Understanding pulverised coal, biomass and waste combustion

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Abstract

Pulverised coal firing has been the dominant technology for generating power in utility boilers for almost a century. During this period, boiler designs have evolved through an accumulating collection of knowledge that has led to many empirical relationships that still guide current and future design directions to some degree. In the late 1940s the developed nations began to undertake coal research based on scientific principles to ensure the most efficient use of the primary energy resource represented by coal. As the body of scientific knowledge on the physics and chemistry of coal combustion grew, it was used to direct the improvements to efficiency required and, later, the control of pollutants produced during the combustion of coal. This involves not only the control of emissions of particulates, SOx and oxides of nitrogen but also of trace elements, polycyclic aromatic hydrocarbons and, increasingly, CO_2. There have been a number of developments in the coal-fired power generation sector including cofiring with secondary fuels, particularly biomass and waste and the development of radically different combustion systems (for example, oxyfuel) to meet carbon capture and storage requirements.

This report sets out the recent advances in this area of coal science and how they are being brought to bear on the current challenges in the field of pulverised coal combustion.

Acronyms and abbreviations

AFT	adiabatic flame temperature
AT	Austria
BE	Belgium
BG	Bulgaria
BOOFA	boosted (or burner) overfire air
CARS	Coherent anti-Stokes Raman Spectroscopy
CCD	charge-coupled device
CCSEM	computer-controlled scanning electron microscopy
CFD	computational fluid dynamic (modelling)
CSIRO	Commonwealth Scientific and Industrial Research Organisation
CZ	Czech Republic
DE	Germany
DK	Denmark
DNS	direct numerical simulation
DSC	differential scanning calorimetry
DTA	differential thermal analysis
DTF	drop tube furnace
EDAX	energy dispersive X-ray spectroscopy
EE	Estonia
EPM	electron probe microanalysis
ES	Spain
EU	European Union
FI	Finland
FC	fixed carbon
FR	France
FMR	full maceral reflectogram
FTIR	Fourier transform infrared (spectroscopy)
GC/MS	gas chromatography/mass spectrometry
GR	Greece
HTF	horizontal tube furnace
HU	Hungary
IE	Ireland
IR	infrared
LDA	laser Doppler anemometer
LES	large eddy simulation
MFC	multifuel combustor
MICRO	multi-colour integrated receiving optics
NETL	National Energy Technology Laboratory, USA
NL	Netherlands
NMR	nuclear magnetic resonance
NOx	nitrogen oxides
OFC	oxyfuel combustor
OHPLIF	OH planar laser-induced fluorescence
PHOENICS	parabolic, hyperbolic or elliptic numerical integration code series
PKE	Palm kernel expeller
PL	Poland
PRB	Powder River Basin
PT	Portugal
QEMSCAN	quantitative evaluation of Minerals by scanning electron microscopy
RO	Romania

SDPA	shadow doppler particle analyser
SEM	scanning electron microscopy
SI	Slovenia
SK	Slovakia
SOFA	secondary overfire air
SOx	sulphur oxides
SWG	switchgrass
TEM	transmission electron microscopy
TGA	thermogravimetric analysist
TMA	thermomechanical analysis
UK	United Kingdom
VM	volatile matter
XRF	X-ray fluorescence analysis

Units used

TWh/y	terawatt hours per year
cm^{-1}	wavenumber
MW	megawatt
nm	nanometre
mJ	millijoule
mm	millimetre
MWth	megawatt thermal
°C	degrees celsius
wt%	weight per cent
ppm	parts per million
K	degree kelvin
m	metre
cm	centimetre
g/min	grammes per minute
m^2	square metres
m^3	cubic metres
MWe	mega watts electrical
kg/s	kilograms per second
t/h	tonnes per hour
vol%	volume per cent
th%	per cent based on thermal input
µm	microns

Contents

1 Introduction

Pulverised coal firing has been the dominant technology for generating power in utility boilers for almost a century. During this period, boiler designs have evolved through an accumulating collection of knowledge that has led to many empirical relationships that still guide current and future design directions to some degree. In the late 1940s the developed nations began to undertake coal research based on scientific principles to ensure the most efficient use of the primary energy resource represented by coal (US DOE, 2012). As the body of scientific knowledge on the physics and chemistry of coal combustion grew, it was used to direct the improvements to efficiency required and, later, the control of pollutants produced during the combustion of coal. The environment of pulverised coal combustion is highly complex, in which carbonaceous components, mineral components and gaseous arisings interact with each other and the boiler components at high temperatures as they pass through the boiler.

Today, there is an increasing requirement to burn coal worldwide in an environmentally acceptable manner. This involves not only the control of emissions of particulates, oxides of sulphur and oxides of nitrogen but also of trace elements, polycyclic aromatic hydrocarbons and, increasingly, CO_2. Given the importance of this topic the state-of-the-art' was reviewed in a keynote IEA CCC study (Morrison, 1986), and updated more recently by Wu (2005). However, there have been a number of developments in the coal-fired power generation sector that make a further update timely including;

- cofiring with secondary fuels, particularly biomass and waste;
- the requirement to utilise a wide range of coals of differing and varying quality, efficiently;
- the need to predict and control emissions (for example, NOx, trace elements) to meet ever-tighter legislative standards;
- the development of radically different combustion systems such as oxyfuel to meet carbon capture and storage requirements;
- changes in the pattern of operation of plant for example flexible load following.

At the same time the research tools available to investigate the system have continued to develop particularly in the field of mathematical modelling and non- or semi-invasive monitoring of the environment within the power plant.

This report sets out the recent advances in this area of coal science and how they are being brought to bear on the current challenges in the field of pulverised coal combustion.

2 Overview of previous studies

2.1 Understanding pulverised coal combustion

In his review on *Understanding pulverised coal combustion* Morrison (1986) reviewed the then current state of knowledge with respect to coal structure, and the species involved in coal combustion and their interactions. He concluded that the overriding characteristic of pulverised coal combustion is the sheer complexity of the processes involved, where a multitude of interacting heterogeneous and homogeneous reactions take place simultaneously in and around coal particles whose initial physical and chemical structures are not only ill-defined but change during the combustion process. This situation is further complicated in that studies undertaken on a specific coal may not be readily transferrable to other coals, even those that closely resemble the original fuel.

Morrison's principal conclusions from his study were as follows:

2.1.1 Coal structure

Our lack of understanding of the molecular structure of coal is impeding progress in coal combustion research. This knowledge is fundamental to our understanding of the processes involved in the evolution of products from coal and the changes which occur during the combustion process. In particular we need to quantify the influence of mineral matter on the particle break- up process and hence on the particle size of char.

2.1.2 Species involved in combustion

Volatile species

It is now possible to predict the ratio of major volatile species evolved from different ranks of coal. This information needs to be extended for the fuel-rich conditions of staged combustion and to include sulphur and nitrogenous species. Attempts have been made, with some success, to predict the species evolved and their rates of evolution from a detailed knowledge of the chemistry of coal. However, much more work is required to validate these claims on a wider range of coals of known structure.

Tar formation

As an extension of the need to predict volatile species it is essential to be able to predict the fraction of the total volatile yield evolved as tar and the effect of changes in devolatilisation conditions and coal characteristics on the yield of tar. There is evidence that volatile nitrogen evolves with the tars. Hence, factors which influence the fraction of tars evolved also have important implications for the evolution of NOx. Our understanding of the possible relationship between tars, soot and polycyclic aromatic hydrocarbons is virtually non-existent.

2.1.3 Ignition, kinetics and diagnostics

Ignition mechanism

There is evidence of both heterogeneous and homogeneous ignition mechanisms. There is, as yet, no means of predicting the conditions under which each mechanism can exist. If heterogeneous ignition is the dominant mechanism, this casts serious doubts on our understanding of the role of volatiles in combustion.

Reaction rate data for volatile species

There is a general lack of confidence in reaction rate data on the oxidation of volatiles. In 1981 Essenhigh (1981) stated that: 'In the last 15 years there has been substantial advance in understanding in virtually all elements of the problem (of coal combustion), except for the volatiles kinetics'. He went on to conclude that the lack of knowledge of the volatiles combustion kinetics in any form needs no further comment. Four years later Smoot and Smith (1985) concluded that the situation with regard to knowledge of volatiles combustion remains essentially unchanged. Furthermore, they state that a rigorous treatment of the volatiles reaction process is not a realistic expectation in a heterogeneous turbulent flow involving hundreds of chemical species and many more reactions.

Reaction rates and the sequence of volatile evolution are particularly important in determining the local environment in which nitrogen is evolved and hence in the formation of NO. The efficiency of NO formation may be smaller in the case of medium rank (or medium volatile) coals as the reaction of volatiles with oxygen is reduced in these cases. This lack of information on reaction rates is, to a large extent, the result of our poor understanding of the reaction mechanisms involved. Recent advances in non-intrusive diagnostic techniques such as those based on lasers should help to improve this understanding.

Char reactivity

Intrinsic reactivity varies widely among chars for a given temperature. No satisfactory explanation for this can be found in the literature. It has been suggested that such variations may be due to differences in maceral composition, coal rank, the molecular structure of carbon and to the effects of impurities in the solid and gaseous reactants. This is clearly an area which requires further attention.

Effect of heating rate on char reactivity

Very high combustion rates have been observed with high heating rates (10^6 °C/s) which were achieved with intense mixing. Enhanced char reactivity was attributed to decreasing chemical reaction resistance with respect to diffusion. This is particularly interesting as it is the opposite of what is generally predicted as the result of intense mixing where turbulence might increase boundary layer transfer with expected enhancement of the diffusional kinetics rather than of the chemical kinetics. If it is correct that chemical kinetics are being enhanced it will be extremely important to establish the cause.

Char reaction rate

Kinetic studies of the reaction between carbon or char and oxygen have given values of the reaction order varying from zero through fractional orders, usually½ to 1, and possibly some indication of reaction order two. Verification of these reaction orders and the conditions under which they exist is required.

Because of the complex nature of both devolatilisation and char oxidation the two processes have largely been studied independently. Work is required to relate pore development, and hence char reactivity, to the devolatilisation stage and also to the structure of the original coal. Contrary to expectations, initial findings indicate that total surface area does not increase during the first 0.2 s of devolatilisation. The relationship between char porosity and the maceral content of coal may provide a tentative explanation of the differences in combustion properties of coals with otherwise similar properties.

Coal particle temperature

Determination of coal particle temperature under a wide range of combustion conditions is required. Whilst techniques such as colour pyrometry have permitted accurate temperature determination, we need to be certain of what we are measuring with this technique. The effects of homogeneous reactions, soot oxidation, inter-particle radiation and devolatilisation must be identified.

SO_2-NOx interactions

Both inhibition and enhancement of thermal NO production in the presence of high concentrations of SO_2 have been identified. A mechanism to account for these opposite effects is required.

Pyritic-CaO reaction

Pyrite/CaO chemistry and fuel ash chemistry of sulphide and sulphate formation in staged combustion remains an area not fully explored or understood.

2.2 Fundamentals of pulverised coal combustion

In updating Morrison's study, Wu (2005), addressed the processes and their underlying mechanisms involved in pulverised coal combustion, namely: drying and heating, devolatilisation, volatile oxidation and char oxidation. Pollutant formation during combustion was also reviewed. The relationship between these mechanisms and coal properties was discussed and the areas where further research may be required were identified. Wu concluded that significant advances in understanding pulverised coal combustion had been achieved, especially through modelling. However, he considered that there were still a number of areas requiring further work. These included in particular:

- further studies on the effect of coal rank on the relative yields of gases and tar during coal devolatilisation;
- further investigations into the volatiles oxidation kinetics;
- modifications to char oxidation models by incorporating the effects of:
  - change in the char surface area during combustion;
  - ash diffusional resistance;
- further research on the conversions of tar-N and soot-N as well as the effect of minerals in coal chars on NO reduction;
- further understanding on the conversion of organic sulphur to SO_2;
- improvements to ash formation models by incorporating the effect of organically-bound inorganic elements, therefore extending applications to low-rank coals.

Other recent IEA CCC studies that have addressed issues germane to the present investigation include those by:

- Barnes (2009, 2010) on *Slagging and fouling in coal-fired boilers, and Ash utilisation – impact of recent changes in power generation practices*;
- Nalbandian (2009) on *NOx control for coal-fired plant*;
- Sloss (2010) on *Emissions from cofiring coal, biomass and sewage sludge*;
- Fernando (2012) on *Cofiring high ratios of biomass with coal*.

2.3 Summary

The importance to world energy production of pulverised coal firing for power generation has stimulated a significant research activity aimed at understanding the transformations occurring during combustion. The presence of complex carbonaceous structures in close combination with a range of mineral components subjected to an extremely aggressive temperature-time profile leads to a very large number of reaction pathways, even before interactions with boiler components are considered. The previous IEA studies have collated and discussed the results of this extensive body of work on pulverised coal combustion. Individual aspects of the combustion process have been isolated by well chosen experimental techniques and characterised in detail, but others have defied clarification. In addition while these individually-focused studies were capable of giving valuable insights into pulverised coal behaviour, and could be used to guide specific aspects of the combustion process (such as pollutant formation and amelioration) a unified model capable of genuine predictive capacity has not emerged and many coal users contained to rely on empirical correlations to predict coal behaviour and for plant design. The overall complexity of the pulverised coal environment remains extremely challenging and a comprehensive theoretical description is considered likely to remain elusive for the immediate future.

3 Recent changes in the power generation sector

3.1 Developments

As outlined above the last twenty years have seen some very significant changes in the power generation sector that impact on the way in which coal is burned to generate power. These factors include:

- power generation sector deregulation;
- technological developments;
- cofiring with biomass and other alternative fuels;
- environmental protection technologies;
- new technologies;
- increased international coal trading.

Deregulation and privatisation in the power generating market of many countries has put increasing pressure on plants to reduce the cost of generation. As fuel is by far the largest cost factor, power plants are required more than ever to be able to utilise a wide range of coals of differing quality, often far outside the plant's original design fuel range. Additionally, there are increasing demands from legislation to increase boiler efficiency and to reduce emissions such as CO_2, NOx and SOx which require operators not only to switch fuel (for instance from high sulphur to low sulphur coals) but to make plant modifications (for instance fitting low NOx burners and implementing other combustion zone modifications for NOx reduction, for example overfire air ports).

Power plant may be operated on a more flexible basis, with coal-fired plant previously used for base load operation competing against other fuels (for example gas) depending on the relative fuel price. It is now increasingly common for coal-fired plant to operate on a 'two-shifting basis' where a plant is started and shut down twice a day. These new patterns of operation put pressure on plant components and much work has been undertaken to ensure long, reliable and efficient operation under these conditions. An important development in plant fuelling is the cofiring of coal plant with additional fuels such as biomass and waste that pose additional technological challenges. Typical biomass fuels for power generation include wood-based fuels such as wood chips, sawdust bark, tree trimmings, paper and cardboard; agricultural wastes such as straw, rice husks and nut shells; sludges from paper mills and municipal sources and energy crops specially grown for use as biofuels such as switchgrass, eucalyptus, willow and poplar trees (Fernando, 2012). Significant progress has been made in the utilisation of these co-fuels in coal-fired power stations and, currently, over 234 units have either tested or demonstrated cofiring of biomass or are cofiring on a commercial basis (Cremers, 2009). Coal is often replaced by biomass in pulverised coal plants up to 20% biomass, as in Belgium, Canada, Denmark, Finland, The Netherlands, Sweden, the UK and the USA. Currently, approximately 30% of cofiring is considered the maximum, but the aim of many new and existing coal fired power stations will be to increase the cofiring percentage, in some cases up to 50% or higher. Hansson and others (2008, 2009) have assessed the near-term technical potential for biomass cofiring with coal in existing coal-fired plant in the EU-27 member countries using various assumptions on plant life, load factor etc. They estimate that between 87 and 52 TWh/y could be generated corresponding to 2.5% and 1.5% of total gross electricity generation in EU-27 (*see* Figure 1).

The continuous drive for low emissions from power plant requires the adoption of technologies for emission reduction or capture. The first generation of NOx abatement technologies, low NOx burners, are now being followed by improved devices such as BOFA (boosted overfire air) and SOFA (secondary overfire air), together with full-boiler staging for reducing NOx through combustion modification. All of these technologies modify the combustion environment and change the way in which coal particle transformations occur. Further emissions reductions require post combustion processes such as catalytic conversion and flue-gas scrubbing and, in the longer term, carbon capture for compliance with climate change driven legislation.

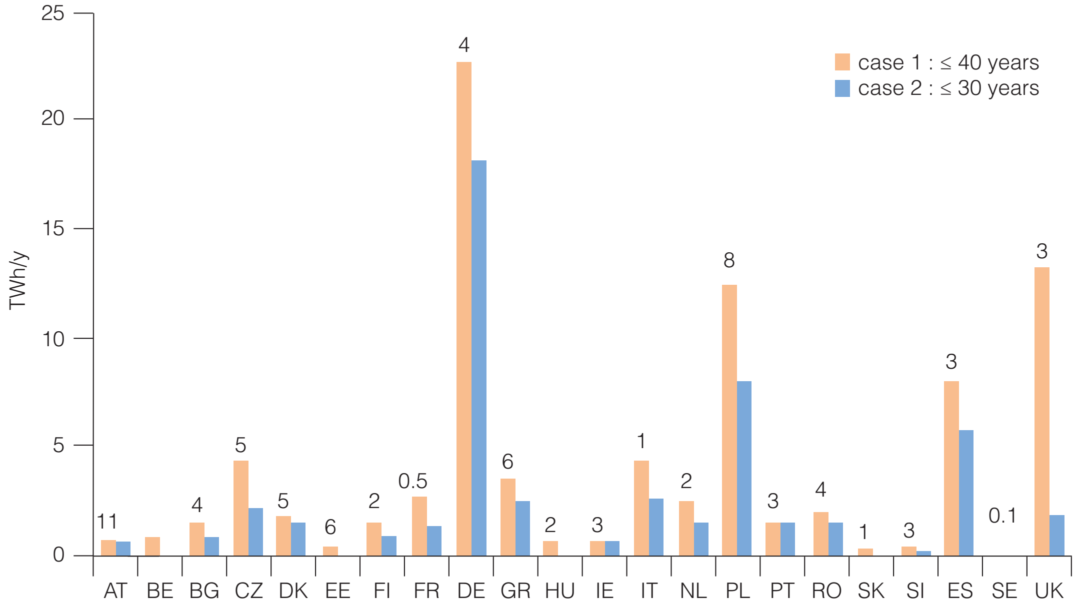


Figure 1 **Technical potential of electricity generation from biomass cofiring the EU** (Hansson and others 2008, 2009)

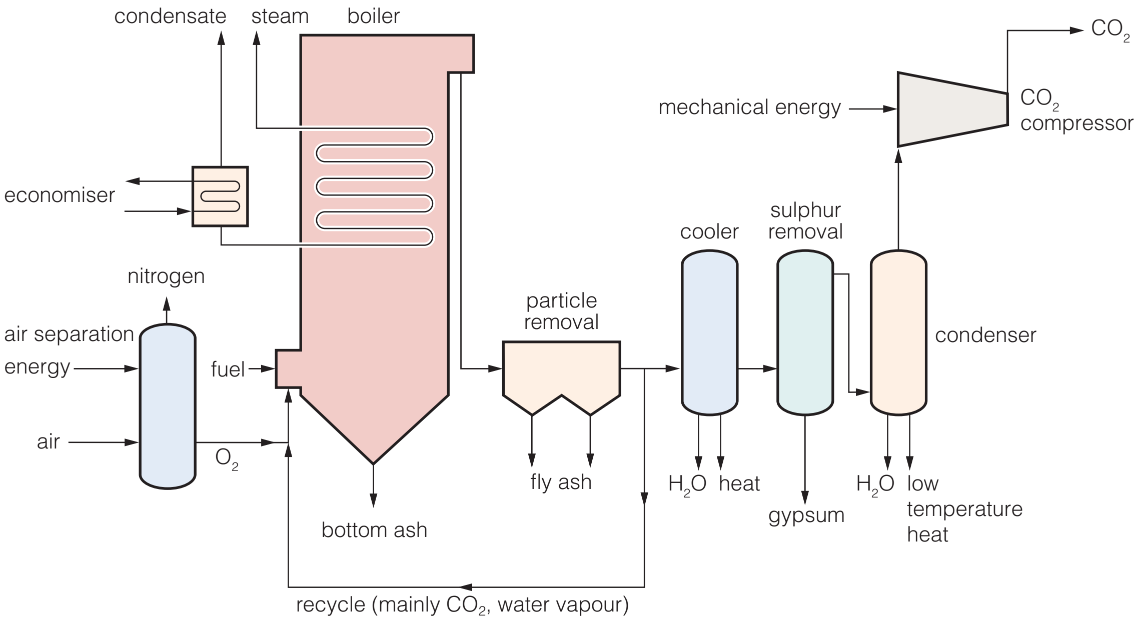


Figure 2 **Schematic diagram showing oxyfuel combustion** (Barnes, 2009)

Carbon capture and storage is the issue facing coal-fired plant worldwide and has generated major research efforts to identify and demonstrate efficient carbon reduction technologies for existing and new plant. Oxyfuel combustion technology is one such technology being developed for pulverised coal plants to facilitate carbon capture where coal is burnt in a mixture of pure oxygen and carbon dioxide from recycled flue gas (*see* Figure 2). The products of oxyfuel combustion are carbon dioxide, the other pollutants normally associated with coal combustion (NOx and SOx, etc) and water – and since the water is easily separated, a stream of CO_2 ready for sequestration is obtained.

Temperatures in an oxyfuel system are controlled by recycled flue gas in a complete power system. In both pulverised coal and power cycle applications, the current state-of-the-art is such that a greenfield oxycombustion plant could be built or an existing boiler could be retrofitted using current technologies.

However, such plants would not be optimised due to a lack of data or proven computer models of oxyfuel combustors, boiler systems or carbon dioxide recovery. Multiple oxyfuel-combustion facilities at various scales are being constructed or are in operation in a number of countries.

The environment in an oxyfuel boiler is very significantly different from that in a conventional air-based combustion system. Gaseous partial pressures and temperature profiles will be significantly modified and this will have a strong influence on the physical and chemical behaviour of burning coal particles and their progeny. Hence it is an important area for study as noted by Davidson and Santos (2010).

3.2 Summary

The last twenty years have seen some very significant changes in the power generation sector that affect the way in which coal is burnt to generate power. In addition to the way in which plant is operated, a new tranche of co-fuels have been introduced into the pulverised coal combustion environment, further complicating an already challenging picture of the fundamental transformation occurring during combustion. Many of these new fuels are themselves highly variable in composition and exhibit behaviour during combustion that can be significantly different to coal. They may also contain high concentrations of species that can interact with coal combustion products, sometimes with deleterious results. The most recent changes to pulverised coal fired boiler plant include modifications to the gaseous atmosphere within the boiler during oxycombustion which are highly likely to produce concomitant changes in reaction mechanisms and pathways that are only just beginning to be explored by research workers. An understanding of the ways in which oxycombustion affects combustion is currently a major driving force in coal research and development.

4 Developments in studying pulverised coal combustion

4.1 Computer-based modelling developments

Since the 1970s, developments in the field of microelectronics have seen the emergence of high-performance, low-cost computing power. The performance of the basic microprocessor components has doubled roughly every two years – an observation embodied in the rule of thumb known as Moore's Law (Moore,1965). Similar developments in associated components have produced desktop computers capable of running programs that would have required a dedicated computer suite even a decade earlier. The emergence of these powerful computing facilities has enabled the realisation of a technique whose principles have been established for two hundred years, but which required modern low-cost computers to realise – computational fluid dynamic modelling (CFD) (Batchelor, 1967).

4.1.1 Computational fluid dynamics

Fluid flows such as the entrained solid-in-gas flows of pulverised coal combustion are governed by partial differential equations that represent conservation laws for the mass, momentum, and energy in the system. In Computational Fluid Dynamics these partial differential equations are replaced by a set of algebraic equations which can be solved using digital computing techniques. CFD provides at least a qualitative, and increasingly a quantitative prediction of fluid flows by means of:

- mathematical modelling using partial differential equations;
- numerical methods such as 'discretisation' and solution techniques;
- software tools including solvers, pre- and post-processing utilities.

CFD can give an insight into flow patterns that are difficult, expensive or impossible to study using traditional experimental techniques by enabling scientists and engineers to perform 'numerical experiments' in a 'virtual flow laboratory'.

Kuzmin (2009) summarised the strengths and weaknesses of CFD compared to traditional experimental techniques as follows (Table 1). The first significant CFD modelling system applicable to coal combustion was CHAM formed initially as Combustion, Heat and Mass Transfer Ltd by Spalding of Imperial College in 1969, and later renamed as Concentration Heat and Momentum Ltd (Spalding and Cole, 1973). The early CFD applications were process-specific and relatively hard to use. A few years later, building upon experience with CHAM, Spalding developed a single CFD code capable of handling all fluid-flow processes, and during late 1978 the company began creating the world's first general-purpose CFD code, PHOENICS, which is an acronym for Parabolic, Hyperbolic

Table 1 Experiment versus CFD simulation (Kuzmin, 2009)

Experiments	Simulations
Quantitative description of flow phenomena using measurements • for one quantity at a time • at a limited number of points and time instants • for a laboratory-scale model • for a limited range of problems and operating conditions	Quantitative prediction of flow phenomena using CFD software • for all desired quantities with high resolution in space and time • the actual flow domain • for virtually any problem and realistic operating conditions
Error sources: measurement errors, flow disturbances by the probes	Error sources: modelling, discretisation, iteration, implementation

Or Elliptic Numerical Integration Code Series. PHOENICS was launched commercially in 1981. Since then a large number of CFD systems have been developed for use in the modelling of combustion processes, and together with pre- and post-processing submodels are used for studying many combustion issues including, flows in and around coal burners, flows around heat exchanger surfaces and emissions from plant. CFD has evolved to the point where confidence in its predictions is sufficiently high to enable its use in the design of new combustion plant (Gillespie, 2001).

In setting up a CFD model to address problems in a real system such as a power plant boiler, a grid-based model must be constructed to represent the flows in the system. Figure 3 shows a simple flow model where the real world situation is mapped onto a grid of discrete boxes ('discretisation') whose inputs and outputs are solved by calculating the solutions to the controlling differential equations.The number of grid points (or control volumes) available determines the complexity of the problem that can be solved and the accuracy of the solution (*see* Figure 4). When CFD flow models are combined with complementary models that describe the other physical and chemical processes occurring during combustion such as devolatilisation, burn-out, and mineral interactions very sophisticated simulations are possible (*see* Figure 5). As with all models, validation of predictions

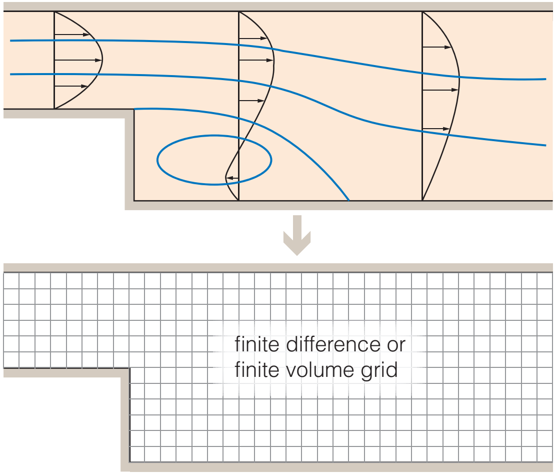


Figure 3 Mapping flows onto a CFD modelling grid (Kuzmin, 2009)

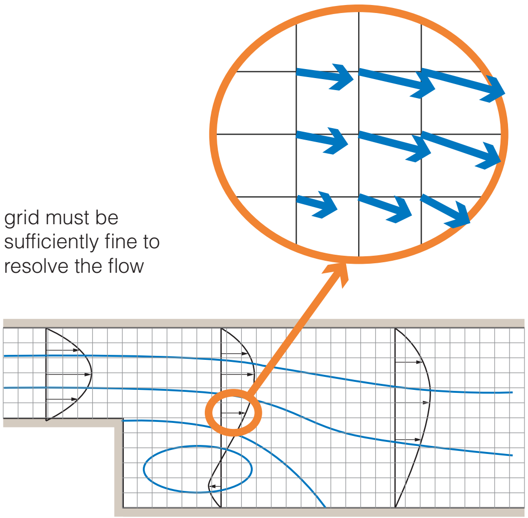


Figure 4 CFD modelling grid resolution (Kuzmin, 2009)

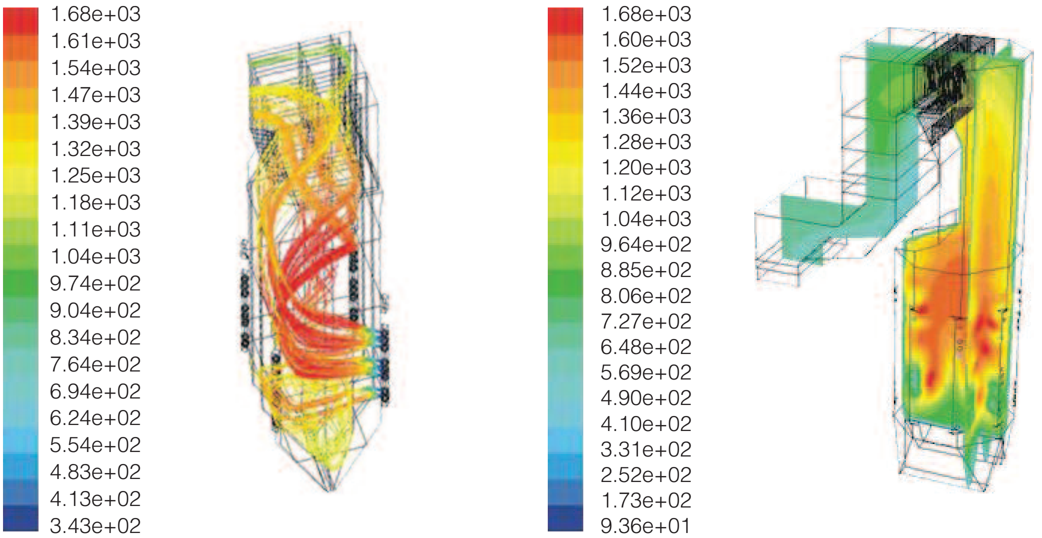


Figure 5 Coal particle temperatures and flows (left) and gas temperatures and flows (right) in a pulverised coal fired boiler model (Mancini, 2012)

against experimental data is a crucial part of the predictive development, but the availability of these models enables high confidence predictions based on a relatively small experimental data set to be achieved at relatively low cost.

Today, a large number of software packages are available that allow sophisticated computer modelling of flows and related phenomena. These include codes developed and marketed as commercial packages with full technical back-up, codes developed by companies (for example boiler manufacturers) for internal use, codes developed by universities and colleges, and free licensed codes made available by enthusiastic users.

4.1.2 Coal characterisation techniques

Gupta (2006) has recently reviewed the physical and chemical analyses that are currently used to give a deeper understanding of coal structure and reactions before and during combustion and which are being used to give a deeper understanding of the complex and challenging environment in contemporary coal-fired plants. While the conventional analytical techniques such as proximate and ultimate analysis, ash fusion temperature and petrographic analysis are still of great value, several advanced analytical techniques that can be used for determining specific properties of a coal from a ‘bulk sample’ have proved themselves useful.

Differential thermal analysis (DTA)

Differential thermal analysis (DTA) is conducted under controlled atmospheric and heating conditions and provides a method of mineral identification in coal (Warne, 1979; Sharkey and McCartney, 1981). The method offers advantages in that the samples can be used directly for analysis without any pre-treatment. DTA is based on heating an unknown sample with a reference sample under controlled conditions and measuring the temperature of the samples with respect to the temperature of the furnace. The difference in these temperatures displays peaks according to exothermic or endothermic reactions occurring inside the sample. The characteristic peaks of various mineral groups have been identified, and by a comparison with the database, the peaks obtained from the unknown sample can be identified as specific mineral groups.

Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) is based on the heat needed or released during a phase change. It measures energy necessary to establish a close to zero temperature difference between a substance and an inert reference material, as the two specimens are subjected to identical temperature regimes by being heated or cooled at a controlled rate. There are two types of DSC systems in common use. In power compensation DSC, the temperatures of the sample and reference are controlled independently using separate, identical furnaces. The temperatures of the sample and reference are equalised by varying the power input to the two furnaces; the energy required to do this is a measure of the enthalpy or heat capacity change in the sample relative to the reference.

In heat flux DSC, the sample and reference are connected by a low-resistance heat flow path. The assembly is enclosed in a single furnace. Enthalpy or heat capacity changes in the sample cause a difference in its temperature relative to the reference. The resulting heat flow is small compared with that in differential thermal analysis (DTA) because the sample and reference are in good thermal contact. The temperature difference is recorded and related to enthalpy change in the sample using calibration experiments. Hansen and others (1999) have used DSC to assess the thermal behaviour of ash.

Thermomechanical analysis (TMA)

Slagging and formation of ash deposits inside furnaces is a major problem faced during the coal conversion process. Thermomechanical analysis (TMA) is a technique which can be used to characterise the melting and slagging properties of coal ash (Saxby and Chatfield, 1996; Bryant and others, 2000). It allows the comparison of the tendency of coal particles to coalesce and sinter and

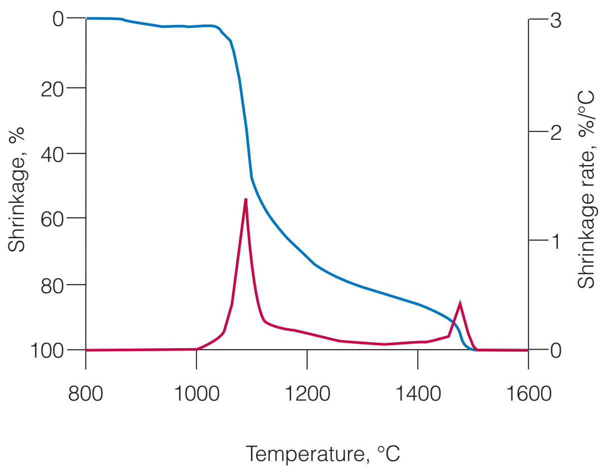


Figure 6 Typical TMA trace of a coal ash and its derivative (Gupta, 2006)

provides information on the fusibility, melting, and sintering behaviour as well as information such as deposit strength, and gives useful information on the influence of ash deposits on heat transfer. TMA involves heating an ash sample under load and measuring the penetration of a mechanical probe into the sample. The results are obtained in the form of increase in percentage penetration with increasing temperature. The TMA results provide an indication of the extent of melting in an ash sample. Figure 6 shows a typical TMA curve for an ash sample. The sharp peaks in the derivative curve in this figure represent distinct phase changes during heating. A scanning electron microscopy (SEM) examination of a sample and comparison with TMA data show an increase in melting with the increase in percentage penetration of the samples.

Chemical fractionation

Chemical fractionation is a technique that provides species-specific information using selective extraction of elements based on solubility that reflects their association in the coal. The process consists of three successive extractions:

1. using water to remove water-soluble salts containing elements such as sodium;
2. using ammonium acetate to remove elements such as sodium, calcium, and magnesium that are ion exchangeable;
3. using hydrochloric acid to remove acid-soluble species such as alkaline earth sulphates and carbonates. The residual material typically consists of silicates, oxides, and sulphides.

This wet-chemistry technique is not ideal in that it can easily be biased by incomplete penetration of the sample by the solutions, resulting in partially-soluble compounds. However, when carefully performed, it can be both accurate and precise, nearly within the limits of the elemental analysis procedures themselves. Many of the mineral species commonly found in coal can be distinguished by chemical fractionation by comparing the elemental composition of the materials extracted at each stage of the process, based on their solubility in the three solutions (Steel and others, 2001). In general, the solubility for each of the elements can be used to construct a matrix to determine the species composition of the sample. The results of chemical fractionation analyses can be used to estimate the overall species composition of both minerals and non-mineral inorganic components in coal. This technique is particularly useful for lignite and biomass fuels. Chemical fractionation has also been used to study the effect of minerals based on elements such as Na and Cl in coal on slagging and fouling characteristics and also to study the formation of fine particles in ash from combustion.

X-ray fluorescence analysis (XRF)

X-ray fluorescence is a particularly valuable technique for the analysis of trace elements because of its ability to perform a rapid simultaneous quantitative analyses of a large number of elements. It offers several advantages over conventional techniques of trace element analysis, such as atomic absorption spectroscopy, including fully automated analytical routines. It can be used to ‘fingerprint’ mixtures of trace elements sourced from coal combustion.

Mössbauer spectroscopy

Mössbauer spectroscopy is used in the analysis of iron containing minerals in coal. These are of particular importance owing to their role in the formation of slagging deposits in pulverised coal fired plant. Huggins and Huffman (1979) have undertaken extensive studies of coal and coal deposits using Mössbauer spectroscopy in coal characterisation.

Electron probe microanalysis

Electron probe microanalysis (EPM) is based on the principle that a sample will emit X-rays characteristic of the elements present in the sample when exposed to a finely focused electron beam. The electron column and basic instrumentation for EPM are very similar to those used in scanning electron microscopy (SEM). The major difference is that while SEM describes the surface morphology by visual magnification of the surface, EPM is able to describe the chemical composition of the sample. A scanning electron microscope, when equipped with an X-ray spectrometer, can carry out the same analysis as that of an EPM. Modern scanning electron microscopes are commonly equipped with energy dispersive spectrometers (EDS) that allow qualitative and quantitative chemical analysis. EPM can be used as a powerful analytical tool in coal research if used in conjunction with other analytical techniques such as SEM, transmission electron microscopy (TEM) and optical microscopy, X-ray diffraction, and Mössbauer spectroscopy.

X-ray diffraction analysis of mineral matter in coal

X-ray diffraction (XRD) of coal reveals important qualitative and quantitative information on the mineral matter composition of coal and the interaction of mineral matter during conversion processes. High-temperature XRD is widely used for the investigation of the mineral reactions that occur during coal combustion in power-plant boilers. In the past, the nature of these reactions has been deduced either from a study of the chemistry of the reaction products or from phase-equilibria modelling. The sample is heated under controlled conditions to simulate combustion processes when the mineral reactions can be studied dynamically and the effects of parameters such as variations in heating rates and variable gas atmospheres can be evaluated. This technique offers a particular advantage to the power-generation industry in that it provides knowledge of the melt phase, both the temperature at which it first formed and the abundance, because first appearance and nature of a melt phase is of critical importance in the formation of slagging and fouling deposits. XRD has also been useful in obtaining the structural information of coal and chars (Lu and others, 2001). The changes in the crystalline structure of coal during conversion can be observed by an analysis of the XRD spectra of the char/ash. X-ray diffraction analysis of the chars can also reveal significant changes in crystallite size for samples produced at different temperatures in a wide temperature range (900–1500°C).

Thermogravimetric analysis (TGA)

In this technique, a small sample of coal is heated in a controlled environment at a specified heating rate. TGA is commonly undertaken to understand the pyrolysis behaviour of coal. The rate of mass loss in TGA has been widely used to determine the reactivity and kinetic parameters of char combustion or gasification. There are two modes of TGA analysis for estimating the reactivity of char: isothermal and non-isothermal. When used for assessing the performance of coals in pulverised coal combustion, care must be taken in interpreting the results as volatile yields under the relatively low heating rate of the analysis can be significantly lower than those under the high heating rates experienced by coal particles in a boiler.

^{13}C and 1H NMR spectroscopy

^{13}C NMR spectroscopy is a powerful non-destructive analytical tool for identifying structural parameters in coal. The carbon NMR spectra are derived from the resonance of the C-13 isotope of carbon, which is the only carbon isotope with a magnetic moment. Coal is thought to consist of a matrix of aromatic clusters connected by aliphatic bridging groups, aliphatic and carbonyl side chains attached to the aromatic cluster, and solvent-extractable components referred to as the ‘mobile phase’. ^{13}C NMR has been used to quantify the average carbon skeletal structure of a given coal with twelve parameters that describe the aromatic and aliphatic regions of the coal matrix. From these structural parameters, combined with an empirical relationship between bridgehead carbons and aromatic carbon per cluster, a description of the lattice structural of coal can be attained. Useful structural parameters determined from these analyses include the number of carbons per cluster, the number of attachments per cluster, the number of bridges and loops, the ratio of bridge to total attachments, the average aromatic cluster molecular weight, and the average side chain molecular weight. A recent development is the use of proton NMR (1H NMR) spectroscopy for coal characterisation. The sensitivity of hydrogen atoms to magnetic resonance, the ease in measuring the spectra, and fast data acquisition on relatively cheap lowfield NMR instruments makes this characterisation technique particularly useful. Research conducted on Australian coals has produced promising relationships between NMR measurements and coal properties (Harmer and others, 2000).

FTIR spectroscopy

FTIR is a powerful tool for probing the functional groups in coal and chars. As a non-destructive analytical tool, it identifies molecular vibration, both stretching and bending, due to the absorption of infrared radiation. A sample exposed to continuously changing wavelengths of infrared radiation absorbs light when the incident radiation corresponds to the energy of a particular molecular vibration. Energies of the stretching vibrations correspond to infrared radiation with wavenumbers between 1200 and 4000 cm^{-1}, while the bending vibration is in the range of 500–1200 cm^{-1}. This part of the infrared spectrum is particularly useful for detecting the presence of functional groups, because these groups have characteristic and invariant absorption peaks at these wavelengths. FTIR has been extensively used in the identification of the chemical structure of coal (Gilfillan and others, 1999). FTIR and other chromatographic instruments such as GC/MS have been coupled to TGA or other similar techniques, providing controlled conditions to study pyrolysis or combustion by-products.

Chromatographic techniques

Analytical pyrolysis techniques such as gas chromatography/mass spectrometry (GC/MS), along with multivariate data analysis techniques, are powerful analytical tools for simultaneously investigating coal structure and reactivity of organic materials. During pyrolysis, complex mixtures are released from coal because of distillation, desorption, and thermal degradation. The chemical nature of these products depends on both the chemical composition and the structure of the coal and on the heating condition. Consequently, the result of a chemical analysis of these devolatilised coal products provides information on the origin structure of the coal. The chromatographic techniques have contributed significantly to the environmental impact of combustion and pyrolysis by providing excellent emission-monitoring tools for qualitative and quantitative analysis.

Scanning electron microscopy (SEM)

The morphology and cross sectioned samples of coal and char/ash have been studied widely using SEM, and the analysis of the SEM image can provide valuable information such as particle size, swelling of the particles during conversion, and the structure of char/ash. This information can be correlated to the fundamental properties of parent coal and the process parameters. Figure 7 shows typical SEM images for the morphology and cross section of a coal char particle.

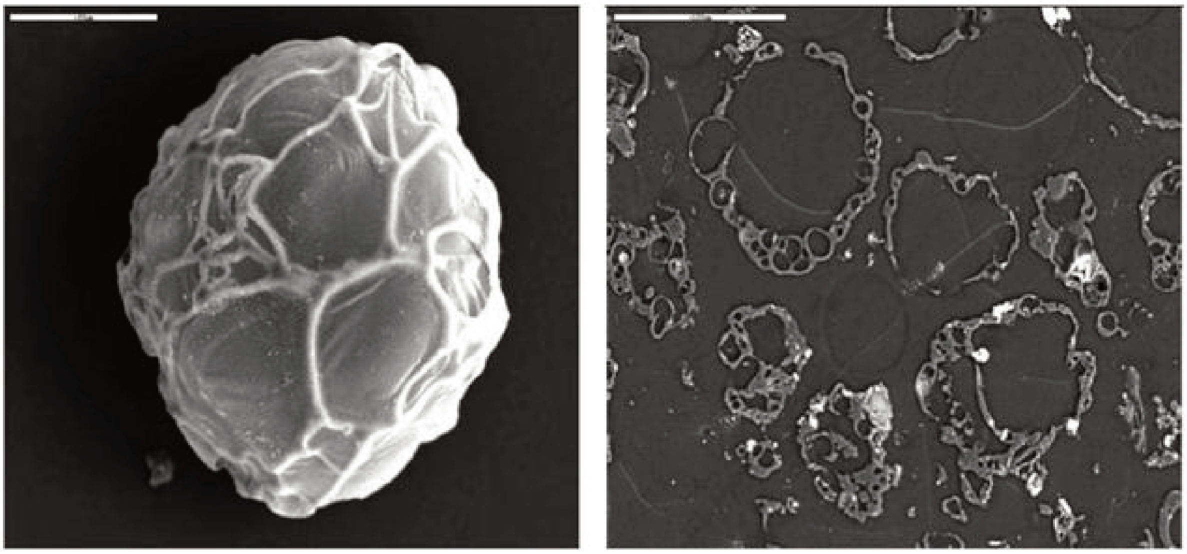


Figure 7 SEM micrograph showing morphology (left) and cross section characteristics (right) of coal char particles (Gupta, 2006)

Image analysis of SEM images has been used to estimate the porosity of coal char particles. It has been stated earlier that the intermediates and products of coal combustion may contain various quantities and types of mineral matter, and it is necessary to assess the beneficial and detrimental effects that the mineral matter may have in plant during subsequent disposal or utilisation. Scanning electron microscopy and transmission electron microscopy (TEM) have also been utilised to identify maceral composition and mineral matter in coal and to explore the relationships between coal minerals and certain maceral types.

Advanced microscopic analytical techniques

Recent advances in analytical techniques have resulted in a multidimensional approach to the characterisation of coals. The correlation of the extensive coal structure data from these approaches has led to an extensive database of fundamental measurements that can be used to model the behaviour of coal during its combustion. Two valuable techniques that use this approach and which are throwing light on the complexities of pulverised coal combustion are:

1. Automated reflectogram (AR) which provides the reflectivity distribution in coal, or the heterogeneity in organic matter.
2. Computer-controlled scanning electron microscopy (CCSEM) analysis which provides the distribution of minerals in coal at the individual particle level, or the heterogeneity in inorganic matter. They are particularly valuable in elucidating the mechanism operating during the combustion of coal blends (Rushdi and others, 2005).

Automated reflectogram

Coal petrography is a standard tool for the characterisation of the organic (maceral) and inorganic (mineral) constituents of coal. Two types of data are derived from this method: rank (defined by vitrinite reflectance) and composition (maceral composition). Both of these can be related to the chemical composition of the coal and will control the physical behaviour of coal during processing and utilisation. The overall maceral composition of coal is valuable in predicting conversion behaviour of coal, but the models based on such predictions have limitations of accuracy; therefore, there is a need to characterise the coal heterogeneity based on a more fundamental property of coal so that the model predictions can be improved. Automated reflectogram provides the possibility of characterising coals based on single-particle composition and modelling their conversion behaviour more accurately.

O'Brian and others (2003) have developed a method to reduce operator subjectivity and improve the accuracy of petrographic analysis, for the fully automated coal petrographic analysis of a single-seam coal. Full maceral reflectograms (FMR) were collected using image techniques and then processed to produce a vitrinite and inertinite group abundance, a combined minerals plus liptinite abundance, and random vitrinite reflectance information. The technique involves obtaining a number of 256 grey-scale images of a polished surface of coal particles. For a given sample, approximately 2 million pixels were taken. Then the grey scale is calibrated with the samples of standard reflectance, and finally, these images are processed to give a distribution of reflectance. Within the FMR, inflection points in the cumulative frequency format coinciding with the commencement and end of the vitrinite proportion can be used to determine maceral group proportions. This form of analysis may be used to 'fingerprint' coals by producing a reflectance signature of the bulk constituents in a representative sample. The full signature exhibits inflections that coincide theoretically with the boundary between the different maceral and mineral groups. The vitrinite content is given by the area under the vitrinite peak in as shown in the example in Figure 8. The material with

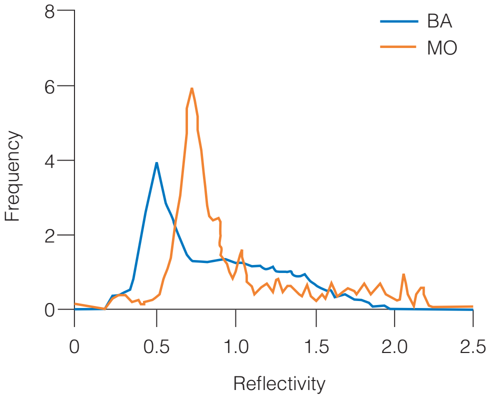


Figure 8 Automated reflectogram showing the maceral composition of two coal samples (Gupta, 2006)

reflectivity values less than this range may be mineral matter or liptinite or microporosity, whereas the material with reflectivity values greater than this are either inertinite maceral or brighter mineral matter.

Computer-controlled scanning electron microscopy (CCSEM)

CCSEM is a technique that combines a scanning electron microscope (SEM), X-ray analyser (EDS) and digital scan generator controlled by intelligent software. The principle of operation of a CCSEM is the interaction between an incident high-energy electron beam and the coal sample specimen. Signals generated such as secondary electrons, backscattered electrons and characteristic X-ray photons are collected by different detectors, and interaction of movement of electron beam and signal measurement is controlled by computer software. Using this technique, large numbers of individual particles can be located, sized and characterised very quickly with scanning times often less than one second per particle required. These particles can then be grouped into particle type classes based on their elemental composition and shape. The resulting CCSEM data on the size, association, composition and abundance of mineral components in coal can be used to study the transformations of the inorganic constituents in chars, fly ash and ash deposits. Thus CCSEM can follow the changes in the size, chemistry and shape of the mineral grains through the various stages of combustion to fly ash formation. An important advantage of CCSEM over the more conventional methods of coal mineral analysis, is that it avoids the need for separation of the mineral matter from the coal by low temperature ashing, thereby eliminating the inherent problems that can be caused by transformation and reactions of the coal mineral matter during the ashing process. Many complete CCSEM systems are commercially available, incorporating all the necessary computer hardware and software and they have become an established tool in understanding coal and coal ash. Figure 9 shows the configuration of a typical CCSEM.

The first CCSEM was developed by White and others (1972) at the Pennsylvania State University in the early 1970s and was used for the analysis of particulate minerals in coal and coal liquefaction residues. The machine was called a Computer Evaluation of Scanning Electron Microscopy Images (CESEMI), which established a prototype platform for the following CCSEM development. The basic

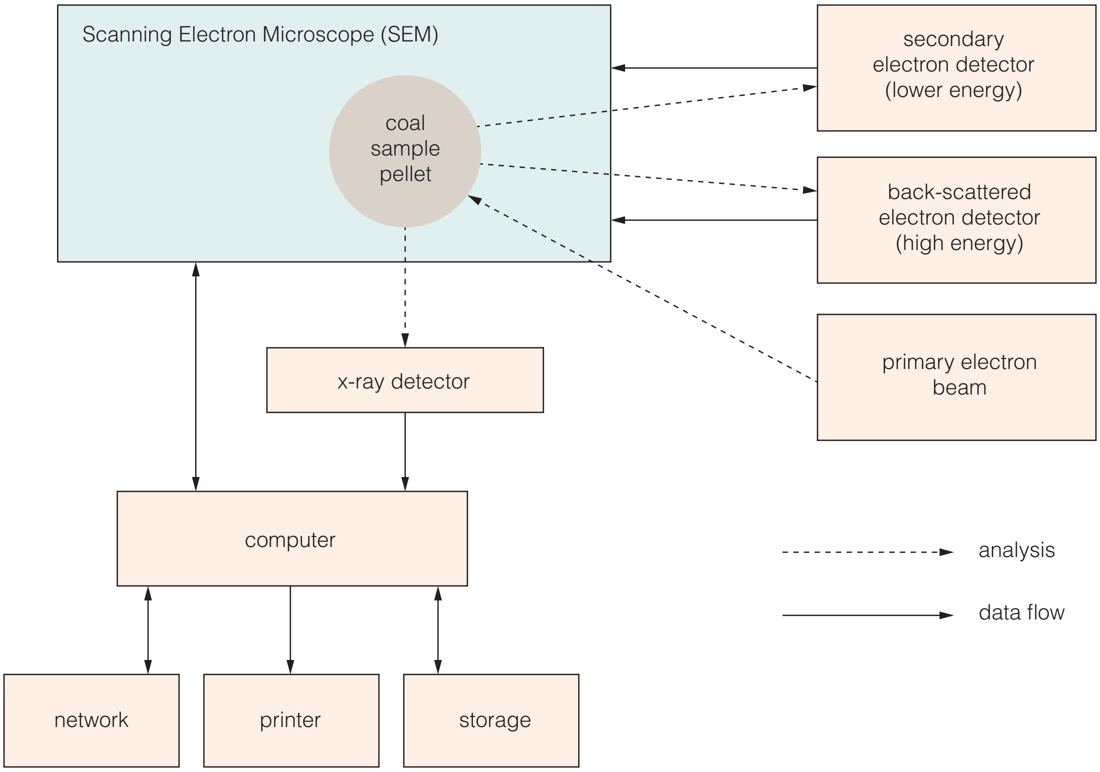


Figure 9 Configuration of a typical CCSEM (Butcher and others, 2003)

methodology for analysis of a coal sample by CCSEM is as follows:

- **sample preparation:** ground particles of coal are mounted and polished in an epoxy resin;
- **mineral location**: mineral grains are determined in the polished section of coal on the basis of their brightness in the back-scattered electron image which is a function of average atomic number;
- **compositional analysis:** in this system, when mineral grains are located, they are sized by their cross-sectional area and their elemental compositions are determined by monitoring 7 X-ray channels (Al, Si, S, Ca, Fe, K, and Ti) by EDAX. From the various combinations of relative X-ray intensities of these elements, it is possible to identify most of the commonly-occurring minerals in coals;
- **statistical consideration:** in a typical run, as many as 2000 particles are examined for their composition and size;
- **data output:** after the data are recorded, the computer presents the results in a summary file, which lists average size, size distribution, shape factor, volume and number percentages for each mineral type;
- **limitations:** for quantitative analysis the method can be applied only to mineral grains larger than about one micron in diameter because it is limited by the lower limit of resolution of the X-ray system.

Table 2 CCSEM mineral and compositional categories

Quartz	Apatite
Aluminosilicate	Pyrite
K-aluminosilicate	Gypsum
Ca-aluminosilicate	Barite
Fe-aluminosilicate	Gypsum/barite
Iron oxide	Aluminosilicate/gypsum
Spinel	Calcium aluminate
Aluminium oxide	Iron sulphate/pyrrhotite
Calcium oxide	Calcium-rich
Dolomite	Silicon-rich
Ankerite	Periclase
Rutile	Unknown
Calcium silicate	

As a result of the study of a large number of different coal samples, a set of compositional categories for most coal common minerals has been developed (*see* Table 2). The major advantage of using CCSEM over other mineralogy analytical methods for characterising coal mineralogy is that it provides information on the structure and association of mineral matter in the coals, such as mineral grains size, chemical composition and whether the mineral grains are within the coal matrix or external to it. Additionally, the measurement is not affected by crystal structure as required by XRD analysis, making it is possible to trace mineral transformations during coal utilisation processes no matter whether the mineral experienced phase changes, became amorphous or even completely molten. However, the technique also has a number of drawbacks, specifically:

- it is a surface analysis rather than bulk analysis technique;
- a significant percentage (<10%) of 'Unknown' minerals is usually reported by CCSEM;
- CCSEM measures discrete mineral grains above 0.5 µm in size, omitting organically associated inorganic elements;
- it identifies a mineral phase from its chemical composition and this approach has limitations due to variations in the chemical composition of naturally-occurring minerals;
- CCSEM does not differentiate polymorphs thus quartz, cristobalite and tridymite are reported under a single heading. Pyrite and marcasite are reported as Fe-Sulphide. This can be partially resolved through the use of additional techniques such as Mössbauer spectroscopy (for iron-containing species) and XRD analysis;
- the threshold setting of the backscattered electron images is a subjective, operator-dependant variable. Clay minerals such as kaolinite have the lowest BSE grey level of minerals in coal and are therefore the most difficult to detect and size. Pyrite is usually of the highest BSE intensities in the coal minerals and is less likely to be missed.

Developments based on CCSEM have been partially successful in addressing these deficiencies and the QEMSCAN technology conceived at CSIRO is worth of note in this context (Butcher, 2003). In QEMSCAN each particle is individually located and is distinguished from the mounting medium by its Backscattered Electron contrast. This is achieved by setting a Backscattered Electron Brightness threshold. Material that is darker than the threshold is classified as mounting medium, that lighter than the threshold is considered as a particle. Once an individual particle is located, it is scanned by a grid of points and the backscattered electrons and the X-ray photons emitted from a given point are used to identify the elements present and thus classify the mineral species present. The identification of a particular mineral or phase at any given point is achieved by comparing, on-line, a rapidly collected (typically 5 milliseconds) X-ray spectrum (normally only 1000 total counts) with a look up table of minerals and phases that are defined by their chemical compositions. Matching X-ray spectra to a mineral is done whilst the next spectrum is being acquired, thus allowing for about 100,000 spectra to be processed and identified in one hour of measurement. The target list of mineral species used (known as the Species Identification Program, or SIP) can be added to or refined. The image of the particle section is built up point-by-point in this way in which each pixel corresponds to a mineral species, or phase, in a region under the electron beam. When all particle sections in a given field of view have been measured the stage is positioned to bring the next field into view and the measurement process is repeated. Many hundreds of particle sections are measured on each sample and their images stored. Liu and others (2007) compared the performance of CCSEM and QEMSCAN in a study of fifteen samples prepared from three coals, concentrating on mineralogy, ash chemistry, mineral-matter organic matter association and particle size distribution of mineral matter. They concluded that:

- both CCSEM and QEMSCAN can positively identify the major minerals occurring in coals including quartz, kaolinite, siderite, calcite, pyrite, dolomite, ankerite, apatite, illite and chamosite;
- the particle size distribution reported by QEMSCAN is in a good agreement with CCSEM data, showing that size of minerals decreases as size of coal particles decrease and size of included minerals is finer than the size of excluded minerals;
- both CCSEM and QEMSCAN can quantify the major minerals occurring in the coals, generally following the order: Clay minerals > Quartz > Siderite > Calcite in the samples studied;
- both CCSEM and QEMSCAN techniques can positively identify the relative abundance of the elements Si, Al, Fe, Ca and Ti in the order of Si>Al>Fe>Ca>Ti in samples studied. And both techniques give information on the distribution of major elements into different mineral phases;
- CCSEM was found to be better for estimating the proportions of included mineral and excluded mineral grains;
- accuracy of CCSEM and QEMSCAN results can be improved if all the bias in sample preparation, measurement process and offline data processing can be minimised;
- CCSEM and QEMSCAN can be used as quantitative tools for mineralogy analysis, combined use of other analytical techniques to predict coal ash performance.

4.2 Summary

The traditional coal characterisation techniques (for example density, proximate and ultimate analysis, ash fusion temperatures, ash chemical composition) have served coal users well for several decades and remain important ‘first step’ tools in assessing coal behaviour under pulverised coal combustion conditions. These techniques have been joined by an impressive array of developments that give detailed information on coal properties, often under dynamic (combustion) conditions in real time. The ability to observe and measure coal reactions as they occur is a valuable step forward as coal behaviour under the demanding temperature-time history in a boiler can be markedly different to that observed in a laboratory under different conditions.

Perhaps the most significant development is the emergence of computer modelling which allows the prediction of fluid and entrained particle flows through a burner and subsequently the boiler to be predicted with a high degree of accuracy. By incorporating submodels of coal behaviour an understanding of ‘real time’ coal behaviour is becoming increasingly possible with the benefits of true predictive capability.

5 Transformations during combustion

5.1 Measurements in coal flames

Developments in electronics have enabled the production of increasingly sophisticated instruments capable of taking direct measurements in coal flames. Examples of some relevant developments are summarised below.

Tsuji and others (2004) set out the results of a study to investigate the combustion characteristics of a pulverised coal combustion flame using advanced optical diagnostics. A laboratory-scale pulverised coal combustion burner was specially fabricated. The velocity and shape of non-spherical pulverised coal particles and light emissions from a local point in the flame were measured by a shadow Doppler particle analyser (SDPA) and multi-colour integrated receiving optics (MICRO), respectively. In addition, to examine the spatial relation of the combustion reaction zone and pulverised coal particle, OH planar laser-induced fluorescence (OHPLIF) and the Mie scattering image of pulverised coal particles were measured simultaneously. Particle velocity measurements with laser Doppler velocimetry (LDV) were carried out to compare with the accuracy of those obtained with SDPA. The particle velocity by SDPA was very consistent with that determined by LDV. The particle velocity did not change for different particle sizes on the centre axis of the flame. However, the particle velocity increased with particle size at the edge of the flame. The axial distributions of OH chemiluminescence, CH band light emission and Mie scattering intensity by MICRO was considered reasonable. The Mie scattering images provided particle motions in the flame and showed that the coal particles radially spread on progressing along the flame. This radial spread in the non-combusting case is more apparent than that in the combusting case.

Pickett and others (1999) used a two-colour Laser Doppler Anemometer (LDA) to obtain axial and tangential velocity information in a 0.2 MW pulverised coal flame. In addition to the reacting flow data, a study on the accuracy of using coal as a seed particle to measure gas phase velocity using LDA was undertaken. Non-reacting flow velocity measurements were obtained near the fuel inlet and in the quarl region of a geometrically identical burner to identify the velocity profile at several burner settings and to assist in establishing modelling inlet conditions. Both the reacting and non-reacting velocity data were obtained at three or more swirl settings and various axial positions allowing a study of the effect of swirl on inlet turbulence and flame structure. The velocity results were compared with effluent NOx measurements. At the flow rates and accelerations experienced in this study, the coal particles were shown to be useful as seed particles for LDA gas phase velocity measurements. The coal-flame velocity indicated a centreline flame at zero swirl transitioning to a radially directed flame with a central recirculation zone at swirl settings of 0.5 and 1.5. The transition of the flame structure to a central recirculation zone was also seen at the fuel inlet plane in the non reacting flow studies and was found to correlate with a decrease in measured effluent NOx. Measured axial velocity profiles 5 mm below the fuel inlet showed negative axial velocities (in the opposite direction of the average flow velocity). These were produced along the primary tube as swirl was increased from 0 to 1.5 with the transition occurring between 0.5 and 0.75 swirl. Transition in the flow near the fuel inlet correlated well with a drop in effluent NOx and with transitions in the recirculation zones measured further downstream. The strong interaction with burner velocity profiles and NOx suggest velocity profile, in addition to swirl number, is an important measured boundary condition for modelling.

Bradley and others (2003) drew attention to the importance of securing reliable temperature measurements as a major requirement for the understanding of combustion processes and the validation of mathematical models. Although thermocouples have been used successfully to measure temperatures in combustion processes they have several disadvantages due to their intrusive nature and, in transient systems, due to thermal inertia. Laser techniques offer the means of circumventing many of the disadvantages of physical probes and, for temperature measurements Coherent

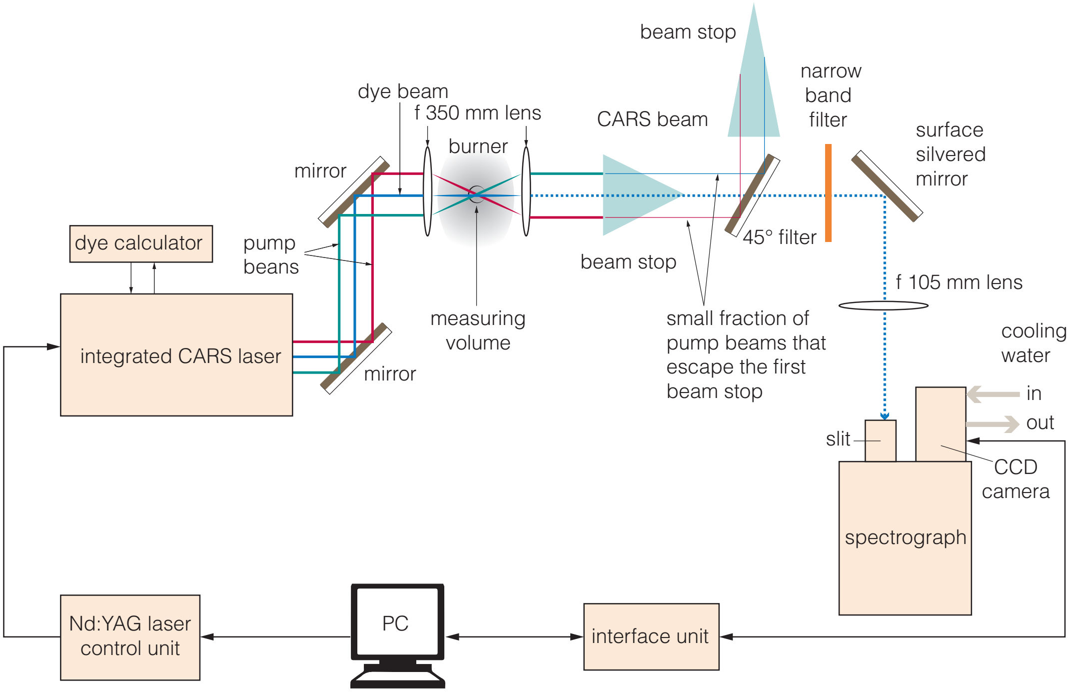


Figure 10 Schematic of CARS equipment used for the study of coal flames (Bradley and others, 2003)

Anti-Stokes Raman Spectroscopy (CARS) has proved to be reliable and robust in a wide range of combustion systems ranging from laboratory flames through industrial applications to rocket motors. The rapid growth in the application of the technique can be attributed to improved lasers, an enhanced understanding of the CARS process, and the development of sophisticated spectral-synthesis codes, which are necessary for the quantitative interpretation of CARS data.

The CARS technique has been applied very successfully for clean flames. However, in the environment of sooty and coal flames, interpretation of the resulting spectra has proved to be difficult. This is due to particle-induced optical breakdown, which alters the shape and intensity of the experimental spectra and causes a reduction in signal strength by attenuation of the laser and signal beams as they pass through the flame. In addition, laser or flame generated C2 emission, which resides inside the N2-Q branch spectrum, disturbs the N2-CARS signal.

Eckbreth (1979) realised that measurements in a highly sooty, laminar propane diffusion flame produced a coherent spectral interference arising from electronic resonance CARS generation from C2 which was produced by the laser vaporisation of soot. He concluded that a reduction in the Stokes laser bandwidth and use of polarisation filters resulted in low distortion N2 CARS spectra. Beiting (1986) found that coal particles induce optical breakdown, creating strong, non-resonant signals.

The optical arrangement of the CARS system employed is shown in Figure 10. The Spectron Laser Systems integrated CARS source comprised a Q-switched frequency doubled (512 nm) Nd:YAG laser, with an energy of 350 mJ in 15 ns pulses at 10 Hz and a 35 mJ broad band (150 cm^{-1}) dye laser with a centre frequency of 607 nm. The folded BOXCARS phase matching geometry was used due to its good spatial resolution (small measurement volume) and ease of signal collection. The ellipsoidal control volume, 3 mm long, was aligned along isothermal planes, and was 100 mm in diameter. A B&M Spectronic BM100 Spectrograph was employed, with a CCD camera, a controller (Model ST-120) and associated software supplied by Princeton Instruments Inc. Nitrogen spectra were analysed with the AERE Harwell computer codes CARP-PC and QUICK to produce single shot temperature measurements. The CARS system was employed to measure temperatures in a coal flame. The burner had optical access through two windows, each 60 mm in diameter, which were mounted on opposite flanged openings. An important improvement in the experimental set-up was to provide good optical access to the coal flames while minimising contamination of the windows by coal particles. For this, two manually operated shutters were fixed to the inside of the windows. The shutters were opened only for a short period of time for each measurement. This allowed adequate window cleanliness to perform a complete set of measurements before cleaning was necessary.

Astrup and Clausen (1995) described a method for the application of laser sheet visualisation to power station flames where the laser light sheet is photographed under a very small angle. The camera was positioned close to the sheet generating cylindrical lens and observed through the same opening as the one through which the laser sheet is introduced. With camera and optics built into a unit that is small enough to enter the burner centre tubes of power station burners, the method was thought applicable to all flames in a multi-burner furnace. The method has been tested on oil and coal flames in an experimental furnace and on two 36 MW power station pulverised coal flames. For both laboratory and power station flames, different flame types have given clearly different pictures and even for the very dense power station low-NO flame it has been possible to distinguish regions with a diminished coal concentration around the periphery of the burner. The workers consider that problems related to such variations or to variations between burners in a furnace might be traced with this technique.

Lu and others (2002) set out a novel instrumentation system for the concurrent measurement of temperature and soot concentration of pulverised coal flames. The system operated on the two-colour principle, combining CCD camera optical sensing and digital image processing techniques. The temperature and its distribution in a flame were calculated from the ratio between the grey-levels of corresponding pixels within two images captured at two carefully selected wavelengths. The soot concentration distribution of the flame was represented and estimated using the KL factor that is derived from intermediate information obtained during the temperature measurement. The system was calibrated using a tungsten lamp as a standard temperature source. The maximum relative error in the temperature measurement was 1.83%. Experimental results obtained on a 0.5 MWth combustion test facility show that the temperature distribution of a coal-fired flame ranged from 1380°C to 1700°C, while the KL factor ranged from 0.18 to 0.33.

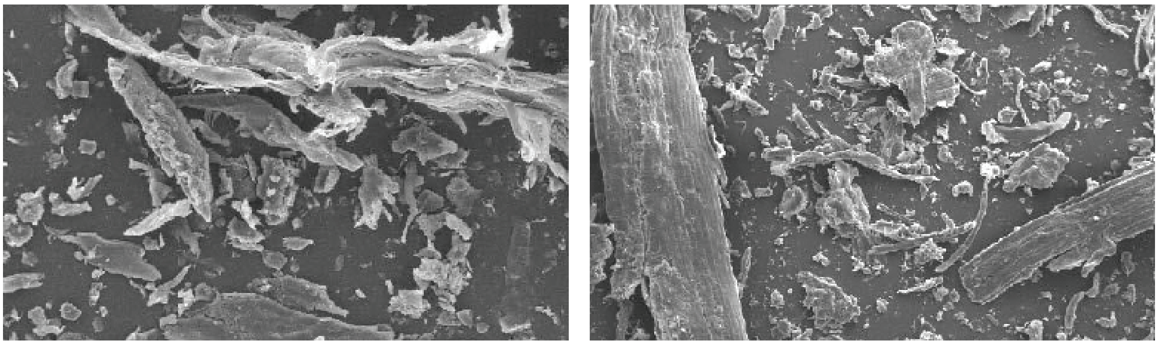
In further work undertaken in 2005, Lu and others (2002) described a system based on a multi-colour pyrometric system for the monitoring of temperature and its distribution in a coal-fired flame. An optical splitting/filtering device is designed and used to split the light of flame into three beams at three selected wavelengths as required in the multi-colour principle. A high-resolution CCD camera was employed to collect the three beams. The three resulting images provide the basis for the determination of temperature and its distribution in the flame field. Again the system was evaluated on a 0.5 MWth coal-fired combustion test facility under various combustion conditions. Results obtained demonstrate that the system is capable of measuring the temperature and its distribution concurrently in the flame field.

5.2 Biomass cofiring

Gil and others (2010) studied the thermal characteristics and kinetics of coal, biomass (pine sawdust) and their blends which were evaluated under combustion conditions using a non-isothermal thermogravimetric method (TGA). Biomass was blended with coal in the range of 5–80 wt% to evaluate their co-combustion behaviour. They observed that biomass combustion takes place in two steps: between 200°C and 360°C the volatiles are released and burnt, and at 360–490°C char combustion takes place. In contrast, the coal was characterised by only one combustion stage at 315–615°C. When the biomass/coal blends were studied, they were found to present three combustion steps, corresponding to the sum of the biomass and coal individual stages. Several solid-state mechanisms were tested by the Coats-Redfern method in order to find out the mechanisms responsible for the oxidation of the samples. The kinetic parameters were determined assuming single separate reactions for each stage of thermal conversion. The combustion of coal was found to consist

Table 3 Test coal and cofiring blends studied (Williams and others, 2008)

Gascoigne Wood (GW) coal – used as a test coal for the CFD model
Russian coal
Russian/ Palm Kernel Expeller (PKE)
South African coal
South African coal/milled wood(20% blend based on thermal input)
South African/Miscanthus Giganteus (20% blend based on thermal input)
South African/Olive waste (15% blend based on thermal input)
South African/Torrefied wood (20% blend based on thermal input)



milled wood

milled miscanthus

Figure 11 Electron micrographs of milled wood and milled miscanthus (Williams and others, 2008)

of one reaction, whereas, in the case of the biomass and coal/biomass blends, the process consists of two or three independent reactions, respectively. The results showed that the chemical first order reaction is the most effective mechanism for the first step of biomass oxidation and for coal combustion. However, diffusion mechanisms were found to be responsible for the second step of biomass combustion.

Williams and others (2008) studied burn-out and NOx formation in blends of several coals and biomass feedstocks (Table 3).

The work was prompted by the observations that when biomass was co-milled with coal, the tough fibrous biomass led to the production of larger particles as compared with the relatively easily fractured coal. This effect can be seen in the electron micrographs of milled wood and miscanthus (*see* Figure 11).

Coal and biomass blends were burnt in an experimental combustion test facility operated by RWE npower and modelled using Fluent CFD software and models for burn-out developed at Leeds. The experimental and computed data for single coals and coal/biomass blends are summarised in Table 4.

Reasonable agreement was observed for exit temperatures, NO, unburnt carbon-in-ash and the authors concluded that the cofiring of wood, miscanthus, PKE and olive wastes with a number of coals had been modelled with reasonable success. However agreement with the radiation measurements was not good. A more detailed examination of the influence of heating-up of the fuel particles, and the devolatilisation and soot models led to the conclusion that the aerodynamic modelling of the test rig burner required improvement.

Table 4 Comparison of experimental and computed data for coal and coal/biomass blends (Williams and others, 2008)

Fuel	Calculated NO, ppm, (dry)	Measured NO ppm, (dry)	Calculated C-in-ash, wt%	Measured C-in-ash, wt%	Calculated exit temp, °C	Experimental exit temp, °C
Gascoigne Wood coal	300	325	1.32	3.0	1332	1324
Russian coal	296	325	1.24	3.4	1344	1134
Russian/PKE	316	321	3.5	4.8	1214	1215
South African coal	292	312	5.87	6.7	1395	1151
South African coal/ wood	288	319	5.6	5.9	1310	1254
South African/ Miscanthus (20%)	250	242	8.9	1.94	1391	1197
South African/Olive waste (15%)	276	230	0.62	0.98	1373	1266
South African/Torrefied Wood (20% thermal)	264	Not available	0.3	Not available	1451	Not available

Yin and others (2009) undertook a comprehensive CFD modelling study to investigate the cofiring of pulverised coal and straw biomass in a 150 kW fuel swirl-stabilised burner, claimed to produce flow patterns similar to those in a typical low NOx burner. The object of the study was to derive a reliable modelling methodology for design and optimisation of low NOx burners cofiring pulverised coal and biomass. In meeting this aim, the effects of grid size, global reaction mechanisms for homogeneous combustion, turbulence models, turbulence-chemistry interactions, properties of the solid fuels, and solid-fuel particle conversion models were studied in detail. The results from the modelling exercise were compared with a detailed mapping of molar fractions of main species, obtained from FT-IR and a Horiba gas analyser. Compared with pulverised coal particles, straw particles are relatively large, of low density, and are non-spherical, which greatly affect the motion and conversion of fuel particles during combustion. In Yin and other's work, the effect of non-sphericity of the fuel particles on their motion and conversion was not accounted for, and both the coal and straw particles are assumed to be spherical. The CFD simulations (62,600 cells, steady, axisymmetric swirl) were undertaken using FLUENT v.6.3.26 with user-defined sub. Comprehensive gas species measurements were determined at the grid points (6 x 6 = 36 along the axis direction and 9 along the radial direction, as shown in Figure 12).

Figures 13 and 14 show the comparison between the measured main species and the CFD predicted values on two representative measuring lines, y = 0.075 m and y = 0.225 m, respectively.

The workers concluded that the discrepancies between the measured data and the CFD results, could be attributed to both the experimental and modelling errors. Based on the geometry of the burner and reactor and the operational conditions, they expected an axisymmetric combustion flow in the reactor, which was the basis for the axisymmetric swirl flow used in the CFD modelling. However, the measured mapping of the species indicates that the flow in the reactor is not axisymmetric. The measurements were also done on different days, and although efforts were taken to maintain the same operation conditions throughout the measuring period, differences in operations were inevitable, which would lead to inconsistencies in the measured results. For the CFD modelling, the uncertainties with the fuels may be one of the major sources of the discrepancies. The two fuels are not yet sufficiently characterised to carry out reliable CFD modelling of such a cofiring flame, although the proximate analysis, the ultimate analysis and the particle sizes of both the fuels are known. A more detailed knowledge of the kinetic parameters (for example appropriate devolatilisation and char oxidation submodels) and the physical properties such as particle density and specific heat was thought necessary for a more accurate modelling of the system and was reported to be the subject of planned future work.

Gera and others (2001) outlined work aimed at supporting the commercial utilisation of biomass in the northeast region of the USA. Specifically, biomass combustion CFD modelling routines were developed using available data and first principles to provide accurate kinetic and model parameters of devolatilisation and diffusion-controlled char burn-out process. The CFD model was being validated with various cofiring experiments so that full-scale 3-D simulations could address site-specific boiler considerations relative to biomass fuel sizing and moisture requirements. The mathematical model is based on the commercial CFD code, FLUENT, where the gas flow is described by the time-averaged equations of global mass, momentum, enthalpy and species mass fractions. The standard k-c turbulence closure, finite rate chemistry, and the Discrete Ordinate radiation models were used for the gas phase in the present simulations. The coal and biomass devolatilisation was incorporated using an Arrhenius-type, first order kinetic rate model. The coal-char oxidation was modelled as the kinetics controlled surface reaction developed by Hurt and others (1998). The biomass char oxidation was controlled by diffusion-limited surface reaction, and was modelled as a constant density process. The standard FLUENT code was updated with the modified char oxidation submodels for coal and biomass via an externally defined function. To test the model, CFD simulations were compared to measurements of unburnt carbon in biomass/coal experiments in the multifuel combustor (MFC) at Sandia National Laboratories. The MFC is a pilot-scale (30 kW), 15-cm diameter and 420 cm-high, down-fired, turbulent flow reactor that simulates gas temperature and composition histories experienced by particles in combustion systems.

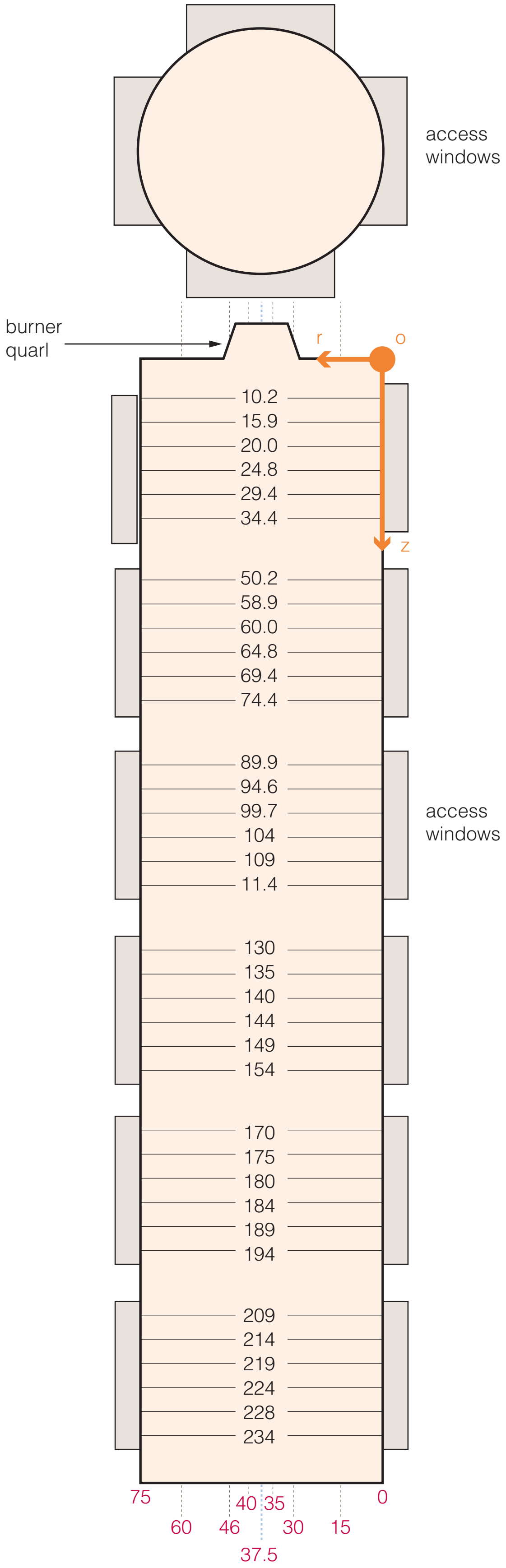


Figure 12 A scaled view of the reactor interior used for the investigations. (Yin and othes, 2009)

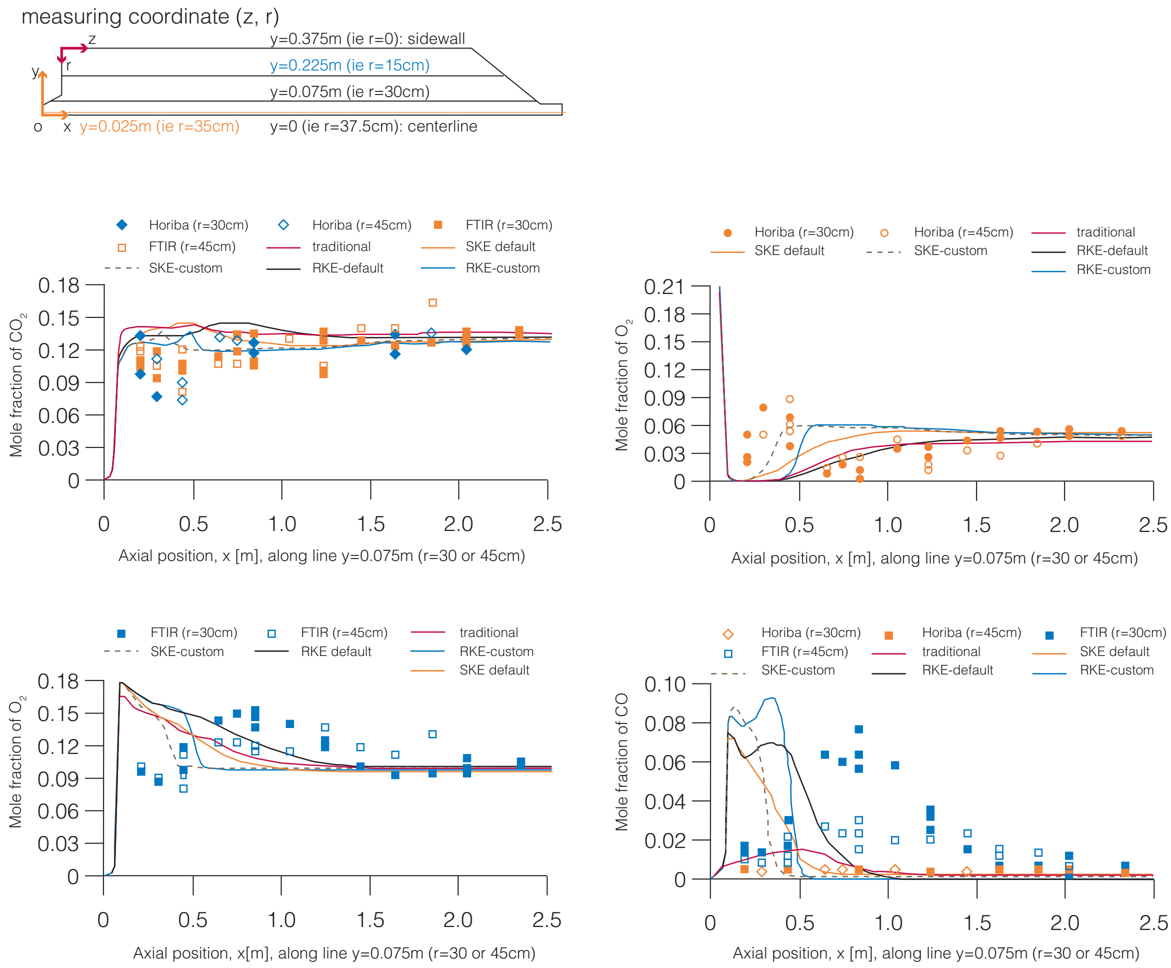


Figure 13 CFD versus measurements on line y = 0.075 m (Yin and others, 2009)

Table 5 compares measured and predicted unburnt carbon for unblended fuels and three different fuel blends under conditions to accentuate differences between coal and SWG combustion at higher levels of unburnt carbon. There is a good agreement between the measurements and the model predictions, which is expected given that MFC data were used in the model development and various kinetic expressions, such as biomass and coal devolatilisation. A noteworthy result was that, despite the presence of larger biomass particle sizes relative to coal, blending biomass reduced the unburnt carbon. This was attributed to the high volatile content of the SWG that burns very rapidly in the combustor.

Table 5 Predicted and measured unburnt carbon in SNL multifuel combustor (MFC) (Gera, 2001)

% SWG (energy basis)	Fuel feed rate, g/min	Predicted unburnt carbon loss, wt%	Measured unburnt carbon loss, wt%	Predicted carbon-in-ash, %	Measured carbon-in-ash, %
100	44.4	2.3	2.3	19.9	13.5
66	36.6	2.3	2.3	19.6	17.0
33	25.5	2.6	3.3	22.9	25.6
15	22.4	3.8	3.6	32.1	28.6
0	19.6	4.8	4.8	37.8	34.2

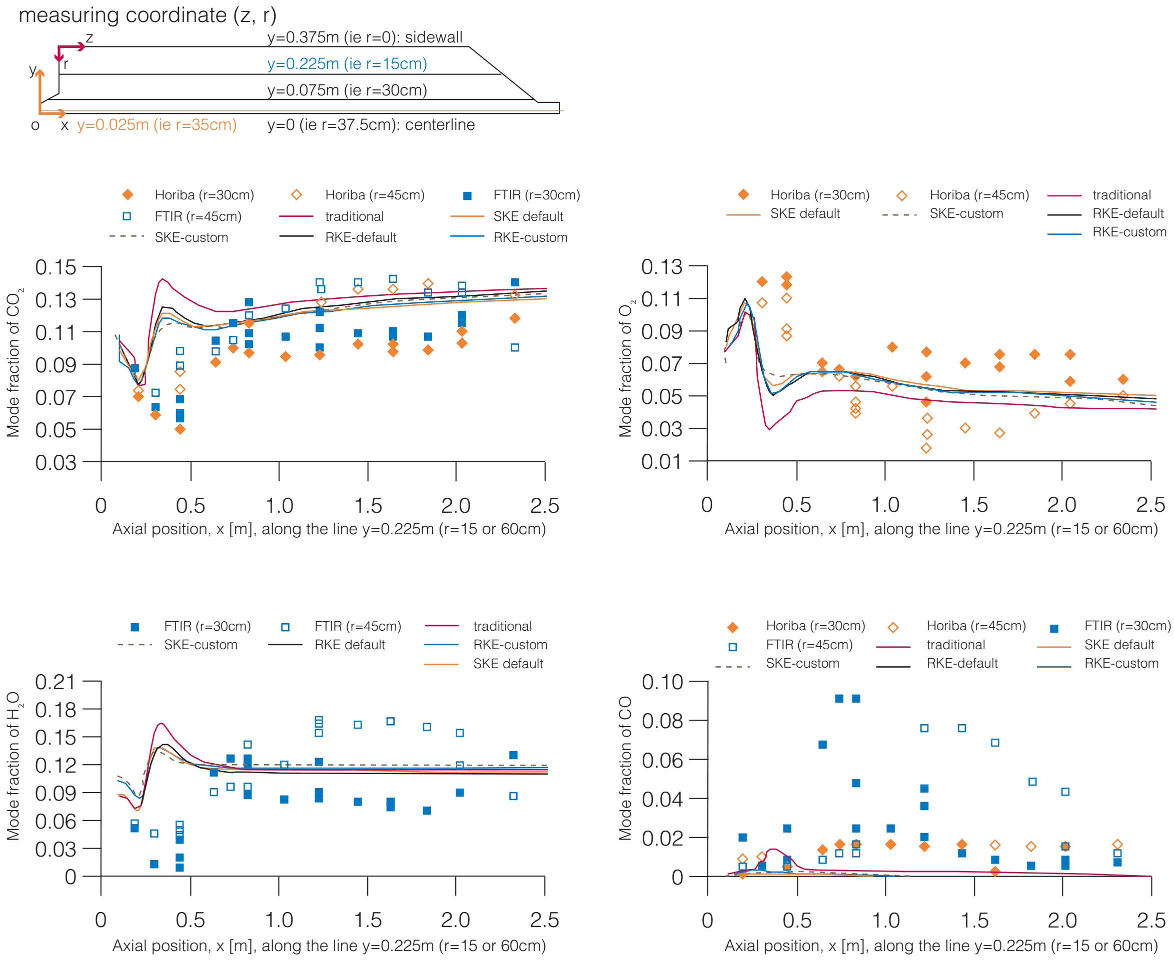


Figure 14 CFD versus measurements on line y = 0.225 m (Yin and others, 2009)

Wu and others (2008) described a methodology based on automatic image analysis for characterising the combustion intermediates, especially chars in coal-biomass mixed fuel. An extensive database of part-combusted coal maceral chars has been used to develop of an algorithm based on reflectance and particle shape to classify part-combusted material. The algorithm is outlined in Figure 15, and an example classification in Figure 16.

Used in conjunction with a combustion model developed by Nottingham University, burn-out profiles for mixtures of several biomass feedstocks with coal were predicted with reasonable accuracy (Lester and others, 2009).

Mitchell and others (2006) worked to develop models that predicted accurately coal and biomass gasification and combustion. Several previous studies have shown that during the combustion of coal particles in conditions typical of those existing in pulverised coal fired boilers and furnaces, char particles burn at rates limited by the combined effects of chemical reaction and pore diffusion. Due to the oxygen concentration gradients established inside particles, and the associated distribution of rates of mass loss due to chemical reaction, particle diameters, apparent densities, and specific surface areas decrease with mass loss when burning in this regime. The writers have developed a char conversion model to account for these variations in the physical structure of the char during the mass loss process. In the direct numerical simulation of a burning spherical char particle, the particle is divided into a number of concentric annular volume elements, each of which contains a portion of the initial total mass of the particle. The mass in each volume element gasifies at a rate governed by the local conditions. An oxygen transport equation is solved to determine the oxygen concentration in each volume element. Account is made for the combined effects of bulk and Knudsen diffusion of oxygen

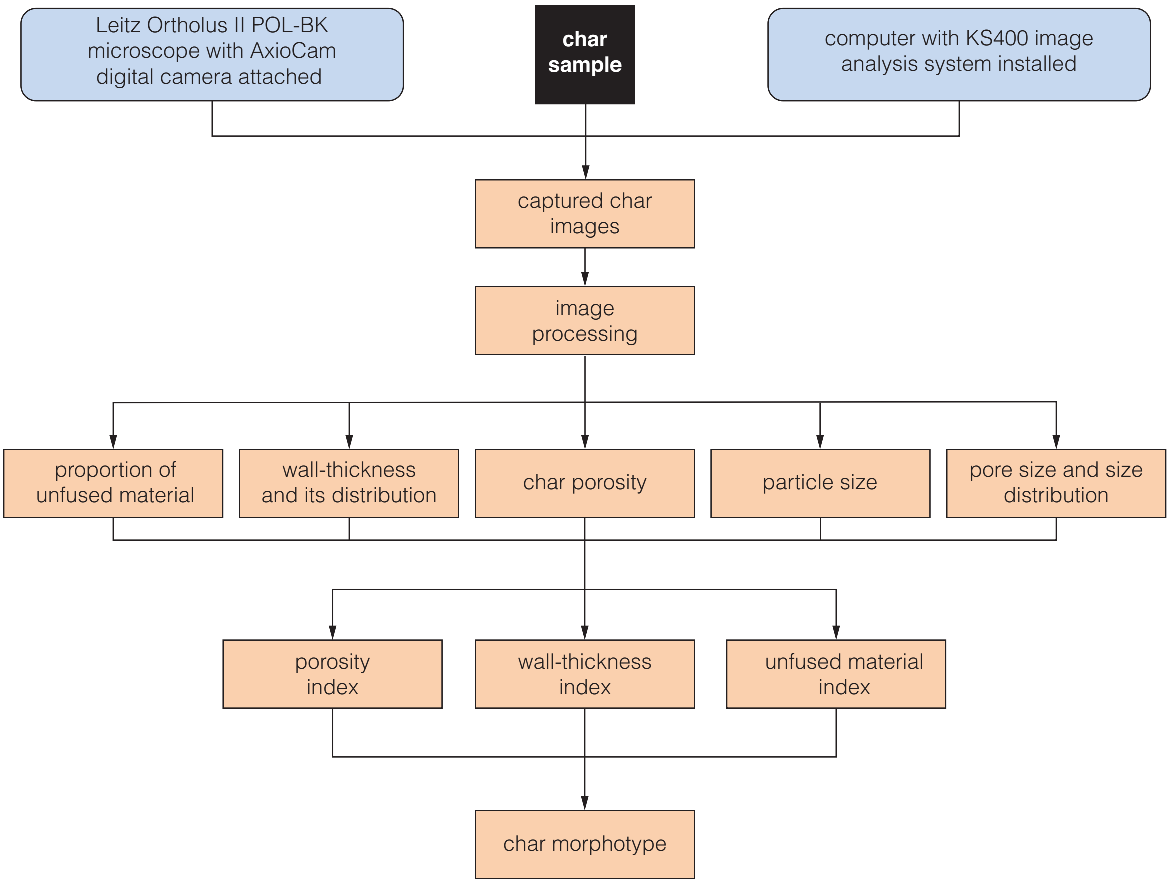


Figure 15 Classification algorithm (Lester and others, 2009)

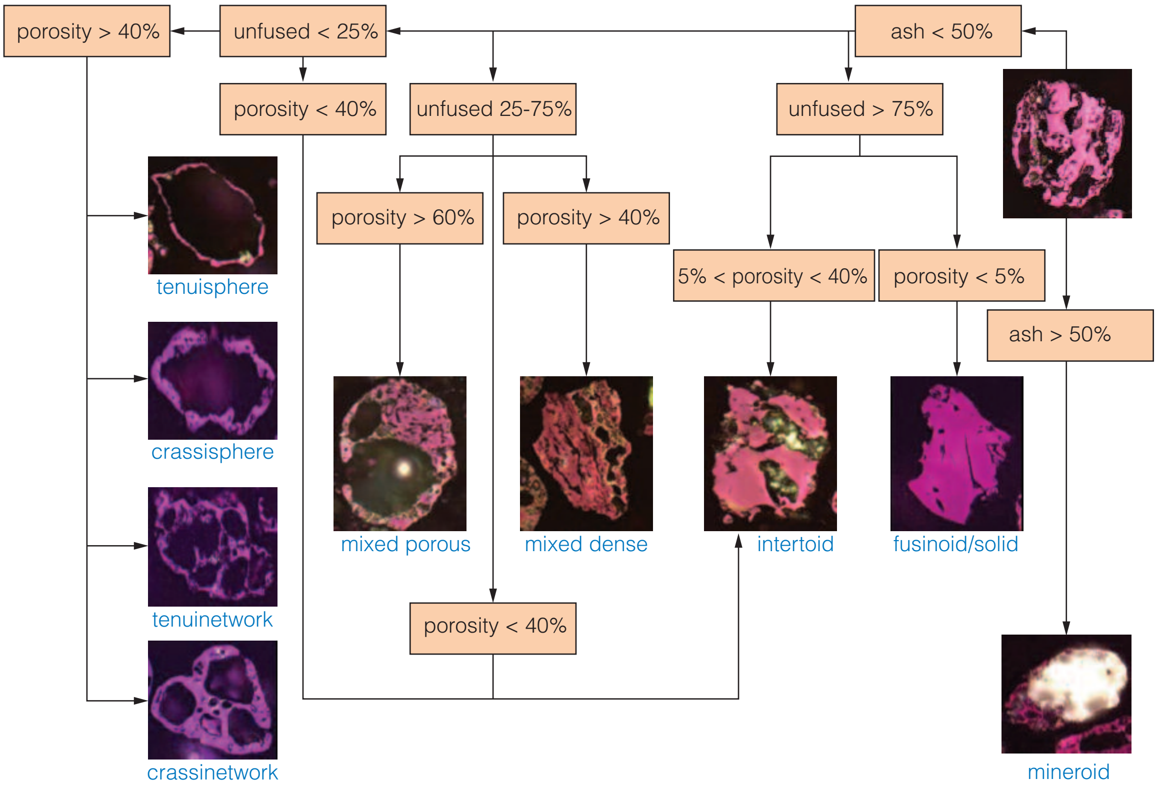


Figure 16 Combustion intermediates (Lester and others, 2009)

Table 6 Revised modelling for early CO_2 evolution (Mitchell and others, 2006)

		A_i [a]	E_i (kJ/mol)	σ_i (kJ/mol)
$2C_f + O_2 \rightarrow C(O) + CO$	(R1a)	3.87e04	60	0
$\rightarrow C_2(O_2)$	(R1b)	1.95e03	55	0
$C_b + C_f + C(O) + O_2 \rightarrow CO_2 + C(O) + C_f$	(R2)	1.18e09	120	0
$C_b + C_f + C(O) + O_2 \rightarrow CO + 2C(O)$	(R3)	3.74e16	250	0
$C_b + C(O) \rightarrow CO + C_f$	(R4)	1.00e13	320	26
$C_b + C_2(O_2) \rightarrow CO_2 + 2C_f$	(R5)	1.00e13	280	45

[a] $k_i = A_i \exp(-E_i/RT)$, units of A_i in mol, m^2-surface/m^3-fluid, s

Table 7 Test conditions of biomass cofiring (Gubba and others, 2001)

Case	Case 0	Case 1	Case 2
Total output power, MWth	629	652	660
Coal mass flow rate, kg/s	31.94	31.11	29.44
Straw mass flow rate,kg/s	0.00	3.33	6.67
Cofire thermal load, %	0.00	6.21	12.35
Excess oxygen, dry vol%	3.0	4.1	3.7
NOx emissions, ppm	242	222	214

through pores, surface roughness, the local porosity, and the particle tortuosity when evaluating an effective diffusivity for oxygen inside the particle. The local adsorption rate of O_2 is dependent on the local adsorbed oxygen concentration and the available surface area within the volume element, which is followed using a specific surface area sub-model. As carbon oxides desorb from the surface as CO and CO_2, the local particle density decreases and the local porosity increases. As conversion progresses, eventually all the mass in the volume element is consumed. Since the oxygen concentration is highest at the particle periphery, reactivity is greatest near the particle perimeter and mass in the outer-most volume element can be consumed prior to complete mass loss in inner volume elements. Consequently, the particle diameter can decrease as burning progresses. Char-particle temperature is calculated from an energy balance, wherein the rates of energy generation due to char oxidation are balanced by the rates of energy loss by conduction, convection, and radiation. Particles are assumed to burn at uniform temperature, an adequate assumption for the small particles sizes (<150 µm) for which the model is applicable. In their more recent work Mitchell and others (2006) modified the reduced heterogeneous reaction mechanism employed in the model in order to better reflect the understanding of the chemistry controlling the carbon oxidation process. The modified mechanism, shown in Table 6, is claimed to account for the early CO_2 evolution observed during the oxidation of some coal chars and nearly all biomass chars.

Gubba and others (2011) used CFD to model a full-scale 300 MWe tangentially-fired furnace for pulverised fuel comprising coal and wheat straw. The main objective of this investigation was to simulate various test conditions as presented and to understand various physical and chemical processes by analysing the CFD data. The experiments were performed on a 300 MWe furnace at the Baoji power station, Shaanxi, China. The furnace employs three distinct banks of burners, each composed of three secondary air inlets interposed by two primary air inlets. The highest of these banks also incorporates a close-coupled overfire air (OFA) inlet above. The OFA is injected into the boiler to give an opposite rotational direction of the fireball, in the recirculation zone, compared to the other inlets. The three banks are present in the four corners, which total 64 inlets, although these are not all operated simultaneously under the firing conditions described in this study. The system provides the means for air staging and a recirculation zone above the burners. The cases studied are summarised in Table 7.

A baseline test of typical operation of the furnace, firing coal only (Case 0), was first performed. Thereafter a battery of coal mills, used to supply the top primary air conveyers, was devoted to biomass processing at 12 or 24 t/h (3.33 or 6.67 kg/s; Cases 1 and 2, respectively). For comparison, the system used for the wheat straw is capable of handling approximately 9 kg/s of coal. In the separate injection method of cofiring the cofired fuels are mixed only upon entrance to the boiler. It is important to note that the power station was designed to burn only coal and that no modifications have been made to the hardware, except the biomass storage and onsite handling. This represents a simple and cheap retrofit cofiring configuration for many similar furnace designs that have burners with dedicated upstream fuel systems.

Despite the simplifications assumed in the CFD modelling, the predictions were, in general, in reasonable agreement with measurements. In particular, the predicted temperature profiles and excess oxygen at the exit were very promising, considering the uncertainty that exists for the thermal boundary conditions both in terms of wall temperature, emissivity, and no air leak-in in large-scale industrial boilers. An increase in the gas temperature along the furnace height with the increase in biomass feed rate from 12 t/h to 24 t/h was clearly demonstrated by the CFD model and is in good agreement with experiments.

It is postulated that the discrepancies in predicted carbon burn-out compared to the measured data in Cases 0, 1 and 2 is mainly due to the particle shapes and unrepresentative particle size distributions

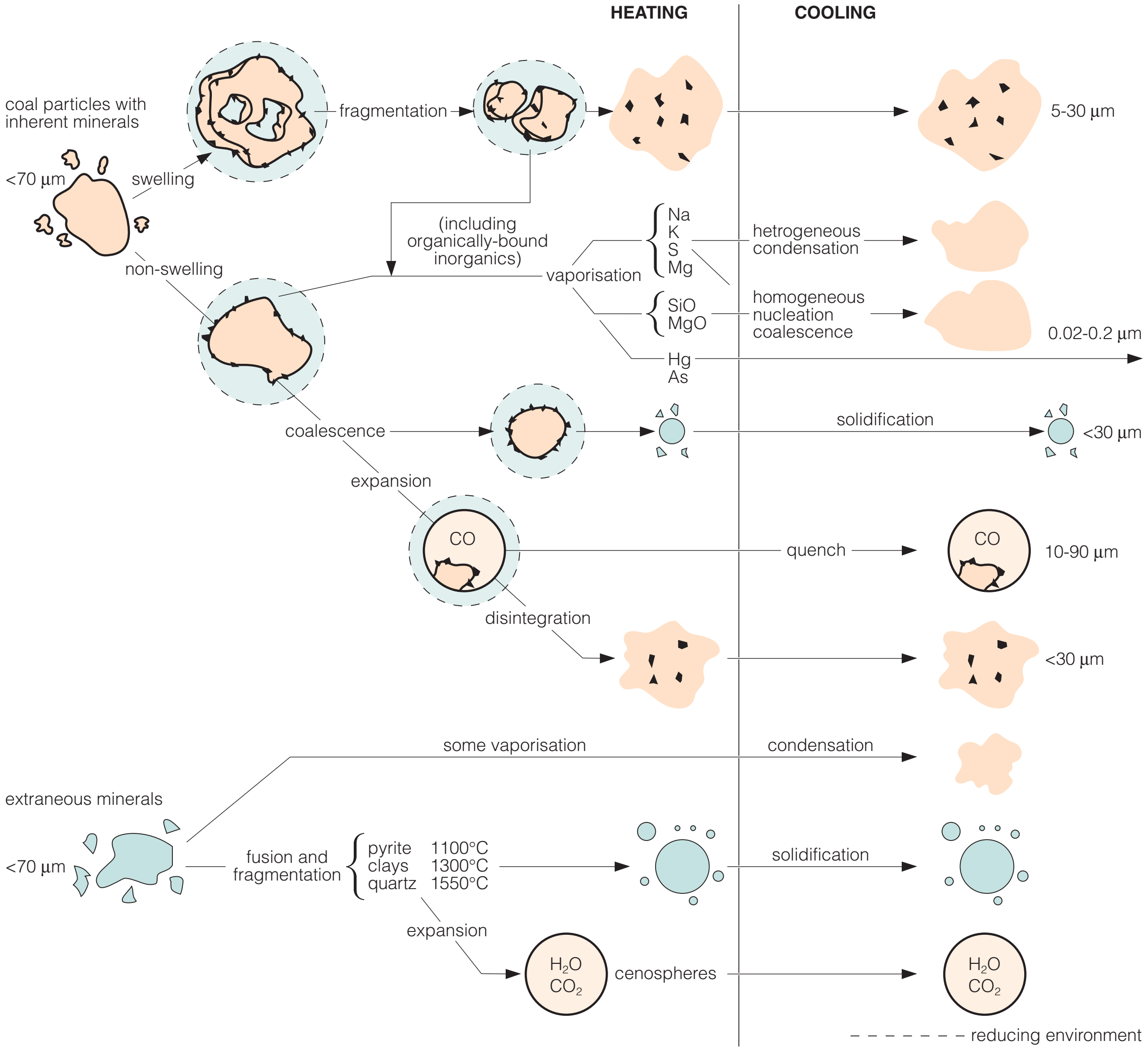


Figure 17 Ash-forming mechanisms (Barnes, 2009)

considered. Further, the devolatilisation and char combustion parameters used for wheat straw are expected to greatly influence the predictions. NOx predictions for all the cases considered in this investigation are in good agreement with the measurements demonstrating the reduction in NOx with cofiring of biomass. Overall, the workers considered that the results were encouraging. Further work was proposed to address the detailed inputs of the biomass particles shape, distribution and their thermal conversion.

Ash formation and its fate during pulverised coal combustion has been the subject of a recent IEA CCC report (Barnes, 2009). The processes of ash formation and the interaction between different species is very complex. Some of the salient pathways are summarised in Figure 17. When coal is cofired with a second fuel such as biomass, the complexity increases and accurate prediction of ash behaviour becomes very difficult.

Stam and others (2010) set out an overview of the existing models and tools, which have been developed largely for pulverised coal combustion systems, and to review their application for the description and prediction of the slagging and fouling behaviour of the biomass ash and the mixed coal-biomass ashes in biomass firing and cofiring applications.

In general terms, three approaches to the development of predictive models for ash deposition in furnaces and boilers are apparent:
- The empirical approach by traditional methods based on the use of simple Slagging or Fouling Indices; using the data normally available on fuel specifications, for example the ash chemical composition and the ash fusion temperatures. These relatively simple, practical methods are used by designers and operators, particularly when no fuel sample for more detailed analysis is available, as input to their normal design or fuel assessment procedures.
- The mechanistic approach involves the use of relatively simple models of combustion and other processes that may occur in combustors and boilers, in an attempt to provide a general assessment of the ash deposition tendency and the nature of the ash deposit in a specific application.
- In principle the more advanced models based on computational fluid dynamics (CFD) can provide detailed information about the combustion process and the fluid dynamics. For the simulation of ash deposition processes, the CFD models have submodels of the ash transformation process, particle deposition and adhesion and the impacts on heat transfer.

To date, much of the biomass cofiring in coal-fired utility boilers has been at relatively low cofiring ratios, less than 20%. The impact on the combustion process, boiler performance, and boiler integrity, has been modest. The current empirical methods for the assessment of fuel characteristics have proven to be adequate in most instances. With increased cofiring levels, it is anticipated that the fuel-related impacts on plant performance increase. The principal technical concerns are with the behaviour of the mixed ashes and the potential impacts on ash deposition on surfaces in the furnace, the boiler and the associated equipment.

The ash deposition process that occurs when biomass is cofired with coal, is a complex phenomena, which occurs over a wide range of flue gas and surface temperatures. The process is dependent on the characteristics of the ash, and on the design and operation of the combustor or boiler plant. The prediction of the growth rate and the nature of the ash deposits for plant design or operational purposes is therefore a complex task.

Traditionally, for routine fuel specification, equipment design and operational purposes, relatively simple empirical methods have been applied. Alternatively, more complex technical approaches to the modelling of these processes have been attempted over several decades. It is fair to say that the deposition models have not been widely adopted for these applications. The use, within the industry, of the predictive models and the associated descriptions of the ash generation and deposition processes, has largely been for development and investigative purposes. The principal reason for this is that the quantitative, predictive capabilities of even the best of the analytical models are limited. It has proved very difficult to provide practically useful simulations of the development of mature ash deposits within the furnace and in the convective sections of a boiler, without proper consideration of natural ash shedding and sootblowing, and of the secondary deposition processes. This has been recognised recently by some of the research groups involved in the development of the mechanistic ash deposition models, and also described by Zbogar and others (2009). The workers report that on a more practical level, there has been significant improvement over the past few years in the techniques available for the monitoring of ash deposition in operating plant and for the optimisation of the use of the on-line cleaning systems. Some of the recent work on the use of on-line plant monitoring with advanced data analysis techniques to predict the effectiveness of the on-line cleaning systems may be of some interest to plant operators, initially to provide additional information to the operating staff, and in time it may be possible to introduce systems for the automatic optimisation of the on-line cleaning equipment.

They concluded that various relatively simple empirical deposition models have been developed for coal-firing applications. More complex models for coal and biomass cofiring applications have been developed or are under development. The deposition models have not been widely adopted for these applications today. In addition, improvement has been made in the techniques available for the monitoring of ash deposition and online cleaning systems for the radiative and convective section of a pulverised fuel fired boiler.

Korbee and others (2009) reviewed the chemical and physical transformations (devolatilisation, char oxidation, fragmentation and gas to particle conversion followed by nucleation, coagulation and condensation, etc) that occur milliseconds after the fuel enters to the furnace. These transformations depend on several operating parameters (temperature, pressure, heating rate, etc) along with several chemical and physical properties (ash, moisture content, density, porosity, mineral matter composition and their association in the fuel matrix, particle size, shape and density, etc). The resultant ash formed from the physical and chemical transformations that occur during combustion will have different particle sizes and mineralogical composition as compare to the original fuel. An extensive experimental study was undertaken in the laboratory-scale combustion simulator at ECN with six biomass and two coals (bark, wood chips, waste wood, saw dust, olive residue, straw, UK and a Polish coal.) under typical pulverised coal firing conditions. Ash release, conversion, size reduction and size distribution along with the change in inorganic chemical compositions, were derived at different char burn-out levels in the reactor at residence times of 20, 90, 210 and 1300 milliseconds. A qualitative predictive tool has been developed to model the extent of first line physical transformations. Based on the extensive data pool obtained from the study, a simple but reliable (R2 >0.95) set of linear correlations have been proposed to predict the elemental release of potassium, sodium, chlorine and sulphur from single and mixed fuels. The predictions were reported to be particularly effective for elemental release from the fuels of similar characteristics, such as woody biomass. A mathematical model has been developed to predict the particle size after combustion by simplifying Dunn-Rankin's particle population balance model analytically and kinetically. It is claimed that the models can be further used for the investigations of several ash related problems during combustion and cofiring such as slagging, fouling, corrosion and erosion.

5.3 Oxyfuel combustion

Wall and others (2009) recently presented an overview on research activities and technology development through a fundamental research underpinning the Australia/Japan Oxyfuel Feasibility Project. Studies on oxyfuel combustion on a pilot-scale furnace and a laboratory-scale drop tube furnace were presented and compared with computational fluid dynamics (CFD) predictions. From pilot-scale and laboratory-scale experimental studies, oxyfuel combustion has been found to differ from air combustion in several ways, including reduced flame temperature, delayed flame ignition, reduced NOx and SOx emissions. Many of these effects can be explained by differences in gas properties between CO_2 and N_2, the main diluting gases in oxyfuel and air respectively. CO_2 has different properties from N_2 which influence both heat transfer and combustion reaction kinetics, specifically:

- **Density:** The molecular weight of CO_2 is 44, compared to 28 for N_2, thus the density of the flue gas is higher in oxyfuel combustion.
- **Heat capacity:** The heat capacity of CO_2 is higher than N_2.
- **Diffusivity:** The oxygen diffusion rate in CO_2 is 0.8 times that in N_2.
- **Radiative properties of the furnace gases:** Oxyfuel combustion has higher CO_2 and H_2O levels, both having high emitting power. The following list identifies differences for oxyfiring compared to airfiring:
- To attain a similar adiabatic flame temperature (AFT) the O_2 proportion of the gases passing through the burners is higher, typically 30%, than that for air (of 21%), necessitating that about 60% of the flue gas is recycled.
- The high proportions of CO_2 and H_2O in the furnace gases result in higher gas emissivities, hence similar radiative heat transfer for a boiler retrofitted to oxyfuel 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 to an extent depending on the flue gas recycle ratio. The volume of flue gas emitted from power plant is reduced by about 80%.
- Typically, when air-firing coal, 20% excess air is used. Oxyfuel requires a percentage 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%.
- Due to the recycling of flue gases to the furnace, species (including corrosive sulphur gases) have higher concentrations than in air firing, if these species are not removed prior to recycle.
- As oxyfuel combustion combined with carbon storage must provide power to several significant unit operations, such as flue gas compression, that are not required in a conventional plant without sequestration, oxyfuel combustion/carbon storage is less efficient per unit of energy produced.

  Three Australian coals were studied in furnaces at laboratory-scale and pilot-scale facilities experimentally and using mathematical modelling to compare and interpolate the difference in air combustion and oxyfuel combustion. Heat transfer, coal reactivity and emissions in oxyfuel combustion differed from air combustion because of differences in combustion conditions resulting from reduced volumetric flue gas, enhanced oxygen level and recycled flue gas.

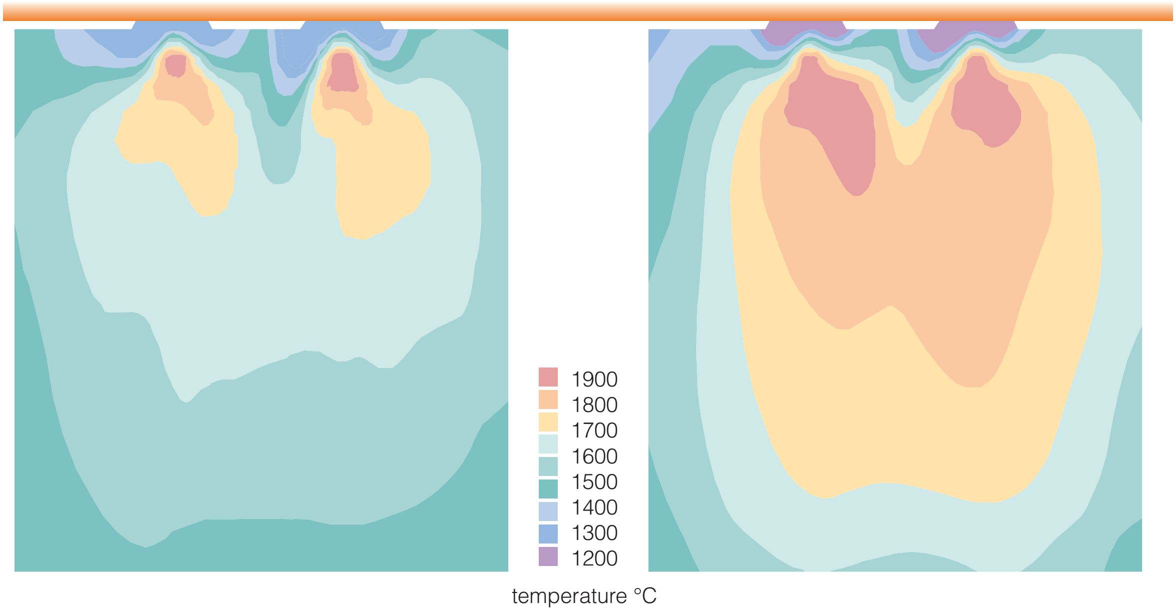


Figure 18 Predicted horizontal burner plane for air-combustion (left) compared to the oxycombustion (right) for a 3 MWe furnace (Wall and others, 2009)

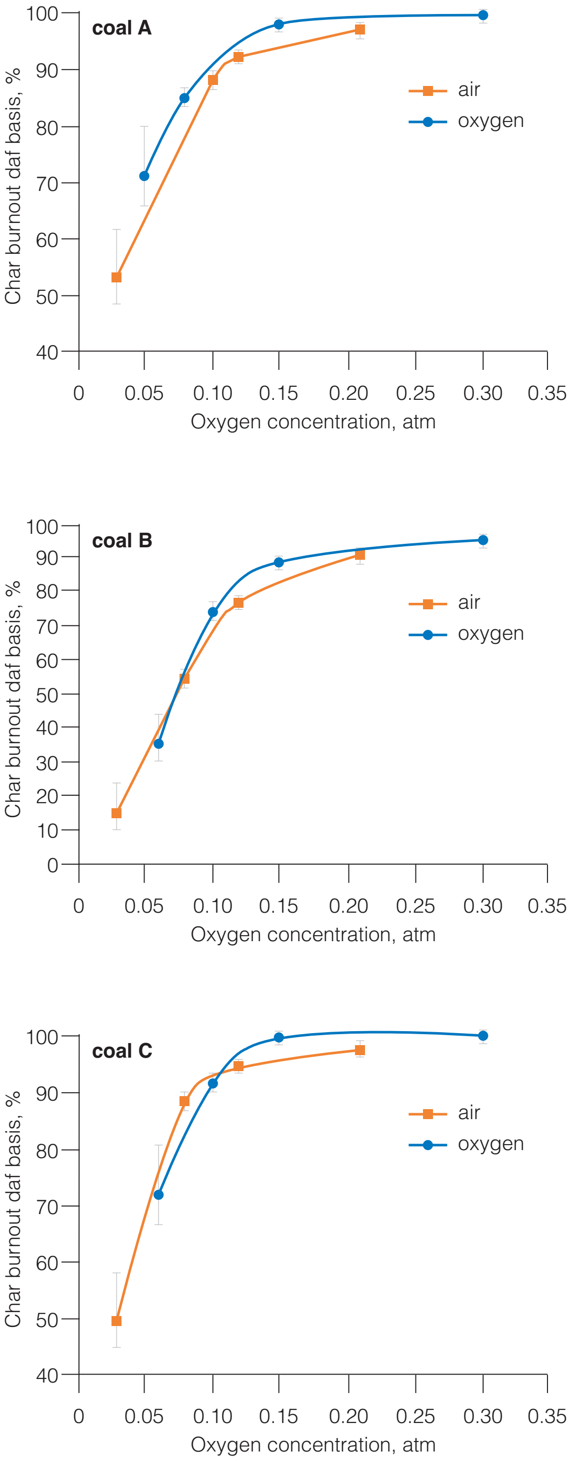


Figure 19 Comparison of char burn-out of three experimental coals in air and oxy atmospheres in a drop tube furnace (Wall and others, 2009)

The research has made several contributions to knowledge, including:

- New measurements in a pilot-scale oxyfuel furnace comparing temperatures, burn-out, and gas compositions have been obtained simulating air-firing retrofitted to oxyfuel, when furnace heat transfer is matched.
- The use of AFT as a design criterion for furnace design for an oxy retrofit has been evaluated, and modified with a criterion of matching heat transfer considered more appropriate.
- The emissivity of the gases in oxyfired furnaces has been predicted by a new 4-grey gas model, which is required as a furnace model input for CFD predictions.
- The first measurements of coal reactivity comparisons, including high-temperature volatile yields and coal burn-out, at several O_2 levels in air and oxyfuel combustion conditions at pilot-scale and laboratory-scale have been obtained, showing a higher reactivity in oxyfuel at the same O_2 concentrations.
- Observed delays in flame ignition in oxyfiring have been shown by mathematical modelling to be due to both gas property differences and aerodynamic effects, due to the differing momentum flux ratio of primary to momentum levels associated with a retrofit.

Results for furnace temperature modelling and are given in Figures 18 and 19.

Rathnam and others (2009) undertook a programme of work to investigate their hypothesis that the reactivity of pulverised coal is significantly different during oxyfuel combustion when compared to air combustion under high temperature and low oxygen partial pressure conditions. They set out to:

- measure and compare the reactivity of a range of coals in air and oxyfuel conditions and evaluate the impact of these differences on the design and operation of oxyfuel technology;
- identify the conditions under which the reactivity is significantly different in air and oxy conditions;
- obtain the intrinsic and apparent kinetic parameters (activation energy, pre-exponential factor, reaction order) of char combustion.It was hoped that a better understanding of the processes would help to estimate differences in furnace operation and performance between air and oxyfuel for a range of coals, leading to the ability to propose modifications to obtain better burn-out in an

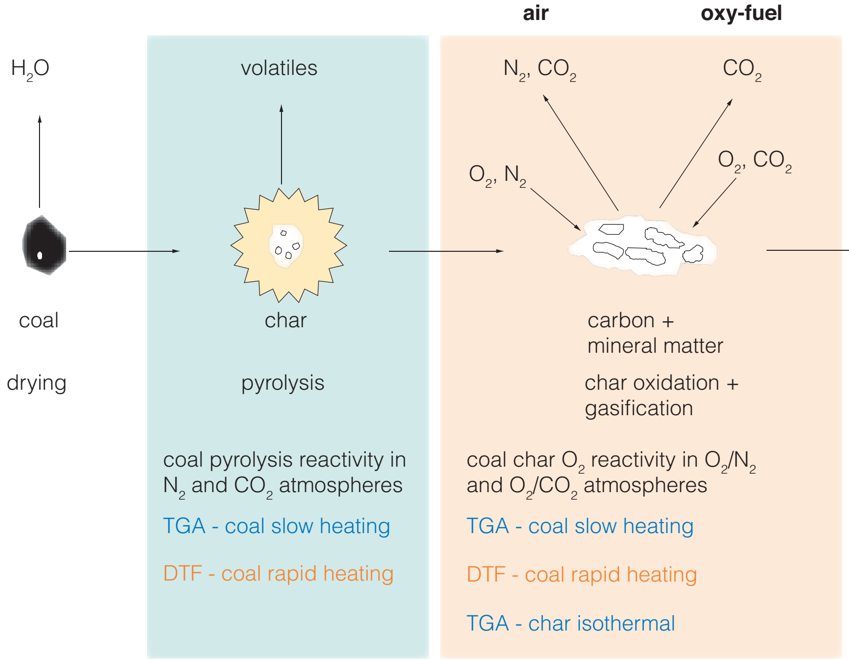


Figure 20 Coal combustion parameters for study under air and oxyfuel conditions (Rathnam and others, 2009)

oxyfuel combustor or a reduction in O_2 usage. The areas for study are set out in (Figure 20).

Eight coals of varying rank were selected for study; three international coals (Coals A, B, C) and five Australian coals (Coals D, E, F, G, H). The behaviour of the coals was studied using a range of techniques and methodologies:

- pyrolysis and char reactivity measurements;
  - thermogravimetric analyser (TGA);
  - drop tube furnace (DTF);
- coal and char characterisation;
- proximate and ultimate analysis, ash analysis, maceral content analysis;
- scanning electron microscope (SEM) analysis – char structure characterisation;
- internal surface area measurements – char internal surface area;
- particle size analysis – coal and char particle size distribution. The basic properties of the coals

Table 8 Test coal properties (wt% air dried basis) (Rathnam and others, 2009)

Coal	Proximate analysis				Ultimate analysis				
	Moisture	Ash	VM	FC	C	H	N	S	O
Coal A	11.20	5.40	47.70	35.70	56.30	4.16	0.55	0.96	21.43
Coal B	2.00	17.20	29.50	51.30	67.80	4.08	1.19	0.68	7.05
Coal C	3.80	22.90	23.90	49.40	60.00	3.29	1.46	1.94	6.61
Coal D	8.00	19.90	25.60	46.50	57.03	3.25	0.84	0.17	10.81
Coal E	5.20	28.60	24.50	41.70	49.65	3.08	0.80	0.22	12.45
Coal F	1.70	19.60	40.50	38.20	64.22	5.38	0.99	0.50	7.60
Coal G	5.90	5.00	33.80	55.30	69.85	4.57	1.91	0.46	12.30
Coal H	1.70	9.80	8.70	79.80	80.89	3.34	1.66	0.67	1.95

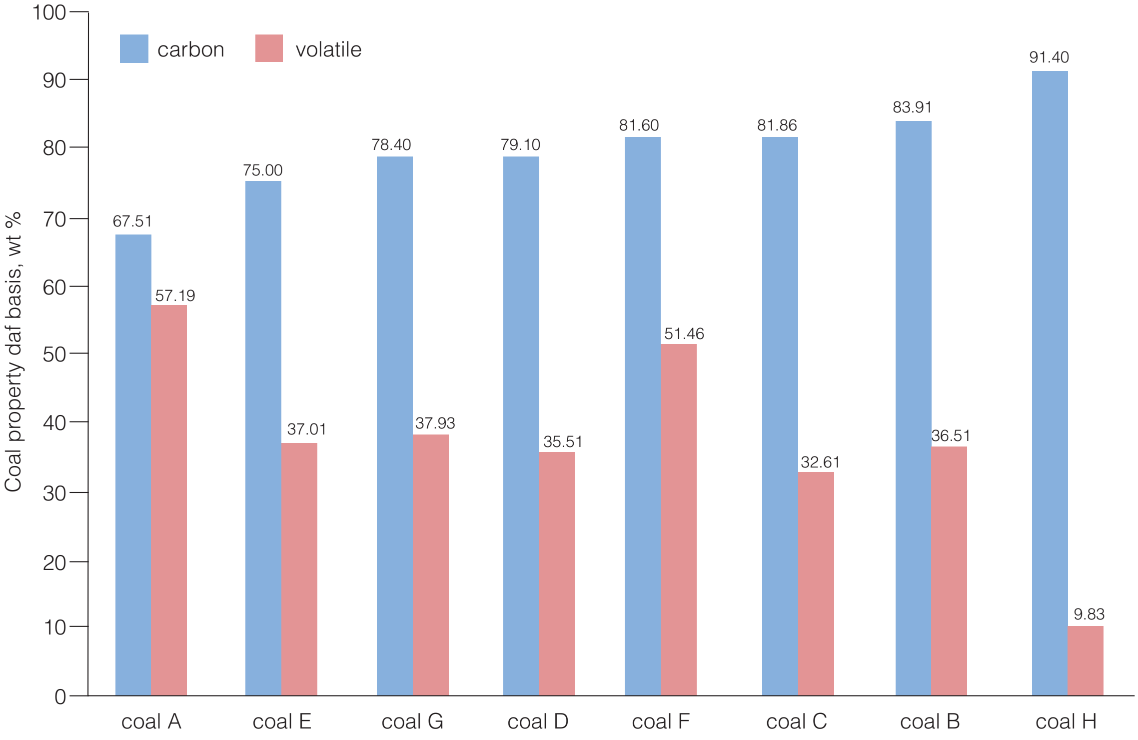


Figure 21 Test coal carbon and volatile matter contents (Rathnam and others, 2009)

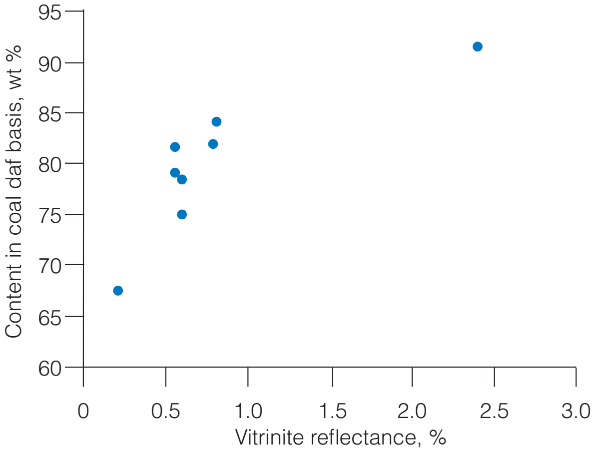


Figure 22 Test coal carbon content versus vitrinite reflectance (Ratham, 2009)

studied are given in Table 8. Carbon and volatile matter contents are displayed graphically in Figure 21, vitrinite reflectance against carbon content in Figure 22.

The study showed that there are significant differences in pulverised coal reactivity in air and oxyfuel conditions. The extent of the differences depends on the coal type (rank). The pyrolysis reactivity of coal in N_2 and CO_2 was found to be similar as shown by TGA results while the apparent volatile yield appeared to be higher in CO_2 due to mass loss during the char CO_2 gasification reaction. Depending on the coal type, there were also significant differences in the characteristics of char formed in N_2 and CO_2 atmospheres. Some coals exhibited greater swelling in a CO_2 atmosphere. Higher char reactivity in O_2/CO_2 conditions, especially at high temperatures and low O_2 levels, was thought to be due to the char CO_2 gasification reaction. The TGA and DTF results complemented each other and were found to be consistent with literature data. The workers report that the reactivity parameters for the char combustion needed to be estimated separately for oxyfuel conditions including the char CO_2 gasification reaction and other relevant differences need to be accounted for when modelling pulverised coal combustion in O_2/CO_2 conditions (*see* Figures 23 and 24).

The coal stream ignition process is critical to the performance of modern pulverised coal burners, particularly when operating under novel conditions such as those experienced in oxyfuel combustion. However, experimental studies of coal stream ignition are lacking, and recent modelling efforts have had to rely on comparisons with a single set of experiments in vitiated air. To address this gap in knowledge, Liu and others (2011) have conducted experiments on the ignition properties of two US

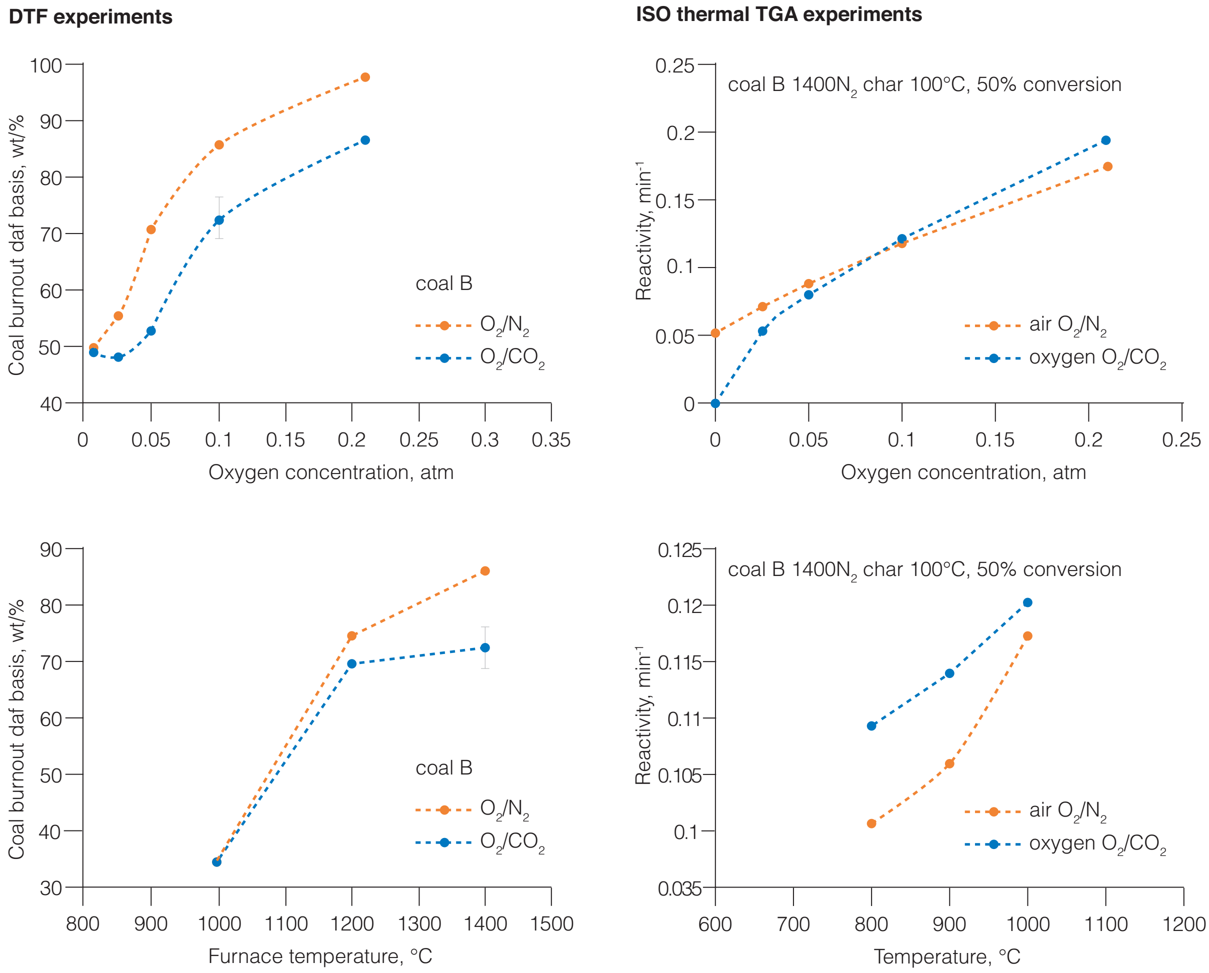


Figure 23 Coal B burn-out/reactivity in O_2/N_2 and O_2/CO_2 atmospheres (Rathnam and others, 2009)

and two Chinese coals in a laminar entrained flow reactor. The majority of the measurements focused on varying the coal feed rate for furnace temperatures of 960–1050°C and for 12–20 vol% O_2 in nitrogen. The influence of coal feed rate on ignition with a carbon dioxide diluent was also measured for 20 vol% O_2 at 1005°C. A second set of measurements was undertaken for the ignition of a fixed coal feed rate in N_2 and CO_2 environments at identical furnace temperatures of 927°C, 1067°C, and 1397°C. An industrial charge coupled device camera equipped with a 431 nm imaging filter was used to monitor the ignition process. Under most conditions, the ignition delay decreased with increasing coal feed rate until a minimum was reached at a feed rate corresponding to a particle number density of approximately 4×10^9 m^{-3} in the coal feed pipe. This ignition minimum corresponds to a cold flow group number, G, of 0.3. At higher coal feed rates the ignition delay increased (Figure 25). The ignition delay time was shown to be sensitive to the temperature of the hot co-flow into which the coal stream is introduced, and the coal particle size. The three high volatile bituminous coals showed nearly identical ignition delay as a function of coal feed rate, whereas the subbituminous coal showed slightly greater apparent ignition delay. Bath gas CO_2 content was found to have a minor impact on ignition delay.

Davis (2011) has described a multi-partner collaboration led by Reaction Engineering aimed at improving the understanding of coal combustion under oxyfuel conditions. The main objective was to predict the performance and operational impacts of oxycombustion retrofit designs on existing coal-fired boilers using multi-scale testing and theoretical investigations. It was hoped that fundamental data could be collected that describe combustion characteristics, corrosion rates, and ash properties during oxycoal firing to enable the development of validated mechanisms that describe the oxycombustion processes. These data could then be used to guide the development of new firing

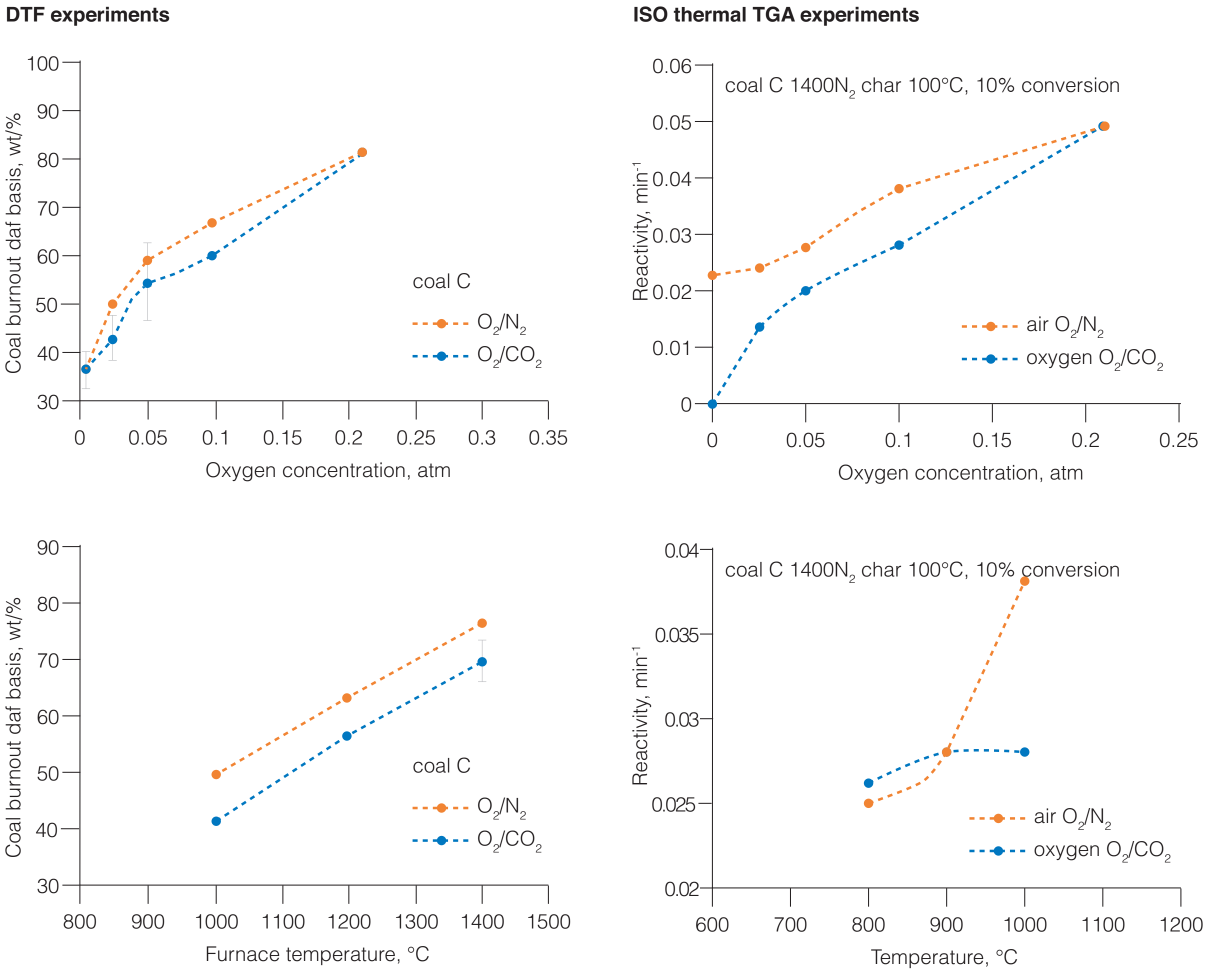


Figure 24 Coal C burn-out/reactivity in O_2/N_2 and O_2/CO_2 atmospheres (Rathnam and others, 2009)

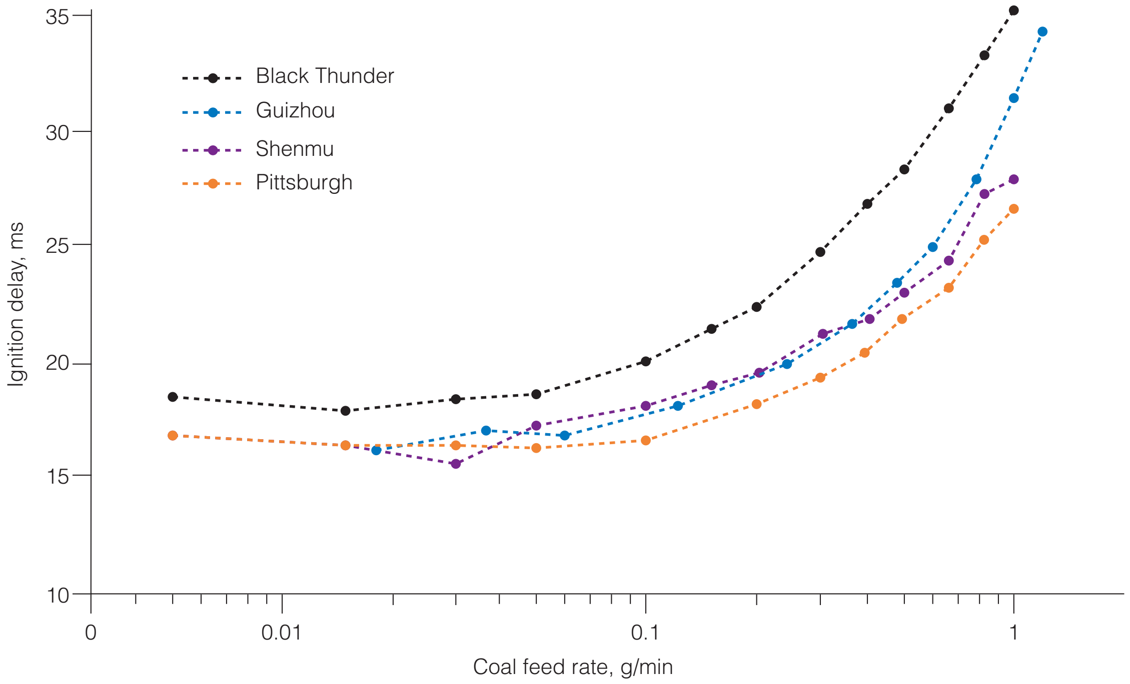


Figure 25 Ignition delays for 75–105 µm coal streams as a function of coal mass feed rate for the four different coals investigated for 12 vol% O_2 in N_2 at 1047°C (Liu, 2011)

system principles that could be used in the design of oxyburners and flue-gas recycle systems. Also, these validated mechanisms could be incorporated into CFD software to evaluate full-scale oxycombustion retrofit designs. The following experimental techniques were used to gain basic data, the results of which were compared with predicted measurements from Reaction Engineering's CFD proprietary 'GLACIER' software:

- Bench-Scale Optical Entrained Flow Reactor;
  - char oxidation kinetics;
- 100 kW Oxyfuel Combustor (OFC) Tests;
  - ash deposition and characterisation;
  - soot evolution;
- 1.2 MW Pilot-Scale Furnace (L1500) Tests;
  - impacts of burner configuration;
  - heat flux, corrosion and particle deposition;
  - flue gas chemistry, sooting.

Radiative emission modelling was undertaken with the proprietary RADCAL code. Given the importance of achieving optimum burn-out of coal char during combustion, special attention was paid to modelling this aspect of the work using an extended model based on that developed by Shaddix and Geier (2011). Results to date indicate that:

- predicted gas temperature trends were correct, including temperature cross-over;
- oxyfired predictions were higher than measured data in staged zone;
- enhanced char oxidation model showed increased CO production in staged zone and better agreement with air data;
- refined gas emissivity model had negligible impact on results;
- model comparisons are on-going, and will also include soot and corrosion data;
- Current activity includes oxycombustion assessment in full-scale boilers.

Furnace heat flux and temperature predictions and measurements for Skyline coal are given in Figures 26 and 27.

Gharebaghi and others (2011) undertook an investigation using a commercial computational fluid dynamics code for the simulation of an air-fired coal combustion and an oxyfired coal combustion with recycled flue gas in a 1 MWth combustion test facility. Reynolds-averaged Navier-Stokes (RANS) solutions were obtained for both cases. The results indicated that the CFD code with existing physical submodels could provide a reasonable prediction for the air-fired combustion. However, the prediction for the oxyfired case was not as satisfactory as expected. In order to assess the impact of the turbulence treatment in CFD on the predictions, large eddy simulations (LES) were carried out for the oxyfired case and compared with the results from the RANS simulation and the available experimental data. Although the results suggested that LES could provide a more realistic prediction of the shape and the physical properties of the flame, significant improvement in the prediction of the temperature was not observed. In addition, the complexity of the problem was thought to require more detailed experimental data for the validation of the LES. In setting out the principal finding of the study, the authors concluded that the numerical simulations for oxyfired pulverised coal combustion used have pointed out the need for improvement and development of specific physical submodels, and have raised several challenges for oxyfuel combustion simulations:

- **Chemistry:** The presence of CO_2 attributes to a different combustion pattern by strengthening the char gasification reactions. These reactions are slower by three orders of magnitude in the flame temperature; however, they are endothermic and would affect the overall heat of reaction.
- **Heat transfer:** Due to the high concentration of CO_2 (>60%) in the flue gas, it is essential to consider a non-grey gas model in order to correctly predict the absorption and the emission and subsequently the temperature in the furnace. Also, CO_2 has a different heat capacity in comparison with N_2 and therefore a different convective heat transfer pattern from an air-fired combustion is expected in the furnace. In the study, measured cooling water temperatures were used as boundary conditions for calculating the heat flux through the furnace wall. However,

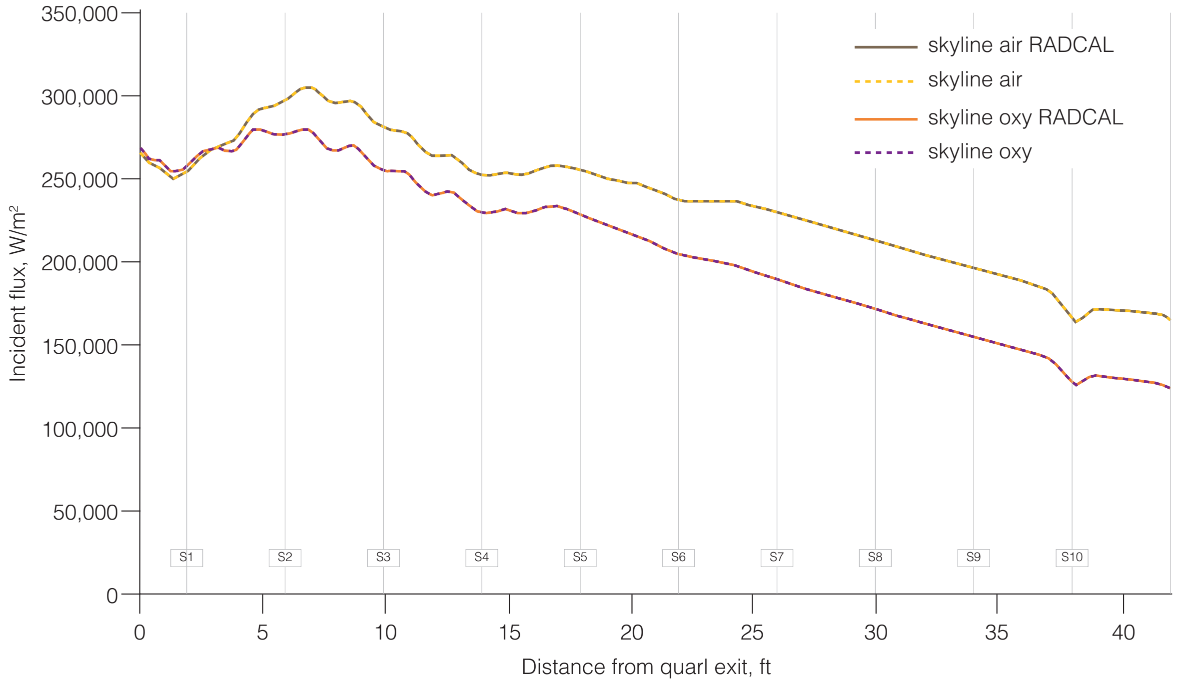


Figure 26 Incident radiative heat flux comparison (Shaddix and Geier, 2011)

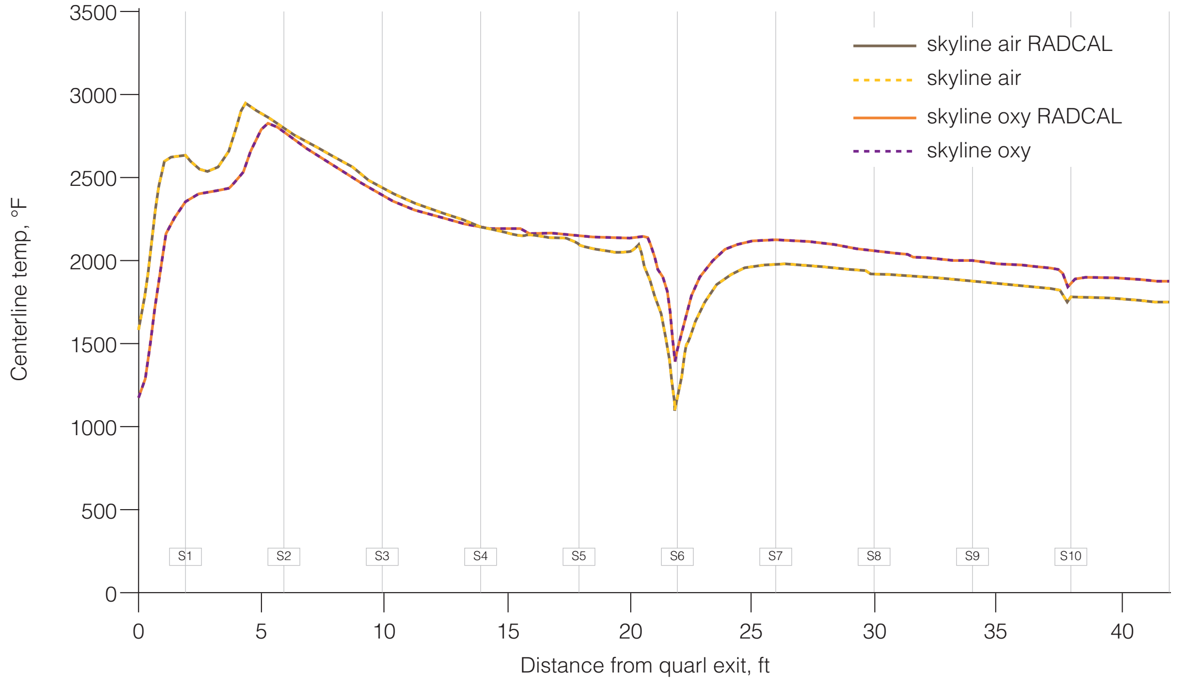


Figure 27 Furnace centreline temperature comparison (Shaddix and Geier, 2011)

larger temperature discrepancies, both inside the furnace and at the furnace exit, have been observed for the oxycoal case than the air-coal case, indicating a larger error in the heat transfer calculations for the oxycoal combustion.

- **Turbulence-radiation interaction:** It has been reported that radiation smoothes the temperature fluctuations and its effect is strengthened by the increase of the temperature. On the other hand, the effect of the turbulence on the radiation in the flame, and the interaction of radiation, density and temperature fields with the turbulence, should ideally be taken into consideration. However, this is a very complex task and involves high computational requirements for coupling of turbulence and radiation. Currently, there is not a generally accepted turbulence-radiation interaction model available for direct numerical simulation (DNS) or LES of reacting flow. The use of time-averaged solutions for the radiative transfer equations is efficient, but requires detailed probability density functions for relevant variables and a number of assumptions. The authors consider that such an approach is a promising candidate for future work.

Kahre and others (2008) described a series of combustion tests undertaken in a vertical pilot-scale furnace (1.2 MWth) at the IHI test facility in Aioi, Japan, to compare the performance of an air-fired swirl burner retrofitted to oxyfired pulverised coal combustion with the oxyfired feed conditions established to match the furnace heat transfer for the air-fired case. A turn down test at a reduced load was also conducted to study the impact on flame stability and furnace performance. Experimental results included gas temperature measurements using pyrometry to infer the ignition location of the flames, flue gas composition analysis, and residence time and carbon burn-out. Theoretical computational fluid dynamics (CFD) modelling studies using the Fluent 6.2 code were made to clarify mechanisms for flame ignition changes. Previous research has identified that differences in the gas compositions of air and oxy systems increase particle ignition times and reduce flame propagation velocity in laminar systems. The current study also suggests changes in jet aerodynamics, due to burner primary and secondary velocity differences (and hence the momentum flux ratio of the flows), also influence flame shape and type. For the oxyfuel retrofit considered, the higher momentum flux of the primary stream of the oxyfuel burner causes the predicted ignition to be delayed and to occur further from the burner nozzle, with the difference being accentuated at low load. However, the study was limited to experimental flames being all Type-0 (low swirl with no internal recirculation), and future work planned will address higher swirl flames (with internal recirculation) that are more common in industry.

Chen and others (2011) reviewed oxycoal combustion work covering the most recent experimental and simulation studies, to highlight the differences between combustion in an oxidising stream diluted by nitrogen and one diluted by carbon dioxide. They concluded that distinct effects on heat and mass transfer, as well as reaction kinetics, arise from the difference between the physical and chemical properties of CO_2 and N_2, which in turn change the coal flame characteristics. Operation under elevated pressures has also been proposed for oxycoal combustion systems in order to improve the overall energy efficiency and the authors opine that this may cause problems with combustion. Narrower flame regimes and lower laminar burning velocity under oxyfuel combustion conditions may lead to new stability challenges in operating oxycoal burners.

Shaddix and Molina (2009) described work aimed at providing important experimental data for the development of coal ignition models for use in CFD simulations. In the work reported, the ignition and devolatilisation characteristics of both a high-volatile bituminous coal and a Powder River Basin subbituminous coal were analysed in detail through single-particle imaging at a gas temperature of 1430°C over a range of 1236 vol % O_2 in both N_2 and CO_2 diluent gases. The bituminous coal images showed large, hot soot cloud radiation whose size and shape vary with oxygen concentration and, to a lesser extent, with the use of N_2 versus CO_2 diluent gas. Subbituminous coal images showed cooler, smaller emission signals during devolatilisation that have the same characteristic size as the coal particles introduced into the flow (nominally 100 µm). The measurements also demonstrated that the use of CO_2 diluent retards the onset of ignition and increases the duration of devolatilisation, once initiated. For a given diluent gas, a higher oxygen concentration yields shorter ignition delay and devolatilisation times. The effect of CO_2 on coal particle ignition is explained by its higher molar specific heat and its tendency to reduce the local radical pool. The effect of O_2 on coal particle ignition results from its effect on the local mixture reactivity. CO_2 decreases the rate of devolatilisation because of the lower mass diffusivity of volatiles in CO_2 mixtures, whereas higher O_2 concentrations increase the mass flux of oxygen to the volatiles flame and thereby increase the rate of devolatilisation.

In further work, Shaddix and Molina (2011) investigated NOx formation during combustion of pulverised coals and pulverised coal char in N_2 and CO_2 environments under isothermal and nearly constant oxygen conditions (for example using dilute coal loading). Three different oxygen concentrations (12% O_2, 24% O_2, and 36% O_2) and two representative US coals were investigated, at a gas temperature of 1050°C. To investigate the importance of NO reburn reactions, experiments were also performed with an elevated concentration (550 ppm) of NO in the gases into which the coal was introduced. For low levels of background NO, the fractional fuel-nitrogen conversion to NOx increased dramatically with increasing bath gas oxygen content, for both N_2 and CO_2 environments, though the fuel conversion was generally lower in CO_2 environments. Char N conversion was lower than volatile N conversion, especially for elevated O_2 concentrations. The results were claimed to highlight the importance of the volatile flame and char combustion temperatures on NOx formation. For the high background NOx condition, net NOx production was only observed in the 36% O_2 environment. Under these dilute loading conditions, NO reburn was found to be between 20% and 40%, depending on the type of coal, the use of N_2 or CO_2 diluent, the bulk O_2 concentration, and whether or not one considers reburn of volatile-NOx. The resulting dataset is thought to provide an opportunity to understand and differentiate the different sources and sinks of NOx under oxyfuel combustion conditions.

Table 9 Properties of Uthan, Illinois and PRB coals (Yu and others, 2011)

	Utah coal	Illinois coal	PRB coal
Proximate analysis, ar, wt%			
Moisture	3.18	9.65	23.69
Volatile matter	38.6	36.78	33.36
Fixed carbon	49.39	45.58	38.01
Ash	8.83	7.99	4.94
Ultimate analysis, ar, wt%			
C	70.6	64.67	53.72
H	5.41	5.59	6.22
N	1.42	1.12	0.78
S	0.53	3.98	0.23
O (diff)	13.21	16.65	34.11
Ash analysis, wt%			
Al_2O_3	14.52	17.66	14.78
CaO	6.11	1.87	22.19
Fe_2O_3	5.09	14.57	5.2
MgO	1.39	0.98	5.17
MnO	0.02	0.02	0.01
P_2O_5	0.59	0.11	1.07
K_2O	0.57	2.26	0.35
SiO_2	60.89	49.28	30.46
Na_2O	1.41	1.51	1.94
SO_3	2.33	2.22	8.83
TiO_2	0.88	0.85	1.3
Combustion parameters			
Coal flow rate, kg/h	4.5	4.89	6.26
Coal firing rate, kW	36.64		

Ash deposition is still an unresolved problem when retrofitting existing air-fired coal power plants to oxyfuel combustion. Experimental data are fundamental for the validation of mechanisms and model development. Yu and others (2011) undertook work designed to obtain laboratory combustor data on ash and deposits from oxycoal combustion, and to explore the effects of oxyfiring on their formation. Two bituminous coals (Utah coal and Illinois coal) and one subbituminous coal (Powder River Basin - PRB coal) were burnt on a down-fired combustor under both oxyfiring and airfiring. The coal properties are given in Table 9. Two oxyfired cases, at gas compositions 27 vol% O_2/73 vol% CO_2 and 32 vol% O_2/68 vol% CO_2, were selected to match the radiation flux and the adiabatic flame temperature of air combustion, respectively. Once-through CO_2 was used to simulate fully-cleaned recycled flue gas. The flue gas excess oxygen was fixed at 3 vol%. For each case, both size-segregated fly ash and bulk fly ash samples were obtained. Simultaneously, ash deposits were collected on an especially designed un- cooled deposition probe. Ash particle size distributions and chemical composition of all samples were characterised. Data showed that oxyfiring had insignificant impacts on the tri-modal ash particle size distributions and composition size distributions in the size range studied. Bulk ash compositions also showed no significant differences between oxyfiring and airfiring, except for slightly higher sulphur contents in some oxyfired ashes.

The oxyfired deposits were thicker than those from air-firing, suggesting enhanced ash deposition rates in oxyfiring (Figure 28). Oxyfiring also had apparent impacts on the deposit composition, especially for those components (for example CaO, Fe_2O_3, SO_3, etc) that could contribute significantly to ash deposition. Based on these results, aerodynamic changes in gas flow and changes in combustion temperature seemed more important than chemical changes of ash particles in

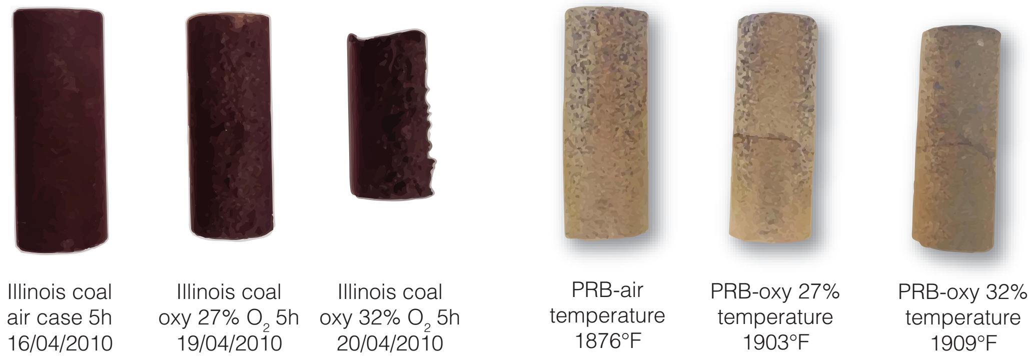


Figure 28 Ash deposits from Illinois and PRB coals (Shaddix and Geier, 2011)

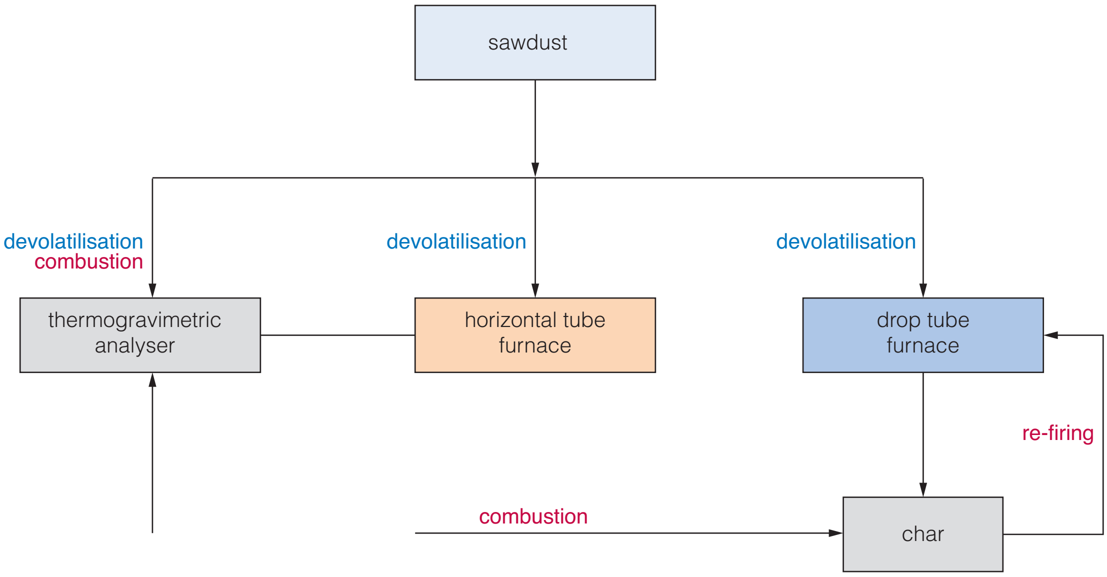


Figure 29 Experimental scheme (Farrow, 2011)

determining deposit behaviour during oxycoal combustion. Farrow (2011) has presented the results of a fundamental study into the behaviour of biomass oxyfuel combustion and co-combustion. Studies were undertaken using thermogravimetric analysis, (TGA), a horizontal tube furnace (HTF) and a drop tube furnace (DTF). Samples of biomass (sawdust) and coal were studied to investigate the behaviour of biomass under oxyfuel conditions in comparison to airfired condition in terms of:

- volatile yield;
- the associated nitrogen partitioning between char and volatiles in order to monitor NOx emissions;
- kinetic parameters which are useful for design of biomass oxyfuel combustion system. Additionally, an investigation was undertaken to determine how biomass will affect coal char burn-out during cofiring under oxyfuel and air firing with particular emphasis on the catalytic effect of biomass-contained alkali and alkaline metals on coal char burn-out.

The experiment approach taken is outlined in Figure 29. Volatile yields were determined for a range of particle sizes (–45 µm – 250 µm) at 700°C, 900°C and 1100°C. There was no particle size effect at both conditions except for the smallest particle size at 1100°C. TGA reactivity tests in an atmosphere of CO_2 showed that the simulated oxyfuel environment did not affect the combustion reactivity of the chars at low temperature hence the burn-out is identical with air-fired condition. Insignificant particle size effect is seen during burn-out in both conditions except for the smallest particle size. Burn-out studies of blends of coal and biomass chars showed an improved burn-out of blend but this was slightly more pronounced under oxyfuel condition. This was suggested to be due to strong synergetic effect: an indication of interactions (*see* Table 10 and Figure 30).

Farrow concluded that:

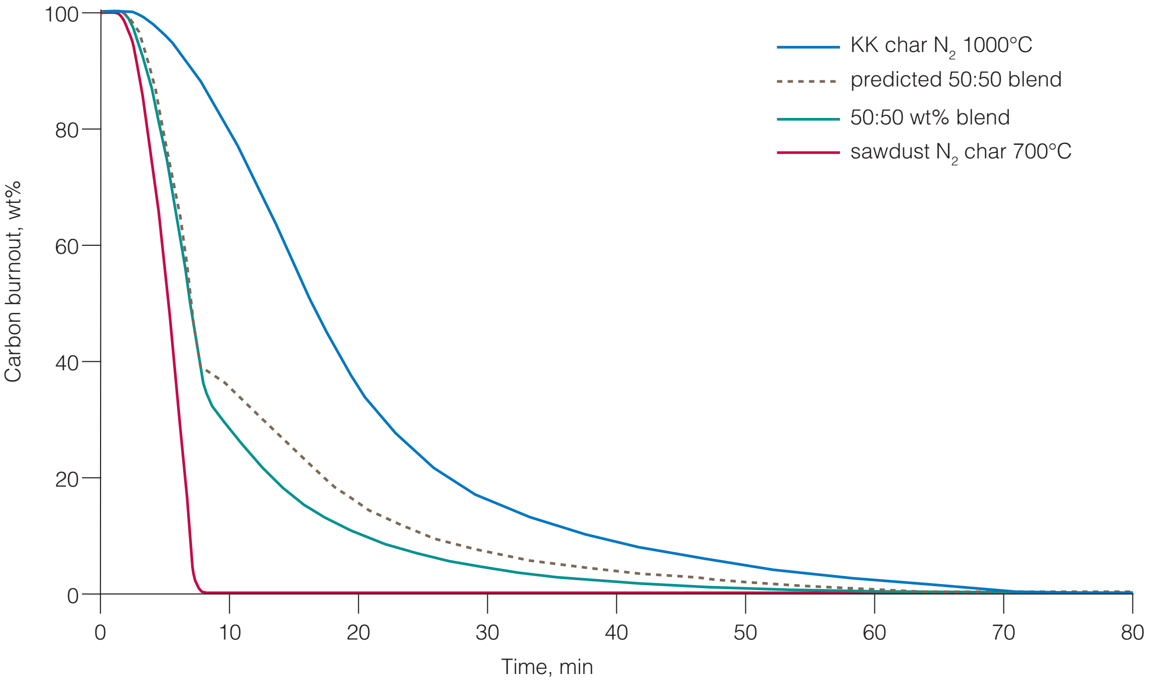
- high reactivity observed for CO at high temperature was due to a gasification reaction;
- no particle size effect, can use bigger particle size for pulverised biomass fuel combustion systems;
- biomass improved coal combustion. There is chemical interaction between the two fuels during co-combustion;
- inorganic minerals in biomass catalysed coal char combustion.

5.4 Summary

Research efforts on coal combustion are now largely focused on important developments such as cofiring and oxyfuel combustion, and how these affect conditions and reaction pathways within the boiler. Despite the wide variability of cofiring fuels, and the radically different environment in an oxyfuel configured boiler, impressive progress has been made in understanding these new systems. In particular, CFD-based approaches that bring together the detailed understanding of basic coal transformations are being used to give a deeper understanding of the new environments and to drive the development of more efficient and less polluting plant.

Table 10 Co-combustion interactions – air and simulated oxyfuel atmospheres (Farrow, 2011)

Samples	Nitrogen chars and air combustion		CO_2 chars and 21%O_2/79%CO_2 combustion	
	1st order rate constants	90% burn-out time, min	1st order rate constants	90% burn-out time, min
Sawdust char 700°C	0.4901	6.60	0.3114	7.85
Kleinkopje coal (KK) HTF char 1000°C	0.0734	38.70	0.0526	48.00
Sawdust/KK char blend 50:50 wt%	0.1002	22.15	0.1089	20.65
Predicted Sawdust KK char blend	0.0829	25.60	0.0720	31.60



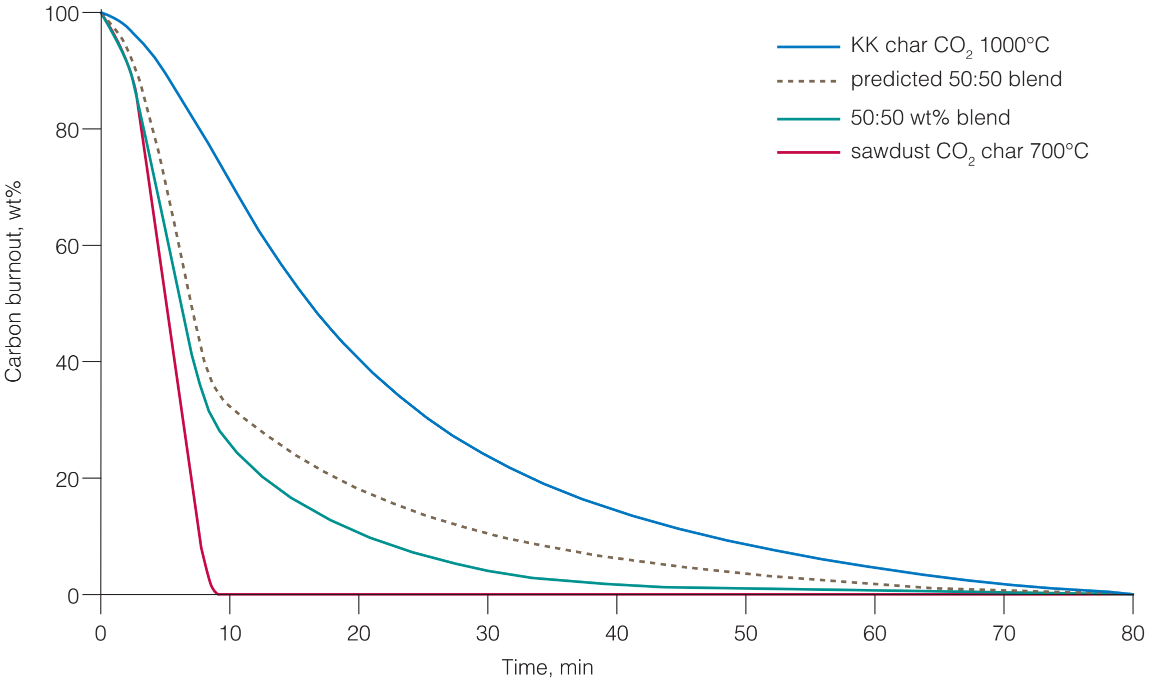


Figure 30 Co-combustion interactions – air (top) and simulated oxyfuel (bottom) atmospheres (Farrow, 2011)

6 Research and development needs

Worldwide, the major thrust for coal research and development is focused on developing and commercialising high-efficiency low-polluting plant. In particular, coal-fired plant capable of carbon capture and storage is a high priority. Work on fundamental coal science therefore tends to be organised to support these aims. In the USA, NETL (2012) is concentrating on two principal areas; the development of novel sensors and advanced process controls for advanced near zero emission power systems, and computational systems dynamics through its Advanced Research Program. The Advanced Research Program work on sensors is currently supporting research to develop:

- a suite of high-temperature, harsh environment sensors to measure temperature, pressure, and other process variables;
- novel sensors to measure synthesis gas (for example hydrogen), flue gas constituents such as nitrogen oxides, and trace contaminants such as mercury;
- advanced process control strategies for near-zero emissions in processes such as gasification and chemical looping.

The area of research on computational system dynamics has three main areas. Ongoing tasks in this area include:

- integration of co-simulator models with virtual engineering plant walk-through environment models;
- expansion and validation of multiphase fluid flow models for simulation of advanced coal-based power systems;
- investigation of basic combustion and gasification chemistry to determine mechanisms that affect coal or emissions behaviour under advanced and conventional combustion/gasification.

In a survey of coal research and engineering needs in the UK, the UK Coal Research Forum (2011) reported the following activities as relevant to improving the understanding of pulverised coal combustion:

- Basic coal science will remain important to the understanding of all coal utilisation processes. Means of readily evaluating coals and of predicting the behaviour and characteristics of coals and coal blends in advanced clean coal technologies continue to be needed. For example, in advanced PC plants, particularly those with, say, oxyfuel firing, plant manufacturers will need simple (low cost) tests to help in plant designs. Standard tests will need to be defined for simulated process conditions, for example true volatile matter measured at realistic heating rates and temperatures, tests to predict NOx emissions, improved techniques for collection of in-flame data, development of reliable cost effective techniques to measure corrosion and deposition rates.
- Equipment and systems for online monitoring of various species and conditions in coal-fired plants will need to be developed. Examples include non- intrusive techniques for the temperature monitoring of coals and flames. There is also a need for suitable fast response techniques for the monitoring of various gaseous species and carbon-in-ash levels. However, the needs now extend much further to encompass the CO_2 injection and storage issues in order to understand what is happening in these deep geological formations. In addition, while underground coal gasification is making rapid development progress, the need for robust monitoring techniques to understand and control the reactions in deep coal seams is of great significance if this technique is to be deployed.
- The development of computational fluid dynamics (CFD), other software tools and powerful computers means that modelling techniques can increasingly be of value. For example, there is a need for mathematical modelling (static, dynamic) of components and their integration into full plant. CFD modelling needs to be improved to reflect the latest findings of coal science such as the development of particle structure, pore diffusion and reaction within particles.
- Emissions of trace elements and volatile organic species are of increasing concern. There is merit in being able to predict trace element mobilisation in combustion and gasification systems from the composition of the coal mineral content as well as being able to predict their removal capability in various plant components.

7 Conclusions

The importance to world energy production of pulverised coal firing for power generation has stimulated a significant research activity aimed at understanding the transformations occurring during combustion. The presence of complex carbonaceous structures in close combination with a range of mineral components subjected to an extremely aggressive temperature-time profile leads to a very large number of reaction pathways, even before interactions with boiler components are considered. The previous IEA CCC studies have collated and discussed the results of this extensive body of work on pulverised coal combustion. Individual aspects of the combustion process have been isolated by well chosen experimental techniques and characterised in detail, but others have defied clarification. In addition while these individually-focused studies were capable of giving valuable insights into pulverised coal behaviour, and could be used to guide specific aspects of the combustion process such as pollutant formation and amelioration, a unified model capable of genuine predictive capacity has not emerged and many coal users continue to rely on empirical correlations to predict coal behaviour and for plant design. The overall complexity of the pulverised coal environment remains extremely challenging and a comprehensive theoretical description is considered likely to remain elusive for the immediate future.

The last twenty years have seen some very significant changes in the power generation sector that affect on the way in which coal is burnt to generate power. In addition to the way in which plant is operated, a new tranche of co-fuels have been introduced into the pulverised coal combustion environment, further complicating an already-challenging picture of the fundamental transformation occurring during combustion. Many of these new fuels are themselves highly variable in composition and exhibit behaviour during combustion that can be significantly different to coal. They may also contain high concentrations of species that can interact with coal combustion products, sometimes with deleterious results. The most recent changes to pulverised coal fired boiler plant include modifications to the gaseous atmosphere within the boiler during oxycombustion which are highly likely to produce concomitant changes in reaction mechanisms and pathways that are only just beginning to be explored by research workers. An understanding of the ways in which oxycombustion affects combustion is currently a major driving force in coal research and development.

The traditional coal characterisation techniques (for example density, proximate and ultimate analysis, ash fusion temperatures, ash chemical composition) have served coal users well for several decades and remain important ‘first step’ tools in assessing coal behaviour under pulverised coal combustion conditions. These techniques have been joined by an impressive array of developments that give detailed information on coal properties, often under dynamic (combustion) conditions in real time. The ability to observe and measure coal reactions as they occur is a valuable step forward as coal behaviour under the demanding temperature-time history in a boiler can be markedly different to that observed in a laboratory under different conditions.

Perhaps the most significant development is the emergence of computer modelling which allows the prediction of fluid and entrained particle flows through a burner and subsequently the boiler to be predicted with a high degree of accuracy. By incorporating submodels of coal behaviour an understanding of ‘real time’ coal behaviour is becoming increasingly possible with the benefits of true predictive capability.

Research efforts on coal combustion are now largely focused on important developments like cofiring and oxyfuel combustion and how these affect conditions and reaction pathways within the boiler. Despite the wide variability of cofiring fuels, and the radically different environment in an oxyfuel configured boiler, impressive progress has been made in understanding these new systems. In particular, CFD-based approaches that bring together the detailed understanding of basic coal transformations are being used to give a deeper understanding of the new environments and to drive the development of more efficient and less polluting plant.

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