution by combustion air, with CO_2 provided at elevated pressure, both aspects reducing CCS energy requirements and costs. More efficient separation methods than those for PCC can be employed, such as pressure-swing-absorption as physical solvents, and methanol or polyethylene glycol (with commercial brands called Rectisol and Selexol). The technology is applied in IGCC power plants, with an illustrative flowsheet on Fig. 2. The gasifier provides a synthesis gas of CO and H_2, and has a syngas cooler following with solids removal and gas treatment; reacting the CO with water in a shift reactor produces CO_2 and H_2; CO_2 is captured: the H_2 is combusted in a gas turbine with heat recovery and a steam turbine following. The flowsheet differs from standard IGCC systems by the additional shift conversion and CO_2 capture operations.

Some 160 gasification plants exist, with about 35 in planning [21], with products including electricity, ammonia, chemicals, methanol and hydrogen. For power generation, initial projects were coal based, with recent focus on refinery waste use. For power generation, many technology variants are available for IGCC, including entrained flow (the most common), fluidised bed and moving bed gasifiers; oxygen or air blown; dry or wet (slurry) fed: high temperature gas cooling or quench, some being suited to particular fuels [18].

The USDoE has identified oxygen-blown IGCC as offering advantages over other CCS technologies [19], with the FutureGen [20] program aimed at the development of a 275 MWe coal-fuelled IGCC power station, demonstrating integrated H_2 production and CO_2 separation and geological sequestration. In contrast, Japan is progressing an air-blown IGCC system for power, without CO_2 capture, and the European Commission has provided limited support for IGCC development [21]. R&D to improve availability and operational flexibility, while reducing energy use and capital costs is required.

Most gasification technologies react coal in pulverised form in entrained flow at high pressure, with fluidised bed technologies operating at lower temperatures being suited to low rank coals. Air may be used as the oxidant when power is generated, but O_2 is used when CO_2 is to be captured. The present paper reviews recent research on pressure effects on coal reactions in entrained flow and updates our recent review [22]. In particular, the effect of pressure on coal pyrolysis and char formation, char combustion and gasification reactivity, and subsequent ash formation and slag flow.

4.2.1. Reactions at high pressure

4.2.1.1. Pyrolysis and char character. Volatile release and yield is a critical aspect of coal reactivity in gasification. Coal pyrolysis at elevated pressures has been extensively investigated and reviewed over the last few decades. Most studies are at the 2–3 MPa of IGCC, not at 7–8 MPa potentially required for IGCC-CCS.

The effect of pressure on gas and tar yields has been observed for a variety of coals under a wide range of operating conditions. The observed effects of pressure on devolatilisation behaviour vary with the coal rank, gas environment and operating conditions. General trends observed from experiments are that the total volatile and tar yields decrease with increasing pressure. The reduction in tar and total volatile yields appears to be most significant for bituminous coals, but less pronounced for lignite [23,24]. The pressure effect on the tar and total volatile yields appears to be less pronounced at high pressures [25–27]. Increasing pressure results in higher yields of gases, particularly in a hydrogen atmosphere [28–31]. Increasing pressure improves the fluidity of the coal melt and reduces char reactivity [25,32,33]. Secondary reactions and mass transport limitations explain the influence of ambient pressure [34,35], and the major effect of pressure on the tar yields is the evaporation of tar precursors [24,33].

Coal swelling as char is formed is the most significant feature of softening coals during heating, which determines the particle size, porosity, density, and thereby reactivity of the residual char [36]. Attempts have been made to understand the effect of ambient pressure on swelling of coal particle during pyrolysis [25,32,37–41]. A review by Solomon and Fletcher [36] based on experimental and theoretical investigations concluded that swelling ratio (ratio of particle radius after swelling to the initial radius of particle) does not change monotonically with increasing applied pressure. The swelling ratio increases as pressure increases, reaches a maximum value, then decreases. At very high heating rates (10^5 K/s) swelling is greatly diminished [42]. Bailey et al. [43,44] studied char morphology based on experiments at atmospheric pressure, and the work has been extended [45–48].

Very little work on char morphology at pressure has been published until recent comprehensive studies [49–51]. Classification of chars according to geometric parameters and porosity has been previously described [43,50]. Typically, Group I char particles have a very porous structure, with large voids inside the particle and a thin wall, Group II char particles have a medium porosity and wall thickness, while Group III char particles have low porosity. In general, as furnace pressure increases, the overall proportion of Group I chars formed increases, while the proportions of Group II and III chars decrease. From the results the inertinite maceral is capable of displaying high fusibility similar to vitrinite, under high-pressure conditions.

4.2.1.2. Char reactivity. The pressure at which the parent coal is devolatilised also plays an important role in the reactivity of the resulting char. A recent advance in this area has been reported by Roberts [52], who measured the apparent and intrinsic gasification rates of a char made in a pressurised drop tube furnace (PDTF) under various pressures. Char apparent rates vary significantly with pyrolysis pressures, whereas the intrinsic rates, which were obtained by normalising the apparent rates by internal surface area, are almost independent of pyrolysis pressure over a pressure range from 1 to 15 atm. The conclusion has a significant implication for interpreting char reaction rates and mathematical modelling of char burnout [49].

A further recent finding of practical significance is the effect of inhibition of CO on gasification kinetics, as identified by van Heek and Muhlen, giving the CO_2 gasification rate r_s of char as

$$r_s\left(\frac{1}{s}\right) = \frac{k_1 P_{CO_2}}{1 + k_2 P_{CO} + k_3 P_{CO_2}}, \tag{1}$$

where s is the reaction area and k the chemical reaction rate.

This equation quantifies inhibition by the partial pressure term P of CO in the denominator, associated by the competition for active sites on the char surface. Recent experiments have confirmed the inhibition in both CO_2 and H_2O gasification kinetics [53]. With the same term also being included in the denominator for H_2O gasification of char, a mathematical model of an entrained flow IGCC gasifier by Bockelie et al. [54] predicts that the increasing CO during gasification reduces gasification rates dramatically. Increased operating temperature is then necessary for satisfactory carbon conversion, with temperature limits imposed for refractory lined gasifiers, due to the increased frequency for refractory repair and replacement.

Regarding the effect of pressure on coal reactions in gasification, the following conclusions are drawn:

- Generally, the char combustion and gasification reactivity increases with increasing reactant pressure. The magnitude of effect reduces at elevated pressures. Such a effect can be explained by an adsorption-desorption reaction mechanism, which is composed of several elementary reaction steps, and a saturation of the reacting surface at sufficiently high pressures.
- Char oxidation rate at elevated temperatures increases with an increase in total pressure from 1 to 10 atm. Further increase in pressure reduces the rate.
- Char gasification rate with H_2O is higher than that of char-CO_2 gasification. The inhibiting effect of H_2 and CO are considerably higher at elevated pressures. CO inhibition is often overlooked, with recent measurements and mathematical models of gasifiers suggesting its effect on char gasification kinetics may determine operating temperature.
- Char character, and swelling, is influenced by both pressure and heating rate, with impact on char reactivity.

4.2.1.3. Ash formation. Ash formation is strongly associated with char fragmentation behaviour [55,56] and included mineral coalescence [57] during combustion. However, very little work has been published on ash formation at pressure. Recently published advances at the authors laboratory [58,59] has advanced this understanding, through careful characterisation of char particles obtained from DTF and PDTF experiments, with evidence of char fragmentation effects in ash formation [55,56]. Extensive fragmentation is associated with reduced coalescence of included minerals during combustion. It is also possible that at high pressures, char fragmentation will be more violent, as more cenospherical char particles are formed in high-pressure pyrolysis [49,51].

A mechanism for ash formation has been proposed [59,60] with porous Group I type char particles fragmenting extensively during the early and middle combustion stages and burn out early. The extent of coalescence for the included mineral particles is very low. Group I type char particle produce a large number of small ash particles, Dense Group II type char particles fragment less. Char fragmentation is still the dominant mechanism

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for ash formation but the included mineral particles undergo some coalescence. One Group II type char particle may produce several ash particles with a relatively larger size. Group III type char particles exhibit little or no fragmentation. The particle size distributions for ashes produced during the combustion of coals at pressure are consistent with the impact of char Group proportions [60], indicating that ash formed at high pressure has a finer size.

The gas exiting a gasifier may pass into a gas cooler where cooled tubes and walls reduce its temperature. The solids contained in the gas comprise ash as well as unburnt char, and this solid matter may foul cooled surfaces. Ash deposition is an ongoing issue in solid fuel utilisation, and the stickiness and adhesion of char to form deposits is not well understood. The expectation is that char stickiness will increase with burnout, as ash is progressively exposed on the char outer surface as combustion proceeds. Fundamental research on this issue is needed.

4.2.1.4. Status of knowledge.

Most of the reactivity experiments to date have been at the lower temperatures (typically <1000 °C), which can be achieved in experiments involving captive solid samples. Experiments in pressurised TGA and wire mesh systems at these low temperatures are the most commonly reported, with some experiments for entrained flow system reported at the higher temperatures typical of IGCC conditions. Although the difficulty and cost has restricted these experiments, further entrained flow data is needed. Relevant devolatilisation and char reactivity studies have been undertaken for some time, with the state of knowledge and predictive ability, while being far from complete, is reasonably well developed. Char and ash formation mechanisms at pressure, however, are not well understood. The structure of the char generated has now been related to reactivity and ash formed, but the mechanisms leading to the effect of pressure on this structure are not understood. Progressing the understanding of the formation of char structure at pressure and its relation to coal properties and deposition and retention of char on heat transfer surfaces is necessary.

4.2.2. Slag flow

The viscosity of molten coal ash slag is one of the important factors affecting the performance and operating conditions in entrained-flow coal gasification plant, because the slag should be liquid, and fluid enough to be tapped.

Some predictive models have been developed to estimate the viscosity of slags, however, most of these are generally formulated for synthetic slag mixtures (typically SiO_2, Al_2O_3, CaO, MgO, and FeO). The empirical viscosity predictor [61], which provides successful agreement for homogeneous molten slags in the Newtonian region below 1000 Pa s, has been developed at the University of Newcastle based on experimental data sets for coal ash slags.

However, actual gasification process can operate at conditions when some heterogeneous material is present in the liquid phase. Highly reducing atmosphere inside a gasifier can lead to the reduction of iron oxides to form metallic iron. When the iron is reduced to its metallic form, it is separated from the slag into dispersed globules [62]. Because of this separation, the liquid slag becomes depleted in iron causing the viscosity to increase. Therefore, it is important to describe the viscosity of not only completely liquid slag phase, but also of the partly crystallized slag systems having solids suspensions. The viscosities should be predicted over a wide composition and temperature ranges for selection of coals, flux additions, and to avoid related troubles. Undissolved ash particles and crystals can also be present.

Measurements [63–65] and empirical models [66–69] have been developed for the prediction of homogeneous slag viscosity. The most commonly used method for predicting slag viscosities was proposed by Urbain et al. [70] and Kalmanovitch and Frank [71] based on fitting experimental data from a SiO_2–Al_2O_3–CaO–MgO system. Browning et al. [61] proposed the empirical viscosity predictor which was used to determine the viscosity of slags in the Newtonian region below 1000 Pa s. This method was found to be the most accurate in the comparison for use with fluxed and unfluxed coal ash slags, but can also be used with reasonable accuracy over a wide range of compositions.

4.3. Oxyfuel

Buhre et al. [72] have reviewed the status and research needs of oxy-fuel technology. The understanding of oxy-fuel combustion has been established primarily from pilot-scale studies, as it has not been applied at practical scale, and there have been few fundamental studies. Demonstrations of a retrofit of a pf unit involving electricity generation at 30 MWe [73] and of the combustion train 30 MWt [74] are planned, both involving CO_2 compression and possibly sequestration.

The characteristics of oxy-fuel combustion with recycled flue gas differ with air combustion in several aspects primarily related to the higher CO_2 levels and system effects due to the recirculated flow, including the following:

- To attain a similar adiabatic flame temperature (AFT) the O_2 proportion of the gases passing through the burner is higher, typically 30%, than that for air (of 21%), necessitating that about 60% of the flue gas is recycled.

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- The high proportions of CO_2 and H_2O in the furnace gases result in higher gas emissivities, so that similar radiative heat transfer for a boiler retrofitted to oxy-fuel will be attained when the O_2 proportion of the gases passing through the burner is less than the 30% required for the same AFT.
- The volume of gases flowing through the furnace is reduced somewhat, and the volume of flue gas (after recycling) is reduced by about 80%.
- The density of the flue gas is increased, as the molecular weight of $CO_2$is 44, compared to 28 for N_2.
- Typically, when air-firing coal, 20% excess air is used. Oxy-fuel requires a percent excess O_2 (defined as the O_2 supplied in excess of that required for stoichiometric combustion of the coal supply) to achieve a similar O_2 fraction in the flue gas as air firing, in the range of 3–5% [75].
- Without removal in the recycle stream, species (including corrosive sulphur gases) have higher concentrations than in air firing.
- As oxy-fuel combustion combined with sequestration must provide power to several significant unit operations, such as flue gas compression, that are not required in a conventional plant without sequestration, oxy-fuel combustion/sequestration is less efficient per unit of energy produced.

4.3.1. Heat transfer

Predictions of heat transfer are critical to oxy-fuel technology. By recycling the CO_2 (and possibly H_2O, if the recycled gas is not dried) from the outlet back to the furnace inlet, several changes in furnace heat transfer can be expected due to the changes in gas properties. These changes are affected by two main properties that change during oxy-fuel combustion:

- Gas radiative properties.
- Gas heat capacity.

During oxy-fuel combustion, the concentration of tri-atomic gas molecules in the flue gas increases drastically and will change the emissivity of the gas. The major contributor of the heat transfer from a flame from conventional fuels (and conventional combustion) is thermal radiation from water vapor, carbon dioxide, fly ash, soot, and carbon monoxide [76]. When the concentration of carbon dioxide and water vapor is increased significantly, such as is the case for oxy-fuel combustion, the radiative heat transfer from the flame will change. However, typical heat transfer calculations in cfd codes such as FLUENT use a "3 grey-one clear gas" model to estimate flame emissivity [76,77]. Traditionally, this model is based on air combustion with conventional partial pressures of CO_2 and H_2O. To calculate the radiative heat transfer from a flame resulting from oxy-fuel combustion, the "3 grey-one clear gas" model should be validated and/or modified or replaced by a more accurate model.

Carbon dioxide and water vapor also have high thermal heat capacities compared to nitrogen. This increase in thermal capacity increases the heat transfer in the convective section of the boiler. However, the amount of gas passing through the boiler in the oxy-fuel case is lower, and (for a retrofit) increased heat transfer in the radiative section of the boiler results in lower gas temperatures entering the convective pass. The heat transfer in the radiative and convective sections of the boiler will need to be optimized to ensure efficient operation. Different authors have observed conflicting heat transfer results due to this required optimization. However, for a retrofit where furnace heat transfer is matched and a given flue gas oxygen concentration of say, 3% typical for air firing, the oxy-fuel case will result in a lower furnace exit gas temperature [75].

4.3.2. Combustibility

Recent measurements of coal devolatilisation by Renu Kumar et al. [78] indicate that devolatilisation in an atmosphere of O_2/CO_2 is greater than in O_2/N_2 due to char gasification by CO_2.

The elevated CO_2 concentration surrounding the burning char particles could also result in gasification reactions contributing to the char mass loss. Várhegyi and co-workers observed that the kinetics of the char with O_2 reaction was not influenced by the presence of a high amount of CO_2 both in an atmospheric thermogravimetric analyzer (TGA) [79] and in a pressurised TGA [80]. They measured the reaction rate of the coal char in O_2–CO_2 mixtures with varying O_2 concentrations. The negligible effect of CO_2 on the char reaction rate was attributed to the much lower reaction rate of the char-CO_2 reaction than that of char-O_2 [79,80], at the low reaction temperatures (400–900 °C) used in the experiments.

Shaddix and Murphy found that gasification reaction of the char by CO_2 becomes significant under oxygen-enriched char combustion at temperatures prevailing in practical processes [81]. Experiments were performed to burn coal particles in Sandia's entrained-flow reactor at a gas temperature of $\sim$1700 K and oxygen concentrations in nitrogen ranging from 6% to 36%. A char combustion model, which considered CO oxidation in the particle boundary layer, was used to interpret the experimental data, demonstrating that significant CO oxidation in the boundary layer occurred for results at high oxygen levels and higher char combustion temperatures. Model

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calculations indicated that the observed char particle temperatures and mass loss rates under oxygen-enriched char combustion could be matched well when the char-CO_2 reaction was included.

Measurements by Kumar et al. [78] indicate that coal and char reactivity can differ at the same O_2 levels in O_2/N_2 and O_2/CO_2 environments. Even if the reactivities in the two environments are the same, coal burnout will improve in an oxy-fuel retrofit due to the higher O_2 partial pressures experienced by the burning fuel, possible gasification by CO_2, and longer residence times due to the lower gas volumetric flows. Lower gas temperatures (both flame and furnace exit temperatures) will worsen burnout. For the same flue O_2 for oxy-fuel and air firing, the overall effect [78] is an improvement in burnout, so that lower flue O_2 levels, and therefore lower XS O_2 levels, can be used in oxyfuel.

4.3.3. Emissions

Gaseous pollutant formation and emissions change during oxy-fuel combustion; the SO_x emissions per energy of fuel combusted may be lowered by sulfur retention in ash and deposits (typically by less than 20%, depending on ash composition); NO_x emissions generated per unit of energy are reduced (by up to 70% but dependant on burner design and operation) as the recycled NO is reduced or reburned as it is recirculated through the flame (even though volume proportions of NO_2 may be increased due to the lower glue gas volume). The effect of oxy-fuel combustion on trace elements emissions and on fly ash size distribution are uncertain, but it can be expected that the behaviour of certain minerals (in particular carbonates) will be affected by the change in environment. (The decomposition temperature of carbonates will be increased due to the high carbon dioxide partial pressures in oxyfuel [82]). The changes in gaseous pollutant formation during oxy-fuel combustion have been analysed by several researchers and is discussed in more detail in the following sections.

During oxy-fuel combustion, the amount of NO_x exhausted from the system can be reduced to less than one-third of that with combustion in air [83,84]. The NO_x reduction is thought to be the result of several mechanisms [85]: Decrease of thermal NO_x due to the very low concentration of N_2 from air in the combustor, the reduction of recycled NO_x as it is reburnt in the volatile matter release region of the flame, and the reaction between recycled NO_x and char.

Okazaki and Ando used a bench-scale reactor to examine the effects of the latter two factors during oxy-fuel combustion with an O_2 concentration of 21% (i.e., recycling ratio as high as 80%) at a maximum flame temperature of 1450 K [85]. They concluded that the reduction of recycled NO_x is the dominant mechanism for the reduction in NO_x emissions. They estimated that more than 50% of the recycled NO_x was reduced when 80% of the flue is recycled.

It has also been found that oxy-fuel combustion can decrease the SO_2 emissions compared to that in air combustion [83,86]. Croiset and Thambimuthu [83] observed that the conversion of coal sulphur to SO_2 decreased from 91% for the air case to about 64% during oxy-fuel combustion. The reason they suggested is that high SO_3 concentrations in the flue gas during oxy-fuel combustion can result in sulphur retention by ash or deposits in the furnace. SO_2 concentration from oxy-fuel combustion is known to be higher than that from air combustion due to flue gas recirculation [87].

Potential corrosion of the furnace and CO_2 transportation systems due to high SO_2 concentrations in the flue gas could result in the need for desulphurization of the recycled flue gas for oxy-fuel combustion [88].

4.4. Other technologies

Other means of CO_2 capture from PCC and IGCC systems are under development [7] to achieve reduced costs and energy, including membrane contactors and gas separation. Other technologies [7] under development are based on "looping" of gases. These include chemical looping—which uses a metal oxide oxygen carrier to transfer oxygen extracted from air to the fuel, to achieve a concentrated CO_2 gas without requiring an ASU, and the HyPr-RING process—which is being developed in Japan, which transfers (and thereby concentrates) CO_2 using a calcium sorbent. While the target fuel for these technologies is coal, at present the experiments to develop them are gas based. The impacts of gaseous and solid impurities will challenge their future application for coal.

5. Implications of combustion processes

The previous section has outlined the status of the understanding of the combustion and related mechanisms in CCS technologies; in this section the use of these mechanisms in developing the technologies is outlined.

There has been considerable research on prediction of pilot-scale and practical gasifier performance which use fundamental combustion mechanisms and rates, incorporated into CFD models.

The two combustion related factors of greatest impact on gasifier design and operation are fuel reactivity and the slag flow as it runs down refractory walls and out of the bottom of the reactor under gravity (R. Boyd, Private Communication Connel Wagner, Australia (2001)). In fact, coal selection for gasifiers has been made based on coal properties influencing these factors, with coal rank used to characterise combustibility and an ash fusibility temperature used to characterise slag flow (Y. Yun, Private communication Institute for Advanced Engineering, Yongin, Kyungi-do, Korea (2002)). These two factors have economic impacts, as operational costs are related to the recycling of unburnt fuel and maintaining slag temperatures and the addition of limestone to reduce slag viscosity in order to attain satisfactory slag removal.

In estimating the heat balance for a gasifier, the gases leaving may be considered to be at thermal equilibrium with major species determined by the water-gas shift reaction, with combustion complete apart from unburnt char [89]. The elements comprising the product gases then contain all the fuel elements (including H and O) apart from carbon. Therefore a heat balance with an estimation of char burnout to provide the carbon in the product gases (which requires knowledge of the combustion kinetics) is a good approximation. Although the gas is at equilibrium at the exit of an entrained flow slagging gasifier reactions do continue at lower temperatures of any quench zone following. The water gas shift temperature of the product gas can be 100–200 K lower than the gasifier exit temperature. Predictions of syngas quality, thermal efficiency and cold gas efficiency can then be made in terms of design variables such as O_2/coal fed using this approximation.

CFD based models [89–93] include sub-models for combustibility and heat release and provide more detail, including prediction of local temperatures, gas compositions and burnout and velocity profiles which are essentially impossible to measure in high pressure reactors. These can also indicate the sensitivity, and therefore the importance of the sub-models [92], for example, the importance of combustion kinetics [93].

Time varying slag flow models [94] have been interfaced with CFD gasifier models (to provide the incident heat flux to the slag which determines slag temperature) to predict the impact of temperature (by an O_2 increase) and extent of limestone addition. Such models have provided insights into the slag removal problem, but assume the slag to be fully liquid and of uniform composition when, which may not be the case [62]. In addition the ash deposition processes onto the slag may be selective, that is, the slag may not have the composition of the ash of the fuel [62]. This does not seem to have been considered by Seggiani [94].

Models of oxy-fuel furnaces have established design parameters for oxygen supply, heat transfer performance, with combustion and emission impacts. The emphasis has been on refrofitted furnaces. However, in contrast to IGCC, most studies use simplified models and there have been few studies using fundamental combustion mechanisms and rates incorporated into CFD models.

In oxyfuel, the oxygen supplied in oxy-fuel technology mixes with the recycled gas before entering the boiler furnace through the burner. Defining the excess O_2 as the O_2 supplied in excess of that required for stoichiometric combustion of the coal, it is noted that as O_2 is recycled, this also contributes to the O_2 through the burner. The design requirements of an air fired furnace retrofitted to oxyfuel are to establish the O_2 proportion of the gases through the burners for matched furnace heat transfer performance of the retrofit, that is, by fixing two factors: the same % v/v O_2 in the flue gases (which is the measurement used to control the combustion performance of boilers, and is typically 3.3 % for air firing) with the same radiative heat transfer performance of air-fired furnaces retrofitted to oxyfuel.

Valid models must allow for the higher emissivity of the furnace gases of the oxy-fuel firing, and a study using a simple well-mixed furnace model has shown [75] that, considering retrofit of different size furnaces from air to oxyfuel: Oxyfuel requires an % excess O_2 to achieve the same O_2 fraction in the flue gas as air firing, in the range from 3% to 5% for dry and wet recycle. Also, oxygen concentrations at the burner inlet range from 25% to 38% (v/v) to achieve matched furnace heat transfer depending on the use of dry or wet recycle with some impact of furnace size. For matched heat transfer, lower temperatures for the gases entering the convective section for oxyfuel are the result of the different heat capacities of the flue gases. These oxygen concentrations are lower than the 30% required to match the adiabatic flame temperature, agreeing with results from a previous 2D model developed by Payne [95], which also allowed for the higher emissivities.

Simple combustion models [78] based on laboratory measurements also show that the 3.3% flue O_2 typical for air firing can also be reduced in oxy-firing, with satisfactory burnout still achieved, this being due to the higher oxygen partial pressures in the furnace gases. CFD models of oxy-fuel combustion have been published for flame models [96] to predict NO_x formed in a pilot-scale furnace, and are currently being developed [97] for heat transfer prediction. These are considered to be an essential tool for heat transfer and combustibility design of retrofits, pilot-plants and purpose built units. A model has been developed to aid interpretation of differences in flame ignition and propagation in air and oxy-fuel environments [98].

Laboratory measurements of NO_x reduction in oxyfuel have been scaled to practical systems using simple models to identify reduction mechanisms [98], to predict magnitudes agreeing with pilot-scale experiments [85], but CFD modeling of flames at practical scale will be a necessary next

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development, as burner throughput is known to influence NO_x levels.

Given this background, oxyfuel is an emerging technology where combustion science and modeling is needed to advance the technology and optimise operations, particularly when this effort is linked to pilot-plant trials [99] and design of plant [97].

6. Final comments

Carbon capture developments are primarily adaptations of conventional combustion and gasification systems, with additional unit operations such as bulk oxygen supply, CO_2 capture by sorbents, CO_2 compression, and storage.

The R&D challenges identified for the combustion scientist and engineer, with current understanding being detailed, are those of design, optimisation and operation of new combustion and gasification plant, controlling the gas quality required by CCS related units and associated emission compliance, and gas separations. Fundamental research topics include fuel reactions at pressure (which may be higher in IGCC-CCS than IGCC), and in O_2/CO_2 atmospheres, as few studies have been made in these conditions. Laboratory results interpreted and then included in CFD models of combustion operations are necessary. Also identified, but not detailed, are combustion issues in gas turbines for IGCC and IGCC-CCS.

Fundamental studies should be a component of pilot-plant and demonstrations at practical being planned. Concepts for new designs of combustion equipment are necessary for the next generation of technologies. The challenges involved with the design and operation of these integrated systems, while supplying electricity on demand, are considerable.

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