EXPERIMENTAL INVESTIGATIONS ON COMBUSTION AND EMISSION BEHAVIOUR DURING OXY-COAL COMBUSTION

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NOMENCLATURE

Latin Symbols

D	Diameter	[µm]
H	Calorific Value	[kJ/kg]
M	Molecular Weight	[kg/kmol]
m	Mass	[kg]
n	Oxygen Ratio	[-]
V	Specific volume at STP	[m^3/kg]
v	NCV Loss	[%]
$\dot{V}$	Volume flow rate at STP	[m^3/hr]
y	Volumetric Concentration	[ppm]

Greek Symbols

β	Percentage Reduction	[%]
φ	Emission Rate	[mg/MJ]
ρ	Density	[kg/m^3]
η	Conversion of Substance i in the Fuel to Species k	[%]
γ	Mass Fraction	[%]

Subscripts

0	Stoichiometric Combustion
A	Ash
bur	Burner
C	Carbon
c	Char
d	Dry
el	Electrical
G	Flue Gas
f	Fuel
i	Substance i (N, S, C etc.)
inj	Injection
k	Species k (NO, SO_2 etc.)
MB	Mass Balance
m	Molar
max	Maximum
n	Standard (norm)

NO	Nitrogen Oxide
O	Oxidant
O_2	Oxygen
OFP	Over-fire Port
PO	Pure Oxygen
S	Sulphur
s	Stable
th	Thermal
u	Net or Lower
wi	With Injection
woi	Without Injection

Abbreviations

ar	as received
ASU	Air Separation Unit
CFR	Coal Feeding Rate
CS	Carrier Stream
DIN	Deutsches Institut für Normung
EN	Ensdorf Bituminous Coal
EOR	Enhanced Oil Recovery
ESP	Electrostatic Precipitator
FTIR	Fourier Transform Infrared Spectroscopy
HVB	High Volatile Bituminous
IGCC	Integrated Gasification Combined Cycle
IR	Infrared

KK	Klein Kopje Bituminous Coal
LA	Lausitz Brown Coal
LHV	Lower Heating Value
MEA	Monoethanolamine
NDIR	Nondispersive Infrared
OF21	O_2/CO_2 combustion with 21% O_2/79% CO_2 by volume
OF27	O_2/CO_2 combustion with 27% O_2/73% CO_2 by volume
OF35	O_2/CO_2 combustion with 35% O_2/65% CO_2 by volume
OTM	Oxygen Transport Membranes
PF	Pulverised Fuel
PS	Primary Stream
RH	Rhenish Brown Coal
RFG	Recycled Flue Gas
SS	Secondary Stream
SCR	Selective Catalytic Reduction
TGA	Thermogravimetric Analysis
V	Volatile Content
vol.	Volumetric
waf	Water Ash Free
wf	Water Free
XRF	X-Ray Fluorescence

SUMMARY

As the most abundant non-renewable energy source available, coal has traditionally played a major role in ensuring the security of energy, and will continue to play a key role in the world energy mix. The burning of coal has however always been a subject of environmental concern. In recent years, the emission of green house gases and global climate change has emerged as the largest environmental challenge. As coal fired power plants are categorised among the least carbon efficient energy producer in terms of CO_2 emission per unit of electricity generated, an immediate technological response is anticipated. Although, improving the efficiency of coal fired plants can decrease CO_2 emissions to some extent, fossil fuel based carbon capture and storage technologies will have to bear the significant share in power generation, if reduction or even stabilisation of CO_2 emission is to be envisaged.

One promising technology with a potential for near complete capture of CO_2 is the oxy-coal combustion process with flue gas recirculation. This technology is however still at an early stage of development, and until now there are no full-scale commercial plants based on this technology. The combustion of coal in this process takes place with almost pure oxygen and recycled flue gas resulting in a flue gas stream of almost pure CO_2, ready for geo-sequestration. The flue gas is recycled back into the furnace to control the temperature and maintain the heat flux profiles within the furnace. Research efforts are in progress for a better understanding of the oxy-coal combustion process. However, many issues still need to be addressed in order to obtain improved fundamental understandings. The primary objective of this study is therefore, a comprehensive and well-planned experimental investigation to further understand the emission and combustion behaviour during O_2/CO_2 combustion using a series of fuels, and is sub-divided into:

I. Determination of combustion and emission behaviour during un-staged combustion.
II. Determination of NO_x reduction potential during oxidant staged combustion.
III. Determination of the fate of recycled NO.
IV. Determination of the fate of SO_2 and its impact on oxy-coal combustion.

A 20 kW electrically heated, once through furnace was used for this investigation, which enabled highly flexible parametric studies as well as reliable and repeatable measurements. To simulate an oxy-coal combustion environment, almost pure O_2 and CO_2 supplied from tanks were mixed in a highly flexible mixing station and were supplied to the furnace via three different streams of the burner. Parametric studies were also performed for air-blown combustion to compare the combustion and emission behaviour in an O_2/N_2 and an O_2/CO_2 mixture. In addition, measurements during simulated O_2/RFG (dry recirculation) environment was also conducted to investigate the behaviour of recycled flue gas species i.e. NO and SO_2 by injecting known concentrations of NO and SO_2 into the furnace along with the O_2/CO_2 mixture or air. Four coals (ranging from medium volatile bituminous coal to pre-dried brown coal), natural gas and char were used for various parametric studies.

As the initial application of oxy-coal combustion technology will most likely be a retrofit in existing pulverised coal furnaces, modifications are required to match the flame and heat transfer characteristics of air-blown furnaces. An investigation was therefore commenced with detailed in-flame and furnace exit measurements during un-staged combustion, using two bituminous coals (Klein Kopje and Ensdorf) and two pre-dried brown coals (Lausitz and Rhenish). Emission and combustion behaviour were determined at different O_2/CO_2 volumetric concentrations i.e. 21% O_2/ 79% CO_2 (OF21), 27% O_2/ 73% CO_2 (OF27) and 35% O_2/ 65% CO_2 (OF35). To further establish the emission and combustion behaviour during oxy-coal combustion, investigation in explicitly gas-phase using natural gas was also performed. This investigation was able to develop a further understanding of the combustion behaviour of volatiles in O_2/CO_2 environment, whilst avoiding the influence of particles. This is thought to aid in improved prediction of homogeneous reactions taking place during oxy-coal combustion for scale-up and modelling purpose. Similar flame temperature profile and gaseous concentration profile along the length of the reactor was observed for coals as well as natural gas firing during OF27 and air-blown combustion. The ash/char composition collected along the reactor length during coal firing was also observed to be similar for OF27 and air-blown combustion. This indicates that approximately 27 vol. % oxygen will be required during O_2/CO_2 combustion (representing oxy-coal combustion with dry flue gas recirculation) to achieve similar combustion performance of air-blown pulverised coal furnaces. The result further reinforces the findings from previous authors that oxygen concentration if properly adjusted gives the heat transfer and flame character similar to air-fired furnaces. It was further found that, the conversion of fuel-N to NO for all 4 coals tested is lower in a CO_2 environment, and is in agreement with most historical studies. When a comparison of the NO emission rate and the fuel nitrogen conversion rate between different coals during OF27 combustion is made, a trend typical to a conventional air-fired, fuel lean combustion scenario was observed, i.e. the higher the fuel-N content (for coals with comparable volatile content), the greater the NO emission, and the higher the volatile content (for coals with comparable fuel-N content), the greater the conversion of fuel-N to NO. It is however noted that this investigation was carried out in a once through furnace.

As the purity requirement of CO_2 for storage is still uncertain, it is rational to minimise impurities in the furnace when possible. The next focus of this investigation was therefore on the reduction of nitric oxide by oxidant staging during oxy-coal combustion. Detailed investigation of NO_x formation mechanisms during oxidant staged combustion in CO_2 (27% O_2/73% CO_2 by volume) and N_2 (air-blown) environment was conducted by firing two pre-dried brown coals (Lausitz and Rhenish) and two bituminous coals (Klein Kopje and

Ensdorf). Investigations of oxidant staged combustion in a CO_2 environment of 27% O_2/73% CO_2 was carried out as the initial results during un-staged combustion indicated that the combustion and emission behaviour for OF27 combustion was comparable to air-blown combustion (it is however noted that as the technology matures, future applications will be with reduced flue gas recycle resulting in higher combustion temperature). Gaseous concentration profile measurements for different burner oxygen ratios and residence times in the reduction zone were conducted. Measurement of in-flame HCN and NH_3, using a FTIR was also performed to determine the NO_x formation mechanisms during O_2/CO_2 combustion. This investigation not only aided in understanding the NO_x reduction potential during O_2/CO_2 combustion but also provided design features required for a low NO_x oxy-coal burner. Fuel NO_x formation mechanisms in a fuel rich environment during O_2/CO_2 combustion, as demonstrated by the formation and destruction of HCN and NH_3 is similar to air-blown combustion. NO formed in the mixing zone reacts with hydrocarbon radicals to produce HCN or NH_3, which are converted to N_2 in the oxygen deficient reduction zone for both cases. As with conventional air-blown combustion, the formation of HCN and NH_3 is also dependant on the coal rank, as only HCN was detected for a medium volatile bituminous coal, Klein Kopje while both HCN and NH_3 were detected for the Lausitz brown coal. Furthermore, results indicate that oxidant staging for NO_x reduction is equally or even more effective for O_2/CO_2 combustion in terms of NO_x reduction potential, as the conversion of fuel-N to NO and NO_x emission rate is lower than corresponding air-blown combustion. However, as mentioned earlier, this investigation was carried out in a once through furnace. As with conventional air-blown combustion, the reduction of NO was observed to be proportional to the partitioning of fuel-N into the gas-phase. This is seen as an encouraging result from oxy-coal combustion perspective, as the amount of fuel-N partitioned into the gas-phase is a function of temperature, and manipulation of local temperature is considered to be simpler during oxy-coal combustion. Direct injection of O_2 into the flame in order to increase the devolatilisation rate without affecting the overall heat transfer performance could be one viable option that can take advantage of existing infrastructure of an oxy-fuel plant for further reduction of NO.

Oxy-coal combustion also requires recirculation of the flue gas to moderate the furnace temperature. Apart from CO_2 and water vapour, the recycled flue gas also contains pollutants from coal combustion and the impact of such pollutants recycled back into the furnace needs to be evaluated for successful application of oxy-fuel process. The next focus of this investigation was therefore the determination of the fate of nitrogen oxide recycled back into the furnace. Fate of NO recycle back into the furnace was determined by injecting a known concentration of pure NO via the burner or the over-fire port, along with air or O_2/CO_2 mixture, depending upon the investigation being carried out. A medium volatile bituminous coal (Klein Kopje) and a brown coal (Lausitz) were used for this investigation. Homogeneous and heterogeneous reduction of recycled NO was also determined by firing natural gas and char of a brown coal. Investigations were carried out during OF27 and air-blown combustion, with and without oxidant staging. This investigation has not only enhanced the understanding of NO_x re-burning mechanism during oxy-coal combustion, but may also provide the design features of low NO_x oxy-coal burner and assess the requirements of flue gas clean-up devices. Reduction of recycled NO by heterogeneous reactions with active carbon sites as indicated by measurements with char of brown coal is prominent when oxygen is in excess. However, as oxygen availability decreases with a decrease in burner oxygen ratio during staged combustion; homogeneous reactions (reactions with active hydrocarbon radicals) become prominent. Similarly, concentrations of recycled NO within the range of 1200 ppm showed no influence on recycled NO reduction efficiency during char and coal combustion, indicating that the reduction efficiency will remain unaffected with an increase in the concentration of recycled NO. Also, the reduction of recycled NO during coal combustion for both air-blown and oxy-coal combustion was seen to be entirely dependent on combustion conditions i.e. the burner oxygen ratio and residence time in the reduction zone. Recycled NO reduction of almost 100% was achieved during staged combustion with a burner oxygen ratio of 0.75, and approximately 50% reduction was achieved during un-staged combustion. Similarly, a longer residence time in the reduction zone during staged combustion had a positive influence on recycled NO reduction when NO was introduced via the burner. The reduction of recycled NO, at a burner oxygen ratio of 0.75 is almost similar for air-blown and oxy-coal combustion, indicating that the combustion media has little influence on recycled NO reduction when oxygen availability is low, or when homogeneous reactions are prominent. However, as oxygen availability increases with an increase in burner oxygen ratio (or when heterogeneous reactions are dominant), reduction of recycled NO is higher in a CO_2 media. This is most probably due to the presence of higher in-flame CO concentrations during oxy-coal combustion. Reduction efficiency of recycled NO is also dependent on the location of NO injection, as the reduction of recycled NO when injected via the over-fire port is much lower than when introduced via the burner. By considering the overall reduction of recycled NO and stable NO concentration thus achieved, the NO_x emission rate is between 0.24 to 0.37 times lower during oxy-coal combustion with 73 vol.% flue gas recycle when compared to corresponding air-blown combustion. This is in agreement with historical investigations carried out during oxy-coal combustion with flue gas recycle, further confirming that the reduction of NO recycled back into the furnace is the most important factor resulting in lower NO_x emissions rate during oxy-coal combustion.

Besides the emission of CO_2, NO_x, CO, etc., the combustion of coal is also associated with the conversion of fuel sulphur into compounds such as SO_2, SO_3, H_2S, etc. The presence of sulphur components, especially H_2S and SO_3 are associated with high temperature corrosion at the furnace walls and super heater sections, and low temperature corrosion through the condensation of sulphuric acid in the economiser or air heater. Primary emphasis of the next investigation was therefore to assess the impact of combustion media (N_2 or CO_2) and recycled SO_2 on the formation of gaseous sulphur components in the furnace (SO_2 and

H_2S). The SO_2 retention capacities of coals (ash) in the radiative and convective section of the furnace were also investigated. Investigations were carried out during air-blown and OF27 combustion, with and without oxidant staging. The impact of recycled SO_2 was investigated by injecting a known concentration of synthetic SO_2 through the secondary stream of the burner. This investigation not only assisted in understanding the risk of corrosion during oxy-coal combustion, but also aided in understanding the SO_2 retention capacity of different coals in the low temperature convective section of the furnace and the flue gas recycle path. Lower temperature window in the convective and recirculation path before the ESP offers a potential for SO_2 retention by sulphate forming elements in the ash. Regardless of a combustion media (CO_2 or N_2), if high concentration of active sulphate forming elements are present in the ash, the SO_2 retained by the ash increases with an increase in SO_2 concentration up to a certain concentration of SO_2 in the flue gas. As SO_2 concentration is much higher during O_2/RFG combustion, the SO_2 retained by the sulphate forming elements in the ash will also be higher. The most important information from these results is that, if the coal being used has high concentration of active sulphate forming elements, the opportunity of retaining maximum possible SO_2 in the convective section and flue gas recirculation path leading to decreased SO_2 accumulation needs be considered, when designing a cost effective oxy-coal plant. Similarly, the H_2S/SO_2 formation mechanism in a CO_2 environment is seen to be basically similar to a N_2 environment. However, the fraction of H_2S with respect to SO_2 is lower in a CO_2 environment as well as in an O_2/RFG environment, when compared to air-blown combustion. This may be due to the enhanced consumption of H_2 to produce CO by the water shift reaction resulting in a lower reaction rate of sulphur and hydrogen molecules to form H_2S. The concentration of H_2S in an O_2/RFG scenario on the other hand is much higher than air-blown combustion due to high in furnace SO_2 concentrations. Therefore, from corrosion perspective, special attention needs to be given to oxy-coal operated furnaces. Low rank (high volatile), high sulphur coals might require even more attention, as both H_2S fraction and the concentrations are seen to be much higher than medium volatile bituminous coal.

KURZFASSUNG

Fossile Energieträger haben aufgrund ihrer weltweiten Verbreitung und wirtschaftlichen Verfügbarkeit einen großen und verlässlichen Beitrag an der Energieversorgung. Die Technologien wurden ständig weiterentwickelt um zum Einen den spezifischen Verbrauch zu reduzieren und zum Anderen die Umwelteinflüsse wie Staub-, Schwefel- und Stickstoffoxidemissionen zu minimieren.

Moderne Kohlekraftwerke emittieren ca. 750g/kWh CO_2 bei einem Wirkungsgrad von rd. 46%. Diese hohen spezifischen CO_2-Emissionen und die Tatsache, dass Kohle weiterhin eine weltweit hohe wirtschaftliche Verfügbarkeit besitzt, legen nahe für diese Kraftwerke Technologien zur CO_2-Abscheidung und langfristigen CO_2-Speicherung zu entwickeln.

Die in der Entwicklung befindlichen Technologien firmieren unter der Bezeichnung „Carbon Capture and Storage“ kurz CCS-Technologien; diese stellen hierbei eine mittelfristig realisierbare Möglichkeit dar, die Kohle weiterhin klimaverträglich zur Energieversorgung zu nutzen.

Die vorliegende Arbeit beschäftigt sich mit der so genannten „Oxyfuel-Technologie“, hierbei wird Sauerstoff anstelle von Luft für die Verbrennung verwendet. Dies führt zu hohen CO_2-Konzentrationen im Abgas und begünstigt somit die Wirtschaftlichkeit des Gesamtprozesses. Um die Verbrennungstemperaturen im Feuerraum und die Wärmeübertragung zu kontrollieren werden Rauchgase in den Feuerraum zurückgeführt. Eine zentrale Aufgabenstellung der Arbeit bestand darin, die Auswirkungen der Rauchgasrezirkulation auf das Verbrennungsverhalten und auf die Schadstoffbildung zu untersuchen.

Die Schwerpunkte der Untersuchungen bilden die Abbrandcharakteristik und die Bildung und Reduktion von Stickstoff- und Schwefeloxiden in einer CO_2-reichen Atmosphäre. Neben einer Variation der Verbrennungsatmosphäre (Luft bzw. CO_2-reich)

wurden Kohlen mit Unterschieden im Inkohlungsgrad, des Stickstoff- und Schwefelgehalts, der Aschemenge und der Aschezusammensetzung verwendet. Durch die gezielte Auswahl der Einsatzstoffe können aus den Ergebnissen für ein breites Brennstoffband umfangreiche Erkenntnisse abgeleitet werden.

Um die geplanten Parametervariationen erfolgreich durchzuführen, wurde ein für Luftverbrennung am Institut verfügbarer Reaktor um die Erfordernisse der Oxyfuel-Verbrennung erweitert. Adaptionen waren im Wesentlichen bei der Sauerstoff- und CO_2-Zuführung am Brenner sowie für eine Sauerstoffstufung im Feuerraum erforderlich. Darüber hinaus wurden Möglichkeiten geschaffen, um NO und SO_2 gezielt den Verbrennungsgasen beizumischen, um so die Auswirkungen einer Rezirkulation dieser Komponenten auf Feuerraum- und Abgaskonzentrationen zu untersuchen. Neben Standardkomponenten wie O_2, CO_2, CO, NO, NO_x, SO_2 wurden insbesondere im Brennernahfeld die Komponenten NH_3, HCN und H_2S gemessen.

In einem ersten Schritt wurden im Vergleich zu Verbrennungsversuchen mit Luft drei Feuerungseinstellungen mit unterschiedlichen Sauerstoffkonzentrationen (21, 27 und 35 Vol.%) im Verbrennungsgasgemisch (O_2/CO_2) durchgeführt (Kapitel 5). In Übereinstimmung mit anderen Publikationen konnte gezeigt werden, dass die Abbrandcharakteristik der 27% Oxyfuel-Einstellung große Übereinstimmungen mit der konventionellen Luftverbrennung aufweist. Vor diesem Hintergrund konzentrierte sich ein Großteil der vergleichenden Parameterstudien in den folgenden Abschnitten auf diese beiden Einstellungen (Luft bzw. $27\%O_2,73\%CO_2$).

Die Ergebnisse dieser Untersuchungen unterstrichen, dass eine belastbare vergleichende Diskussion und Darstellung der Luft- und Oxyfuel-Einstellungen mit der bisher verwendeten Maßeinheit mg/m^3 i.N nicht zielführend ist. Für vergleichende Betrachtungen wird somit die Schadstofffracht in mg/MJ am Feuerraumende herangezogen.

In den weiteren Kapiteln 6 und 7 wird gezielt auf die Bildung und Reduktion der Stickoxide eingegangen. Umfangreiche Profilmessungen der Komponenten NO, CO, NH_3 und HCN bei variierenden Verweilzeiten (1s, 2s, 3s) und Sauerstoff- zu Brennstoff-Verhältnissen (0,75, 0,85, 0,95, 1,15) in einer Primärreaktionszone bilden hier die Basis der Untersuchungen. Darüber hinaus wurde eine mittelflüchtige und hochflüchtige Steinkohle (Klein Kopje, Ensdorf) sowie zwei Braunkohlen aus dem Rheinischen und Lausitzer Revier eingesetzt. Anhand der umfangreichen Datenbasis konnte gezeigt werden, dass auch in einer CO_2-reichen Oxyfuel-Atmosphäre die sauerstoffgestufte Verbrennung ein probates Mittel darstellt, um die NO-Bildung aus Brennstoff-Stickstoff zu minimieren. Für alle eingesetzten Kohlequalitäten konnten bei Anwendung der Sauerstoffstufung Umwandlungsraten zu NO von weniger als 10% erzielt werden.

In Kapitel 7 wurde untersucht, inwieweit mit den abgekühlten Rauchgasen rezirkuliertes NO in der Primär- und Ausbrandzone einer Feuerung bei ungestufter und gestufter Feuerungsführung reduziert wird. Es konnte gezeigt werden, dass sowohl für die mittel- wie auch hochflüchtigen Kohlen bereits bei ungestufter Verbrennung eine Reduktion von ca. 50% und bei Sauerstoff- zu Brennstoff-Verhältnissen von kleiner 0,95 in der Primärzone Reduktionsraten von 80 bis 100% erzielt werden können.

Die im Rahmen von Kapitel 6 und 7 durchgeführten Untersuchungen verdeutlichen, dass die in einzelnen Versuchsanordnungen mit realer Rauchgasrezirkulation ermittelten verringerten NO-Frachten im Wesentlichen auf die Reduktion von rezirkuliertem NO in der Flamme zurückzuführen sind. Dieser Sachverhalt erklärt auch die starke Schwankungsbreite der bisher veröffentlichten Datenbasis, da das Reduktionspotential sowohl von der rezirkulierten Rauchgasmenge wie auch stark von den lokalen Sauerstoff- zu Brennstoff-Verhältnissen im Brennernahfeld abhängig ist.

Eine Vielzahl der in der Arbeit erzielten Ergebnisse unterstreichen, dass eine primärseitige NO-Reduktion durch gestufte Verbrennung unter Oxyfuelbedingungen ein großes Potential hat und für ein breiteres Brennstoffband effizient angewendet werden kann.

Das Verhalten von Schwefel im Hochtemperaturbereich der Feuerung und entlang des Rauchgasweges wird in Kapitel 8 betrachtet. Grundsätzlich konnte gezeigt werden, dass unabhängig von der Verbrennungsatmosphäre der im Brennstoff enthaltene Schwefel weitgehend zu SO_2 umgewandelt wird. Es lässt sich auch kein nennenswerter Zusammenhang zwischen einer CO_2-reichen Atmosphäre und der Bildung von H_2S im Brennernahbereich ableiten.

Es werden vielmehr aufgrund der deutlich erhöhten SO_2-Konzentrationen unter Oxyfuel-Bedingungen insbesondere für hochflüchtige Brennstoffe höhere H_2S-Konzentrationen im Brennernahfeld gemessen. Neben dem Sauerstoff- zu Brennstoff-Verhältnis im Brennernahfeld hängt die erzielte H_2S-Konzentration vor allem von der SO_2-Konzentration im Feuerraum und der Kohlequalität ab. So wurde z.B. für eine hochflüchtige Steinkohle (Ensdorf) eine Umwandlungsrate zu H_2S von 44% bestimmt, während für die mittelflüchtige Steinkohle (Klein Kopje) nur eine Umwandlungsrate von 11% ermittelt wurde.

Um das Potential der Eigeneinbindung von Schwefel in die Flugasche der jeweiligen Kohle zu untersuchen wurde die SO_2-Konzentration im Rauchgas über einen Bereich von 500 vppm bis 4000 vppm variiert. Das Ca/S-Verhältnis der Brennstoffe lag zwischen 1,03 und 3,96. Die Eigeneinbindung des Schwefels steigt unter Oxyfuel-Bedingungen deutlich an und ist verursacht durch die prozessbedingten höheren SO_2-Konzentrationen.

Die Untersuchungsergebnisse unterstreichen, dass für eine Betrachtung der Schwefelbilanz die Eigeneinbindung verstärkt zu berücksichtigen ist. Die erhöhte Eigeneinbindung und der damit verbundene erhöhte SO_3-Anteil in der Asche sollte auch im Hinblick auf die weiteren Verwertungswege berücksichtigt werden. Dieser Sachverhalt gilt insbesondere für die Steinkohleaschen, die üblicherweise unter Berücksichtigung der EN 450 der Zementherstellung zugeführt werden.

Abschließend werden die Untersuchungsergebnisse kapitelübergreifend zusammengefasst und diskutiert sowie Empfehlungen für ein weiteres Vorgehen abgeleitet.

CHAPTER 1

INTRODUCTION

A rapid growth in the world population and a desire for a higher standard of living has led to an increased demand for energy throughout the world. The energy demand is projected to expand by almost 60% between 2002 and 2030 [IEA04]. Fossil fuels are, and will remain the backbone of power generation to fulfil this energy demand. As the most abundant fossil fuel energy source available, coal has and will play a major role in ensuring the security of energy. With reserves geographically diversified across the globe and expected to last another 200 years, international coal has a strong track record of stability. Coal accounted to 33.7% of the primary energy demand in Europe in the year 2002 [IEA04] and more than half of the electricity generated today in USA is based on coal. Coal will therefore continue to play a key role in the world energy mix. The burning of coal has however always been a subject of environmental concern. First it was the particulate matters, followed by NO_x and SO_2 emissions. Suitable control technologies have been successfully implemented to reduce these pollutants. In recent years, the emission of green house gases and global climate change has emerged as the largest environmental challenge. Power generation is expected to contribute to approximately half the increase in carbon dioxide emissions over the years 2002 to 2030 [IEA04]. As coal fired power plants are among the least carbon efficient energy producer in terms of CO_2 emission per unit of electricity generated, an immediate technological response is anticipated. Although improving the efficiency of coal fired plants can decrease the CO_2 emission to some extent, fossil fuel based carbon capture and storage technologies will have to bear the significant share in power generation, if reduction or even stabilisation of CO_2 emission is to be envisaged [She07].

One promising technology with a potential for near complete capture of CO_2 is the oxy-coal combustion process with flue gas recirculation. This technology is however still at an early stage of development and until now there are no full-scale commercial plants. The combustion of coal in this process takes place with almost pure oxygen and recycled flue gas resulting in a flue gas stream of almost pure CO_2. The flue gas is recycled back into the furnace to control the temperature and maintain the heat flux profiles. The characteristic of an oxy-fuel plant will therefore differ from an air-blown combustion plant in several aspects, most important of which are:

I. The density of gases through the furnace as well as that of the flue gas will be increased due to the presence of higher proportion of CO_2 during oxy-coal combustion.

II. The volume of gases through the furnace will be reduced due to recirculation of the flue gas.

III. The adiabatic flame temperature in a CO_2 media will be lower than in a N_2 media for a given oxygen concentration, due to the higher specific heat capacity of CO_2. To achieve a similar adiabatic flame temperature as in an air-blown combustion scenario, the oxygen concentration will have to be more than 21 vol. %.

IV. Higher concentrations of tri-atomic molecules (CO_2 and H_2O) in the furnace will result in higher gas emissivities. To attain similar radiative heat transfer as in air-blown furnaces, the O_2 proportion passing through the furnace will have to be optimised.

V. The concentration of contaminants such as sulphur containing compounds, hydrogen chloride (HCl) and mercury (Hg) will increase due to the re-circulation of the flue gas and reduction in net flue gas volume.

VI. The velocity of primary gases carrying the coal to the burner will have to be similar to air-blown combustion since a certain minimum velocity is required to keep the pulverised fuel in suspension. The volume of oxidant through the secondary stream of the burner will therefore be reduced, as the total oxidant volume is lower during oxy-coal combustion. This will result in a lower velocity through the secondary stream of the burner, and a burner with swirled secondary stream will experience a lower overall swirl and altered aerodynamics.

Although research activities are in progress for a better understanding of the oxy-coal combustion process, issues that need to be addressed in more detail to obtain improved fundamental understanding of oxy-coal combustion process are:

I. Determination of the oxygen concentration or recycle ratio (ratio of the mass of recycled flue gas to the mass of total flue gas flow in the system) that yields the optimum flame temperature and heat transfer characteristics for a retrofit and for purpose built plants.
II. A detailed investigation of the combustion behaviour for coals of different rank in O_2/CO_2 environment along with ignition, burn out and emission behaviour.
III. Requirements for flue gas cleanup and options for emissions reduction.
IV. Issues associated with materials and corrosion.
V. Requirements for plant start-up, shut down and boiler control systems.
VI. A full appraisal of the slagging and fouling nature of the ash arising from the oxy-combustion process and their impact on boiler heating surface arrangement and choice of boiler material.
VII. Burner performance due to changes in aerodynamics and properties of the media and options for optimum burner design for all ranks of coals.

Furthermore, demonstration of pilot and full-scale plants will be necessary to improve the confidence of utilities for successful commercialisation of this technology. Due to time constraints, the present study is unable to investigate all the aspects previously identified. The primary aim of this study is therefore, a comprehensive and well planned experimental investigation to further understand the emission and combustion behaviour of a series of fuels during O_2/CO_2 combustion and is sub-divided into:

I. Determination of combustion and emission behaviour during un-staged combustion.
II. Determination of NO_x reduction potential during oxidant staged combustion.
III. Determination of the fate of recycled NO.
IV. Determination of the fate of SO_2 and its impact on oxy-coal combustion.

With the above objectives in prospective, this dissertation is organised as follows:

Chapter 2 summarises the literature review of the general aspects and techno-economic analysis associated with the oxy-coal combustion process. Chapter 3 presents a literature review on combustion and emission behaviour during oxy-coal combustion. Chapter 3 is mainly focused on NO_x and SO_2 emissions. Chapter 4 describes the experimental parameters and the test facility used for this study. Chapter 5 provides the results on combustion and emission behaviour during un-staged combustion. Chapter 6 presents the results of NO_x reduction potential during oxidant staged combustion. Chapter 7 presents the results on fate of recycled NO during oxy-coal combustion. Chapter 8 provides the results on the fate of SO_2 during oxy-coal combustion. Chapter 9 summarises the present work with conclusions and recommendations for further investigation. The definition of unique terms used for the evaluation of the results is included in Appendix A.

CHAPTER 2

OVERVIEW OF OXY-COAL COMBUSTION TECHNOLOGY

2.1. OPTIONS FOR CO_2 REDUCTION

Reduction and capture of CO_2 from fossil fuel power plants has been a subject of intense discussion among policy makers in recent years due to its association with climate change. There are three main options for reducing CO_2 emission from fossil fuel based energy conversion systems:

1. Improving the fuel conversion efficiency.
2. Switching to less carbon intense fuels.
3. Capture and storage of CO_2

Improving a plants thermal efficiency will not only reduce the CO_2 emission per unit of energy generated but will also lower emissions of NO_x and SO_2, by an amount directly proportional to the efficiency improvement. Modest efficiency gains can be achieved for existing plants through relatively simple measures such as steam turbine upgrades and boiler upgrades. More complex options like re-powering to higher temperature and pressure steam conditions are also currently being investigated [Mar04]. Modern fossil fuel fired plants are however technologically mature and increasing the fuel conversion efficiency further will be challenging. Furthermore, increasing the plant efficiency alone cannot achieve the current target of CO_2 reduction and therefore will have limited effect on climate change. Switching to less carbon intense fuels like natural gas is not considered a long-term solution due to the depleting reserves, security of supply and increasing price. Around three quarters of power generation costs of gas-fired plants are fuel cost [Vos01]. Public support, which is crucial for the future of another carbon neutral technology i.e. nuclear energy, is almost non existent in many European countries. Renewable energy alone will not be able to replace the world energy demand. As the most abundant non-renewable energy source available with reserves geographically diversified across the globe, major exporters in every continent and a healthy, highly competitive and expanding international market, coal is expected to play a vital role as a primary source of energy. To address the issue of global warming, the largest environmental challenge of our time, the third option i.e. the capture and sequestration of CO_2 is expected to have the most significant impact on reduction of this green house gas in the short and medium term.

The capture and storage of CO_2 emitted from coal fired power plants has been a subject of intense research work in recent years. The concept of CO_2 capture however is not new to the industries. The capture processes have been widely applied in the natural gas and chemical processing industries for over 60 years but the unused CO_2 was vented to the atmosphere. The concept of capture with the purpose of storage is relatively new, especially when decoupling the fossil application cycle from carbon dioxide emissions to the atmosphere [Gup05]. There are different potentially viable options available for the capture and storage of CO_2 and the best technology will be expected to economically capture the maximum possible CO_2 for sequestration. The technologies for CO_2 capture from coal-fired power plants as illustrated in Figure 2.1 can broadly be divided into the following three categories.

1. Post-combustion capture
2. Pre-combustion capture
3. Oxy-coal combustion

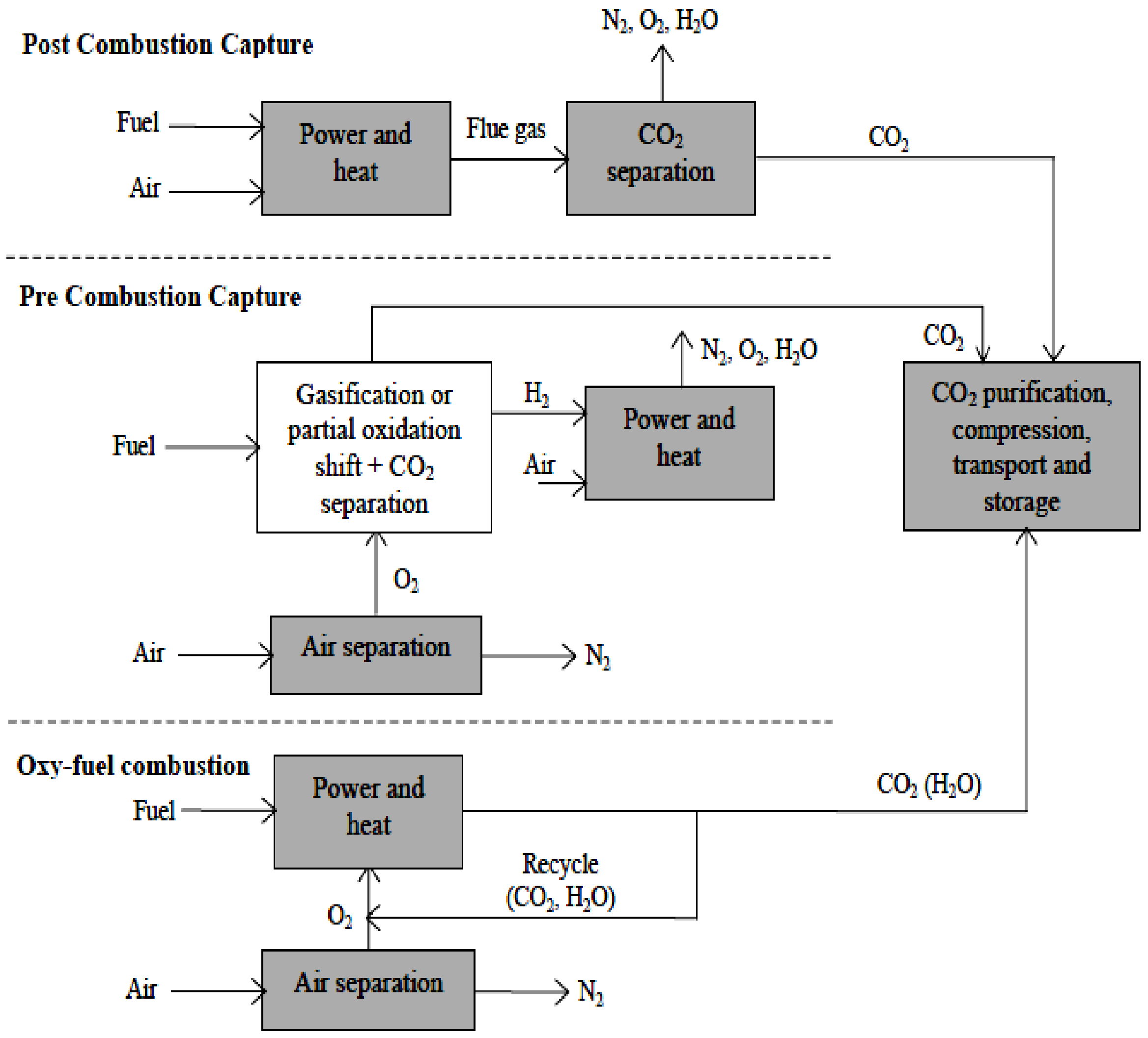


Figure 2.1 Options for CO_2 capture.

2.1.1. Post-Combustion Capture

Post-combustion CO_2 capture mainly applies to conventional coal-fired power generation, but may also be applied to gas-fired generation using gas turbines. Post combustion capture technology involves separation of CO_2 from the flue gas produced by combustion of fuel. One of the main advantages of this process is that it is considered convenient for retrofit to existing facilities. The major challenge with this approach, however is that the flue gas is at near atmospheric pressure and the CO_2 concentration is low i.e. typically in the range of 13-18 vol. % in coal-fired systems and in the range of 3-4 vol. % in gas-fired turbines. Low atmospheric pressure of the flue gas and low partial pressure of CO_2 results in a large volume of flue gas to be treated, and a small driving force for traditional adsorption/absorption processes. On the other hand, compressing captured or separated CO_2 to pipeline pressure represents a large auxiliary power load on the overall power plant system. Auxiliary power load for compression of the captured CO_2 for storage however will be required for all major carbon capture processes currently being considered.

Amine scrubbing is a widely applied state-of-the-art post-combustion capture technology but poisoning of amine due to flue gas components like SO_2, NO_2, O_2 and particulate matter affects the long term stability of the solvent. Solvent regeneration is also highly energy intensive and is responsible for an efficiency penalty of 14-18% points when compared to reference steam plants with a net efficiency of 43-46% [She07]. However, significant research work is being carried out to develop alternative chemicals with the aim of minimising the poisoning and reducing the energy for regeneration. Like pre-combustion and oxy-coal combustion technologies, although still not an economically proven option of CO_2 capture, it is considered a potentially viable option if the above mentioned issues can be resolved.

2.1.2. Pre-Combustion Capture

Pre-combustion CO_2 capture, also called decarbonisation relates to gasification plants, where fuels such as coal are converted into gaseous components by applying heat under pressure in the presence of steam. In a gasification reactor, the amount of air or oxygen (O_2) available is carefully controlled so that only a portion of the fuel burns completely. This partial oxidation process provides the heat necessary to chemically decompose the fuel and produce synthesis gas (syngas), which is composed of hydrogen (H_2), carbon monoxide (CO), and minor amounts of other gaseous constituents. The syngas is then processed in a water-gas-shift reactor, which increases the CO_2 and H_2 molecular concentrations. At this point, the CO_2 has a high partial pressure (and a high chemical potential), which improves the driving force for various types of separation and capture technologies. After CO_2 removal, the H_2 rich syngas can be used to produce electrical or thermal power. One application is to use H_2 as a fuel in a combustion turbine to generate electricity. Additional electricity is generated by extracting energy from a combustion turbine flue gas via a heat recovery steam generator. Another application, currently being developed is to utilise the H_2 to power fuel cells with the intent of significantly raising overall plant efficiency. However, there are few gasification plants in full-scale operation. When compared to a reference 1000 MW_{el} (gross), brown coal fired power plant and a 600 MW_{el} (gross) bituminous coal fired power plant without CO_2 capture, the IGCC based pre-combustion plant using the same fuel will result in a net efficiency loss of 8.8% points and 9.1% points respectively [Sch08]. Furthermore, high priority needs to be devoted towards availability improvements to a reasonable level.

2.1.3. Oxy-Coal Combustion

The objective of oxygen-fired pulverised coal combustion (oxy-coal combustion) is to combust coal in an enriched oxygen environment using almost pure oxygen diluted with recycled flue gas consisting of CO_2 and/or H_2O [Figure 2.2]. Under these conditions, the primary products of combustion are CO_2 and H_2O, and the CO_2 can be captured economically by condensing the water vapour out of the exhaust stream. Part of the flue gas consisting mainly CO_2 is recycled back to the furnace to maintain the temperature and heat flux profiles, and to entrain the pulverised coal. Significant reduction in NO_x formation is possible mainly due to the absence of thermal NO_x and reduction of NO_x recycled back into the furnace along with the flue gas. Furthermore, the key process principles involved in oxy-coal combustion have been demonstrated commercially, including air separation and flue gas recycle. Both pre-combustion and oxy-coal combustion utilise air separation to combust coal in an enriched oxygen environment. However, it is important to note that the amount of oxygen required during oxy-combustion is significantly higher than in pre-combustion applications. Oxygen is typically produced using low-temperature cryogenic air separation process but novel oxygen separation techniques such as oxygen transport membranes (OTM) and chemical looping systems are being developed to reduce the costs.

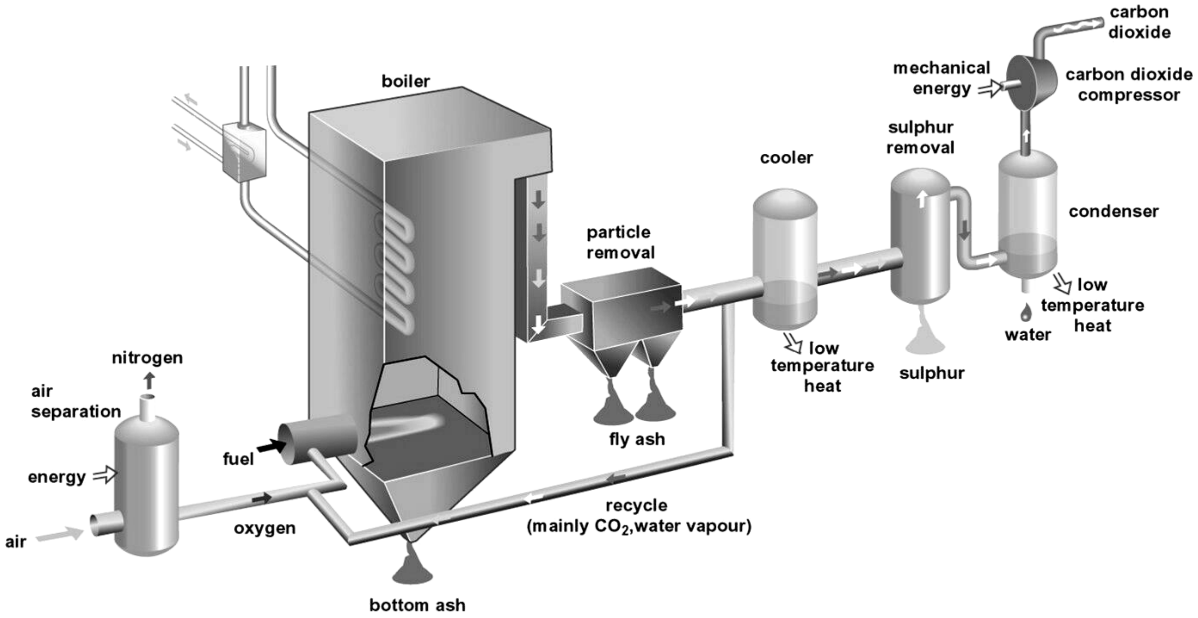


Figure 2.2: Schematic of oxy-coal combustion technology [Rad06].

Currently, there is no single, all-encompassing, long-term option for greenhouse gas mitigation and break-through developments are required. As can be seen from Table 2.1, which summarises the techno-economic analysis of different CO_2 capture options, oxy-coal combustion, the main focus of this work, is comparable with other CO_2 capture options, shows promising potential and merits further development.

Table 2.1: Comparison of options for CO_2 capture.

Feature	**TECHNOLOGY OPTIONS**		
	Post Combustion	**Oxy-coal Combustion**	**Pre Combustion (IGCC)**
CO_2 in the flue gas [vol. %]	3-18%	80-90%	15- 60%
CO_2 capture efficiency [%]	MEA: 90+ [Mar04]	90+ [Mar04]	90+ [Mar04]
Fuel flexibility	Like traditional PF plants	Like traditional PF plants	Depends on gasifier type
Potential for retrofit	High	Good with modifications like recycle path and ASU.	Not applicable
Commercial maturity	Partially proven	Not yet commercial	Partially proven
Net efficiency [LHV Based]	34.5% with MEA compared to baseline 1000 MW_{el} (gross) brown coal plant of 49.4% net efficiency (based on LHV) [Mej07] 34% with MEA, compared to baseline 600 MW_{el} (gross) bituminous plant of 45% net efficiency (based on LHV) [Mej07]	41% compared to baseline 1000 MW_{el} (gross) brown coal plant of 49.4% net efficiency (based on LHV) [Sch08] 36.4% compared to baseline 600 MW_{el} (gross) bituminous plant of 45% net efficiency (based on LHV) [Sch08]	40.6% compared to baseline 1000 MWel (gross) brown coal plant of 49.4% net efficiency (based on LHV) [Sch08] 35.9% compared to baseline 600 MW_{el} (gross) bituminous plant of 45% net efficiency (based on LHV) [Sch08]
CO_2 avoidance cost	40.5 €/ton with MEA compared to baseline 600 MW_{el} (gross) bituminous plant of 45% net efficiency (based on LHV) [Abu06]	15.8 €/ton compared to baseline 1000 MW_{el} (gross) brown coal plant of 49.4% net efficiency (based on LHV) [Sch08] 17.9 €/ton compared to baseline 600 MW_{el} (gross) bituminous plant of 45% net efficiency (based on LHV) [Sch08]	17.7 €/ton compared to baseline 1000 MW_{el} (gross) brown coal plant of 49.4% net efficiency (based on LHV) [Sch08] 24.8 €/ton compared to baseline 600 MW_{el} (gross) bituminous plant of 45% net efficiency (based on LHV) [Sch08]

2.2. THE OXY-COAL COMBUSTION PROCESS

Oxy-fuel combustion can be applied to furnaces, which use pulverised coal, oil or gas as the main fuel for combustion by recirculation of flue gas. Oxy-fuel combustion may be an attractive option for new builds as well as a retrofit to existing steam cycle power plants. It has attracted the interest of industries for applications in furnaces, process heaters and power plants [Dil04, Mar03, Wil01, Zan04]. Oxy-fuel combustion could also be applied to gas turbines with the use of MATIANT cycle, but the turbines that use CO_2 as the working fluid would have to be substantially different to conventional gas turbines. This would require development of a new CO_2 compressor, turbine, combustor and control system [Gup05]. Substantial investment would be further needed to develop these components, and for the prospect of large market, there would be a need to persuade manufacturers to make such an investment.

2.2.1. History and Status

Oxy-coal combustion is still at an early stage of development and until now there are no full-scale plants based on this technology. However, oxy-fuel combustion has long been practiced in the glass, cement and steel processing industries. The benefit of oxygen enhancement includes increased thermal efficiency, improved heat transfer, reduced specific fuel consumption and reduced emission [Jen00, Yam00, Rot00]. Research on high temperature oxy-fuel combustion in glass, cement and steel processing sectors were however mainly focused on issues related to material science rather than combustion.

The concept of oxy-fuel combustion with recycled flue gas in the energy sector was first proposed by Abraham et al. in 1982 [Abr82] to produce CO_2 for Enhanced Oil Recovery

(EOR) process. A series of research activities were organised by Argonne National Laboratory (ANL) thereafter during the decade of 1980 and 1990, and included a techno-economic review, pilot-scale studies (3 MW_{th} vertical tower furnace), small demonstration studies (117 kW_{th} furnace) and modelling of heat transfer and combustion behaviour in O_2/CO_2 environment [Wel85, Ber86, Ric87, Wan88, Pay89, Wol91]. Research on oxy-coal combustion with flue gas recycle focusing on capture and sequestration of CO_2 gained momentum during the decade of 1990. This was due to the concern of climate change and regulations driven by international initiatives such as the Kyoto protocol and the Intergovernmental Panel on Climate Change (IPCC). A research consortium led by the International Flame Research Foundation (IFRF) and funded by the European Commission under the Joule II programme performed the first oxy-coal combustion tests with flue gas recirculation in Europe during the early part of 1990 using a 2.5 MW_{th} furnace [Woy95]. Under the same research programme, an attempt was made by Rolls Royce International Combustion Limited to demonstrate the technical feasibility of this technology using a 35 MW burner. Around the same time, a research consortium led by IHI and funded by NEDO (1992-2000) carried out the first pilot scale studies in Japan [Kim95, Kig97, Oka97b]. Around the same period, CANMET [Dou01] in Canada performed pilot scale studies using a 0.3 MW_{th} vertical combustor research facility. During the beginning of 2000, Air Liquid, Babcock and Wilcox and BP [Fab03, Cha03] based in the USA performed oxygen enriched experiments in a 1.5 MW pulverised coal furnace.

Since then, research works concerning oxy-coal combustion have increased exponentially and several pulverised fuel laboratory scale and pilot-scale test facilities are in operation today. They are providing a further contribution to the understanding of the fundamental scientific and engineering issues associated with the application of this technology. Major demonstration projects in Europe, Australia and North America have also been planned for the near future.

In summary, significant research and development activities for the demonstration of this technology are in progress. Although theoretical studies combined with laboratory and pilot-scale studies have provided some understanding of the relevant design parameters and operational issues, uncertainties on issues like heat transfer, ignition, flame stability, emissions, slagging, fouling, corrosion, etc., still remains. On the other hand, concerns such as availability and load following capability of oxy-fuel plants are also significant and requires demonstration and full-scale plant experience [Buh05].

2.2.2. Techno-Economic Review

Most techno-economic reviews are based on the comparison of oxy-fuel technology with air-blown combustion or post combustion scrubbing. The comparisons vary significantly in cost as costs vary between countries and the basis of calculation. Capture of carbon dioxide from an existing large refinery power station boiler by conversion to oxygen firing with flue gas recirculation however has been reported to be feasible, and could be based on proven equipments [Wil01, Yam05, Zhe01]. Furthermore, an air-fired furnace could be converted to oxy-fuel operation without changes in the costly steam pressure parts and without loss of duty [Wil01]. Also, the flue gas volume exiting the boiler, downstream the recycle flue gas take off point during oxy-coal combustion is reduced by almost 70% relative to air-blown combustion, thus minimising the additional processing or treatment costs necessary to prepare a CO_2 rich stream for permanent storage [Far07].

Okawa et al. [Oka97b] reported a net efficiency drop from 39.6% (baseline plant) to 29.1% for an oxy-fuel plant, with an ESP for ash removal, a fabric filter for gas cleaning prior to CO_2 compression and preheated recycled flue gas. This was due to the energy required for air separation unit and CO_2 compression. However, the capital and operation cost was reported to be substantially lower than a standard pulverised fuel plant with amine absorption for CO_2 recovery. Efficiency loss of about 9% points, when compared to an ultra supercritical PF plant of 450 MW capacity, due to the extra energy required for the oxygen production and compression plant have been reported by Cottrell et al. [Cot03] as well. A study conducted by Andersson et al. [And02] for the retrofit on a 865 MW_{el} brown coal fired power plant in Germany using a cryogenic air separation unit for oxygen production concluded that the retrofit and CO_2 recovery decreases the efficiency of the plant by 11.9% points. However with all the identified optimisation possibilities in the whole system, the plant net efficiency increased to 34.3% resulting in an efficiency loss of 8.3% points.

Ochs et al. [Och07] reported that the energy cost of oxygen production is the most important factor influencing the net power output and the single most effective way to improve the performance of an oxy-fuel plant. Lowering the oxygen purity from 99.5% to 95% with the current state-of-the-art technology (cryogenic air separation unit) can lower the power consumption by approximately 10% [Far07]. For oxygen purity higher than 97%, the separation in the main low-pressure distillation column changes from oxygen-nitrogen to oxygen-argon, increasing the operation as well as capital costs significantly [Wil01]. However, during operations below 95%, the capital cost of the ASU increases because of the larger equipment size caused by lower pressure in the system. Therefore, 95% oxygen purity has been chosen in most studies [Dil04]. Okawa et al. [Oka97b] however concluded that the optimum oxygen purity based on minimising CO_2 compression and liquefaction power is around 97%.

Cost of CO_2 separation and compression also contributes to a loss in the net power output. The cost of a CO_2 separation and compression system depends on the level of inerts in the flue gas stream, which in turn is a function of air leakage and excess oxygen. If the air ingress could be eliminated, the level of inerts in the flue gas could be reduced, significantly lowering the cost of separation and compression of CO_2. Although it may be possible to eliminate the air ingress, the efforts needed for boiler refurbishment would be significant. Therefore, a minimum air ingress level realistically achievable over the lifetime of an oxy-coal plant needs to be determined by plant testing and online monitoring [Wil01]. For a completely sealed boiler with oxygen purity of 99.5%, elimination of inert removal process would result in a net CO_2 capture cost reduction of $1.7/tonne. In cases where there is air leakage and oxygen purity of less than 99.5%, a low temperature inert removal system is necessary [Wil01].

In summary, although the efficiency of an oxy-coal plant will be lower than the conventional air-blown plant, the scope of increasing the efficiency is extensive. Besides proper integration of the process, the greatest improvements in heat rate can be achieved through:

I. Lower energy oxygen production

II. Improvements of heat recovery

III. Reducing excess O_2

At present, cryogenic based air-separation unit is the only state-of-the-art oxygen production technology capable of producing the amount of oxygen required for full-scale oxy-coal combustion plants. As discussed earlier, energy loss due to oxygen production is the most important factor contributing to majority of efficiency loss of an oxy-coal operated plant. Although the specific energy requirement in a standard cryogenic separation unit has been reduced significantly in recent years from 270 kWh/ton to 220 kWh/ton at 99% O_2 purity [Och07], breakthrough technologies like ion transport membranes (being developed by Air Products), oxygen transport membranes (being developed by Praxair) and mixed conducting membranes (being developed by ALSTOM and Norsk Hydro) are expected to be available commercially soon. This offers a potential for significant reduction in the cost of oxygen production [Sim04, Wil01]. The efficiency of the oxy-fuel system can also be increased by optimised heat integration or heat recovery. Some of the potential areas of heat recovery are the use of an adiabatic compressor in the ASU, and an adiabatic compressor for CO_2 compression and heat recovery from exhaust flue gas stream [All05, Och07]. A study conducted by Ochs et al. [Och07] reported a loss of heat recovery of approximately 99 MW from a nominal 432 MW plant, which is approximately 23% reduction in power. Furthermore, by employing all beneficial technologies, the loss in capacity was reduced to around 50 MW, a reduction of 12% from air-fired baseline case. A model examining the effect of removing heat recovery by changing the cooling process in the exhaust stream by using cooling water with no energy recovery resulted in a change in thermal efficiency of 1.5%. This further indicates the potential of efficiency improvement within oxy-coal process with optimum heat recovery.

Lowering the excess oxygen might also lower the oxygen production rate for combusting a given amount of fuel. However, more oxygen is brought back into the system through recirculation of the flue gas during combustion with higher excess oxygen. The excess oxygen level therefore needs to be optimised not only from the perspective of lowering the oxygen production rate, but also from the objective of reducing unburned carbon in the ash [Och07]. One of the advantages of using oxygen is that changing the recirculation rate (ratio of mass of recycled flue gas to the mass of total flue gas flow in the system) allows the designer to change the flame character significantly. The lower the recirculation rate, the higher the mole fraction of oxygen. A higher oxygen mole fraction will result in a higher flame temperature, which in turn may allow the reduction of excess oxygen level without affecting the carbon burnout. Reducing the recirculation rate will also result in a lower fan load. Furthermore, the resulting higher flame and flue gas temperature due to reduced flue gas recirculation could possibly lead to more compact boilers.

2.2.3. Possible Configurations of an Oxy-Coal Combustion Plant

The additional components used in an oxy-coal operated furnace i.e. oxygen production, CO_2 compression and purification, all use existing demonstrated technologies, but at a very large scale and an integrated system. In order to allow these conventional combustion equipments to be used in an oxy-fuel boiler, the combustion temperature has to be moderated by recycling a portion of the flue gas and mixing this with incoming oxygen [All05]. Several factors could substantially affect the operation mode of an oxy-coal fired furnace with flue gas recycle and various configurations are possible with the consideration of:

I. Type of recycle flue gas i.e. wet or dry.
II. Location of oxygen injection i.e. mixed with flue gas or direct injection.
III. Degree of clean up required prior to transportation and storage i.e. tolerance regarding non-condensates like Ar, N_2 and O_2.

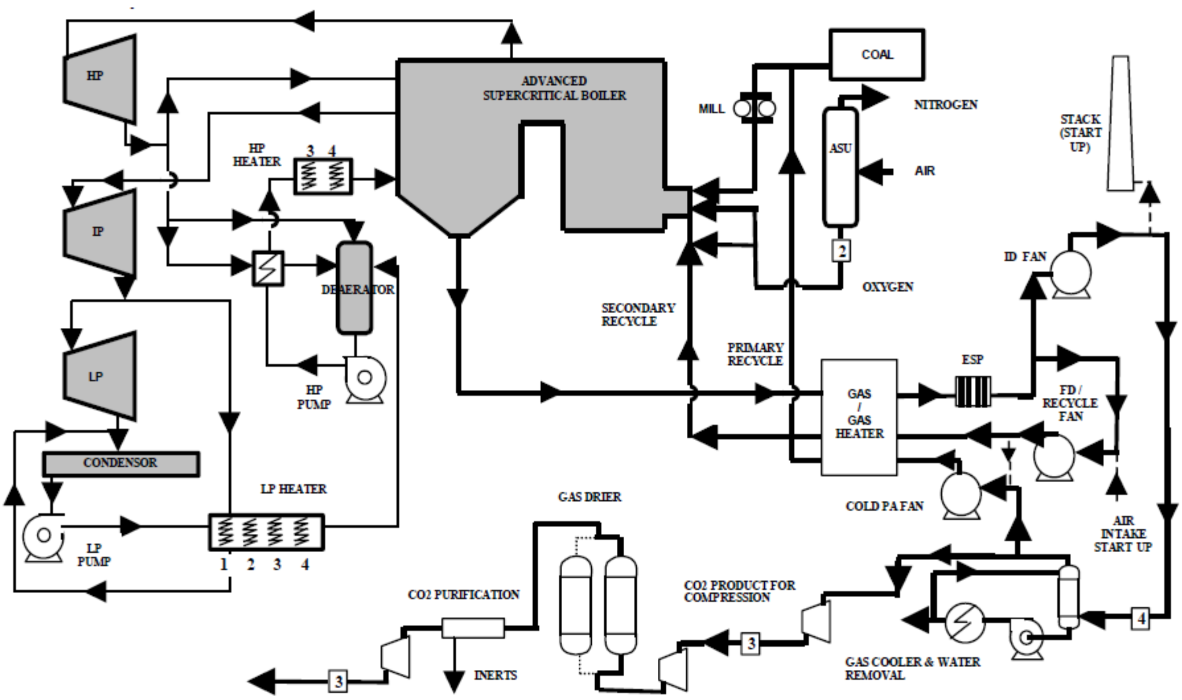


Figure 2.3: Configuration of an advanced supercritical pulverised fuel oxy-combustion plant with CO_2 *capture [All05].*

Several configurations of oxy-coal combustion process have been analysed by Nakayama et al. [Nak92]. Their assessment indicates that a wet recycle process would be more advantageous, as during dry recycle, the hot flue gas needs to be cooled for water vapour removal, and then heated again before it enters the furnace. Wet recycle has also been favoured by Allam et al. [All05] and as seen from Figure 2.3, the recycled flue gas contains a primary flow, which passes through the coal mills to entrain the powdered coal, and a secondary flow, which recycles straight back to the burners. The primary stream is however further cooled in a direct contact water cooler, which not only removes water vapour but also acidic components such as SO_3 and HCl and any residual ash. The drying of the coal carrying recycle stream was favoured to a wet recycle stream as a dry recycle stream makes it easier to dry and transport the coal in a conventional manner. The total flue gas flow is cooled in a gas-

gas heat exchanger against the returning primary and secondary recycle, before passing through an electrostatic precipitator.

The location of oxygen injection is another crucial factor that will determine the optimum configuration of an oxy-coal combustion process. Oxygen may either be mixed with the recycled flue gas or injected directly into the furnace via the burner. Mixing of oxygen with the recycled flue gas or in the burner needs to be carefully addressed. The amount of oxygen injected into the primary recycle stream used for carrying and drying the coal would have limitations due to safety reasons. Most of the oxygen will therefore have to be introduced via the secondary recycle stream. However the pipe works and ducts (normally used in power plants) carrying the secondary stream will also have limitations on the maximum oxygen concentration. The overall oxygen concentration in the furnace required to achieve reasonable ignition behaviour, flame temperature and heat transfer characteristics may not be adequate when oxygen is injected via recycled flue gas only, thereby necessitating additional oxygen injection via the burner.

The required purity of CO_2 in the flue gas prior to transportation and storage is another important factor that will determine the configuration of the process. Questions on how clean the CO_2 must be for transport and storage and how much impurities can be removed with different purification steps such as particle removal, water condensation, dehydration, SO_x removal and removal of non-condensable gases will determine the process layout. Economically, for oxy-coal combustion, it is preferable if, SO_x, NO_x, non-condensable gases and the last fraction of water in the CO_2 rich stream are not required to be removed, since this will reduce the plant investment cost and most likely also reduce the energy penalty caused by the CO_2 capture. However, issues like, whether it is possible to co-capture SO_2 with CO_2, and if the resulting stream has a composition that is acceptable for transport and storage, and is compliant with legal demands must be answered. If yes, the expensive desulphurisation system could be omitted. Theoretically, the critical constants of SO_2 lie close to those of CO_2, therefore SO_2 present in the flue gas should be easily mixed with CO_2 under most operating conditions of the CO_2 processing. The main obstacles for the co-capture of SO_2 with CO_2 will be related to corrosion problems in connection to transport and storage, the concerns of safety, environmental regulation and legal related issues. In addition, the concentration of acid gases in the flue gas is predicted to increase by a factor of approximately 3 times, further aggravating the corrosion problems. On the other hand, although NO_x can be reduced within the furnace by the application of primary measures, the amount that can be removed by CO_2 compression and purification system, and the amount that can be co-captured with CO_2 need to be answered to determine if a selective catalytic reduction unit is required. Similarly, air leakage is a fact of life for large boilers with balanced draught. The boilers operate under suction in the furnace preventing the leakage of hot flue gases out of the furnace and any leakage is of cold air into the furnace. Obviously any air in-leakage has a detrimental effect on the efficiency of the process as it can significantly increase the duty of the CO_2 purification plant. One way to avoid air infiltration would be to run boilers at slight positive pressure. However, there are safety issues involved in operating the boilers at positive pressure as well as uncertainty as to how much CO_2 is lost to the atmosphere through the same leaks that allow the air in when the boiler is running under negative pressure.

In summary, further investigation is required to answer the uncertainties highlighted, as the issues discussed above will determine the final optimum configuration of an oxy-coal combustion plant.

CHAPTER 3

COMBUSTION AND EMISSION BEHAVIOUR DURING OXY-COAL COMBUSTION

3.1. COMBUSTION BEHAVIOUR DURING OXY-COAL COMBUSTION

Due to the recirculation of flue gas, the concentration of tri-atomic molecules (CO_2 and H_2O) during oxy-fuel combustion or combustion with O_2/RFG (Recycled Flue Gas) will be significantly higher than conventional air-blown combustion. As the initial application of oxy-coal combustion technology will most likely be a retrofit in existing pulverised coal furnaces, modifications are required if the flame characteristics and ignition and burn out behaviour is to be matched to air-blown furnaces. For this, the inherent physical properties of the flame temperature moderator i.e. CO_2 and H_2O in oxy-fuel operated furnaces and N_2 in air-blown furnace needs to be accounted for. For example, the thermal conductivity of the media may influence the heat up rate of coal particles introduced into the hot oxidising environment. The mass diffusivity of devolatilised products in the media may influence the volatile consumption rate. Binary diffusion coefficient of oxygen in the media may influence the carbon oxidation rate during char combustion, and thermal capacity of the media may influence the adiabatic flame temperature.

In turbulent flames, representing full-scale pulverised fuel flames where mixing is rapid, flame temperature is considered the most important parameter that can alter the ignition and burnout time. For a particular fuel, adiabatic flame temperature will be lower, when CO_2 concentration is high due to its higher heat capacity. The flame temperature may however be increased by increasing the oxygen concentration or lowering the amount of CO_2. Oxygen concentration of a combustion media is therefore considered the single most important parameter, proper adjustment of which can result in optimum flame-temperature, ignition and burnout characteristics. In O_2/RFG applications, inlet oxygen concentration is adjusted by tuning the recycle ratio (ratio of recycled flue gas to total flue gas leaving the furnace) of the flue gas and is therefore considered the most important parameter for practical applications.

The optimum recycle ratio or consequently the inlet oxygen concentration that results in similar flame temperature profile and heat transfer has been a subject of intense research work in recent years. The optimum value however depends on various parameters like fuel type, recirculation mode (wet/dry, hot/cooled) and O_2 purity, and is therefore specific to the configuration of the system. Earliest study of oxy-coal combustion in a pilot scale [Wel85, Wol89], 3 MW furnace by Environmental Research Corporation (EERC) for Argonne National Laboratory (ANL) reported that a CO_2:O_2 ratio of 2.42, i.e. oxygen concentration of about 29 vol. % during dry recycling matches the overall heat transfer performance of air firing case. Results from experiments conducted by CANMET in a 300 kW vertical combustor during oxy-coal combustion [Cro00] indicate that axial flame temperature matches closely to that of the air-fired case, when O_2 concentration (dry basis) in the wind-box is between 28-35 vol. %. However, measurements conducted at an inlet oxygen concentration of 42 vol. % clearly displayed a much higher axial flame temperature. Tests conducted at IHI [Yam06] in a 1.2 MW_{th} vertical furnace using Australian coals disclosed that with an O_2 concentration of 27 vol. % in the furnace, the peak temperature was approximately 150°C lower than during air-blown combustion. However, the ignition point was observed to be at a similar location for both air and oxy-coal combustion. Likewise, investigation carried out by Babcock and Wilcox [Cha03, Far05] in a 1.5 MW_{th} pilot plant reported that the exit temperature measured for air and oxy cases did not have significant difference, when the heat transfer performance in the furnace and the convective pass were matched. This further supports the suggestions that oxy-firing technology can be implemented as an effective retrofit technology, since it does not significantly alter the heat transfer patterns. Heat and mass balance calculations conducted by maintaining the same exit O_2 concentration levels (3.5 vol. %, dry) in the flue gas for both oxy-fuel and air-firing, and matching the furnace radiative heat transfer indicate that 27 vol. % O_2 levels are required at the burner inlet for oxy-fuel combustion [Kha05]. Similarly, Nsakala et al. [Nsa07] reported that a mixture of flue gas and 30 % oxygen gives thermal conditions in the furnace similar to those of air firing, when different properties of CO_2 and N_2 are taken into account. On the other hand, lower combustibility and higher un-burned carbon in the ash has been reported when oxygen concentration in the wind-box is below 30 vol. % [Kim95, Tan93].

In summary, although the reported oxygen concentration required for attaining a similar flame and heat transfer character to air-blown combustion varies, it is obvious that oxygen concentration higher than 21 vol. % will be required in a CO_2 environment. Much lower flame temperature with unsustainable flame have been reported by Liu et al. and Hjärtstam et al., when the oxygen concentration in the furnace was 21 vol. % [Liu04, Hjär07]. Oxygen concentration in the comburent typically approaching the range of 25-35 vol. % (dry basis) in the wind-box and recycle rate of approximately 61-76% in mass basis (ratio of recycled flue gas to total flue gas leaving the furnace) would therefore most likely give the combustion and heat transfer characteristics of an air-blown PF furnace [Dil04, McD99, Nsa01, Sin03, Tan05].

However, detailed investigations focusing on the combustion behaviour during oxy-coal combustion with different ranks of coals to predict the behaviour of oxy-coal operated furnaces is still lacking, and is one of the scopes of this work.

3.2. EMISSION BEHAVIOUR DURING OXY-COAL COMBUSTION

3.2.1. CO_2 Concentration

Foremost aspect that drives oxy-fuel combustion technology is the high concentration of CO_2 that can be potentially achieved with this process. The concentration of CO_2 is however completely dependant on the air leakage in the furnace and the recirculation path and the purity of oxygen used. Depending upon the tightness of the furnace and the recycle loop, CO_2 concentration between 80-90 vol. % [dry basis] has been reported during oxy-fuel combustion [All97, Cro00, Mön07, Woy95]. To achieve satisfactory level of CO_2 in the flue gas depending upon the intended application, air leakage of less than 3% [All97, Wil06] and oxygen purity of approximately 95 vol. % [And02, Dil04, Far07, McD99, Nsa01, Oka00, Sin03] has been recommended to be most economical for large-scale applications.

3.2.2. Nitrogen Oxide Emission

Besides the possibility of economic capture of CO_2, another advantage that oxy-fuel firing offers is the elimination of thermal NO_x, as N_2 in the air is replaced by recycled flue gas. However NO_x emission from fuel bound nitrogen, first observed by Shaw et al. [Shaw65] is considered dominant during coal combustion in moderate temperature pulverised fuel furnaces, as coal contains significant amount of chemically bound nitrogen (0.5-2% by weight). Although fuel-N is more important for NO_x emission during coal combustion, it is accepted that reduction of NO_x formation is inherent to oxy-coal combustion when combustion performance is matched to air-blown furnaces. It is however noted that, most of the reported values of NO_x are based on the mass of emission per unit of energy input, calculated downstream of flue gas recycle point, and is considered a more accurate way of comparing emissions from completely different combustion scenarios. The definition of NO_x emission in mass of emission per energy input in mg/MJ (referred as NO_x emission rate) generally used during oxy-coal combustion with flue gas recycle, and for this study with once through furnace, is discussed in detail in Appendix A.

The emission concentrations depending on the burner configuration however may be higher when compared to air-blown combustion due to the accumulation of NO_x recycled with the flue gas, and significantly reduced flue gas volume during oxy-coal combustion. For example, investigation carried out by Yamada et al. [Yam06] reported that NO_x generated during oxy-coal combustion has a concentration, one and half times higher than during air-blown combustion. The amount of emission downstream the flue gas recycle location in mg/MJ (NO_x emission rate) is however approximately one third. Croiset et al. [Cro00] reported higher NO_x emission rate during air-blown combustion when compared to oxy-coal combustion with oxygen concentration up to 35 vol. %. An investigation carried out by Babcock and Wilcox in a 1.5 MW oxy-coal fired boiler using a low NO_x burner reported that NO_x emission rate below 65 mg/MJ (which is the expected future US regulation limit) can be achieved during oxy-coal combustion [Cha03]. When compared to un-staged, air-blown combustion, 53% and 69% reductions were reported during un-staged oxy-coal combustion, with low and high recirculation rate respectively. Similarly, approximately 75% reduction in NO emission rate has been reported by Andersson et al. [And07] during oxy-coal combustion when firing a pre-dried brown coal. NO emissions, as reported in open literatures indicating that the reduction of NO emission rate is inherent during oxy-coal combustion is summarised in Figure 3.1. As mentioned previously, the NO emission rate is calculated downstream of flue gas recycle point.

The conversion of the coal-N to NO_x has also been reported to be lower in an O_2/CO_2 environment when compared to air-blown combustion [Kig97, Kim95, Liu04, Mac07]. Increase in oxygen concentrations in the media during oxy-coal combustion however increases the NO_x emission rate, and this increase is linked to the increased flame temperature [Cro00, Cro01, Liu04]. Increased flame temperature tends to increase the partitioning of fuel-N towards the gas phase, resulting in increased NO_x emission during un-staged combustion. A similar influence on NO_x emission rate with increasing oxygen concentration has been reported by Hu et al. [Hu00]. The authors further mentioned that at an oxygen ratio of 1, increasing the gas temperature by 400 K doubled the NO_x produced per kilogram of fuel fed.

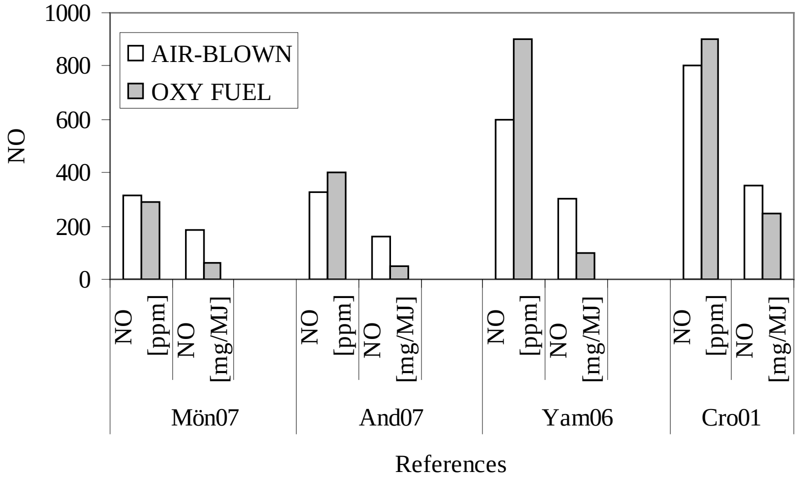


Figure 3.1: Summary of NO emissions reported in open literatures.

Studies have shown that the conversion of volatile nitrogen to NO is the primary path for fuel NO formation [Chen82]. As mentioned earlier, increased flame temperature implies that more nitrogen in the fuel is partitioned towards the gas phase, and depending on the oxygen availability, is either reduced to N_2 or oxidised to NO. Increased flame temperature in oxygen excess flame therefore has negative influence on NO_x emission [Gre96b].

Based on the findings so far, decrease in NO emission during oxy-coal combustion has been attributed to one or more of the following reasons:

I. Interaction between recycled NO and fuel-N

II. Enhanced reduction by char
III. Reduction of recycled NO

Interaction between recycled NO and fuel-N may suppress the formation of fuel-NO. Approximately 18% reduction of NO due to the interaction between fuel-N and recycled NO has been reported by Okazaki et al. [Oka97a] during oxy-fuel combustion in a mixture of 21% O_2 and 79% CO_2 by volume. However, the measurement was carried out with a CH_4 flat flame and fuel nitrogen was simulated by injecting NH_3.

High concentration of CO_2 during oxy-coal combustion results in a high concentration of CO in the flame [Liu04, Hjär07], thereby NO_x reduction by char is possibly enhanced by reductions with CO, when compared to conventional air-blown combustion. Extensive studies on the reduction of NO by carbonaceous solids have been reported [Beer77, Des80] for O_2/N_2 coal combustion scenario. The reduction of NO by carbon has been reported to be through dissociation of NO on the surface with a rapid surface dissociation of the dissociated atoms to form N_2. The kinetic scheme for NO/char reactions has been rationalised by following scheme [Aar97, Suu90, Tom01].

$NO + 2C(\_) \rightarrow C(N) + C(O)$ [R3.1]

$C(N) + NO \rightarrow C(O) + 0.5N_2$ [R3.2]

Reaction R3.1 represents the dissociative chemisorption of NO, with (_) representing empty sites. The active surface sites react with the incoming NO molecules to produce N_2 and CO (reaction R3.2). The oxygen produced by dissociation is strongly chemisorbed and inhibits further reactions. The reaction between NO and char has also been reported to be enhanced in the presence of CO, as the formation of chemisorbed layer is removed by reaction with CO [Levi81, Mas92].

Rapid reduction of recycled NO to HCN in the flame zone when it reacts with hydrocarbon radicals [Noz97] has, in fact been accepted to be the most dominant during oxy-coal combustion by most researchers [Cro01, Hu01, Kim95, Liu05]. The formation of HCN is strongly dependant on the concentration of hydrocarbon radicals, which are decomposed from hydrocarbon fuels at high temperature. Investigation by Liu et al. [Liu05] have shown that up to 92% reduction of recycled NO can be achieved during oxy-coal combustion (30% O_2/70% CO_2 by volume) for staged combustion with a burner oxygen ratio of 0.80. The authors, after testing seven international bituminous coals have concluded that the reduction of recycled NO is dependant on the combustion media, the combustion mode and the location of NO injection. Generally more NO was observed to be reduced in a CO_2 media during oxidant staging and when NO was recycled via the burner. The reduction of recycled NO has also been observed during combustion with direct injection of O_2 [Kim95]. When compared with once through O_2/CO_2 combustion, Croiset et al. [Cro01] observed a decrease in NO_x emission rate by 40-50% with flue gas recycling, and this reduction was associated with re-burning of NO_x recycled back into the furnace. Hu et al. [Hu01] studied the reduction of recycled NO during oxy-coal combustion with low recycle ratios (ratio of recycled flue gas to total flue gas leaving the furnace) ranging from 0 to 0.4 and observed that reduction efficiency of recycled NO increased with increasing fuel equivalence ratio and recycle ratio.

The NO reduction reactions may be summarised as:

$NO + CH^{\cdot} \rightarrow HCN + O^{\cdot}$ [R3.3]

$NO + CH_2{}^{\cdot} \rightarrow NCO^{\cdot} + H_2$ [R3.4]

$NO + CH_3^{\cdot} \rightarrow HCN + H_2O$ [R3.5]

Where, the dot immediately after atomic symbols or molecular formulas represents the free radicals. The HCN formed may then react to form N_2 under oxygen lean condition or it may reform NO if the oxygen concentration is too high.

Above reactions are in fact also the principle behind NO reduction by re-burning in conventional air-fired furnaces, where NO formed in the flame zone is reduced by the injection of hydrocarbons (coal, natural gas or coal pyrolysis gas). This concept of NO reduction by fuel addition was first introduced by Meyerson et al. [Mey57] and patented by Reed [Reed69]. The term re-burning was introduced by Wendt et al. [Wen73] and this concept was established as a practical NO_x reduction method after Takahashi et al. [Tak83] reported greater than 50% reduction of NO during tests conducted at Mitsubishi Heavy Industries in 1983.

However, detailed investigations by considering homogeneous and heterogeneous reduction reactions, combustion condition (staged, unstaged), location of NO injection by using different ranks of coals during oxy-coal combustion are still lacking, and is one of the scope of this work.

3.2.3. Reduction of Nitrogen Oxide during Oxidant Staging

Purity requirement of CO_2 for sequestration is still unclear therefore researchers working in the field of CO_2 capture need to investigate the measures to minimise the impurities in the flue gas. Primary measures like air-staged and fuel-staged (re-burning) combustion have been demonstrated to be cost- effective methods to reduce NO_x emission during conventional air-blown combustion, and has a potential to be applied during oxy-coal combustion as well.

Unlike sulphur in the fuel matrix, nitrogen is much more tightly bound in the molecules and most parts are in the aromatic ring [Levy82]. All fuel nitrogen compounds exhibit C-N or N-H bonding. Studies have shown that volatile nitrogen conversion into NO is the primary path for fuel NO formation [Chen82] and evolution of fuel nitrogen corresponds approximately to the release of carbon or total mass in the gas-phase [Sol78]. NO_x formed from char nitrogen contributes to approximately 25% of the total fuel NO in pulverised coal flames [Per76, Wen80] and offers little or no opportunity of reduction by the application of primary measures of NO_x reduction like oxidant or fuel staging. Most investigations are therefore focused on the understanding of the release of volatile nitrogen and optimising the combustion process so as to partition most of the nitrogen in the coal towards the gas-phase, so that it can be reduced to N_2.

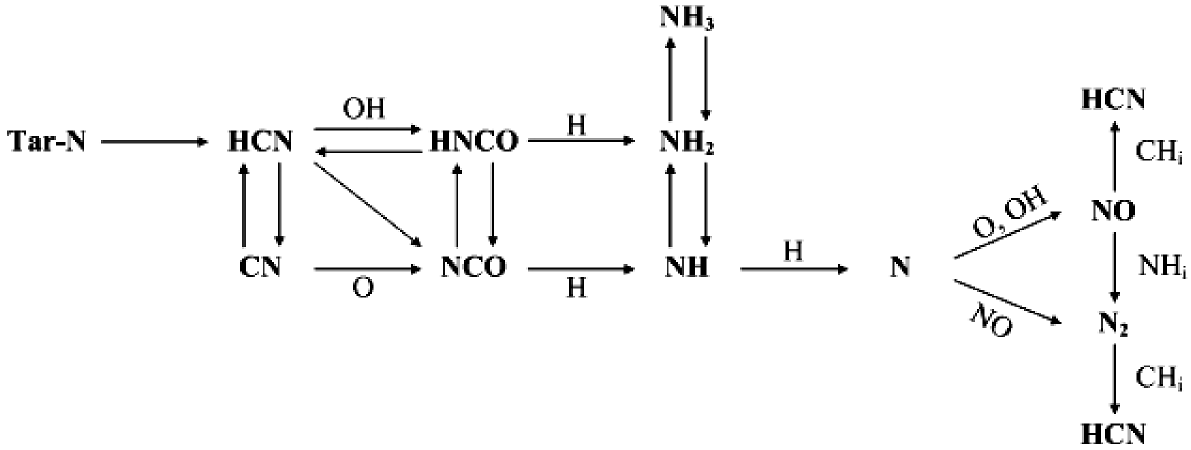


Figure 3.2: Simplified path of homogenous NO formation [Gla86].

The main shuttle of coal nitrogen during devolatilisation is tar [Chen92]. During its decomposition into light gases and soot, tar nitrogen is liberated. Although researchers studying pyrolysis and combustion of coal differ as to the detail, basically tar nitrogen is converted to HCN and NH_3 as primary intermediates [Figure 3.2], which in turn are converted to NO or N_2 depending upon the oxygen availability during combustion. Although highly dependent on the coal rank, predominant intermediate product from tar cracking is HCN with a portion of tar-N remaining in the soot [Bow91, Chen92]. Bartok et al. [Bar72] noted a significant amount of HCN in a well-stirred reactor, which was converted to NO. Other studies have shown that HCN is the single most important precursor of NO for low to medium volatile bituminous coals [Chen83, Nik94] while NH_3 has been observed to be dominant for brown coals [Bose88, Bur94]. Other studies have shown that quaternary and amino-side chain nitrogen produces NH_3 as an intermediate while pyridinic nitrogen, the percentage of which increases with the rank of coal produces HCN [Nor97]. The fate of pyrrolic nitrogen is less clear, but there are evidences that it mostly produces HCN and possibly some NH_3 [Kam95].

Fuel lean condition favour formation of NO from HCN and the most important reactions are [Nor97]:

$HCN + O^{\cdot} \leftrightarrow NCO^{\cdot} + H^{\cdot}$ [R3.6]

$HCN + O^{\cdot} \leftrightarrow NH^{\cdot} + CO$ [R3.7]

$HCN + O^{\cdot} \leftrightarrow CN^{\cdot} + OH^{\cdot}$ [R3.8]

$NCO + O^{\cdot} \leftrightarrow NO + CO$ [R3.9]

$NH^{\cdot} + OH^{\cdot} \leftrightarrow NO + H_2O$ [R3.10]

$CN^{\cdot} + O^{\cdot} \leftrightarrow CO$ [R3.11]

Where, the dot immediately after atomic symbols or molecular formulas represents the free radicals.

Fuel rich condition favours formation of N_2 by reaction of HCN with hydrocarbon radicals and NO, and most the important reactions are [Nor97]:

$HCN + OH^{\cdot} \rightarrow NH_2^{\cdot} + CO$ [R3.12]

$NH_2^{\cdot} + RH^{\cdot} \rightarrow NH_3 + R^{\cdot}$ [R3.13]

[R= C, CH, CH_2CH, etc.]

$NH_2^{\cdot} + NO \rightarrow N_2 + H_2O$ [R3.14]

$CH^{\cdot} + NO \rightarrow HCN + O^{\cdot}$ [R3.15]

Similar set of reactions is also applicable for NH_3, with a fuel lean condition favouring NO and a fuel rich condition favouring N_2.

The knowledge of gas phase fuel NO formation summarised above is implemented technologically for staged combustion, which can be differentiated as oxidant-staged and fuel-staged combustion. Both have been demonstrated to be successful combustion modifications and a cost-effective way to reduce NO_x emission during conventional air-blown combustion. The effect of these measures is established by setting local combustion zones with oxygen deficiency in which the conversion of gaseous NO_x precursors towards NO is low, and already formed NO can be reduced to molecular nitrogen [Spl02]. The most important NO_x control technology applied in modern air-blown furnaces is air-staged combustion or oxidant-staged combustion.

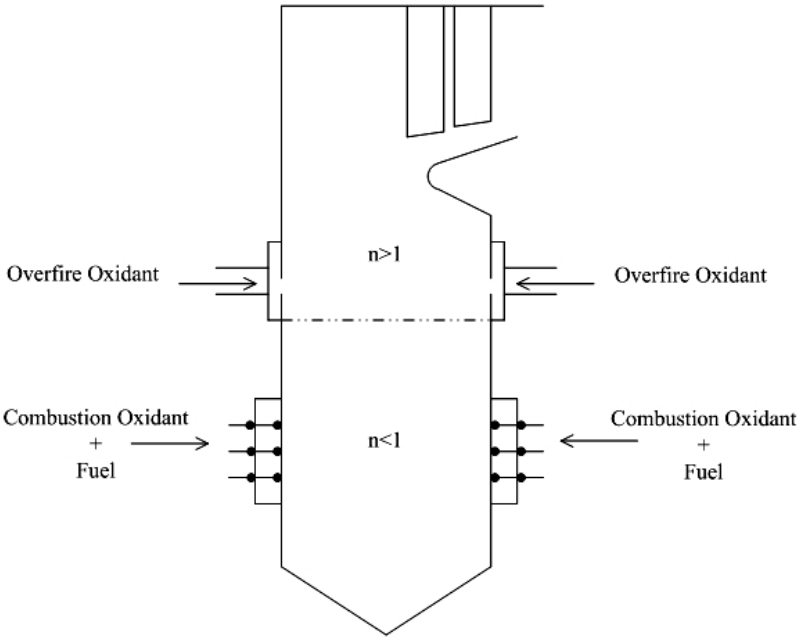


Figure 3.3: Schematic of oxidant staging.

As seen from Figure 3.3, oxidant staging divides the combustion process into 2 zones, the primary zone and the burn out zone. Primary zone operates at oxygen deficient, fuel-rich condition and restricts the formation of fuel NO_x. Whereas the burn out zone operates at excess oxygen condition and encourages complete combustion. However, it is necessary to establish the optimum process condition to achieve specified NO_x emission while minimising the level of carbon in the ash.

Effectiveness of oxidant staging depends primarily on the degree of coalification when other operating parameters are similar i.e. the more is the volatile nitrogen released in the sub-stoichiometric zone, the more is the probability that gaseous nitrogen compounds can be reduced to molecular nitrogen. In fact studies have shown that more reactive European coals (brown coals) with higher volatile content produces less NO_x emission than bituminous coals, and NH_3 intermediate produces less NO_x than HCN intermediate, all during staged combustion [Spl96].

Besides the type of coal used, operating parameters also have significant effect on NO_x reduction during oxidant staging, and the most important parameters are the burner oxygen ratio and the residence time in the reduction zone. At a definite burner oxygen ratio, designated as the optimum oxygen ratio, minimum NO_x emission level is achieved. At higher oxygen ratio, NO is not sufficiently decomposed in the reduction zone. Majority of literatures report this optimum oxygen ratio in the range of 0.75 to 0.85 [Gre96a, Gre98, Klu00a, Spl02], and the total fuel nitrogen concentration i.e. the sum of NO, HCN and NH_3, as well as NO emission were found to be lowest with an oxygen ratio of around 0.7 for brown coals and bituminous coals [Che82]. Reduction of NO_x emission with an increase in residence time in the reduction zone has also been reported in many literatures. A residence time in the reduction zone of 2 to 4 seconds and a burner oxygen ratio of approximately 0.75 in the reduction has been reported as an optimum in most literatures [Gre96a, Klu00b, Spl95, Spl96]. However, for a given furnace size, the longer the residence time in the reduction zone, shorter will be the time available for carbon burnout in the burnout zone, and therefore the location of oxidant addition through the over fire port needs to be optimised appropriately. In summary, the most important reaction mechanisms that determine the overall efficiency of oxidant staging are:

I. Reaction of NO formed in the mixing zone with free radicals of hydrocarbons to produce HCN or NH_3.
II. Conversion of HCN/ NH_3 to N_2 in oxygen deficient reduction zone.

As can be seen from above review, nitrogen oxide formation during conventional air-blown combustion is well understood. However detailed parametric investigations with different burner oxygen ratio and residence time in the reduction zone during oxy-coal combustion are limited. If the conversion mechanism of fuel bound nitrogen is also similar for oxy-coal condition needs to be investigated in more detail, and is one of the scopes of this work.

Tests in a 1.5 MW PC-fired boiler [Cha03, Cha04a] have shown that O_2/RFG combustion combined with oxidant staging can reduce NO_x emission rate by 71-76% relative to un-staged air-blown combustion. The emission rate during staged oxy-coal combustion was observed to be between 54-62% lower than during staged air-blown combustion. Hu et al. [Hu00] reported that the NO_x emission is strongly dependent on the oxygen ratio and the temperature of the inlet gases during oxy-coal combustion, and for a similar oxygen ratio and temperature, emissions in a CO_2 environment is generally lower than that in a N_2 environment. Furthermore, fuel-rich condition was reported to improve NO_x reduction efficiency in an oxy-coal environment as well, and up to 80% reduction with oxygen ratio of 0.7 or lower was achieved [Hu01, Hu03]. Liu et al. [Liu04] and Mackrory et al. [Mac07] also reported that the final NO_x level during staged oxy-coal combustion is lower than that of air-blown combustion at a similar combustion condition. The influence of the burner oxygen ratio and the residence time in the reduction zone on NO_x emission was observed to have an impact similar to conventional air-blown combustion. Inflame measurements of HCN & NH_3 carried out by Nozaki et al. [Noz97] show that the concentration of these species are significantly higher during oxy-coal combustion, and it was concluded that the NO_x recycled back into the furnace is decomposed to HCN and NH_3 in the flame region.

3.2.4. SO_2 Emission

Besides the emission of CO_2, NO_x, CO, etc., the combustion of coal is also associated with the conversion of sulphur in the coal into gaseous compounds such as SO_2, SO_3, H_2S and COS. The presence of sulphur in the fuel is associated with high temperature corrosion at the furnace walls and super heater sections, and with low temperature corrosion through the condensation of sulphuric acid in the economiser or air heater.

Sulphur in the coal is present in elemental, inorganic and organic forms. Inorganic sulphur is found mostly as pyrite (FeS_2) and sulphates, and organic sulphur is mostly structurally integrated in the macromolecular organic matrix of the fuels. Under pulverised coal condition, pyrites release elemental sulphur, which are eventually oxidised to SO_2. The mechanisms of organic sulphur oxidation are less understood, although most of the sulphur is eventually converted to SO_2 with some groups first decomposing into H_2S before finally oxidising to SO_2 [Cou95].

Though NO_x emission has been addressed by several investigators, only a handful of authors have addressed the fate of sulphur during oxy-coal combustion, and is therefore one of the scopes of this work. SO_2 emission during pulverised coal combustion primarily depends on the total sulphur content of the coal, irrespective of organic or inorganic form. Thermodynamic models suggest that the conversion of sulphur would be unaffected in a CO_2

environment, as it is governed by oxygen concentration only [Zhe03]. Most measurements, especially during O_2/RFG combustion report a lower conversion of sulphur to SO_2 [Cro01, Kig97, Woy95]. The authors attribute lower conversion to either more retention of sulphur in the ash, higher conversion of SO_2 to SO_3 or removal with the condensates during dry recycling. Results clearly displaying higher retention of SO_2 in the ash could not be found in open literatures. However, SO_3 concentration has been reported to be about 3 times higher during oxy-coal combustion [Yam06]. Relatively high concentration of sulphate in the condensate water [Cro01] during dry recycle indicating removal with the condensates has also been reported. However, when the difference in conversion of sulphur to SO_2 during air-blown combustion is compared to oxy-coal combustion, (which has been reported to be between 30-40% lower) it is unlikely that the conversion of SO_2 to SO_3 and removal of SO_2 and SO_3 from the condensate (during dry recycling) could alone be responsible for such a huge reduction. It is therefore likely that the retention of SO_2 by the sulphate forming elements in the ash, especially in the convective section and the low temperature recycle loop before the ESP could be the dominant factor.

It is however widely accepted and confirmed by measurements that the SO_2 concentration during O_2/RFG combustion is much higher due to the accumulation of SO_2 from recycled flue gas. As a result, even low sulphur coals produces flue gas with SO_2 concentration more typical of medium sulphur coals. Croiset et al. [Cro01] and Mönckert et al. [Mön07] for example reported about 2 times higher SO_2 concentration during O_2/RFG combustion and pointed out the potential of material corrosion. Similarly, Yamada et al. [Yam06] reported increase in SO_2 concentration by a factor of 3 during oxy-coal combustion. Though the SO_2 concentration is higher, the emission rate has been reported to be lower than air-blown combustion. For example, Yamada et al. [Yam06] and Croiset et al. [Cro01] report about 30% lower emission rate, and Mönckert et al. [Mön07] report 22% reduction. The primary reasons for lower emission rate as discussed earlier might be due to the retention of SO_2 in the ash, conversion of SO_2 to SO_3 or removal with the condensates during dry recycle.

Although the alkaline earth metals (Ca, Mg) and alkali metals (Na, K) may be responsible for the retention of sulphur in the ash due to the formation of sulphates (SO_4), it is widely accepted that calcium in the ash plays a dominant role in sulphur retention, while contribution of other elements are limited [She00]. The sulphates formed are stable at temperature below 1000 °C [Fol04]. It is therefore anticipated that during oxy-coal combustion, some of SO_2 will be retained in the ash at lower temperature regions like convective section and the flue gas recirculation path (before ESP). The amount of SO_2 retained in the ash for a particular operational condition is however dependant on several factors; the concentration of above alkaline elements relative to sulphur content, modes of occurrence of these alkaline elements and competitiveness of other elements besides sulphur to form compounds with above alkaline elements.

However all of the above mentioned alkaline earth metals and alkali metals are not available for SO_2 retention as there exists a mode of occurrence that makes them inactive to react with SO_2. Calcium, which plays the most dominant role on SO_2 retention, has been known to be inactive when present in clay and silicate minerals, whereas carbonate minerals like calcite ($CaCO_3$) are most active. The organic bound calcium is also considered active. Calcite decomposes rapidly at 670-750°C [Fol03] to form lime according to the reaction:

$$\mathrm{CaCO_3 \rightarrow CaO + CO_2} \qquad \text{[R3.16]}$$

Lime formed from calcite as well as from oxidation of organic bound calcium then forms calcium sulphate or calcium sulphite according to the reactions:

$$\mathrm{CaO} + \mathrm{SO_2} + \frac{1}{2}\mathrm{O_2} \rightarrow \mathrm{CaSO_4} \qquad \text{[R3.17]}$$

$$\mathrm{CaO} + \mathrm{SO_2} \rightarrow \mathrm{CaSO_3} \qquad \text{[R3.18]}$$

However during pressurised fluidised bed combustion, it has been reported that the partial pressure of CO_2 exceeds the equilibrium partial pressure for calcination of $CaCO_3$, therefore resulting in direct reaction between SO_2 and $CaCO_3$ according to the reaction [Shi01]:

$$\mathrm{CaCO_3} + \mathrm{SO_2} + \frac{1}{2}\mathrm{O_2} \rightarrow \mathrm{CaSO_4} + \mathrm{CO_2} \qquad \text{[R3.19]}$$

Results indicating direct sulfation behaviour in an O_2/CO_2 environment with measurements conducted in a fixed bed reactor have been reported by Liu et al. [Liu00]. Tests conducted in a fixed bed reactor by Liu et al. [Liu00] as well as during thermo-gravimetric analysis [Haj88, Sno88] report that direct sulfation enables higher degree of sulfation than those observed in CaO-SO_2 sulfation. Higher sulfation rate has been suggested due to the counter diffusion of CO_2 during direct sulfation resulting in a porous product layer, offering less resistance to diffusion. However, results indicating direct and higher degree of sulfation by the ash in an oxy-coal pulverised fuel fired furnace could not be found in open literatures and needs to be investigated in detail.

Like fuel-N, sulphur in the coal is also liberated during devolatilisation and is distributed between the char and the volatiles, depending on the temperature and the coal rank. For a given heating rate, the amount of sulphur released as volatiles has been reported to be higher for low rank coals [Lab95, Pat93]. On the other hand, hydrogen sulphide (H_2S) has been reported to be the most abundant sulphur containing volatile compound [Lab95, Mon99]. As the amount of sulphur released via the volatiles is higher for low rank coals, and the most abundant sulphur containing volatile compound is H_2S, the amount of H_2S released by low rank coals are probably higher. However, literatures reporting on the formation of H_2S in the flame zone in a CO_2 environment could not be found, and is one of the scopes of this work.

3.2.5. CO Emission

Like SO_2 emission during oxy-coal combustion, the emissions of CO have been addressed by only a few investigators. Hjärtstam et al. [Hjär07] using the same pre-dried brown coal (Lausitz coal) as used in the present study, have reported that during oxy-coal combustion with 27 and 29 vol. % oxygen, higher inflame CO concentration (around 8 vol. %) was measured. The CO emission leaving the furnace however was similar to air-blown combustion and was therefore concluded that controlling the CO emission during oxy-coal combustion should not be any more difficult than during air-blown combustion. Liu et al. [Liu04] using a UK bituminous coal reported that the CO emissions are closely related to the gas temperature profile, with combustion in 30% O_2/ 70% CO_2 by volume (for which case highest gas temperature profile was measured) producing the lowest CO emission of 34 ppm at the exhaust. Although the authors have not commented on the in-flame CO concentration, axial profile measurements show a CO peak of approximately 12000 ppm during oxy-coal combustion with 30 vol. % O_2 and approximately 7000 ppm during air-blown combustion. Similarly Croiset et al. [Cro00] also correlate the CO emission rate with temperature and observed faster decrease in CO emission rate during 35 vol. % O_2 than during 28 vol. % O_2 measurements. However, they observed much faster decrease in CO emission rate during air-blown combustion and concluded that temperature is not only the parameter significantly affecting the CO emissions, and is likely that high concentration of CO_2 can also affect CO formation. The higher CO peak in the near burner zone during oxy-coal combustion could be due to the lower flue gas volume. Coal pyrolysis experiments conducted by Al-Makhadmed et al. [Al09] however show a higher CO and lower H_2 concentrations in a CO_2 environment, and has been attributed to enhanced production of CO by reaction of CO_2 with Carbon (Char-CO_2 gasification reaction), and consumption of H_2 to produce CO (reverse water-gas reaction) given below:

$$CO_2 + C \leftrightarrow 2CO \qquad [R3.20]$$

$$H_2 + CO_2 \leftrightarrow CO + H_2O \qquad [R3.21]$$

CHAPTER 4

EXPERIMENTAL SET-UP AND PARAMETERS

4.1. EXPERIMENTAL SET-UP

4.1.1. Description of the 20 kW Once Through Furnace

The once through, pulverised fuel combustion test facility used for this investigation, as illustrated in Figure 4.1, consists of a ceramic tube reaction zone of 2500 mm length and 200 mm diameter. The facility is down fired, and is electrically heated around the reaction zone enabling a constant wall temperature and a uniform temperature profile. A constant wall temperature up to 1400°C can be maintained, therefore enabling reliable investigations at different temperatures. However, all the measurements for this investigation were carried out at a wall temperature of 1300ºC. Pulverised fuel or natural gas is fed into the reactor by means of a carrier air or O_2/CO_2 mixture through the central tube of the top-mounted circular jet burner. The combustion air or O_2/CO_2 mixture simulating oxy-fuel firing are injected through outer concentric tubes of the burner, divided into the primary and the secondary streams. The burnout oxidant, for over-fire oxidant staging experiments can be injected at any position in the ceramic tube reaction zone by means of an over-fire probe inserted from the bottom of the reactor. The flue gas is extracted at the final section of the heated reaction tube at a distance of 2.5 m from the burner opening. Axial profile measurements of the flue gas composition can be carried out by means of a vertically movable oil cooled sampling probe, which transports the extracted flue gas to the standard analysers.

For the investigation of the fate of recycled NO, a defined amount of pure NO from cylinder was injected into the reactor either via the secondary stream of the burner or via the over-fire probe, mixed with O_2/CO_2 mixture or air depending upon the combustion mode. For the investigation of the fate of SO_2, a defined amount of pure SO_2 from cylinder was injected into the reactor via the secondary stream of the burner, mixed with O_2/CO_2 mixture or air depending upon the combustion mode. For the determination of the amount of SO_2 retained in the convective section/flue gas path, gaseous concentration measurements were carried out at the end of the radiative section (2.5 m) as well as at the flue gas path, before the candle filter. Ash samples were also collected at the candle filter and compared with the ash samples collected at the end of radiative section (2.5 m) to further evaluate SO_2 retained in the flue gas path.

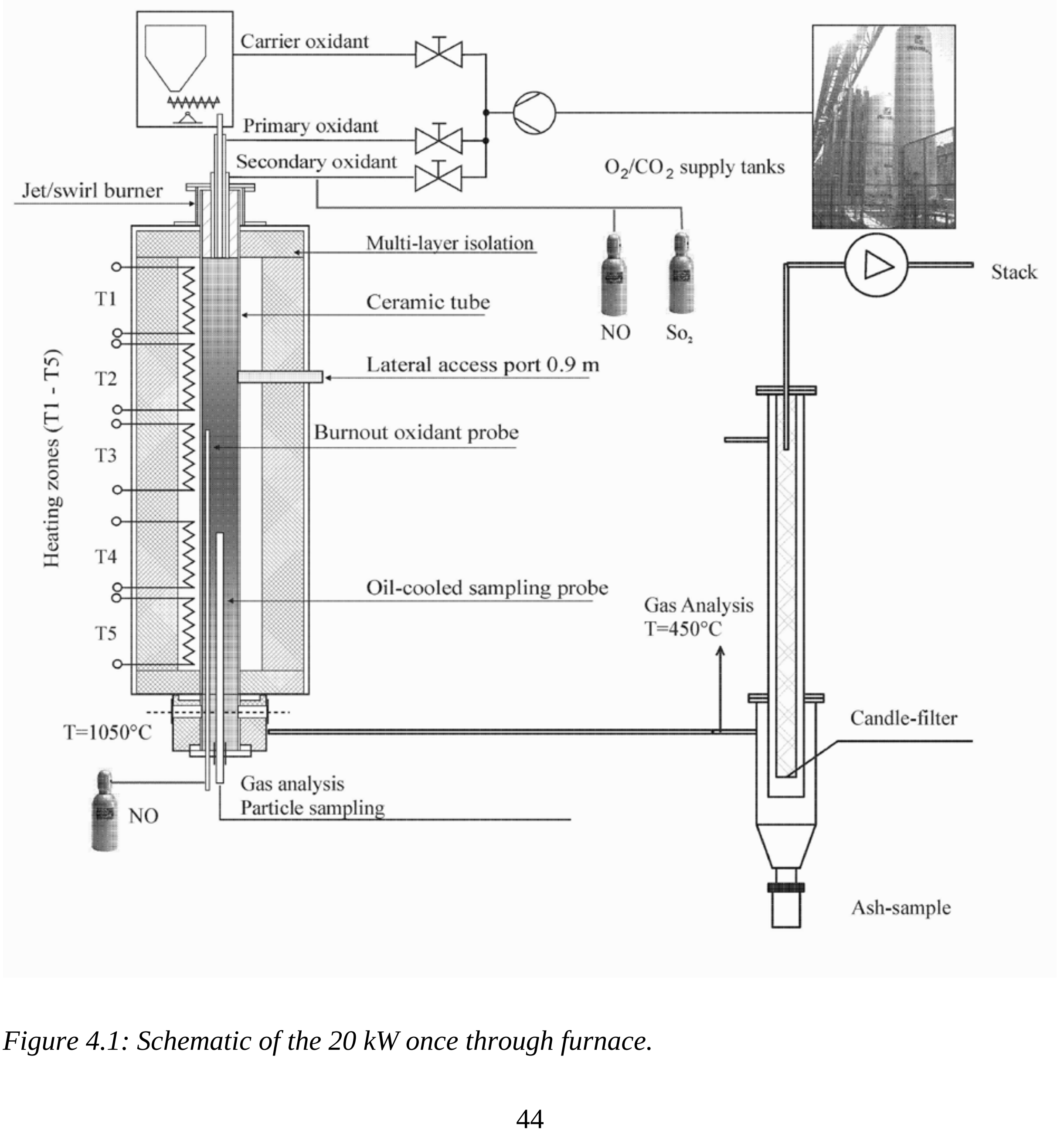


Figure 4.1: Schematic of the 20 kW once through furnace.

4.1.2. Burner Configuration

The burner is mounted at the top of the test facility and is basically a circular jet burner with a provision to operate in a swirl mode. However, all the measurements for this investigations were carried out in a jet mode i.e. without a swirl. The burner consists of three concentric tubes for carrier stream, primary stream and secondary stream. As mentioned earlier, the carrier stream is used for conveying the pulverised fuel or natural gas inside the reactor, and the combustion air or O_2/CO_2 mixture are injected through the outer concentric tubes, divided into primary and secondary streams. For natural gas firing, the central pulverised fuel carrier tube is replaced by a natural gas injection nozzle; otherwise the burner configuration for natural-gas firing is similar to pulverised fuel firing [Figure 4.2].

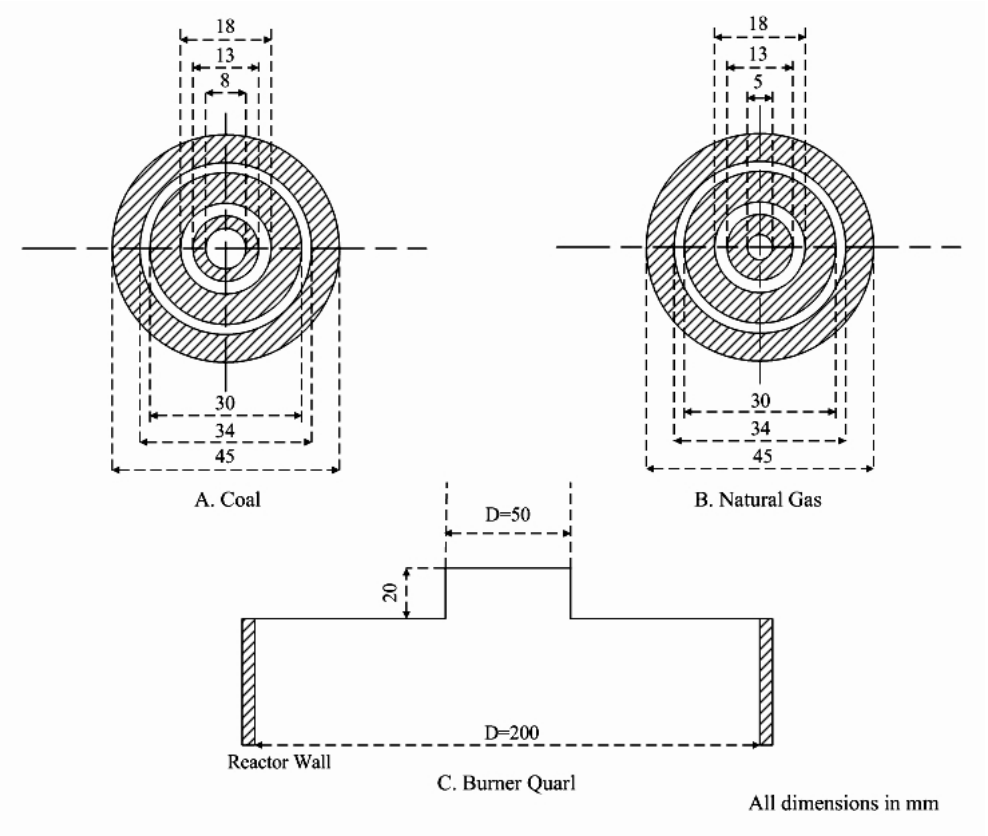


Figure 4.2: Dimension of the burner openings (A) for coal combustion, (B) for natural gas combustion and (C) burner quarl.

4.1.3. Fuel-Feeding System

The fuel feeding system consists of a gravimetric conveyor and a screw feeder. A uniform coal feeding rate up to 5 kg/h is possible. Carrier air or O_2/CO_2 mixture depending upon the type of experiment being carried out was used for conveying the coal from the fuel-feeding system into the test facility. The temperature of the coal in the feeding unit was approximately 20°C. As the fuel-feeding system is volumetric, calibration of the system was carried out before the commencement of measurements to ensure accurate fuel input. A typical calibration curve is shown in Figure 4.3, which illustrates the coal feeding rate against the number of revolution of the screw-feeder.

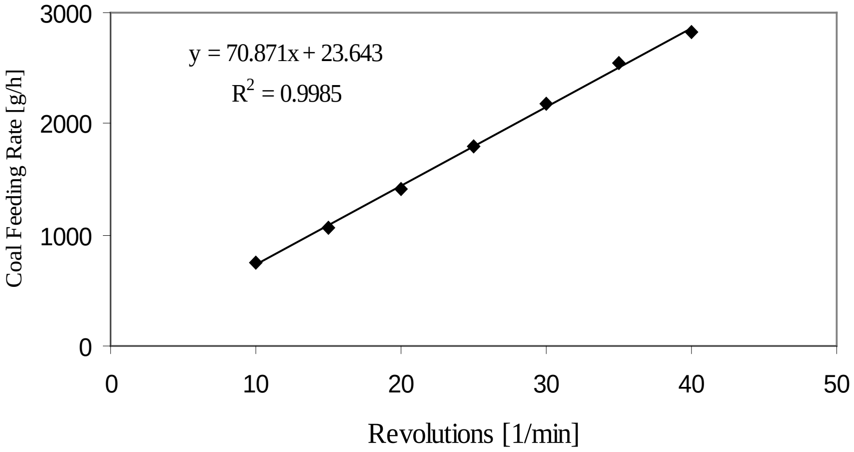


Figure 4.3: Typical calibration curve of the fuel-feeding unit.

Table 4.1 shows a typical fluctuation of the fuel dosing with time, which was carried out by recording the coal feeding rate for a time interval of 5 minutes. As seen from Table 4.1, the mean deviation of the flow-rate is 8.8 g/h when the mean value for the feeding rate is 1799 g/h. The fluctuation of the fuel-feeding system with time can therefore be considered negligible.

Table 4.1: Coal feeding rate based on 5 minutes measurement interval.

No.	1	2	3	4	5	6
Coal feeding rate [g/h]	1804.92	1811.76	1794.24	1786.20	1790.64	1807.08

4.1.4. Oil Cooled Sampling Probe and Suction Pyrometer for Gas Temperature Measurement

Gas as well as ash/char samples were collected by means of an oil-cooled sampling probe, schematic of which is shown in Figure 4.4. It can be moved vertically along the central axis of the reactor from the burnout section to the burner mouth with a high flexibility. The standard operation temperature of the oil-cooled probe is 180°C, and therefore ensures immediate quenching of the flue gas samples. The head of the probe is streamlined and ensures minimum impact on the flow pattern of the reactants inside the combustion chamber. A steel covering surrounds the probe in order to minimise the heat loss. Solid samples are separated from the flue gas at the end of the oil-cooled probe by means of a filter, and are immediately collected in glass containers for lab analysis.

A vertically movable gas temperature measurement probe commonly referred to as ‘suction pyrometer’ can be attached to the oil cooled sampling probe for gaseous temperature measurements [Figure 4.4.A]. During gas temperature measurement, the temperature measurement probe is placed 2 cm above the tip of the oil-cooled probe [Figure 4.4.B]. The pump for sucking in the flue gas is then started. After the completion of gas temperature measurement, the suction pump is switched off and the temperature probe is moved back to its original position as shown in Figure 4.4.A. One of the most important requirements for suction pyrometer is that the velocity of gases between the outer and inner ceramic tube sheathings must be greater than 150 m/s, so that the equilibrium thermocouple temperature is nearly that of the gases without the radiative component.

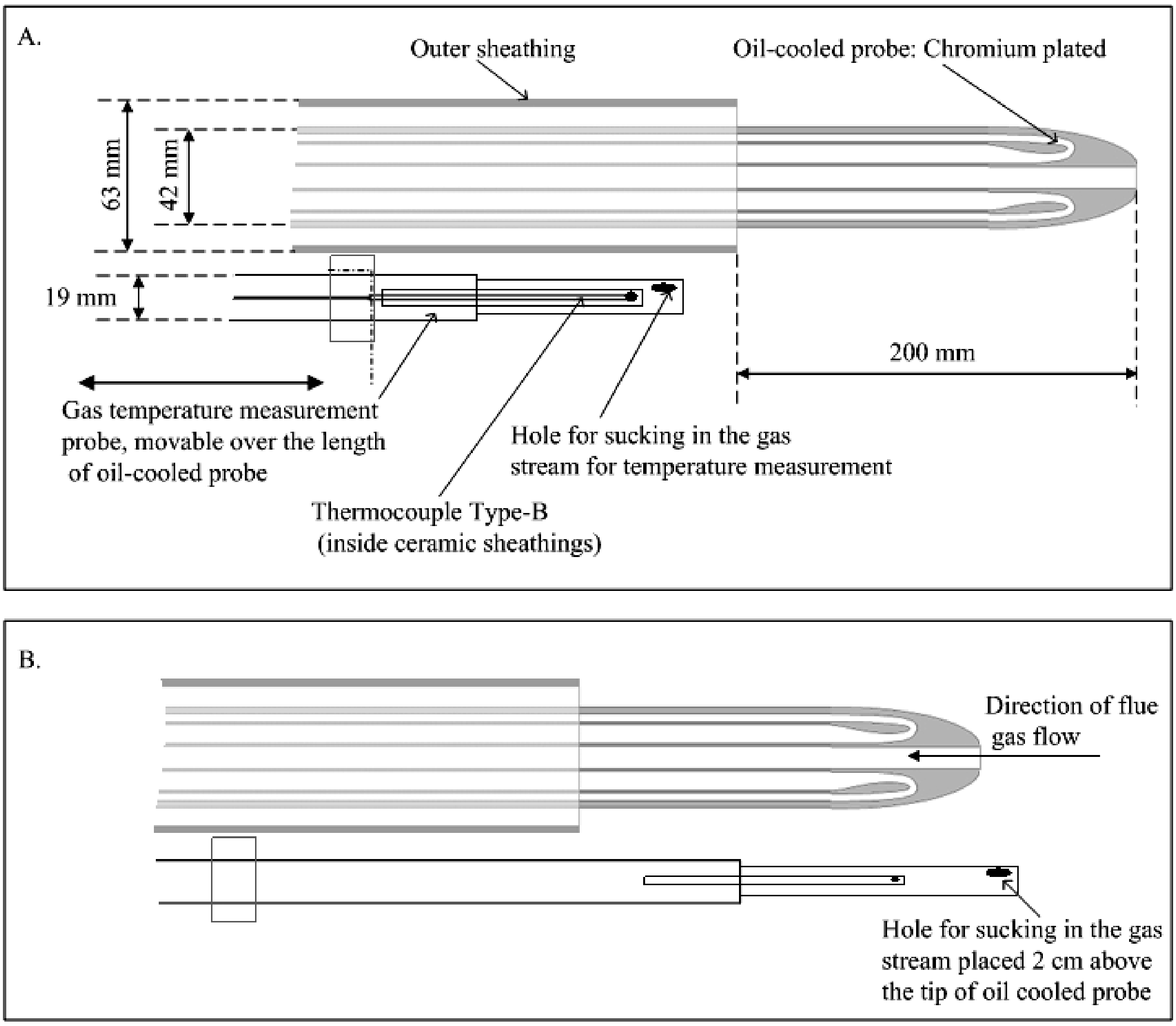


Figure 4.4: Dimensions and position of the oil-cooled probe and suction pyrometer illustrating (A) gas and solid sampling by oil-cooled probe (B) gas temperature measurement by suction pyrometer.

4.1.5. Burnout Oxidant Probe

As mentioned previously, during oxidant staged combustion, the burnout air or oxidant can be injected at any position along the reactor axis with a burnout probe made of

Inconel. The tip of the injector has 3 holes with diameters of 2.8 mm in radial position (angle 30°). The outer diameter of the probe is 21 mm with wall thickness of 2.1 mm and is placed approximately 10 mm from the reactor wall (distance from wall to central axis of the burnout probe is approximately 20 mm) and burnout air/oxidant is injected perpendicular to the gas and coal flow inside the reactor.

4.1.6. Air Supply System

Combustion air can be fed into the reactor by means of four separate rotameters and mass flow meters, thus enabling accurate control of flow through the carrier, primary, secondary and the burn-out stream individually. The combustion air fed into the reactor is supplied from a compressor therefore the moisture content in the combustion air is negligible. The temperature of the combustion air before it enters the flow controllers is approximately 20°C.

4.1.7. O_2/CO_2 Supply and Mixing System

O_2 and CO_2 required for simulating oxy-fuel combustion are supplied from commercially available tanks. The purity of both gases is approximately 99.5%. Mixing and regulating the flow of O_2 and CO_2 inside the reactor is carried out in a highly flexible mixing station. Flow through carrier, primary and secondary stream of the burner can be adjusted individually with high flexibility, therefore enabling investigation of oxy-coal combustion at different O_2/CO_2 concentrations. The temperature of O_2 and CO_2 after the mixing station is approximately 20°C.

4.1.8. Standard Flue Gas Analysis

As mentioned previously, gaseous samples are collected by means of the vertically movable oil cooled probe, which are then conducted to the gas sample preparation and analysis appliances via an electrically heated tube maintained at 180°C. The flue gas is cooled and moisture is removed in a chiller before it enters the standard analysers. Therefore all the standard gaseous concentrations i.e. O_2, CO_2, NO_x, CO and SO_2 are expressed on a dry basis. Table 4.2 lists the standard measurement equipments employed and the calibration gases used for the calibration of the analysers. Careful attention needs to be given to the analysers for oxy-coal combustion measurement as the CO_2 concentration is much higher in the flue gas. NO_x analysers based on chemiluminescence principle have a quenching effect in a CO_2 environment. Therefore NO_x calibration gas in a CO_2 background was used for the calibration of the NO_x analyser for oxy-fuel combustion measurements. Similarly, cross-sensitivity between CO and CO_2 in oxy-fuel environment for CO analysers based on NDIR principle needs to be checked and corrected appropriately [refer to Appendix B for detail].

Table 4.2: Analysers used for standard flue gas analysis.

Comp.	**Measurement technique**	**Manufacturer**	**Calibration gas concentration**	
			Air	**Oxy-Coal**
O_2	Paramagnetism	Rosemount / Oxinos 100	3 % in N_2	--
	Paramagnetism	Sick Maihak	--	3 % in N_2
CO_2	NDIR	Rosemount / Binos 100	16 vol. % in N_2	--
	NDIR / bifrequence	Siemens/Ultramat 21	--	73 vol. % in O_2
CO	NDIR	Rosemount / Binos 100	200 ppm in N_2	200 ppm in N_2
	NDIR	Rosemount / Binos 100	12 vol. % in N_2	12 vol. % in N_2
NO_x	Chemiluminescence	ECO Physics	800 ppm in N_2	800 ppm in CO_2
SO_2	Infrared	Siemens/Ultramat 23	700 ppm in N_2	700 ppm in N_2

4.1.9. FTIR for HCN and NH_3 Measurement

A high resolution FTIR spectrometer from BRUKER Optics (model VECTOR 22), coupled with a high temperature multi-path length gas cell (0.5-5m) was used for the determination of the concentrations of gaseous nitrogen-containing compounds, HCN and NH_3. The instrument was calibrated with an advanced calibration method and all the spectra were acquired with a resolution of 0.5 cm^{-1} and a spectral range of 600-4000 cm^{-1}. Details on the calibration method of this instrument can be found in PhD dissertation from Benöhr [Ben03].

In order to consider the possible interferences of several IR active gas compounds in the flue gas, and to determine the optimum spectral range for the quantification of the sample gas concentrations, reference gases were mixed and measured by the FTIR. Based on these well-defined gas mixtures, the optimum spectral ranges for the calibration of each gas were defined. For the measurement of HCN and NH_3 concentration in the flue gas, a portion of the flue gas was fed into the multi-path gas cell at a constant pressure, via a heated filter and a heated tube, which were all maintained at 180°C in order to avoid any condensation of HCN and NH_3. Additionally, the results can be affected due to the selective adsorption or desorption of measured gases by materials of the gas cell walls and the sampling line walls. A significant effect was only seen for ammonia. Therefore, the memory effect of ammonia on the sampling system and the gas cell, which were both made of electrically polished stainless steel, was determined by feeding ammonia reference gas (499ppm NH_3 in N_2) into the pipes of the sampling system, which were kept at 180°C. Ammonia achieved a stable level (~500 ppm) after approximately 3 minutes. Therefore, in order to minimise any selective adsorption and desorption effects, measurements were carried out only after flushing the sampling system with the flue gas for at least 3 minutes. The errors after correcting the integration areas and determining the concentration are <5% for HCN and <4% for NH_3 in realistic ratios of the interfering and the measured compound possibly present in pyrolysis gases [Ben03].

4.1.10. H_2S Analyser

An analyser from Western Research, Canada, model 921CE was used for H_2S measurement. The analyser measures at two discrete wavelengths, the absorbances of ultraviolet radiation (light) by a gas sample. The concentration of the component absorbing the light is then determined from the relationships developed through the application of ideal gas law in concert with the laws of Bouguer, Beer and Lambert. Like standard analysers used for this investigation, flue gas was dried before it enters the measuring cell, therefore H_2S concentration is also expressed on a dry basis.

The calibration of the instrument was carried out by considering the interference of other flue gas components like CO_2, CO, SO_2 and NO, detail of which is included in Appendix B.

4.2. FUEL AND ASH CHARACTERISATION

4.2.1. Analysis Methods

Fuel as well as the solid samples collected during the experiments were analysed at the laboratory of Institute of Process Engineering and Power Plant Technology, University of Stuttgart. Table 4.3 lists the type of analysis, measurement principle, equipment used and the standard followed.

Table 4.3: Principle and standard for fuel and solid sample analysis.

Analysis	**Measurement Principle**	**Equipment**	**Species**	**Standard**
Higher heating value of coal	Adiabatic calorimeter	IKA C 4000	---	DIN 51900
Particle size distribution	Laser scattered analysis	Malvern 2600	---	---
Proximate analysis	Thermogravimetric analysis	Leco TGA-500	Water	DIN 51718
			Ash	DIN 51719
			Volatiles	51720
			Fixed-C	Calculated
Ultimate analysis (Elemental Analysis)	Incineration with oxygen and thermal conductivity detectors	Vario el (Elementar)	Carbon, Hydrogen, Nitrogen, Sulphur	DIN 51721 to DIN 51727
			Oxygen	By difference
Fuel ash composition	X-Ray Fluorescence spectrometer (XRF)	Philips PW 1480 with Rh-Anode	SiO_2, Al_2O_3, CaO, MgO, K_2O, Na_2O, Fe_2O_3, P_2O_5, TiO_2, Mn, Sr, Ba, Cu, Zn, Cr, C, S	DIN 51729-10

4.2.2. Analysis of the Coals and Char used

It is well established that coal rank is one of the most important factors that determine the combustion and emission behaviour. Consequently, coals of different ranks were chosen for this study. Table 4.4 gives the analysis of a medium volatile bituminous coal, Klein Kopje (KK) from South Africa, pre-dried Lausitz brown coal (LA) from Eastern Germany, pre-dried Rhenish brown coal (RH) from Western Germany, a high volatile bituminous coal, Ensdorf (EN) from Saar basin in Germany, and char of Rhenish brown coal, used for this investigation. The brown coals when received from the mine often contains more than 50% moisture but were pre-dried prior to combustion, as pre-drying of high moisture brown coals is expected to become state-of-the-art for efficiency improvement.

Table 4.4: Analysis of the coals and char used for this investigation.

	Klein Kopje Coal (KK)	**Lausitz Brown Coal (LA)**	**Rhenish Brown Coal (RH)**	**Ensdorf Coal (EN)**	**Char of Rhenish Brown Coal**
H_u[kJ/kg, ar]	24932	21412	20965	30955	30076
PROXIMATE ANALYSIS					
Moisture [%, ar]	3.60	10.20	11.50	2.42	1.00
Ash [%, wf]	19.29	5.46	4.07	7.47	8.48
Volatile [%, waf]	27.76	57.36	54.18	37.21	5.63
Fixed C [%, waf]	72.24	42.64	45.82	61.90	94.37
ULTIMATE ANALYSIS					
C [%, waf]	83.93	66.78	67.96	74.85	98.23
H [%, waf]	4.50	5.26	7.68	5.05	<0.3
N [%, waf]	1.67	0.65	0.73	1.59	<0.3
S [%, waf]	0.72	0.85	<0.3	0.83	0.45
O [by diff]	9.18	26.45	23.63	17.68	1.44
XRF ANALYSIS					
SiO_2 [%, wf]	46.10	9.66	1.60	35.50	---
Al_2O_3 [%, wf]	28.70	5.04	4.80	20.20	---
CaO [%, wf]	7.80	23.78	35.10	10.50	---
MgO [%, wf]	1.70	9.34	17.30	2.70	---
K_2O [%, wf]	0.54	0.30	0.76	1.80	---
Na_2O [%, wf]	<0.5	0.50	2.40	1.00	---
Fe_2O_3 [%, wf]	3.70	22.86	17.20	16.20	---
P_2O_5 [%, wf]	1.30	0.20	<0.2	<0.2	---
TiO_2 [%, wf]	1.50	0.40	<0.4	0.70	---
PARTICLE SIZE DISTRIBUTION					
D_{10} [µm]	4.83	7.46	10.83	5.79	5.23
D_{50} [µm]	28.05	47.91	93.07	23.66	27.79
D_{90} [µm]	72.68	142.54	264.65	92.25	90.96

4.3. EXPERIMENTAL PARAMETERS

The fundamental approach for all the experiments conducted was to keep baseline experiments (air-blown combustion) comparable to oxy-fuel combustion experiments as far as possible. The foremost concern was achieving a similar flame shape between the baseline experiments and oxy-fuel experiments. Therefore, total volumetric flow of oxidants through the burner was kept constant for all experimental cases. This not only ensures a similar flame shape but also a similar gas residence time inside the reactor. Other parameters that were kept constant for all the measurements of this study were reactor wall temperature (1300°C) and overall oxygen ratio (n=1.15). It is noted that, to maintain an overall oxygen ratio of 1.15, the O_2 excess during air-blown, OF21, OF27 and OF35 combustion needs to be 2.74, 2.74, 3.52 and 4.57 vol. % respectively. The calculation method of oxygen ratio is discussed in Appendix A. Furthermore, to maintain a similar oxygen ratio for O_2/CO_2 combustion with higher inlet oxygen concentration (e.g. OF27 and OF35 cases), the coal feeding rate needs to be increased. However, as the reactor temperature is maintained by electrical heating, the impact on combustion behaviour due to the change in coal feeding rate is negligible.

Initial measurements for the investigation of combustion and emission behaviour during oxy-coal combustion (un-staged conditions) were conducted during air-blown as well as O_2/CO_2 combustion with 21% O_2/79% CO_2, 27% O_2/73% CO_2 and 35% O_2/65% CO_2 by volume (referred as OF21, OF27 and OF35 respectively). However detailed oxy-fuel measurements like measurements for the investigation of oxidant staging, fate of recycled NO and the fate of sulphur were carried out at 27% O_2/73% CO_2 (OF27) condition together with base line condition (air-blown combustion). Oxidant staging experiments were conducted at a burner oxygen ratio of 0.75, 0.85 and 0.95 and a residence time in the reduction zone of approximately 1, 2 and 3 seconds, with overall oxygen ratio of 1.15. Investigations on the fate of recycled NO were carried out by injecting a known amount of NO into the reactor either via the secondary stream of the burner or via the over-fire probe, mixed with O_2/CO_2 mixture or air depending upon the combustion mode. Measurements were carried out during staged as well as un-staged combustion. For the investigation of the fate of recycled SO_2, a defined amount of SO_2 was injected into the reactor via the secondary stream of the burner, mixed with O_2/CO_2 mixture or air, depending upon the combustion mode. Other important input parameters are listed in Table 4.5 and 4.6.

Table 4.5: Experimental parameters for un-staged combustion.

Experimental Conditions			**Air**	**O_2/CO_2 Combustion**		
				OF21	**OF27**	**OF35**
O_2:N_2 or O_2:CO_2 ratio	volumetric ratio		21:79	21:79	27:73	35:65
	mass ratio		23:77	16:84	21:79	28:72
Oxidant Flow Rate	m³/h (STP)		6.70 (Carrier Stream=1.5, Primary Stream= 2.08, Secondary Stream=3.12)			
	kg/h		8.04	11.52	11.32	11.12
Fuel Feeding Rate/Thermal Input [LHV based]	Klein Kopje Coal (KK)	kg/h	0.84	0.84	1.07	1.39
		kW_{th}	5.75	5.75	7.41	9.63
	Lausitz Coal (LA)	kg/h	0.98	0.98	1.27	1.64
		kW_{th}	5.83	5.83	7.55	9.75
	Rhenish Coal (RH)	kg/h	0.87	---	1.13	---
		kW_{th}	5.07	---	6.58	---
	Ensdorf Coal (EN)	kg/h	0.81	---	0.99	---
		kW_{th}	6.96	---	8.51	---
	Char of Rhenish Coal	kg/h	---	---	0.89	---
		kW_{th}	---	---	7.44	---
Oxygen Ratio [n]			1.15			
O_2 Excess [vol. %, dry]			2.74	2.74	3.52	4.57
Reactor Wall Temperature [°C]			1300			

Table 4.6: Experimental parameters for staged combustion.

Experimental Conditions			**Air**			**OF27**		
			Burner Oxygen Ratio [n_1]					
			0.75	0.85	0.95	0.75	0.85	0.95
Oxidant flow through the burner at STP [m³/h]			6.70					
Oxidant flow through the over-fire port at STP [m³/h]			3.57	2.37	1.41	3.57	2.37	1.41
Coal Feeding Rate/Thermal Input [LHV based]	Klein Kopje Coal	kg/h	1.28	1.13	1.01	1.65	1.45	1.30
		kWt_h	8.86	7.83	6.99	11.43	10.04	9.00
	Lausitz Coal	kg/h	1.51	1.33	1.19	1.94	1.71	1.53
		kWt_h	8.98	7.91	7.08	11.54	10.17	9.10
	Rhenish Coal	kg/h	1.34	---	---	1.73	---	---
		kWt_h	7.80	---	---	10.07	---	---
	Ensdorf Coal	kg/h	1.24	---	---	1.52	---	---
		kWt_h	10.66	---	---	13.07	---	---
	Char of Rhenish Coal	kg/h	---	---	---	1.36	1.20	1.07
		kWt_h	---	---	---	11.36	10.03	8.94
O_2 excess [vol. %, dry]			2.74			3.52		
Oxygen ratio in burnout zone (n)			1.15					
Reactor wall temperature [°C]			1300°C					

CHAPTER 5

COMBUSTION AND EMISSION BEHAVIOUR DURING UN-STAGED COMBUSTION

Oxy-coal combustion during un-staged combustion has been investigated by several organisations. However, investigations with a wide range of coals are still lacking. From conventional air-blown pulverised coal experience, it is well accepted that each coal behaves uniquely, and an attempt to generalise coal combustion behaviour by testing only a few coals would be impractical. This would be the case for oxy-coal combustion as well. Therefore, with the aim to better understand and predict the behaviour of oxy-coal operated furnaces, results from detailed experimental work during un-staged, O_2/CO_2 and air-blown combustion by firing two pre-dried brown coals, two bituminous coals and natural gas are presented in this chapter.

5. 1. RESULTS

It is noted that, when evaluating emissions associated with O_2/CO_2 combustion, the most important aspect that needs consideration is that a portion of the flue gas needs to be recycled back into the furnace for oxy-coal combustion process. The mass of the flue gas at the end of the system, downstream of flue gas recirculation location will therefore be much lower than at the furnace end. As mentioned previously in Chapter 4, this investigation was conducted in a once through furnace by keeping a similar volume flow through the burner for all experiments. The reported emissions in concentration at the end of the furnace at 2.5 m may therefore be lower than oxy-coal combustion with simulated flue gas recycle.

Furthermore, all the measured concentrations are reported on a dry basis unless otherwise stated.

5.1.1. Combustion Behaviour during O_2/CO_2 Combustion

For the comparison of combustion behaviour during O_2/CO_2 combustion with air-blown combustion, the axial gaseous concentration profiles during un-staged combustion with a medium volatile bituminous coal, Klein Kopje for air-blown, OF21 and OF27 combustion is illustrated in Figure 5.1.

As seen from Figure 5.1.A, the oxygen consumption rate in the near burner region is lower for OF21 combustion when compared to air-blown combustion, and reaches the experimental set-up value of 2.74 vol. % (corresponding to n=1.15) at approximately 2 m from the burner. However, experimental set-up value of 2.74 vol. % and 3.52 vol. % is achieved at approximately 1.1 m from the burner for air-blown and OF27 combustion respectively. When the oxygen consumption rate (relative to the initial input oxygen concentration) at 1.1 m from the burner is compared, approximately 87%, 86% and 82% oxygen is consumed for OF27, air-blown and OF21 combustion respectively. Although, it is generally difficult to clearly distinguish the difference in oxygen consumption profile in an electrically heated furnace like the one used for present study, especially when oxygen concentration of the oxidant is higher than 15 vol. % due to very fast reaction rates, the axial profile measurements clearly indicate a delay in combustion for OF21 case. Furthermore, if a self-sustained reactor was used, it might have been difficult to maintain a stable flame for OF21 case as evident from the results of Liu et al. [Liu04], who observed a destabilized flame and a delay in combustion during OF21 combustion for bituminous coals.

The NO formation rate in the near burner region, as seen from Figure 5.1.B is highest for air-blown combustion, and reaches a peak at approximately 0.5 m from the burner. When compared to air-blown combustion, although the NO formation rate is lower for OF27 combustion, the NO concentration reaches a peak at the same location (0.5 m from the burner). However, for OF21 combustion, the NO formation rate is not only lower than air-blown combustion, the formation of NO peak is also delayed (approximately 0.7 m from the burner). This further indicates a delay in combustion during OF21 firing.

The NO concentration at the furnace exit is also similar for air-blown and OF27 combustion (approximately 670 ppm) but is lower during OF21 combustion (approximately 500 ppm). However, a comparison of emission concentrations during combustion with different input oxygen concentrations would be unfair to cases with a higher input oxygen concentration. This is due to more fuel required during combustion with higher input oxygen concentration, when a similar gas flow and oxygen ratio is maintained. Emission at the furnace exit is therefore discussed separately in section 5.1.3.

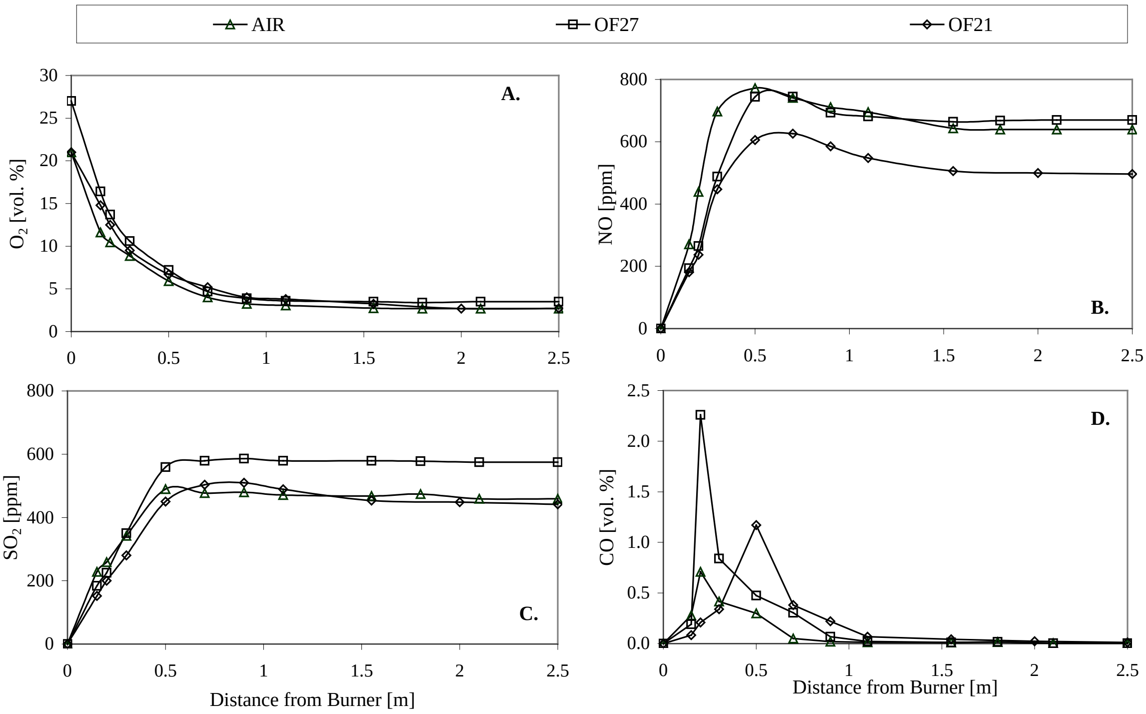


Figure 5.1: Axial (A) O_2, (B) NO, (C) SO_2 and (D) CO concentration profiles during air-blown, OF21 and OF27 combustion for a medium volatile bituminous coal, Klein Kopje.

The SO_2 formation rate, as presented in Figure 5.1.C is similar for air-blown and OF27 combustion and reaches a peak at the same location (0.5 m from the burner). The SO_2 formation rate in the near burner region is however lower for OF21 combustion and reaches a peak at 0.9 m from the burner. The SO_2 concentration at the furnace exit is however approximately 25% higher for OF27 combustion. This is due to the increase in fuel-feeding rate by approximately 30% during OF27 combustion.

The CO emissions at the furnace exit as seen from Figure 5.1.D is lower than 100 ppm for all three conditions tested, indicating that controlling the CO emissions during oxy-coal combustion should not be any more difficult than for air-blown combustion. However, the formation of CO peak is delayed for OF21 combustion (approximately 0.5 m from the burner vs. 0.2 m for OF27 and air-blown combustion), further demonstrating that combustion is delayed during OF21 firing. Furthermore, the peak of CO in the near burner zone is seen to be higher for O_2/CO_2 combustion, and is in agreement with Liu et al. and Hjärtstam et al. [Liu04, Hjär07]. The higher CO peak during OF27 may have been due to 30% higher fuel feeding rate (it is noted that the volume of oxidant for all three experimental cases were similar). However, when air-blown and OF21 combustion are compared, the CO peak is seen to be higher for OF21 combustion, although the fuel feeding rate for these two experiments were similar. This indicates that the increased fuel-feeding rate is not the only factor that contributes to higher peak of CO in a CO_2 environment. A likely reason for the elevated production of CO in the near burner region in a CO_2 atmosphere could be due to an enhanced reaction of CO_2 with carbon and consumption of H_2 to produce CO by the water-gas reaction, as given by reactions R3.20 and R3.21 in section 3.2.5. As mentioned previously in Chapter 3, coal pyrolysis experiments conducted by Al-Makhadmed et al. [Al09] also show a higher CO and lower H_2 concentrations in a CO_2 environment.

Similarly, Figure 5.2 shows axial CO concentration profiles for the Lausitz brown coal during air-blown, OF21 and OF27 combustion. For this coal as well, the location of CO peak is delayed during OF21 combustion. This further demonstrates a delay in combustion when N_2 is simply replaced by CO_2. The CO peak was observed to be higher during O_2/CO_2 combustion for this coal as well. Furthermore, Hjärtstam et al. [Hjär07] reported a CO peak of 1.25 vol. % for air-blown combustion and about 7 vol. % for OF27 combustion, when the same Lausitz brown coal was fired in a 100 kW test facility with flue gas recirculation. This is in good agreement with the measurements conducted for this investigation, as the CO peak of 2 vol. % was observed for air-blown combustion and 6.4 vol. % was observed for OF27 combustion.

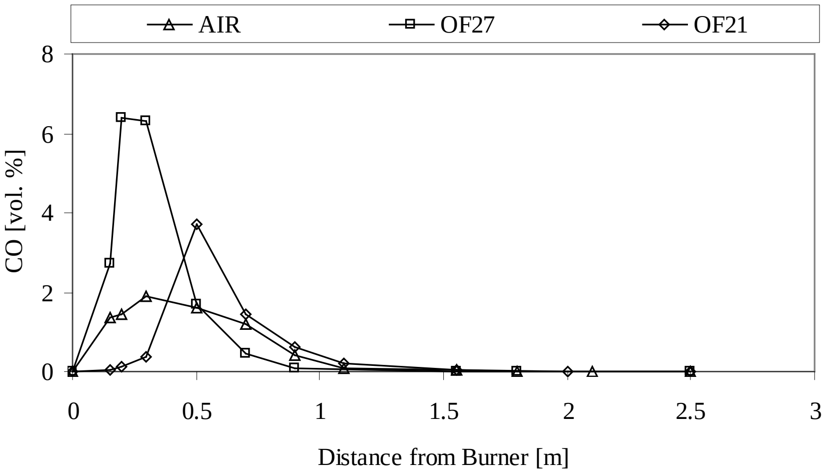


Figure 5.2: Axial CO concentration profiles during air-blown, OF21 and OF27 combustion for Lausitz brown coal.

To further evaluate the progress of combustion during air-blown and O_2/CO_2 combustion, the axial C, H, N and S fractions in the ash/char collected (in mass basis) during air-blown as well as OF27 combustion for a medium volatile bituminous coal, Klein Kopje and the Lausitz brown coal are included in Figure 5.3.

As seen from Figure 5.3.A, the carbon content in the char collected at the near burner region, during air-blown and OF27 combustion are similar for both coals. However, the carbon content in the char collected at 1.1 m from the burner is slightly higher for OF27 combustion, indicating a slight delay in combustion. The carbon content in the ash collected at the reactor exit is however almost similar for both air-blown and OF27 combustion, indicating that the ash may be a marketable product even under oxy-coal combustion.

The H content in the ash/char as shown by Figure 5.3.B is independent of the combustion media. It however shows a dependency on the coal composition, as the coal with a higher H content (Lausitz brown coal) also shows a higher H content in the char collected.

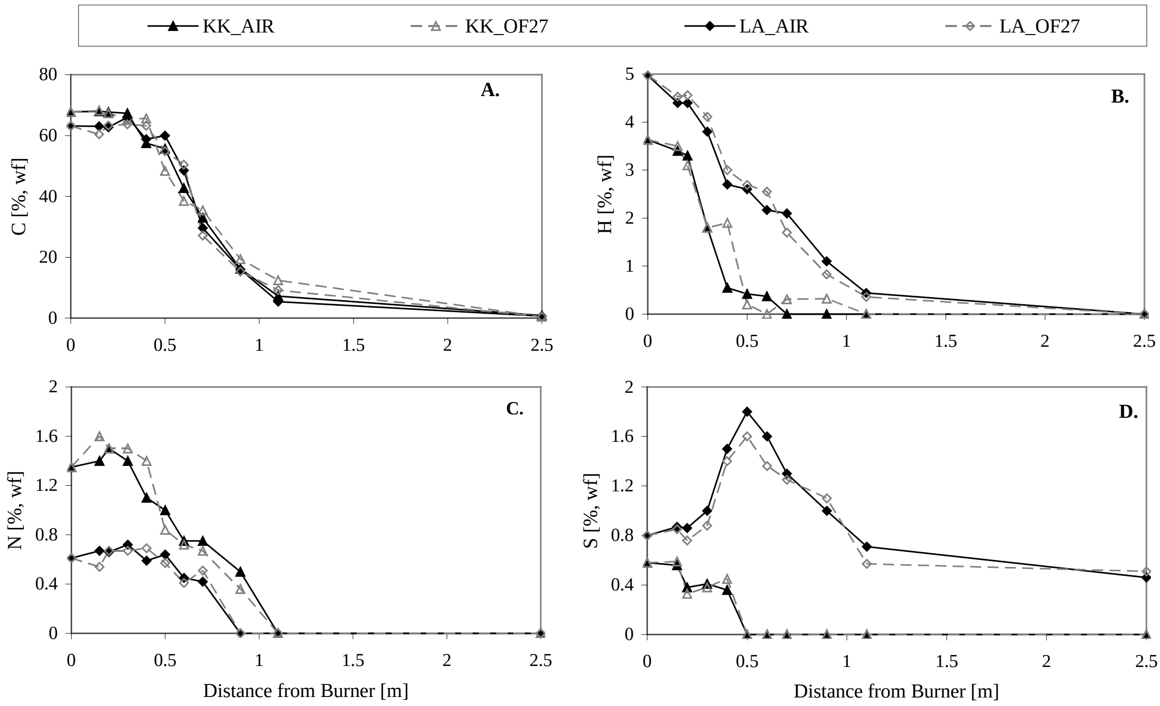


Figure 5.3: Axial (A) C, (B) H, (C) N and (D) S fractions in the ash/char collected during air-blown and OF27 combustion, for a medium volatile bituminous coal, Klein Kopje and the Lausitz brown coal.

The N content in the ash/char collected, as seen from Figure 5.3.C, shows a little influence of the combustion media. It is however dependent on the coal composition, as the coal with a higher N content (Klein Kopje coal) also shows a higher N content in the char collected. This may also be an indication that, less of the fuel-N is released into the gas phase for coals with a lower volatile content, as the volatile content of Klein Kopje coal is lesser than that of Lausitz brown coal. Furthermore, the nitrogen content in the ash/char collected and the NO concentration profiles are in good agreement with each other, as the NO concentration profile becomes flat by the time the nitrogen in the fuel is fully consumed.

Finally, the sulphur content in the ash/char collected, as seen from Figure 5.3.D is also independent of the combustion media and only dependent on the fuel type. It is noted that the mass fraction of sulphur in the Lausitz brown coal (S fraction at 0 m from the burner) appears to be similar to the mass fraction of sulphur in the ash collected at 2.5 m from the burner. This is due to the mass fraction of sulphur in the ash being relative to the ash component only, and the mass fraction of sulphur in the coal being relative to all the components in the fuel.

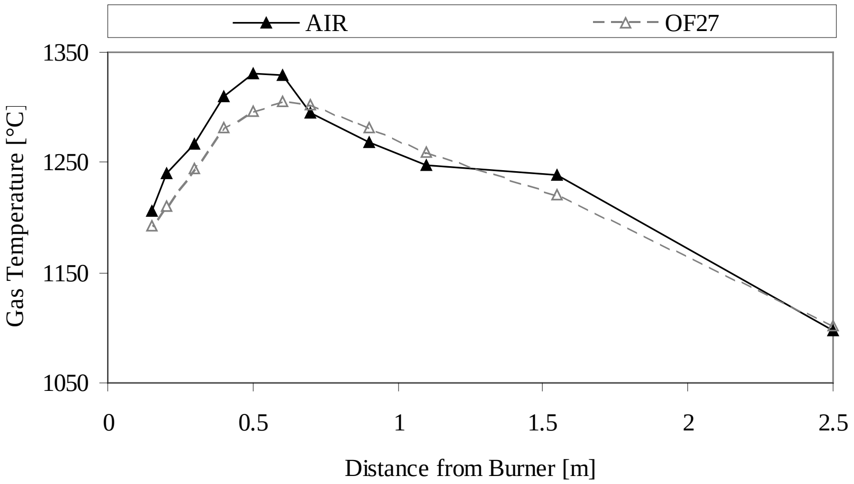


Figure 5.4: Axial flame/gas temperature profiles during air-blown and OF27 combustion for a medium volatile bituminous coal, Klein Kopje.

As seen from Figure 5.4, the axial flame temperature profiles for a medium volatile bituminous coal, Klein Kopje are also almost similar for air-blown and OF27 combustion. A slightly lower flame temperature in the near burner region may be one of the reasons for slightly lower NO formation rate in the near burner region during OF27 combustion [Figure 5.1.B], since NO formation rate as reported in literatures [Cro00, Cro01, Hu00, Liu04, Mac07] is also a function of the flame temperature.

It is evident from the results so far, that combustion is delayed in a CO_2 media when the oxygen concentration in a N_2 and a CO_2 media are similar. Results also indicate that, oxygen concentration of approximately 27 vol. % is required in a CO_2 media to give combustion and emission behaviour similar to air-blown combustion. This is due to the oxygen consumption rates, the NO_x and SO_2 formation rates, the axial flame temperature profiles and the composition of ash/char collected, for these two cases being similar. The optimum oxygen concentration in an O_2/CO_2 mixture that gives a similar flame temperature, heat transfer and emission formation rates has been reported to be in the range of 25-35 vol. % [Cro00, Hjär07, Kha05, Nsa07, Yam06] and is in agreement with the findings of this investigation.

Based on the results obtained so far indicating that combustion in 27% O_2 and 73% CO_2 by volume gives emission and combustion behaviour similar to air-blown combustion, axial gaseous concentration profiles during OF27 combustion of all 4 coals used for this investigation are compared in Figure 5.5. As seen from Figure 5.5.A, the oxygen consumption rate in the near burner region is highest for the Lausitz brown coal. It may be due to the reactive nature of this coal. The oxygen consumption rate of another reactive coal (Rhenish brown coal) is however seen to be lower than that of bituminous coals, and could be due to the larger particle size distribution of this coal (refer to Table 4.4). The experimental set- up O_2 excess of 3.52 vol. % was however achieved for all coals at approximately 1.1 m from the burner.

As generally observed during conventional air-blown, un-staged combustion, the NO concentration profiles as seen from Figure 5.5.B is a function of the nitrogen and the volatile content of a coal, i.e. the more the fuel-N content (for coals with comparable volatile content), the more is the NO formed. On the other hand, the more the volatile content (for coals with comparable fuel-N content), the more is the conversion of fuel-N to NO. Nitrogen remaining in the ash/char collected along the length of the reactor, as shown by Figure 5.3 also indicates that fuels with a higher volatile content releases more of the fuel-N via the gas phase. Coals with higher volatile content imply that more of the fuel-N is released via the gas phase, which is then oxidised to NO during fuel lean combustion. Furthermore, after achieving a maximum concentration at approximately 0.7 m from the burner, the NO concentration remains constant for both pre-dried brown coals. However, a slight decrease in the NO peak was observed for bituminous coals for all experimental conditions [Figure 5.1.B and Figure 5.5.B], and could be due to the heterogeneous capture of NO by active carbon sites in the char.

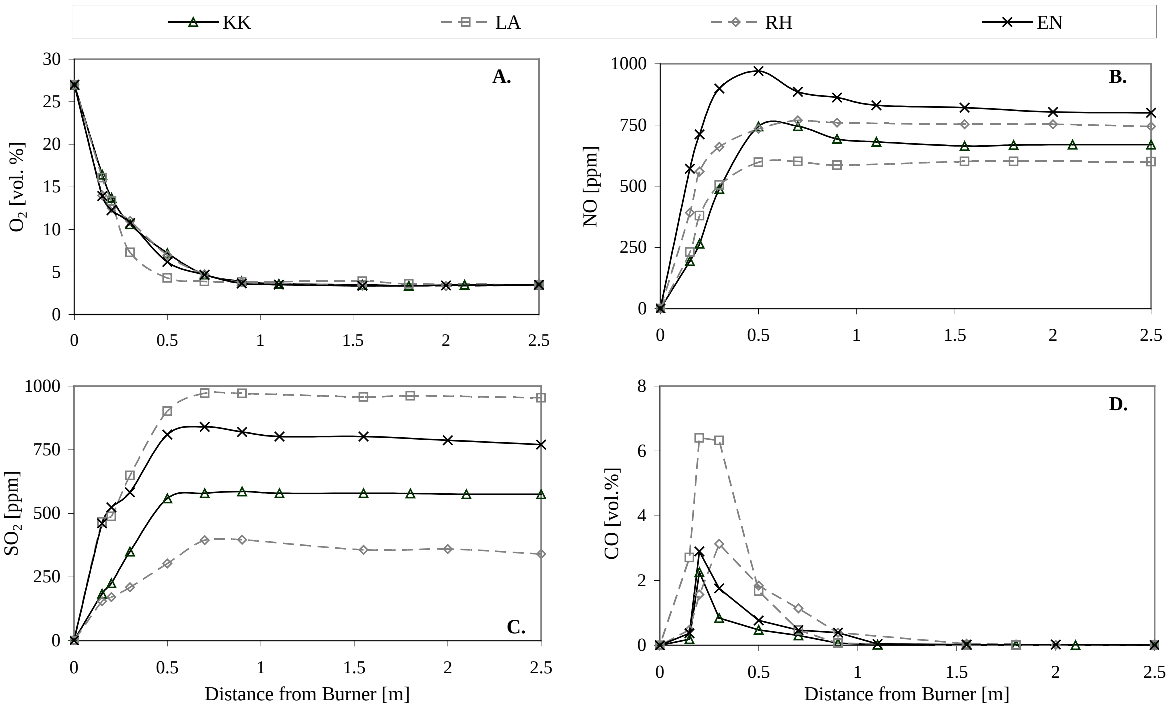


Figure 5.5: Comparison of axial (A) O_2, (B) NO, (C) SO_2 and (D) CO concentration profiles during OF27 combustion, for all 4 coals.

The SO_2 concentration profile as seen from Figure 5.5.C is essentially a function of the sulphur content of the fuel, with the fuel containing highest sulphur (Lausitz brown coal) displaying highest SO_2 concentration. This further reinforces the observations from other authors that conversion of sulphur to SO_2 depends essentially on the sulphur content of the fuel [Cro00, Cro01, Zhe03].

The CO concentration, as seen from Figure 5.5.D, reaches a peak in the flame zone between 0.2-0.3 m from the burner, drops sharply in the post flame zone, and reaches a value of less than 100 ppm at the furnace exit, for all coals. This further demonstrates that controlling CO emissions during oxy-coal combustion should not be any more challenging than during air-blown combustion. However, CO peak is seen to be much higher for high volatile coals and seems to be dependant on the rank of a coal. A higher volatile content in a coal generally imply that more of the hydrocarbons are released via the gas phase, a large part of which are then immediately converted to CO, therefore forming a higher CO peak. For coals with lower volatile content, carbon is released gradually by heterogeneous reaction, therefore avoiding the formation of high CO peak. Furthermore, the volatiles from bituminous coals mainly contain soot-producing heavy hydrocarbons, whereas the volatiles of brown coals mainly contain CO, CO_2, H_2, H_2O and light hydrocarbons [Bej07, Chen92, Fre82]. This could be another reason for the higher CO peak for pre-dried brown coals.

5.1.2. Combustion Behaviour in the Gas Phase

To further establish the emission and combustion behaviour during oxy-coal combustion, investigation in explicitly gas-phase using natural gas was performed. This is considered to develop a further understanding of the combustion behaviour of volatiles in O_2/CO_2 environment, whilst avoiding the influence of particles. This is thought to aid in improved prediction of homogeneous reactions taking place during oxy-coal combustion for scale-up and modelling purpose.

The natural gas was combusted in a balance gas of 27% O_2/73% CO_2 by volume and air. To reflect oxy-fuel combustion with flue gas recirculation, a known concentration of NO was also injected into the furnace through the secondary stream of the burner. Axial gaseous concentration profile measurements inside the furnace were performed to investigate the progress of combustion. Results of such axial emission profile measurements during air-blown and OF27 combustion are illustrated in Figure 5.6.

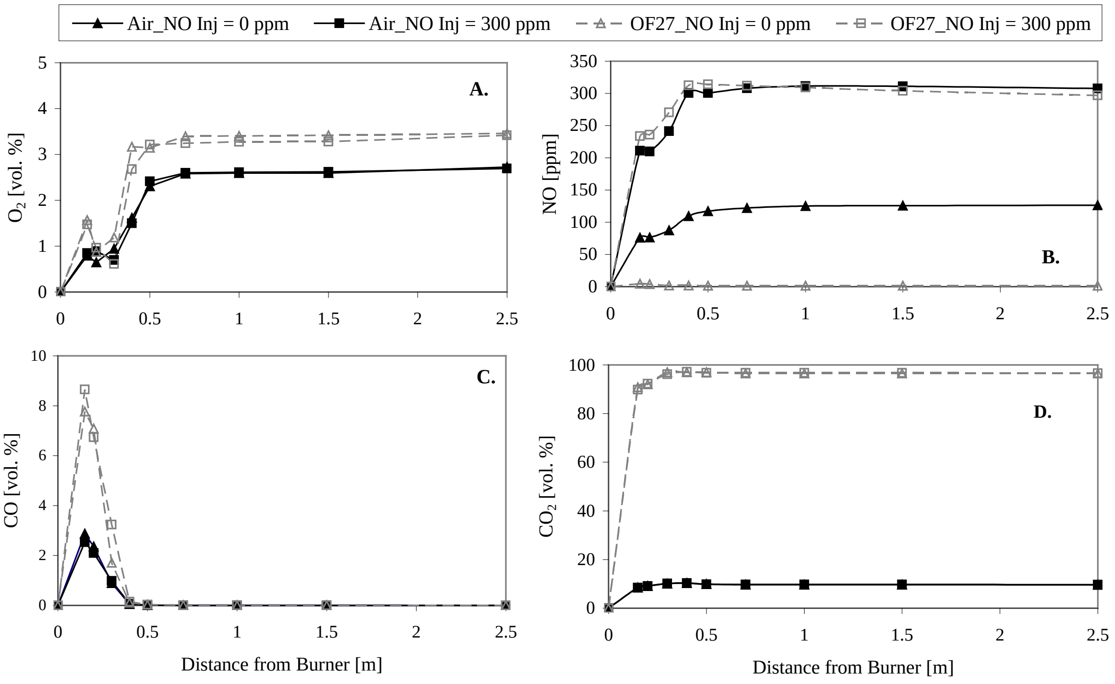


Figure 5.6: Axial (A) O_2, (B) NO, (C) CO and (D) CO_2 concentration profiles during air-blown and OF27 combustion with natural gas.

When oxygen consumption profiles between air-blown and OF27 combustion (Figure 5.6.A) are compared, there seems to be little differences except the difference due to the experimental set-up i.e. the oxygen ratio of 1.15 resulting in exit O_2 concentration of 2.74 and

3.52 vol. %. The oxygen concentration reaches a minimum value between 0.2-0.3 m from the burner for both air-blown and OF27 combustion, and reaches the experimental set-up value at 0.5 m from the burner. This indicates that the gas-phase combustion is complete by 0.5 m from the burner.

Also, as shown by Figure 5.6.B, there is no apparent difference in NO formation rate between air-blown and OF27 combustion, as NO reaches a stable value at 0.5 m from the burner for both cases. One obvious difference is the negligible NO concentration during O_2/CO_2 combustion without injection of NO. This is due to the absence of nitrogen in the fuel as well as in the oxidant which are known to form fuel and thermal NO_x.

As evident from Figure 5.6.C, the CO peak in the flame is clearly higher for OF27 combustion with a peak of around 8 vol. %. This further supports the results from coal combustion demonstrating that the concentration of CO in the near burner zone is higher for O_2/CO_2 combustion. As discussed previously, a likely reason for the elevated production of CO in the sub-stoichiometric region in a CO_2 atmosphere could be due to an enhanced reaction of CO_2 with carbon, and consumption of H_2 to produce CO by the water-gas reaction. However, the location of the peak of CO formation is similar for air-blown and OF27 combustion, indicating similarities in homogeneous combustion rate. The concentration of CO at its peak is highest for natural gas, followed by Lausitz brown coal, Rhenish brown coal, Ensdorf coal and Klein Kopje coal. This further demonstrates a relationship between gas phase combustion and the concentration of CO peak.

The CO_2 concentration as seen in Figure 5.6.D also reaches a stable level within 0.5 m from the burner, for both air-blown and OF27 combustion. Overall, one can conclude that gas phase combustion rate in a balance gas of 27% O_2/73% CO_2 by volume is similar to gas-phase reaction rate during air-blown combustion.

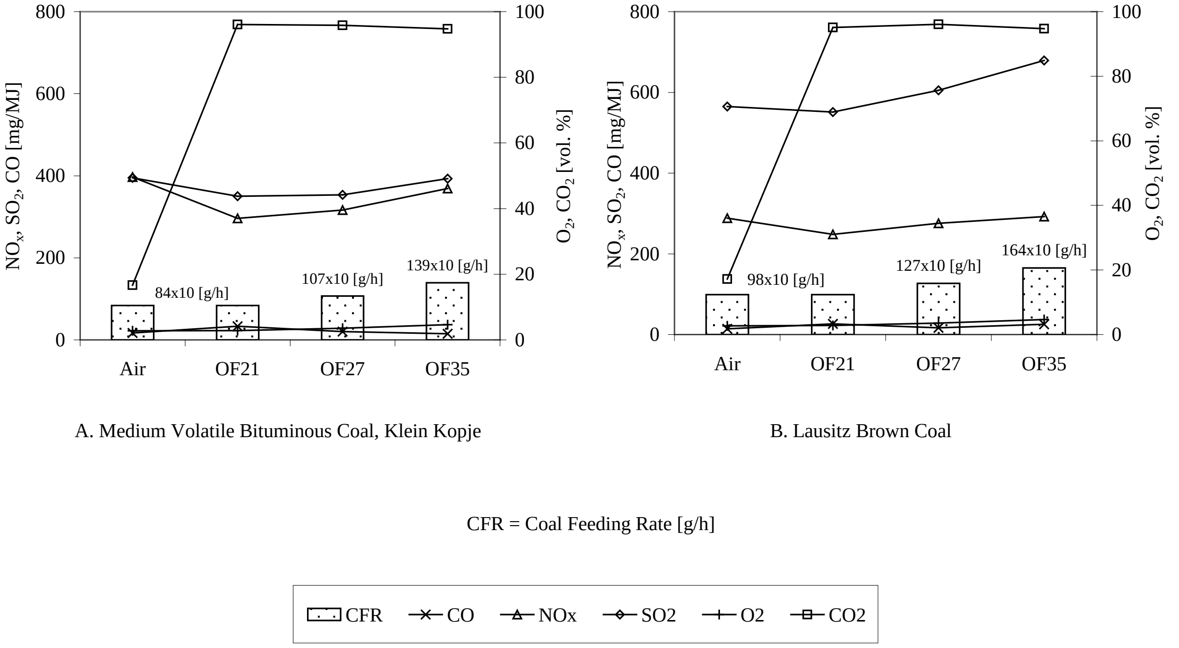
Together with the axial gaseous concentrations and flame temperature profiles during coal combustion, further supported by gas-phase measurements using natural gas, it may be concluded that oxy-coal combustion with approximately 27 vol. % oxygen gives similar combustion behaviour as air-blown combustion, and may be suitable for a retrofit with dry flue gas recirculation.

5.1.3. Emission Behaviour during O_2/CO_2 Combustion

As mentioned previously, a comparison of emission concentrations between combustion cases with a different input oxygen concentration would be unfair to cases with a higher oxygen concentration due to more fuel required when a similar gas flow and oxygen ratio are maintained. Emissions based on the mass of pollutant per energy input, referred to as the emission rate [refer to Appendix A, section A.2] are therefore used when comparing the emissions at the furnace exit. As discussed earlier, it is noted that, since this investigation was carried out in a once through furnace, the reported emission rate (especially NO_x) at the furnace exit may be different from oxy-coal combustion with flue gas recycle, where the emission rates are generally reported at the system end, downstream of the flue gas recycle location.

Figure 5.7.A and 5.7.B shows the emission rate at the furnace exit (2.5 m) during air-blown, OF21, OF27 and OF35 combustion for a medium volatile bituminous coal, Klein Kopje and the Lausitz brown coal. When combustion mode is switched from air-blown to O_2/CO_2 , the volumetric fraction of CO_2 in the flue gas approaches 95% (dry basis). It is noted that the CO_2 concentration achieved is almost equal to the theoretical maximum, as oxy-coal combustion experiments were simulated by using O_2 and CO_2 from tanks and the test facility was operated at a slightly positive pressure. As seen from air-blown and OF21 combustion cases, the NO_x emission rate at the furnace exit is lower in a CO_2 environment (25% lower for the Klein Kopje coal and 14% lower for the Lausitz brown coal). This may be directly associated with the absence of thermal NO_x and a decrease in fuel NO_x formation due to

lower flame temperature in a CO_2 environment. However, as seen from OF21, OF27 and OF35 case, increase in oxygen concentration in a CO_2 environment results in increase of NO_x emission rate. Increase in NO_x emission rate with the increase in inlet oxygen concentration may be associated with the increased flame temperature and further supports the findings of previous investigations [Cro00, Cro01, Hu00, Liu04]. As mentioned previously, increased flame temperature implies that more of nitrogen in the fuel is partitioned into the gas phase, and due to the fuel lean conditions in the devolatilisation region during un-staged combustion, more of volatile-N is oxidised to NO.



A. Medium Volatile Bituminous Coal, Klein Kopje

B. Lausitz Brown Coal

CFR = Coal Feeding Rate [g/h]

Figure 5.7: Emission rate at the furnace end during combustion with (A) medium volatile bituminous coal, Klein Kopje and (B) Lausitz brown coal.

Results from this investigation show that the SO_2 emission rate also increases with increase in oxygen concentration in a CO_2 environment. SO_2 emission rate is a function of heat input and if SO_2 captured by the ash remains constant, the SO_2 emission rate should remain constant for all oxygen concentrations. The current study is therefore unable to answer this phenomenon. However, when SO_2 emission rate during air-blown and OF21 combustion are compared, the difference is negligible, indicating that the SO_2 emission is controlled by the fuel sulphur content and not by the combustion media.

The CO emission rate, as can be seen from the figures, remains constant for all cases further indicating that controlling CO emission during oxy-coal combustion should not be more difficult than during air-blown combustion.

The NO and SO_2 emission and conversion rates during air-blown and OF27 combustion, of all 4 coals used for this investigation are compared in Figure 5.8. As seen from the figures, the NO_x and SO_2 emission rates at the furnace exit are almost similar for air-blown and OF27 combustion. It is however noted that during oxy-coal combustion with flue gas recycle, emission rates are calculated downstream of the flue gas recycle point. Furthermore, investigations have shown that some of the recirculated NO_x will be reduced in the flame [Liu05, Oka97a] during oxy-coal combustion with flue gas recycle, resulting in lower NO_x emission rate. Similarly, some SO_2 may be retained in the ash [Cro01, Kiga97, Woy95] especially in the convective section of the furnace and the flue gas recirculation path resulting in a lower SO_2 emission rate. Reduction of recycled NO depends on the combustion condition and is specific to the burner settings [Liu05]. When the temperature window is appropriate for sulphation, SO_2 retention is fuel specific and depends on the sulphate forming minerals in the ash. Detailed investigation on the fate of recycled NO and SO_2 specific to a combustion condition and a fuel is therefore necessary to fully understand and predict the emission behaviour during oxy-coal combustion. Investigations dealing with these issues are presented in Chapter 7 and 8 where a known concentration of NO and SO_2 are also injected into the furnace to simulate oxy-coal combustion with recycled flue gas.

Figure 5.8.C and 5.8.D compares the conversion of the fuel-nitrogen and the fuel-sulphur to NO and SO_2 respectively during air-blown and OF27 combustion. The percentage

conversion rate is calculated from the ratio of measured concentration of NO or SO_2 to the theoretical maximum NO or SO_2 emissions possible from the fuel-N and the fuel-S content in the coal [refer to Appendix A, section A.3]. It is noted that there will be some thermal NO as well for air-blown combustion case.

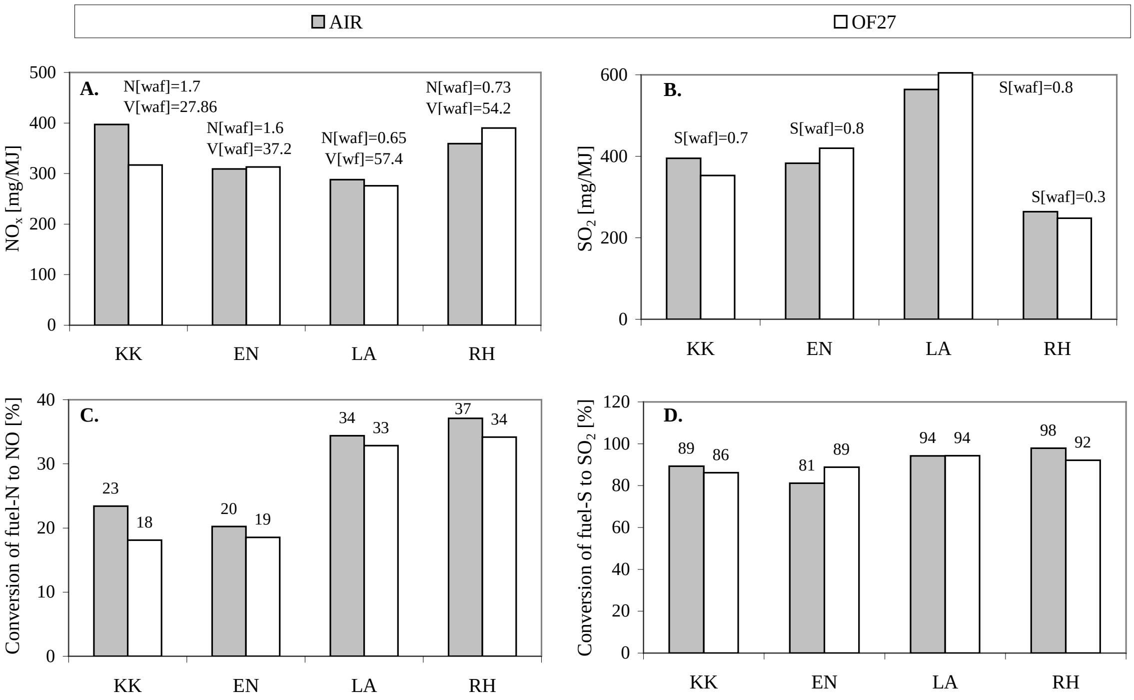


Figure 5.8: Comparison of (A) NO_x emission rate, (B) SO_2 emission rate, (C) conversion of fuel-N to NO (thermal NO for air case is included) and (D) conversion of fuel-S to SO_2 during air-blown and OF27 combustion for all four coals investigated.

The percentage conversion of fuel-N to NO, as seen from Figure 5.8.C is lower during OF27 combustion for all 4 coals, and further supports the previous findings [Kig97, Kim95, Liu04, Mac07] that the conversion of fuel-N to NO is lower in a CO_2 media. Furthermore, for an in-house built burner not optimised for low NO_x operation like the one used for this investigation, a similar conversion rate (approximately 28%) has been reported by Liu et al. [Liu04]. Similarly, previous experimental work carried out by Kluger et al. [Klu98] during air-blown combustion in the same test facility, using 21 different coals, have reported a conversion rate in the range of 20-50% during un-staged combustion, which are also in good agreement with the results from this investigation.

When the conversion of fuel-S to SO_2 for air-blown and OF27 combustion are compared [Figure 5.8.D], a definite trend could not be observed, indicating that the combustion media does not have significant influence on sulphur conversion. SO_2 measurements typically under O_2/RFG firing conditions however show a lower SO_2 emission rate [Cro01, Kig97, Woy95]. During O_2/RFG firing, SO_2 concentration in the combustion media will be much higher and this may result in suppressed conversion of fuel-S to SO_2. Investigations dealing with the possible cause of lower conversion of fuel-S to SO_2 under high CO_2 and SO_2 environment are discussed in Chapter 8.

The influence of coal property on the conversion of fuel-N to NO during OF27 combustion [Figure 5.8.C] shows a trend similar to air-blown combustion, i.e. the more the fuel-N content (for coals with comparable volatile content), the more the emission rate; and the more the volatile content (for coals with comparable fuel-N content), the more is the conversion of fuel-N to NO. When firing 21 different coals during un-staged, air-blown combustion, a similar trend was observed by Kluger et al. [Klu98] as well. Similarly, Chen et al. [Chen82] who investigated 48 coals observed an increase in NO emission by roughly 50% when the fuel-N content increased from 1 wt. % to 2 wt. % leading to a conclusion that the increase in coal nitrogen content results in increase of NO emission. Like for air-blown combustion, the influence of coal property on SO_2 emission rate is dependant on the sulphur content of the fuel i.e. the more the sulphur content in the fuel, the more the SO_2 emission rate. It can therefore be concluded that like in conventional air-blown un-staged combustion, NO_x and SO_2 emission for similar combustion condition is also dependant on the coal quality.

It is however noted that during conventional air staged combustion, more partitioning of fuel-N into the gas phase generally implies that more of nitrogen oxide can be reduced to

N_2. Investigation dealing with the formation and destruction of NO in a fuel rich environment during O_2/CO_2 combustion is therefore presented in Chapter 6.

The carbon content in the ash (CIA) and NCV loss [refer to Appendix A, section A.4] during air-blown and OF27 combustion, giving an indication of burnout and combustion efficiency is included in Figure 5.9. As can be seen, the carbon content in the ash and NCV loss [%] is in general slightly lower during OF27, indicating that ash may be a marketable product under oxy-coal combustion process as well.

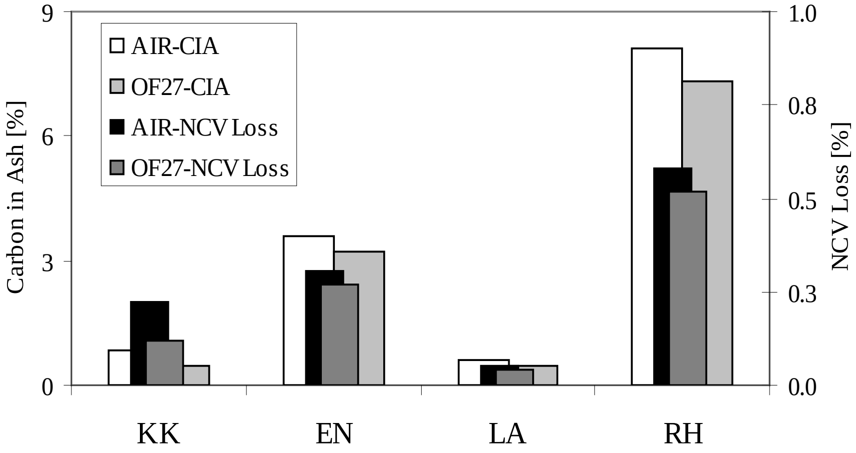


Figure 5.9: Comparison of un-burned carbon in the ash (%) and NCV loss [%] during air-blown and OF27 combustion.

5.2. SUMMARY OF RESULTS

1. For an equivalent oxygen concentration, O_2/CO_2 combustion demonstrates a delay in combustion due to the higher heat capacity of CO_2. Measures such as higher input oxygen concentration and improved mixing are therefore required to match the combustion performance of an air-fired furnace. Similar flame temperature profile and gaseous concentration profile along the length of the reactor was observed for coals as

well as natural gas firing during OF27 and air-blown combustion. The ash/char composition collected along the reactor length during coal firing was also observed to be similar for OF27 and air-blown combustion. This indicates that approximately 27 vol. % oxygen will be required during O_2/CO_2 combustion (representing oxy-coal combustion with dry flue gas recirculation) to achieve similar combustion performance of air-blown pulverised coal furnaces. The result further reinforces the findings from previous authors that oxygen concentration if properly adjusted gives the heat transfer and flame character similar to air-fired furnaces.

2. CO emission at the furnace exit during air-blown and O_2/CO_2 combustion are below 100 ppm indicating that the control of CO emission should not be any more challenging than during conventional air-blown combustion. However, higher CO peak was observed in the flame zone during O_2/CO_2 firing and could be due to enhanced CO_2 shift and water gas shift reactions in a CO_2 environment.
3. The conversion of fuel-N to NO at the furnace end for all 4 coals tested is lower in O_2/CO_2 environment. When the NO emission rate and fuel nitrogen conversion rate for different coals during un-staged OF27 combustion are compared, a trend typical to conventional air-fired, fuel lean combustion scenario was observed. That is, the higher the fuel-N content (for coals with comparable volatile content), the greater the NO emission and the higher the volatile content (for coals with comparable fuel-N content), the greater the conversion of fuel-N to NO. It is however noted that the tests were conducted in a once through furnace without flue gas recirculation.
4. Results from this investigation indicate that the combustion media (N_2 or CO_2) has little influence on the conversion of fuel-S to SO_2. SO_2 emission is dependant on the fuel type i.e. the more is the sulphur content in the fuel, the more is the SO_2 emission. However, it is noted that the tests were conducted in a once through furnace without flue gas recirculation.

5. Carbon content in the ash and NCV loss are in general lower during OF27 firing indicating that the ash can be a marketable product even during oxy-coal combustion.

CHAPTER 6

REDUCTION OF NITRIC OXIDE BY OXIDANT STAGING DURING OXY-COAL COMBUSTION

Besides the possibility of almost complete capture of CO_2, another advantage that oxy-coal firing offers is the elimination of N_2 that forms thermal NO_x, as N_2 in the air is replaced by recycled flue gas. However, NO_x emission from fuel-N, first observed by Shaw et al. [Shaw65] is considered a more important route of NO_x formation during coal combustion, as coal contains a significant amount of chemically bound nitrogen (0.5-2% by weight). Purity requirements of CO_2 for transport and sequestration are still uncertain. Researchers working in the field of CO_2 capture therefore need to investigate the measures to minimise the impurities in the furnace. Primary measures, such as air-staged and fuel-staged (re-burning) combustion have been demonstrated to be cost-effective methods in reducing NO_x emission during conventional air-blown combustion. These proven technologies have the potential to be applied to oxy-coal combustion process. This chapter therefore investigates the NO_x formation/reduction mechanisms during oxidant staged combustion, during O_2/CO_2 and air-blown combustion. Investigations in O_2/CO_2 environment were carried out with a mixture of 27% O_2 and 73% CO_2 by volume (OF27) as results from the un-staged combustion tests during OF27 combustion indicated a similar combustion and emission behaviour to that of air-blown combustion. It is however noted that as the technology matures, future applications will be with reduced flue gas recycle resulting in higher combustion temperature.

6.1. RESULTS

It is noted that, when evaluating emissions associated with O_2/CO_2 combustion, most important aspect that needs consideration is that a portion of the flue gas needs to be recycled back into the furnace for oxy-coal combustion process to moderate the flame temperature. The mass of the flue gas at the end of the system, downstream of flue gas recirculation location will therefore be much lower than at the furnace end. As mentioned previously in Chapter 4, this investigation was conducted in a once through furnace by keeping a similar volume flow through the burner, in all the experimental cases. The reported emissions in concentration at the end of the furnace at 2.5 m may therefore be lower than oxy-coal combustion with simulated flue gas recycle. Furthermore, all the measured concentrations are reported on a dry basis unless otherwise stated.

6.1.1. NO_x Formation Mechanism in a Fuel Rich Environment

As previously mentioned, conversion of fuel nitrogen in the gas phase to nitrogen oxide is the primary path for fuel NO_x formation. NO_x formed from char nitrogen offers little or no opportunity of reduction by the application of primary measures of NO_x reduction like oxidant or fuel staging. Wang et al [Wang96] and Cai et al. [Cai93] reported that, although low NO_x burners operating under the principle of oxidant staging could successfully reduce NO_x originating from nitrogen in the air and the fuel in the gas-phase, NO_x derived from the char-N component could not be successfully reduced. About 60-95% of NO_x after installation of low NO_x burner originated from the char-N component. Therefore, with the objective of improving the understanding of fuel-NO_x formation and destruction mechanisms in the gas-phase during oxy-coal combustion, axial gaseous concentration profile measurements including the measurement of HCN and NH_3 were performed.

Figure 6.1 demonstrates results of such axial concentration profile measurements for a medium volatile bituminous coal, Klein Kopje and the Lausitz brown coal during oxidant-staged combustion with a burner oxygen ratio (n_1) of 0.75 and a residence time in the reduction zone (τ_1) of 3 seconds, during air-blown and OF27 combustion.

As seen from the plots in Figure 6.1, a peak of NO is formed around 0.2 m in the oxidant-fuel mixing region and then reduces rapidly in the reduction zone along with the drop in the oxygen concentration. The mixing zone, where O_2 is not fully consumed even during fuel-rich combustion is the region where most of the coal mass and coal nitrogen are devolatilised [Bose88]. A peak of HCN is formed at approximately 0.3 m from the burner, slightly after the peak of NO (for most cases), then drops rapidly, and is fully consumed by the end of the reduction zone. NH_3 was detected only for the Lausitz brown coal, and its peak is formed slightly after the peak of HCN at approximately 0.5 m from the burner and is also fully consumed by the end of the reduction zone.

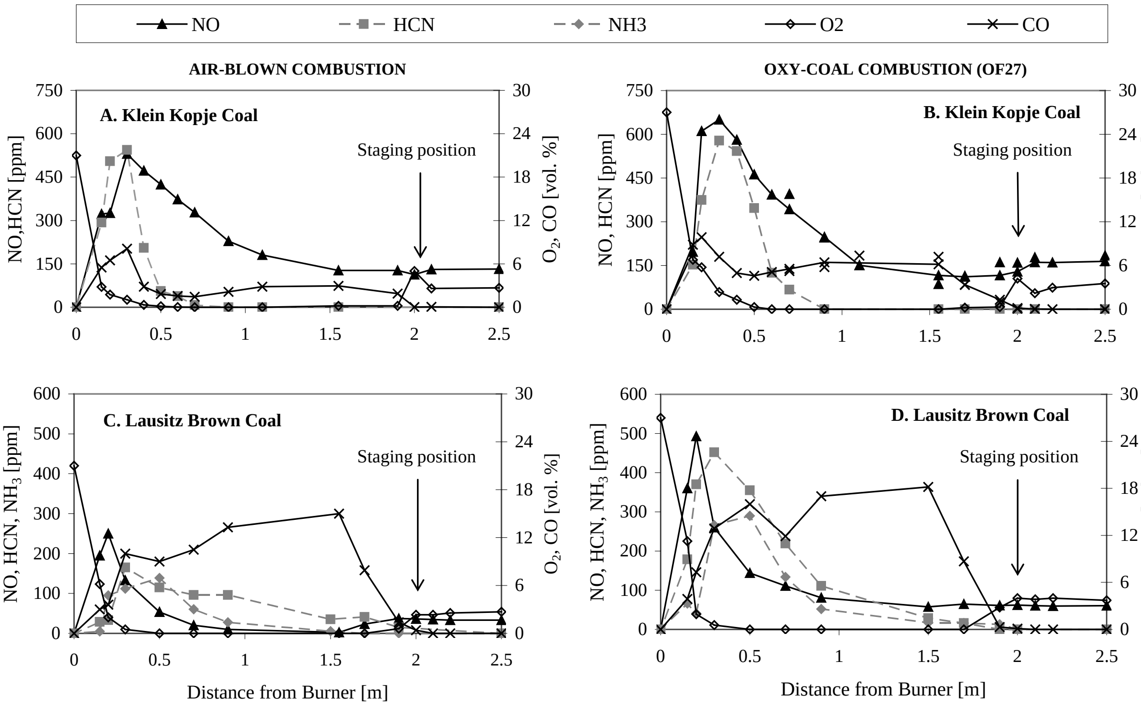


Figure 6.1: Axial gaseous concentration profile for a medium volatile bituminous coal, Klein Kopje and Lausitz brown coal during air-blown and OF27 combustion for a burner oxygen ratio of 0.75 and a residence time in reduction zone of 3 seconds.

Overall, the NO_x formation and destruction profile along with the formation and destruction of HCN and NH_3 are observed to be fundamentally similar between air-blown and O_2/CO_2 combustion. Similarities observed are discussed below and are summarised by Figure 6.2.

I. NO formed in the mixing (devolatilisation) zone reacts with free hydrocarbon radicals to produce HCN and NH_3. In fact, C_2H_2, giving an indication of the presence of free hydrocarbon radicals was detected by the FTIR only in the near burner region. Appreciable quantities of CH_4 and C_2H_2 within the near burner zone during fuel rich combustion in a N_2 environment has also been reported by Bose et al. [Bose88]. The authors have attributed the formation of HCN and NH_3 by reaction of NO with hydrocarbons. It should however be noted that tar nitrogen also contributes to the formation of some HCN and NH_3. Furthermore, for the Lausitz brown coal, as shown by the location of the peak for HCN and NH_3, it seems that HCN appears in the bulk gas phase before NH_3 for both air-blown and OF27 combustion. Although the studies were conducted only in N_2 environment, Bose et al. and Glarborg et al. [Bose88, Gla86] also reported the formation of HCN before $NH_{3.}$ However, it is not clear from the results of present study if NH_3 is formed from the decomposition of HCN or reaction of NO with hydrocarbon radicals, although Bassilakis et al. [Bas93] suggests that HCN can react with coal hydrogen in the coal pores to form NH_3.

II. HCN and NH_3 are then converted to N_2 in the oxygen deficient reduction zone.

III. Formation of HCN and NH_3 is dependent on the coal rank in a CO_2 environment as well, since the medium volatile bituminous coal (Klein Kopje) produced only HCN, while the brown coal (Lausitz) produced both HCN and NH_3. This is in agreement with most literatures, which indicates that quaternary or amino-side chain nitrogen produces NH_3 as intermediate, whereas pyridinic nitrogen (six-ring structure), the percentage of which increases with the rank of coal produces HCN [Bur94, Chen83, Klu98, Nik94, Nor97].

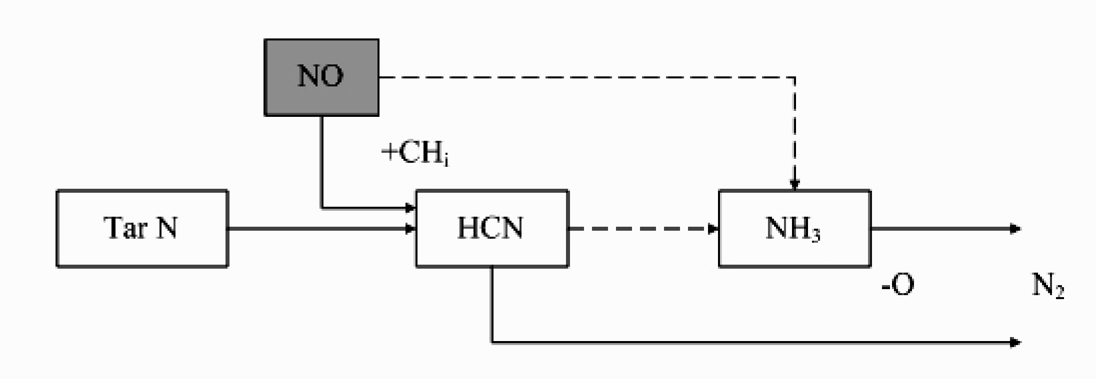


Figure 6.2: Overall fuel-NO reduction route during fuel-rich condition.

For the evaluation of the influence of burner oxygen ratio (n_1) on NO_x formation mechanism during OF27 combustion, NO, HCN and CO concentration profiles when firing a medium volatile bituminous coal, Klein Kopje for a burner oxygen ratio of 0.75, 0.85 and 0.95 with a residence time in the reduction zone of 3 seconds, during air-blown and OF27 combustion are included in Figure 6.3.

As seen from Figure 6.3.A, the lower the burner oxygen ratio, the lower the final NO concentration, for both air-blown and OF27 combustion. This further demonstrates the similarities on NO formation mechanisms in a N_2 and a CO_2 environment. A peak of NO is formed in the fuel-oxidant mixing zone for all experimental conditions included in Figure 6.3.A, as sufficient oxygen is still present in this region. The location of NO peak, for most cases, is slightly delayed for OF27 combustion. The NO reduction rate in the oxygen depleted, sub-stoichiometric region is slightly higher for OF27 combustion for a corresponding burner oxygen ratio (0.76 vs. 0.80 for n_1=0.75, 0.61 vs. 0.73 for n_1=0.85 and 0.52 vs. 0.48 for n_1=0.95). NO reduction rate was calculated by considering the NO concentration at the location of the peak and the NO concentration at the end of reduction zone at 1.9 m from the burner. Higher NO reduction rate during O_2/CO_2 combustion may be due to the presence of higher concentration of hydrocarbon radicals. The final NO concentration at the end of the furnace, however is slightly higher for OF27 combustion, but emissions at the furnace end cannot be compared directly in concentrations, and is discussed separately in section 6.1.2.

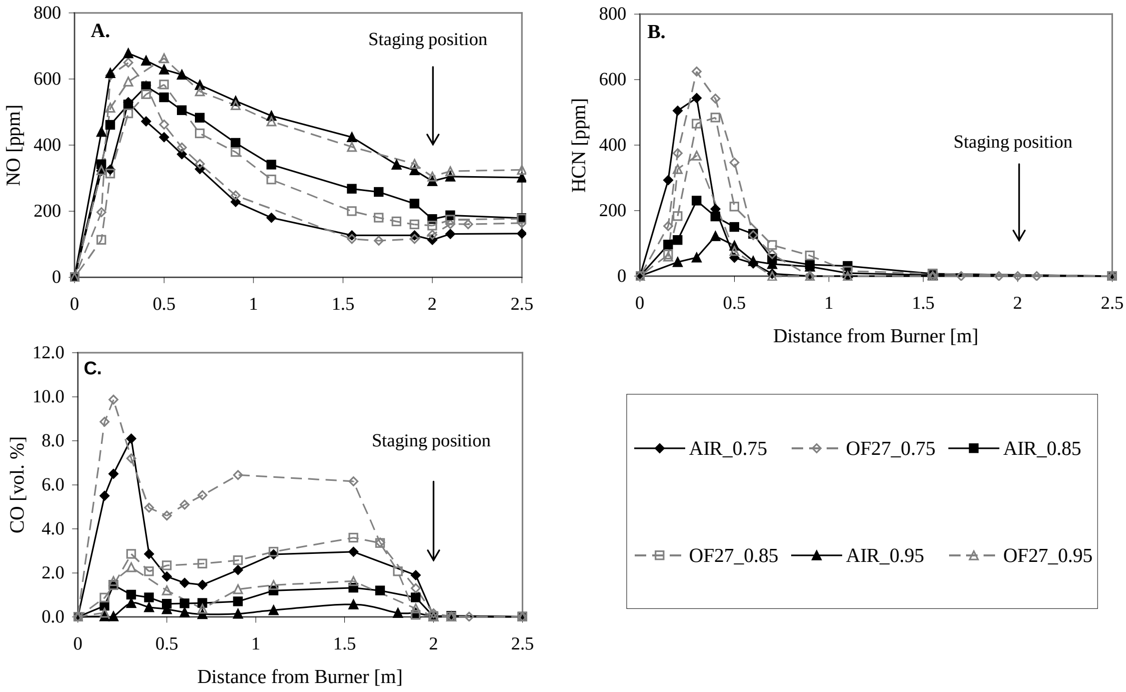


Figure 6.3: Comparison of (A) NO, (B) HCN and (C) CO concentration profiles during combustion with a medium volatile bituminous coal Klein Kopje for different burner oxygen ratios and a residence time in reduction zone of 3 seconds.

As can be seen from Figure 6.3.B, the HCN concentration for a particular burner oxygen ratio is higher for OF27 combustion. Higher HCN concentration corresponds well with a higher reduction rate of NO in the sub-stoichiometric region for OF27 combustion, as NO formed in the mixing zone is primarily reduced to HCN by the reaction with hydrocarbon radicals. A higher HCN concentration was measured for combustion with a lower burner oxygen ratio. NO concentration at the furnace exit on the other hand is lower for lower burner oxygen ratio, suggesting that, the more the formation of HCN, the lower the final NO concentration will be. As is the case with conventional air firing, this further supports the suggestions that NO formed in the mixing zone reacts with hydrocarbon radicals to produce HCN, which in turn is converted to N_2 during fuel-rich combustion. Also, after the formation of a peak in the flame zone, the HCN concentration decreases rapidly and is almost fully consumed at approximately 1.1 m from the burner. The NO concentration on the other hand continues to decrease (although at lower rate especially for n_1= 0.75 case) even after 1.1 m from the burner, until the final section of reduction zone. This may be due to heterogeneous reductions with active carbon sites in the char.

The emissions of CO at the furnace exit as seen from Figure 6.3.C is negligible for all measurements (lower than 100 ppm), during air-blown as well as OF27 combustion. This indicates that controlling the CO emissions, even during oxidant staged, oxy-coal combustion should not be more difficult than during air-blown combustion. However, CO concentrations in the sub-stoichiometric zone are higher for oxy-coal combustion for a similar burner oxygen ratio, and exhibits a CO peak of approximately 10 vol. % during combustion with n_1=0.75. A likely reason, for the elevated production of CO in the sub-stoichiometric region in CO_2 atmosphere, as mentioned in Chapter 5 could be due to an enhanced reaction of CO_2 with carbon and consumption of H_2 to produce CO by the water-gas reaction, as given by reactions R3.20 and R3.21 in section 3.2.5.

Similarly, Figure 6.4 shows the NO, HCN, NH_3 and CO concentration profile of the Lausitz brown coal, during oxidant staged combustion with a burner oxygen ratio of 0.75, 0.85 and 0.95 and a residence time in the reduction zone of 3 seconds, for air-blown and OF27 combustion. As with the case of Klein Kopje coal, a lower burner oxygen ratio results in a lower NO concentration at the furnace exit for OF27 combustion as well, further establishing that NO formation and destruction mechanisms during OF27 combustion is similar to air-blown combustion. Except for combustion with a burner oxygen ratio of 0.75, the peak of NO in the mixing region is higher for OF27 combustion for this coal as well. However, a delay in the formation of NO peak during OF27 combustion is more apparent for this coal. The NO reduction rate, calculated from the difference in the peak of NO and the NO concentration at the end of the reduction zone is also generally higher for OF27 combustion, and corresponds well with higher concentrations of HCN and NH_3. The HCN and NH_3 concentration reaches a peak in the near burner region, diminish rapidly and become negligible after 0.9 m from the burner. Except for n_1=0.95, the NO concentration also ceases to decrease after approximately 0.9 m from the burner, for both air-blown and OF27 combustion. This implies that, not only a negligible amount of NO is reduced to HCN and NH_3 beyond this point; the reduction of NO by the active char surface within the char is also negligible.

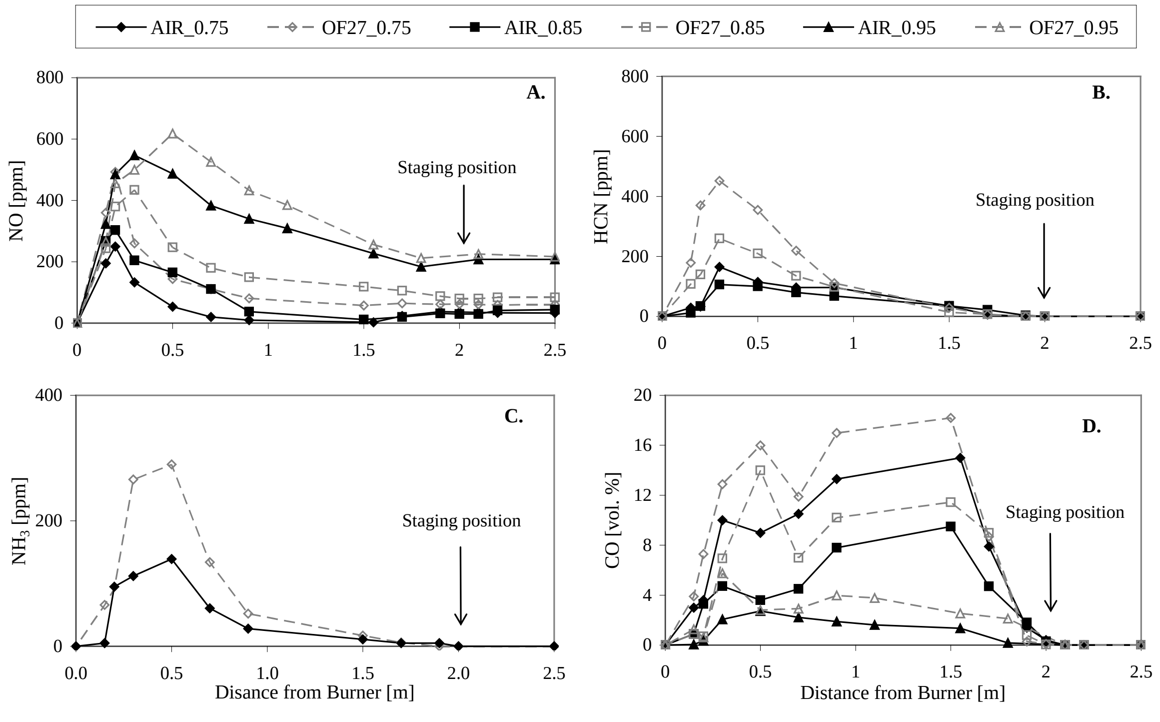


Figure 6.4: Comparison of (A) NO, (B) HCN, (C) NH_3 and (D) CO concentration profiles during combustion with Lausitz brown coal for different burner oxygen ratios and a residence time in reduction zone of 3 seconds.

As with a medium volatile bituminous coal, Klein Kopje, the CO concentrations at the furnace exit as seen from Figure 6.4.D is negligible for all burner oxygen ratios (lower than 100 ppm), during air-blown and OF27 combustion. Like for Klein Kopje coal, the CO concentration in the sub-stoichiometric zone is however higher during OF27 combustion for a similar burner oxygen ratio (n_1).

The NO and CO concentration profiles of all 4 coals during oxidant staged combustion with a burner oxygen ratio of 0.75 and a residence time in the reduction zone of 3 seconds, for air-blown and OF27 combustion, are compared in Figure 6.5. As seen from Figure 6.5.A and Figure 6.5.C, which compares the NO concentration profile of all 4 coals during air-blown and OF27 combustion, the highest peak of NO was measured for a high volatile bituminous coal Ensdorf, and the lowest peak was measured for the Lausitz brown coal. The extent of the NO peak, or the extent of fuel-N released in the gas-phase is seen to be dependent on the volatile and the nitrogen content of the coal. In general, it is seen that, for coals with almost similar nitrogen content (Ensdorf and Klein Kopje), the coal with a higher volatile content (Ensdorf) results in a higher NO peak formation, i.e. releases more fuel-N via the gas phase. Alternatively, for coals with almost similar volatile content (Lausitz and Rhenish brown coals), the coal with lower nitrogen content (Lausitz brown coal) results in lower NO peak. The reduction of NO formed in the mixing region on the other hand is a function of the volatile content or alternatively a function of hydrocarbon radicals available in the gas phase, as the medium volatile bituminous coal, Klein Kopje displays the lowest reduction and the Lausitz brown coal with highest volatile content displays the maximum NO reduction. Kluger et al. [Klu98] have also reported a stronger decrease in the NO concentration during air-staged combustion with coals containing higher volatile content, or coals that release more fuel-N via the gas phase. Investigations have demonstrated that a higher fraction of the fuel-N can be partitioned towards the gas phase by increasing the flame temperature. Manipulation of flame temperature is considered to be simpler during oxy-coal combustion as flame temperature is a function of oxygen concentration. Direct injection of O_2 in the flame (without affecting the overall heat transfer performance) by taking advantage of existing infrastructure of an oxy-fuel plant in order to increase the devolatilisation rate could be one viable option for further reduction of NO during oxidant staged combustion. Low oxygen enrichment by direct injection of O_2 has been demonstrated to be a successful in furnace NO_x reduction option during air-blown combustion [Cha04b].

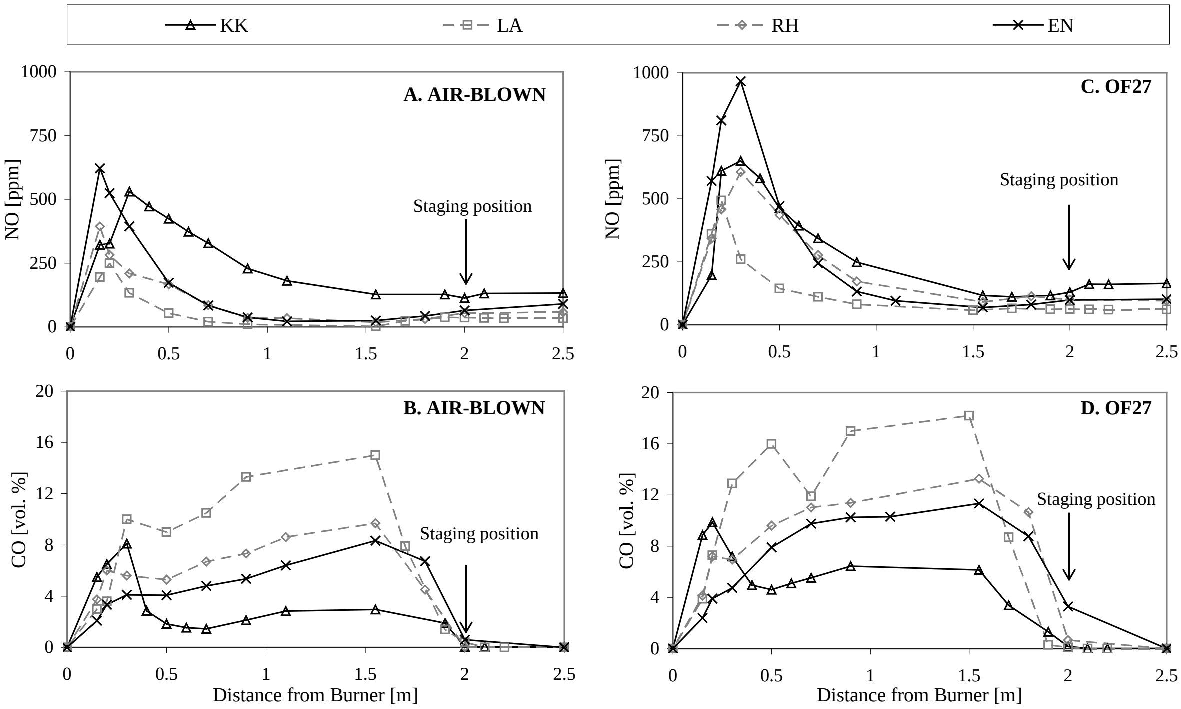


Figure 6.5: Comparison of NO and CO concentration profiles of all four coals during combustion with a burner oxygen ratio of 0.75 and a residence time in the reduction zone of 3 seconds.

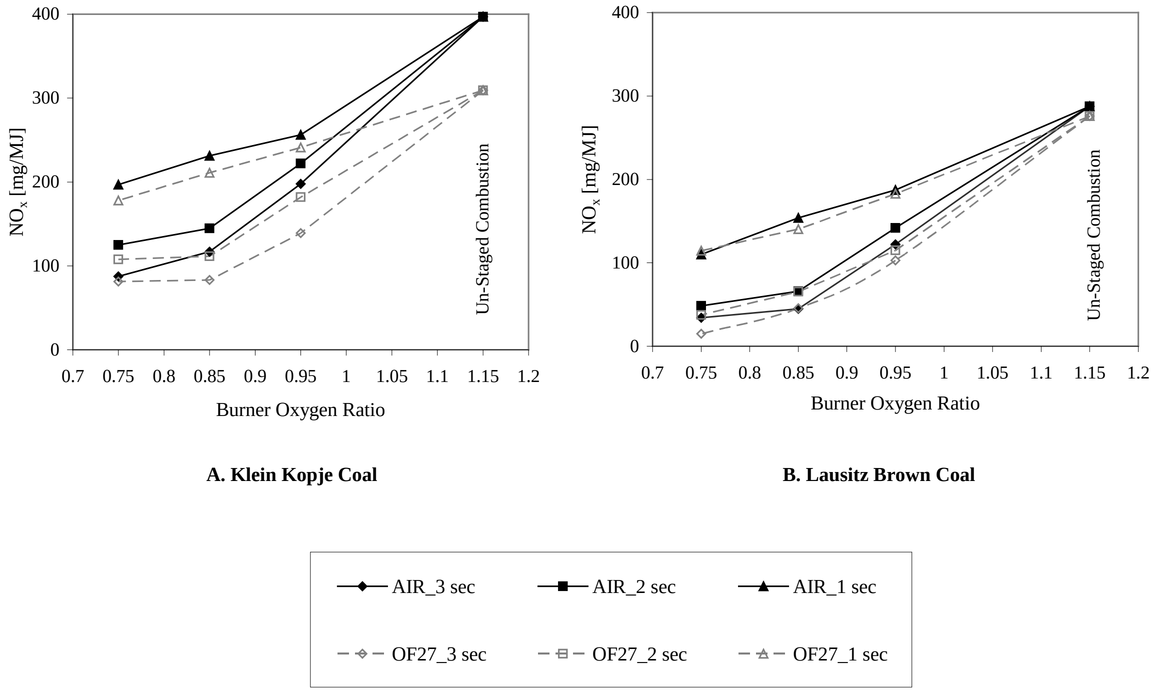
The CO concentration profile, as included in Figure 6.5.B and 6.5.D, reaches a value of less than 100 ppm for all coals at the reactor exit, further establishing that controlling CO emissions should not be any more challenging than in air-blown combustion. However, like during un-staged combustion, the CO peak is much higher for high volatile coals and seems to be a function of the coal rank. As mentioned previously in Chapter 5, a higher volatile content in a coal generally imply that more of the hydrocarbons are released via the gas phase, a large part of which are then immediately converted to CO, therefore forming a higher CO peak. Whereas, for lower volatile coals, carbon is released gradually by heterogeneous reactions, therefore avoids a high CO peak. Furthermore, the volatiles from bituminous coals mainly contain soot-producing heavy hydrocarbons, whereas the volatiles of brown coals mainly contain CO, CO_2, H_2, H_2O and light hydrocarbons [Bej07, Chen92, Fre82]. This could be another reason for the higher CO peak for pre-dried brown coals.

6.1.2. NO_x Emission Rate at the Furnace End

As mentioned previously in Chapter 5, a comparison of emission concentrations between combustion cases with a different input oxygen concentration would be unfair to cases with a higher oxygen concentration due to more fuel input when a similar gas flow and oxygen ratio are maintained. Emission based on the mass of pollutant per energy input, referred to as the emission rate [refer to Appendix A, section A.2] is therefore used when comparing the emissions at the furnace exit. As discussed earlier, it is noted that, since this investigation was carried out in a once through furnace, the reported emission rate (especially NO_x) at the furnace exit may be different from oxy-coal combustion with flue gas recycle, where the emission rates are generally reported at the system end, downstream of the flue gas recycle location.

Figure 6.6.A and Figure 6.6.B shows the influence of burner oxygen ratio and residence time in the reduction zone on NO_x emission rates for a medium volatile bituminous coal, Klein Kopje and the Lausitz brown coal, during air-blown and OF27 combustion. As can be seen, for a similar burner oxygen ratio and a residence time in the reduction zone, the NO_x emission rate is generally lower during O_2/CO_2 combustion for both coals. The similarities

observed when one compares the NO_x emissions between conventional air-staged combustion and O_2/CO_2 combustion in Figure 6.6.A and 6.6.B are as follows:



A. Klein Kopje Coal

B. Lausitz Brown Coal

Figure 6.6: NO_x emission rate during staged combustion for air-blown and OF27 combustion using (A) medium volatile bituminous coal, Klein Kopje and (B) Lausitz brown coal.

I. The NO_x emission rates also decreases with a decrease in burner oxygen ratio and an increase in residence time in the reduction zone for O_2/CO_2 combustion. When compared to un-staged combustion, NO_x reduction of approximately 75% and 90% can be achieved with a medium volatile bituminous coal Klein Kopje and the Lausitz brown coal respectively.

II. The NO_x emission rate is lower for Lausitz brown coal when compared to a medium volatile bituminous coal (Klein Kopje) during O_2/CO_2 combustion as well. This finding further supports the well-established experience that NO_x reduction efficiency during oxidant staged combustion is highly dependent on the coal rank, with coals partitioning more fuel-N into the gas-phase reducing more NO_x.

As seen from Figure 6.6.A, the optimum burner oxygen ratio that results in a minimum NO_x emission rate for Klein Kopje coal during OF27 combustion is around 0.85 when the residence time in the reduction zone is greater than 2 seconds. However, for the Lausitz brown coal, the optimum burner oxygen ratio resulting in minimum NO_x emission rate during OF27 combustion may be lower than 0.75, as indicated by the trend lines in Figure 6.6.B. A low burner oxygen ratio especially for medium to low volatile hard coals could be an issue in achieving efficient burnout. Brown coals, such as Lausitz brown coal have shown a negligible influence of burner oxygen ratio on burnout even up to burner oxygen ratio of 0.65 [Gre98] during air-staged combustion. This indicates that, if necessary, a lower NO_x emission rate for the Lausitz brown coal during OF27 combustion can be achieved by further decreasing the burner oxygen ratio below 0.75, without causing severe burn out problem.

Table 6.1: Conversion of fuel-N to NO [%].

	Medium Volatile Bituminous Coal, Klein Kopje						**Lausitz Brown Coal**					
	Air-Blown Combustion			**OF27**			**Air-Blown Combustion**			**OF27**		
Un-staged Combustion							**Un-staged Combustion**					
n=1.15	23			18			34			33		
Staged Combustion							**Staged Combustion**					
τ_1 n_1	**3 sec**	**2 sec**	**1 sec**	**3 sec**	**2 sec**	**1 sec**	**3 sec**	**2 sec**	**1 sec**	**3 sec**	**2 sec**	**1 sec**
0.95	12	13	15	8	11	14	15	17	22	12	14	22
0.85	7	8	14	5	7	12	5	8	18	5	8	17
0.75	5	7	12	5	6	10	4	6	13	3	4	14

The percentage conversion of fuel-N to NO during un-staged as well as staged combustion for a medium volatile bituminous coal, Klein Kopje and the Lausitz brown coal is included in Table 6.1. Both coals exhibit a lower fuel-N to NO conversion during OF27 combustion, for a similar burner oxygen ratio and residence time in the reduction zone. This is in agreement with Liu et al. [Liu04, Liu05] and Mackrory et al. [Mac07], who have also reported a lower conversion rate during staged as well as un-staged combustion. The percentage conversion rate is calculated from the ratio of measured concentration of NO at the furnace exit to the theoretical maximum NO emission possible from fuel-N content in the coal [refer to Appendix A, section A.3]. It is noted that there will be some thermal NO as well for air-blown combustion case.

It is recognised that the burner used in the 20 kW test facility to conduct the present study has not been optimised for low NO_x. However, it is noted that previous experimental work carried out by Kluger et al. [Klu98] during air-blown combustion in the same test facility, using 21 different coals, have reported a conversion rate in the range of 20-50% during un-staged combustion. A conversion rate below 10% during staged combustion with a burner oxygen ratio of 0.75 and a residence time in reduction zone of 3 seconds was also reported. It is in agreement with this investigation, therefore adds support to the previous experimental work conducted by Kluger et al. [Klu98] and also demonstrates the reliability of the measurements produced.

To investigate the influence of coal property during oxidant staged combustion, Figure 6.7 compares the NO_x emission rate, conversion of fuel-N to NO, mass fraction of carbon in the ash and NCV loss for all 4 coals during air-blown and OF27 combustion. The measurements were conducted with a burner oxygen ratio of 0.75 and a residence time in the reduction zone of 3 seconds.

As seen from the figure, except for the Rhenish brown coal, NO_x emission rate at the furnace exit during OF27 firing is lower than air-blown combustion. The percentage conversion of fuel-N to NO as shown by Figure 6.7.B is also lower during OF27 firing, except for the Rhenish brown coal.

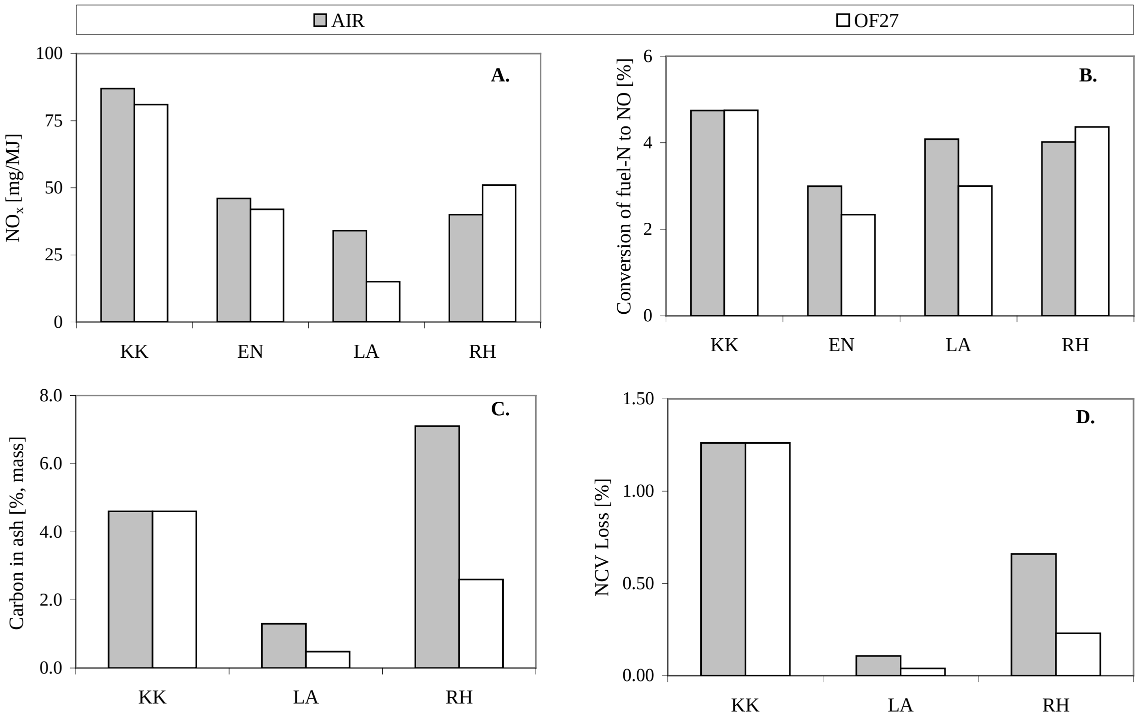


Figure 6.7: (A) NO_x emission rate, (B) Conversion of fuel-N to NO (thermal NO for air case is included), (C) Carbon in ash and (D) NCV Loss for different coals during air-blown and OF27 combustion with a burner oxygen ratio of 0.75 and a residence time in reduction zone of 3 seconds.

Similarly, the carbon content in the ash and NCV loss [refer to Appendix A, section A.4] during air-blown and OF27 combustion as shown by Figure 6.7.C and Figure 6.7.D, giving an indication of burnout efficiency is in general lower during OF27 firing. This indicates that the ash can be a marketable product even under oxy-coal combustion. The carbon content of the Rhenish brown coal is higher than other coals and might be due to a larger particle size distribution of this coal. However, the NCV loss for this coal is lower than that of the medium volatile bituminous coal, Klein Kopje. The carbon content and NCV loss of the medium volatile bituminous coal, Klein Kopje on the other hand is higher than Lausitz brown coal during air-blown and OF27 combustion. Increase in the un-burned carbon from 1.5% during un-staged combustion to 6.5% during air staged combustion with a burner oxygen ratio of 0.65 for a medium volatile bituminous coal have been reported by Greul et al. [Gre96a]. Controlling the carbon content in the ash even for a medium volatile coal Klein Kopje is therefore thought not to be any more challenging than air-blown combustion as carbon content in the ash is around 4.6% for air-staged combustion.

When the NO emission rate is compared between different coals during OF27 combustion, a trend typical to conventional air-staged combustion was observed. That is, the higher the fuel-N content, the greater the emission rate, and the more the volatile content (or the partitioning of fuel-N into the gas phase), the more is the reduction efficiency of NO_x. On the other hand, lower the volatile content (for coals with comparable fuel-N content) or lower the partitioning of fuel-N into the gas phase, lower is the reduction efficiency. This finding is consistent with most experimental investigations carried out during air-staged combustion [Gre96a, Klu98], which report that higher volatile content in a coal implies that more nitrogen in the fuel is partitioned towards the gas phase, which in turn are reduced to N_2 in oxygen deficient, reducing zone resulting in higher NO_x reduction efficiency.

Together with the results of in-furnace NO_x formation mechanisms discussed in section 6.1.1 and the impact of coal type on NO_x emission and conversion rate during air-blown and OF27 combustion as discussed in section 6.1.2, it is concluded that NO_x formation and destruction mechanisms during OF27 combustion are similar to air-blown combustion. Moreover, if required the state of the art in furnace NO_x reduction technologies applied in conventional air-fired pulverised fuel furnaces can also be applied for oxy-coal combustion.

6.2. SUMMARY OF RESULTS

1. The fuel NO_x formation mechanisms during fuel rich combustion, demonstrated by the formation and destruction of HCN and NH_3 is similar for air and O_2/CO_2 combustion, as the NO that is formed in the mixing zone reacts with hydrocarbon radicals to

produce HCN or NH_3. They are then converted to N_2 in the oxygen deficient reduction zone. As with conventional air-blown combustion, the formation of HCN and NH_3 is dependent on the coal rank, as only HCN was detected for a medium volatile bituminous coal Klein Kopje, while both HCN and NH_3 were detected for the Lausitz brown coal.

2. The reduction rate of NO formed in the fuel-oxidant mixing zone is generally higher for OF27 combustion, and is most likely due to the higher concentration of hydrocarbon radicals in the flame during OF27 combustion. Higher concentration of HCN and NH_3 during OF27 firing further indicates more reduction of NO formed in the mixing zone to HCN and NH_3. The influence of burner oxygen ratio on the amount of HCN and NH_3 formed is however similar for air-blown and OF27 combustion, i.e. lower the burner oxygen ratio, higher the concentration of HCN and NH_3. In other words, lower the burner oxygen ratio, more of NO formed in the mixing zone is reduced to HCN and NH_3, which in turn are converted to N_2 resulting in lower NO emission, and is consistent with the NO emission at the furnace end.
3. CO concentration at the furnace exit for all measurements were below 100 ppm, indicating that control of CO emission should not be any more challenging than for conventional air-blown combustion, even for staged combustion. However, higher CO peak was observed in the sub-stoichiometric region during O_2/CO_2 firing and may be due to enhanced CO_2 shift and water gas shift reactions in the CO_2 environment.
4. Oxidant staging for NO_x reduction is equally or even more effective for O_2/CO_2 combustion in terms of the NO_x reduction potential, as the conversion of fuel-N to NO and NO_x emission rate is lower than corresponding air-blown combustion. Furthermore, as observed for air-blown combustion, the reduction of NO is proportional to the partitioning of fuel-N into the gas-phase. This is an encouraging result from oxy-coal combustion perspective, as the amount of fuel-N partitioned to

the gas-phase is a function of temperature and manipulation of local temperature with oxygen is considered much simpler during oxy-coal combustion. Direct injection of O_2 in the flame (without affecting the overall heat transfer performance) in order to increase the devolatilisation rate could be one viable option that can take advantage of existing infrastructure of an oxy-fuel plant for further reduction of NO.

5. The carbon content in the ash and NCV loss during air-blown and OF27 combustion, giving an indication of burnout and combustion efficiency of a combustion process, is in general lower during OF27 firing. This indicates that ash can be a marketable product even during oxidant-staged, oxy-coal combustion.

CHAPTER 7

FATE OF RECYCLED NITROGEN OXIDE DURING OXY-COAL COMBUSTION

During oxy-coal combustion, when flue gas is recycled back into the furnace, pollutants like NO_x, SO_x, CO, etc., are also recycled back along with CO_2 and/or water vapour (depending on wet or dry recirculation mode). The recycled flue gas not only influences the combustion performance, but also effects the formation and destruction of pollutants. Furthermore, due to the recirculation of flue gas, the pollutants tend to accumulate in the furnace. In depth understanding of the fate of pollutants recycled back into the furnace and their effect on the boiler performance is therefore required. The aim of this chapter is to investigate the fate of recycled NO during oxy-coal combustion, and compare the findings with conventional air-blown combustion. This is thought to not only enhance the knowledge on so called NO_x re-burning mechanism during oxy-coal combustion but may also support on the design of a low NO_x oxy-coal burner, and assess the requirements of flue gas clean-up devices like SCR, if required.

7.1. RESULTS

As mentioned in the description of the test facility in Chapter 4, this investigation was carried out in a once through furnace and recirculated NO was simulated by injecting a known concentration of pure NO either via the burner or via the over-fire port, as shown in Figure 4.1. The term ‘NO injected’ used throughout this section is the concentration of NO measured at the furnace end when NO is injected via the burner or the over fire port, without combustion of fuel. The calculation method of another term used throughout this section, i.e. the percentage reduction of recycled NO is presented in Appendix A, section A.5.

Furthermore, when assessing the fate of NO injected via the over-fire port, it is noted that a longer residence time in the reduction zone results in NO injection position being further away from the burner or the flame, and the injected NO having a shorter time in the burn out region [Figure 7.1]. Furthermore, all the emission concentrations are reported on a dry basis unless otherwise stated.

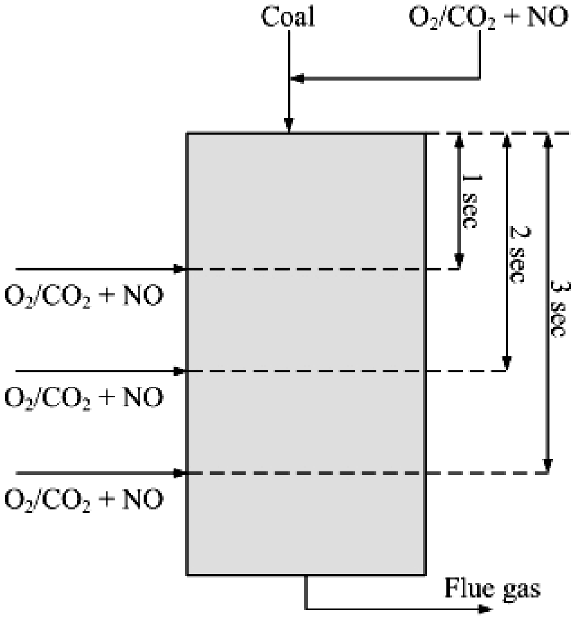
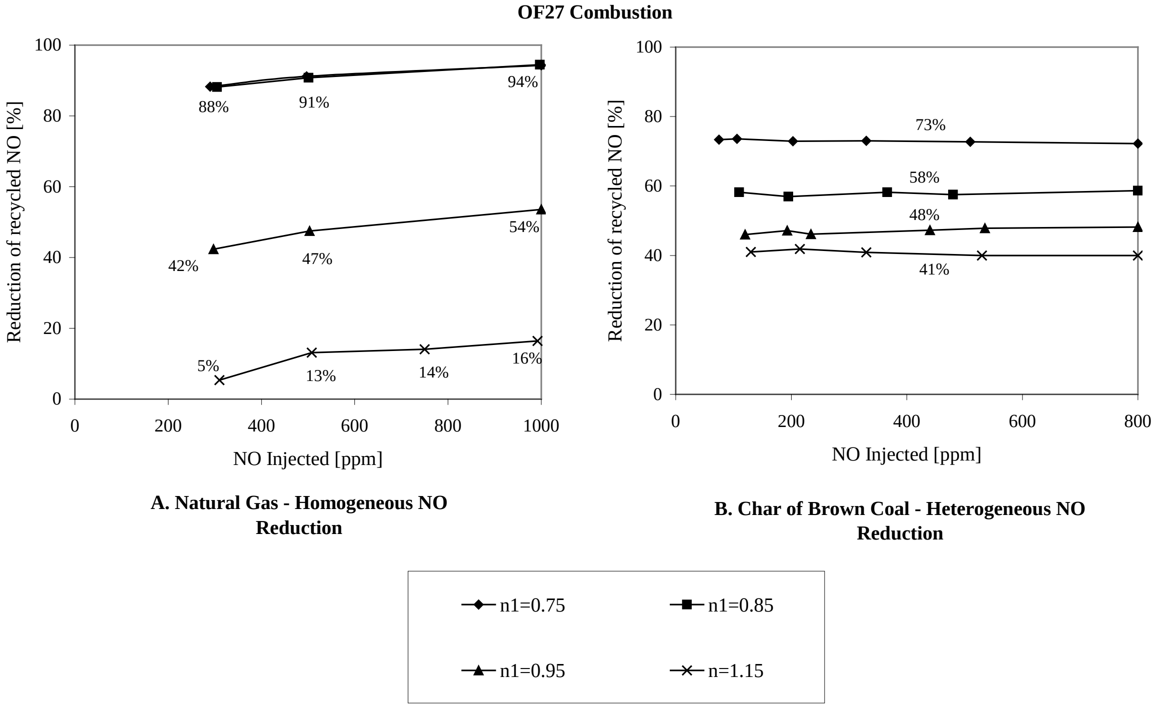


Figure 7.1: Schematic of NO injection position via the over-fire port at different residence time in the reduction zone.

7.1.1. Fate of NO Injected via the Burner

Figure 7.2.A shows the percentage reduction of recycled NO during OF27 combustion with natural gas, which predominantly consists of CH_4, and Figure 7.2.B shows the reduction of recycled NO during OF27 combustion with the char of brown coal, predominantly consisting of carbon. The reduction of the recycled NO during combustion of natural gas provides an indication of reductions taking place by homogeneous reactions, whereas

combustion with char of brown coal gives an indication of reductions by heterogeneous reactions.



A. Natural Gas - Homogeneous NO Reduction

B. Char of Brown Coal - Heterogeneous NO Reduction

Figure 7.2: Reduction of recycled NO during OF27 combustion with (A) natural gas and (B) char of brown coal.

As seen from Figure 7.2, during un-staged combustion (n=1.15), when oxygen availability is significant, the percentage reduction of recycled NO is about 3 times higher for char combustion (reduction efficiency of around 45% during char combustion vs. 15% during natural gas combustion). This indicates that heterogeneous reactions with char play a more important role on the reduction of recycled NO during un-staged combustion. The reduction of NO by carbon, as stated previously in Chapter 3, is probably through dissociation of NO on the char surface, with rapid surface dissociation of the dissociated atoms to form N_2. Investigations focusing on homogeneous and heterogeneous reduction of NO in oxygen rich conditions could not be found in open literatures, even for pulverised coal, air-blown combustion. Most investigations focus on NO reduction during fuel staging or oxidant staging, reflecting reductions in a fuel rich, oxygen deficient environment. However, a study conducted by Chambrion et al. [Cha98] on the C-NO reactions in the presence of O_2 at an experimental condition of 850°C indicate that the presence of O_2 greatly enhances NO reduction rate, while the N_2 and N_2O production rate also increases as the reactivity of C(N) accumulated on char surface is increased by O_2 gasification, resulting in a higher N_2 formation rate. Although, not applicable for a pulverised coal combustion case where the flame temperature is much higher than 850°C, it is a strong indication that heterogeneous reduction of NO may be more prominent during oxygen rich, fuel lean combustion. As reactions between NO and char has been reported to be enhanced in the presence of CO [Levi81, Mas92], the presence of high concentration of CO in the near burner region could be another factor for enhanced reduction of NO with char. Furthermore, a study by Molina et al. [Mol02] in 2002 for an air-blown combustion scenario suggests that the reaction rate of NO with char is approximately two times higher than previous studies and acknowledge that the of role of char on NO reduction might have been under predicted. On the other hand, when oxygen concentration is high, a large part of CH_4, which is dominant in natural gas, is oxidised to CH_3, CH_2O, HCO and finally to CO [Kil92]. Therefore, less of active hydrocarbon derived radicals are available for reaction with NO, consequently diminishing the NO reduction efficiency by homogeneous reactions. However, during staged combustion with a burner oxygen ratio of 0.95, the reduction of recycled NO during char and natural gas combustion are almost similar [Figure 7.2]. As oxygen availability decreases further with a decrease in the burner oxygen ratio to 0.85 and 0.75, reduction of recycled NO is approximately 20% higher during natural gas firing, with percentage reduction of almost 90%. This might be due to the presence of higher concentration of active hydrocarbon radicals in fuel rich conditions, enhancing the reduction of recycled NO. Bose et al. [Bose88] have also reported an enhanced reaction between the NO formed in the flame zone and hydrocarbon radicals when the concentration of the later is sufficiently high. It is noted that the study was conducted in an air-firing environment. Investigations carried out by Wendt et al. [Wen73], Sarofim et al. [Sar78], Song et al. [Song81] and Kilpinen et al. [Kil92] have also confirmed reactions between hydrocarbon radicals and nitrogen oxide in air firing combustion environment. The reactions were observed to be more significant in fuel-rich flames. During 21% O_2/79% CO_2 combustion with a CH_4 flame, increase in reduction of recycled NO from 30% with a burner oxygen ratio of 1.2 to 60% at a burner oxygen ratio of 0.7 have also been reported by Okazaki et al. [Oka97a]. Furthermore, Figure 7.2.A and 7.2.B exhibits a slight increase in the percentage reduction of recycled NO with increased NO injection for natural gas. However, the percentage reduction of recycled NO remains almost constant for char up to 800 ppm of NO injection, indicating that the reduction efficiency is independent of the concentration of recycled NO.

The result from this investigation further demonstrates the relative importance of homogeneous and heterogeneous reduction of recycled NO at different combustion conditions. It is none the less noted that, the hydrocarbon radicals formed in the flame during natural gas combustion do not precisely represent the devolatilised products during coal combustion. Besides hydrocarbon radicals, the devolatilised products during coal combustion also contain tar nitrogen and other gaseous nitrogen containing components. Investigations conducted by Greul et al. [Gre95] during re-burning experiments for air-blown combustion using different re-burn gases indicate a much higher reduction of NO formed in the flame zone, when tar containing pyrolysis gas was used as a re-burn fuel. When CH_4 (similar to natural gas used for the present investigation) was used as a re-burn fuel, approximately 90% of NO (with respect to NO emission during un-staged combustion) was reduced for an oxygen ratio of 0.75 at the re-burn zone, whereas tar containing pyrolysis gas achieved a similar reduction at an oxygen ratio of 0.95. Therefore, during coal combustion, the percentage reduction of recycled NO by hydrocarbon radicals may be higher than with natural gas, or similar reduction efficiency may be achieved with a higher burner oxygen ratio.

Figure 7.3.A to 7.3.D displays the influence of NO injection on the reduction of recycled NO during un-staged (n=1.15) and staged (n_1=0.75 and n=1.15) combustion, during OF27 firing, for a medium volatile bituminous coal, Klein Kopje and the Lausitz brown coal. The first bar in all figures indicates the concentration of NO without recirculation of NO (without injection of NO).

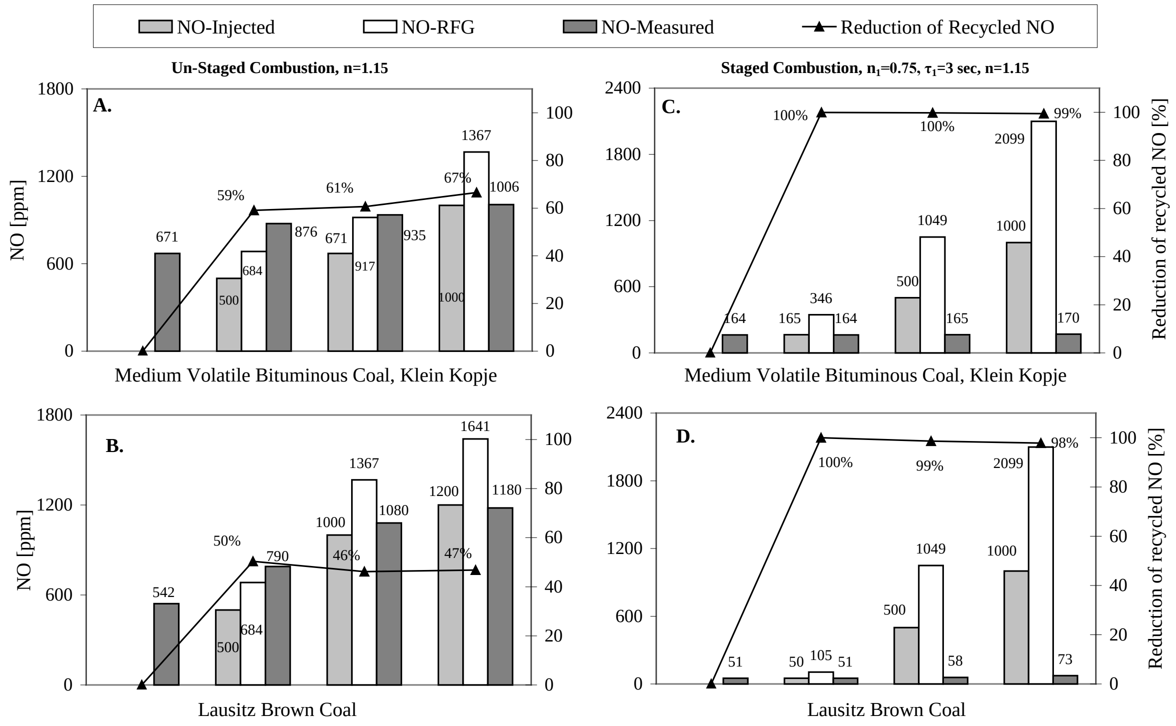
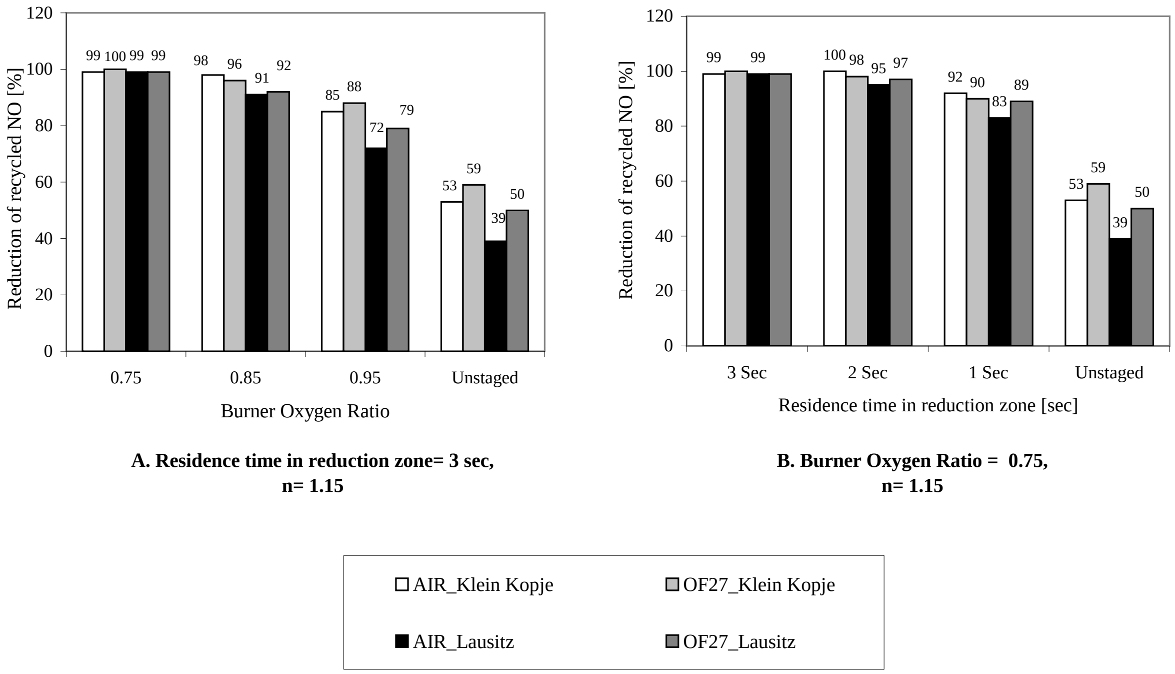


Figure 7.3: Influence of NO injection during (A and B) un-staged combustion and (C and D) staged combustion.

As seen from Figure 7.3.A, which displays the influence of NO injection during un-staged combustion of the Klein Kopje coal, the NO concentration (NO-measured) of 671 ppm was measured when there was no injection of NO. When 500 ppm of NO was injected into the furnace (NO-injected), 876 ppm of NO was measured, resulting in a reduction of recycled

NO of 59% [refer to Appendix A, section A.5]. Injection of NO was then gradually increased from 500 ppm, until a condition of stability in terms of NO emission was achieved. The condition of stability is defined as a condition when there is no more accumulation of recirculated NO in the furnace. For the once-through furnace, this condition is achieved when NO concentration in the imaginary recycled flue gas, before the addition of oxygen (NO-RFG) becomes equal to the measured NO (NO-Measured in Figure 7.3). Such a stable condition was achieved at NO concentration of around 935 ppm, which is approximately 1.4 times higher than the initial fuel-NO concentration of 671 ppm. Although, this indicates a difficulty in achieving NO_x emission limits for sequestration, it is noted that a simple in-house designed burner, that has not been optimised for low NO_x operation was used for this investigation. As seen in the case of char combustion, the percentage reduction of recycled NO remains almost constant with an increase in NO injection, indicating that the concentration of NO in the recycled flue gas has little influence on the reduction efficiency of recycled NO. This is in agreement with Liu et al. [Liu05] who also reported an approximately constant recycled NO reduction efficiency with increased NO injection for bituminous coals.

Similarly, Figure 7.3.B shows the influence of NO injection on the reduction of recycled NO for the Lausitz brown coal during un-staged combustion. The percentage reduction of recycled NO for this coal is approximately 50%, slightly lower than that of bituminous coal, Klein Kopje. A stable condition of NO emission is achieved when NO injection is approximately 850 ppm, which is approximately 1.6 times higher than the initial fuel-NO concentration of 542 ppm. Similarly, Figure 7.3.C illustrates the influence of NO injection during staged combustion for a burner oxygen ratio of 0.75 and a residence time in the reduction zone of 3 seconds, when firing a medium volatile bituminous coal, Klein Kopje. The concentration of NO at the furnace exit was observed to be almost constant with an increase in NO injection up to approximately 1000 ppm. This resulted in almost 100% reduction of recycled NO and may be considered an encouraging result for an economic operation of oxy-coal furnaces. For this combustion condition, a stable NO concentration is achieved in the first cycle itself, i.e. the NO produced from the fuel-N is the final concentration of NO in the furnace, as all the recycled NO is reduced. Figure 7.3.D shows the influence of NO injection for the Lausitz brown coal for a similar combustion condition (staged combustion with a burner oxygen ratio of 0.75 and a residence time in the reduction zone of 3 seconds). The Lausitz brown coal also showed a constant NO concentration when injection of NO was gradually increased up to1000 ppm, resulting in almost 100% reduction of recycled NO. As stated previously, this high reduction efficiency may be due to the availability of high concentration of active hydrocarbon radicals during fuel-rich combustion.



A. Residence time in reduction zone= 3 sec, n= 1.15

B. Burner Oxygen Ratio = 0.75, n= 1.15

Figure 7.4: Influence of (A) burner oxygen ratio and (B) residence time in the reduction zone on percentage reduction of NO recycled via the burner.

The influence of combustion conditions (the burner oxygen ratio and residence time in the reduction zone) on recycled NO reduction efficiency during air-blown and OF27 combustion is demonstrated in Figure 7.4.A and 7.4.B. The air-blown combustion case illustrated in Figure 7.4.A and 7.4.B has no practical significance; it is purely for comparative purposes and scientific interest. The last case in Figure 7.4.A and 7.4.B are for un-staged combustion with an overall oxygen ratio of 1.15.

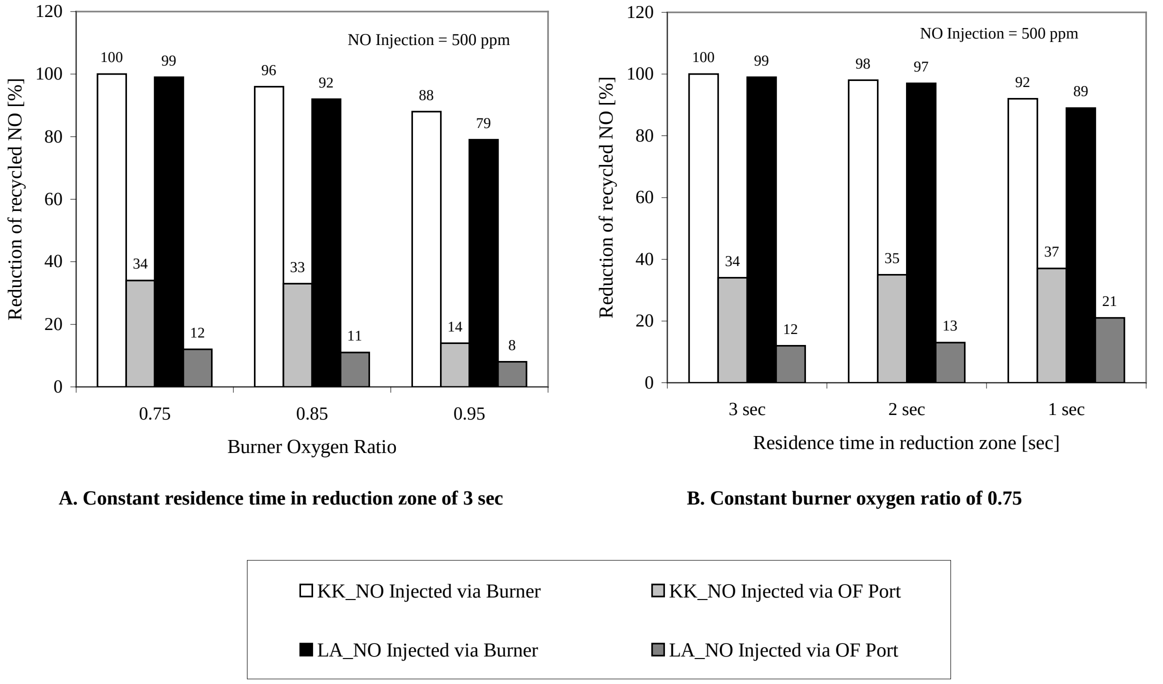
As seen from Figure 7.4.A, the percentage reduction of recycled NO decreases with an increase in burner oxygen ratio for OF27 and air-blown combustion. For a burner oxygen ratio of 0.75 and a residence time in the reduction zone of 3 seconds, the percentage reduction of recycled NO is almost 100%, and decreases with increase in oxygen availability to 40-60% (during un-staged combustion with n=1.15). This may be due to the presence of higher concentration of hydrocarbon radicals in the near burner region during combustion with a lower burner oxygen ratio, resulting in enhanced reduction of recycled NO. When compared to air-blown combustion, the percentage reduction of recycled NO is generally higher for O_2/CO_2 combustion, and the difference is more apparent for oxygen rich conditions. This again is likely to be due to the higher concentration of hydrocarbon radicals and CO in the near burner zone during oxy-coal combustion [Hjär07, Liu04], enhancing the reduction of NO by homogeneous as well as heterogeneous reactions. Kilpinen et al. [Kil92] who studied the NO reduction chemistry using natural gas as a re-burn fuel by applying 225 reversible elementary gas-phase reactions and 48 chemical species also acknowledge that, apart from the reaction of NO with hydrocarbon radicals, the reaction of NO with CO was also effective in the reduction of NO. When compared to a medium volatile bituminous coal, Klein Kopje, the percentage reduction of recycled NO is slightly lower for the Lausitz brown coal (except for a burner oxygen ratio of 0.75). The difference is more discernible for increased fuel lean conditions. As shown from the results of reduction of recycled NO using char, the active carbon sites in the char play a more prominent role on recycled NO reduction in an oxygen rich environment. The lower percentage reduction of recycle NO for the Lausitz brown coal in an oxygen rich environment may therefore be due to the release of majority of carbons with volatiles, rendering the char depleted of active carbon sites. During combustion with a burner oxygen ratio of 0.75, where the concentration of hydrocarbon radicals is high, the reduction of recycled NO with coal combustion is higher than that of natural gas (refer to Figure 7.2.A and Figure 7.4). This may be due to the combined effect of reductions by the hydrocarbon radicals in the fuel rich region as well as the heterogeneous reductions by the char. Another reason could be the nature of hydrocarbon radicals released by coals. As discussed previously, studies conducted during air-blown combustion have shown that tar containing pyrolysis gas from coals is more efficient in reducing NO_x during re-burning [Gre95, Led00, Spl95]. Also, the sum of homogeneous and heterogeneous reduction of recycled NO for un-staged combustion [Figure 7.2.A and 7.2.B] is almost equal to that of coals [Figure 7.4] during un-staged, OF27 combustion. However, as oxygen availability decreases with a decrease in burner oxygen ratio (0.85 and 0.75), and as homogeneous reactions with hydrocarbon radicals become dominant, the recycle NO reduction efficiency for coals exceeds that of natural gas.

The influence of the residence time in a reduction zone on the reduction of recycled NO is illustrated in Figure 7.4.B. The percentage reduction of recycled NO decreases with a decrease in residence time in the reduction zone. Approximately 100% reduction is achieved for a residence time in the reduction zone of 3 seconds, and between 83-93% is achieved for 1 second. This indicates that a longer time available for the recycled NO to interact with hydrocarbon radicals in oxygen depleted region will result in increased reduction of recycled NO. With these findings, it is suggested that not only a high concentration of hydrocarbon radicals in the oxygen depleted zone is necessary, but a sufficient residence time for the recycled NO to interact with hydrocarbon radicals is also required for maximum reduction of recycled NO.

In summary, reduction of recycled NO increases with a decreases in burner oxygen ratio and an increase in residence time in the reduction zone, when NO is injected via the burner.

7.1.2. Fate of NO Injected via the Over-Fire Port

During oxidant-staged combustion, a small fraction of the recycled flue gas including NO_x is also introduced via the over-fire port of the furnace and its impact on overall NO concentration requires careful consideration. The fate of NO injected via the over-fire port was investigated by injecting a known concentration of NO along with a mixture of 27% O_2/73% CO_2 via the over-fire port during staged combustion.



A. Constant residence time in reduction zone of 3 sec

B. Constant burner oxygen ratio of 0.75

Figure 7.5: Influence of NO injection position on reduction of recycled NO for different (A) burner oxygen ratio and (B) residence time in reduction zone.

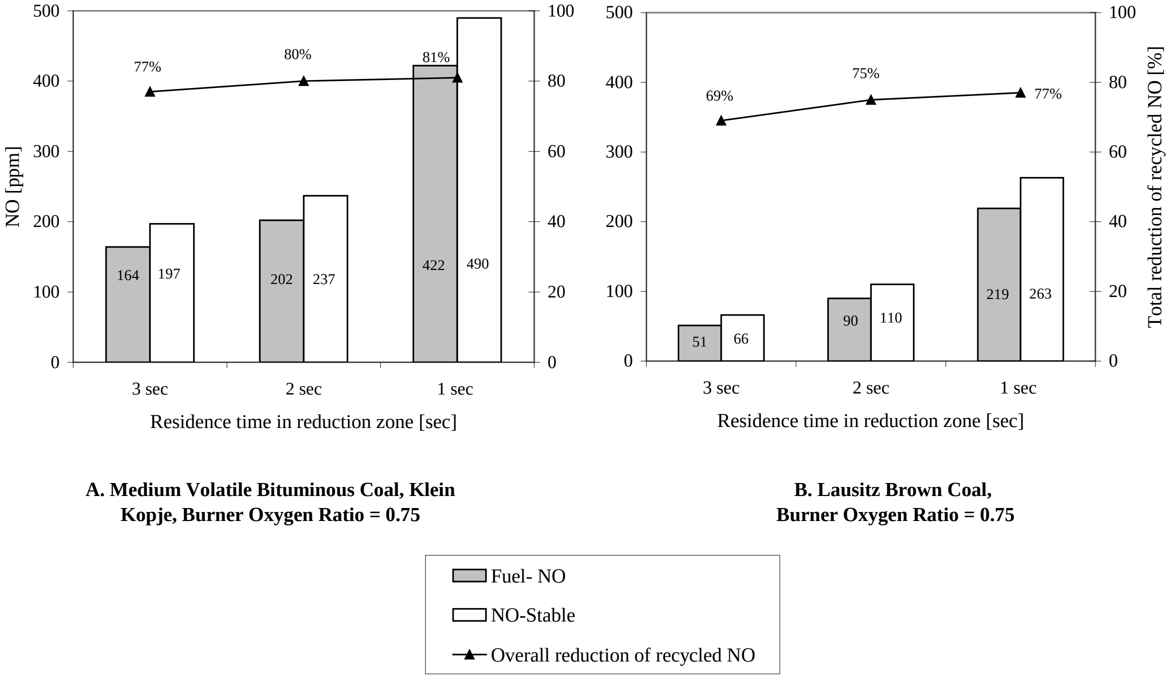
Figure 7.5.A compares the percentage reduction of recycled NO when NO was injected via the burner and the over-fire port, during staged combustion with a burner oxygen ratio of 0.75, 0.85 and 0.95 and a residence time in the reduction zone of 3 seconds. The percentage reduction of recycled NO also decreases with an increase in burner oxygen ratio,

when NO was introduced via the over-fire port. The percentage reduction of recycled NO is however much lower when NO is injected via the over-fire port. The highest reduction efficiency of recycled NO, when NO was introduced via the burner has been reported by Liu et al. [Liu05] during oxy-coal combustion for bituminous coals, and by Zhou et al. [Zho96] during air-blown combustion in a cyclone combustor. This is due to a longer time available for NO introduced via the burner to interact with hydrocarbon radicals in the flame. On the other hand, most of the hydrocarbon radicals at the location of NO injection near the over-fire port are already converted to CO, which immediately reacts with O_2 to form CO_2 at the oxygen rich, burnout zone. Most of the NO introduced via the over-fire port is therefore probably reduced by the heterogeneous reaction with the char. This is further supported by the results demonstrating that the reduction efficiency of NO injected via the over-fire port is approximately 2-3 times higher for the Klein Kopje coal, when compared with the Lausitz brown coal. Due to the reactive nature of the Lausitz brown coal, most of the hydrocarbon radicals responsible for the reduction of recycled NO are released via the gas-phase. By the time the hydrocarbons reach the burnout zone, they are already converted to CO, and the ash is also probably exhausted of its active carbon sites. In contrast, the medium volatile bituminous coal, Klein Kopje, may still have some of the active carbons sites remaining as the particles reach the burnout zone, and hence reduce more of the NO injected via the over-fire port. When NO from the over-fire port is introduced closer to the flame during staged combustion with a shorter residence time in the reduction zone, the reduction efficiency of recycled NO increased from 12 to 21% for the Lausitz brown coal and from 34 to 37% for the Klein Kopje Coal [Figure 7.4.B]. A higher increase in the reduction efficiency with a decrease in residence time in the reduction zone for the Lausitz brown coal may be due to the presence of more hydrocarbon radicals in the gas-phase. However, only a slight improvement in the NO reduction efficiency for Klein Kopje coal, when NO was introduced closer to the flame, gives further indication of the prominent role of NO reduction by char in an oxygen rich condition. As discussed earlier, most of the remaining active hydrocarbon radicals are immediately converted to CO and eventually to CO_2 with the injection of the burnout oxidant [Kil92] before they have a chance to react with NO injected via the over-fire port. On the other hand, large amount of carbons were still present within the ash at end of reduction zone of 3 and 1 second for bituminous coal. The reduction of recycled NO is therefore high (34%) even at 3 seconds and shows a slight improvement (by 3%) for 1 second residence time in the reduction zone. Whereas, almost no carbon was present in the ash at the end of reduction zone of 3 seconds for a reactive coal like pre-dried brown coal, and carbon in the ash was approximately 20 times higher at the end of reduction zone of 1 second. Therefore, for the Lausitz brown coal, recycle NO reduction efficiency is low (12%) for a residence time in the reduction zone of 3 seconds and is approximately doubled when residence time in the reduction zone is reduced to 1 second.

The results presented so far demonstrate that a fuel rich condition favours the reduction of recycled NO introduced via the burner and the over-fire port. The recycled NO is reduced at a higher rate when NO is introduced through the burner as opposed to over-fire port. A longer residence time in reduction zone favours the reduction of recycled NO introduced via the burner. A longer residence time in the reduction zone however has a negative impact on reduction of recycled NO introduced via the over-fire port, especially for high volatile brown coals.

7.1.3. Overall Reduction of Recycled NO and its Implication during O_2-RFG Combustion

It is recognised that, only a small fraction of the oxidant (O_2+RFG) needs to be introduced via the over-fire port during staged combustion. The amount of NO introduced via the over-fire port along with the oxidant is therefore, a fraction of the NO introduced via the burner. The influence of NO injected via the over-fire port on the total or overall reduction efficiency of recycled NO, therefore may not be significant. However, as discussed previously, the reduction of NO introduced via the burner increases with an increase in residence time in the reduction zone. Whereas, the reduction of NO introduced via the over-fire port tends to decrease with an increase in reduction zone residence time. Therefore, the residence time in the reduction zone may require further optimisation for the maximum reduction of NO recycled via the burner and the over-fire port.



A. Medium Volatile Bituminous Coal, Klein Kopje, Burner Oxygen Ratio = 0.75

B. Lausitz Brown Coal, Burner Oxygen Ratio = 0.75

Figure 7.6: Overall reduction of recycled NO during oxidant staged combustion and final stable NO concentration for (A) Klein Kopje and (B) Lausitz brown coal.

Figure 7.6.A and 7.6.B present the calculated overall reduction of recycled NO for NO introduced via the burner and the over-fire port. The main objective of the results presented within Figure 7.6.A and 7.6.B was an attempt to assess the optimum location for NO injection via the over-fire port. The overall reduction of recycled NO is calculated using the equation

EA.11 in Appendix A. The experimentally determined values of the reduction of recycled NO when NO is injected via the burner and the over-fire port are used in the equation EA.11. Figure 7.6.A and 7.6.B further present the stable NO concentration (refer to Appendix A, section A.7) that was achieved, by taking into account the initial fuel NO concentration (NO concentration without injection of NO) and the overall reduction of NO recycled back into the furnace. It is seen that, the overall reduction efficiency of the recycled NO increases from 77% to 81% for the Klein Kopje coal and from 69% to 77% for the Lausitz brown coal, when the residence time in the reduction zone is reduced from 3 to 1 seconds. The final stable concentration of NO in the furnace is approximately 2.5 times lower for the Klein Kopje and 4 times lower for the Lausitz brown coal, when the residence time in the reduction zone is reduced from 3 seconds to 1 second. This demonstrates that the stable NO concentration in the furnace is lower for cases with a longer residence time in the reduction. This is due to the lower production of fuel NO from both coals during staged combustion with a longer residence time in reduction zone, resulting in a lower stable or equilibrium NO concentration in the furnace.

Figure 7.7 compares the NO_x emission rate [refer to Appendix A, section A.2] during oxy-coal combustion (OF27) with air-blown combustion. The combustion conditions considered in Figure 7.7 are un-staged combustion, and staged combustion with a burner oxygen ration of 0.75 and the residence time in the reduction zone of 3, 2 and 1 seconds. The NO_x emission rate during oxy-coal combustion is calculated by taking into account the overall reduction of recycled NO, and the final stable NO concentration thus achieved. Unlike in previous chapters where the NO_x emission rate was calculated at the end of the furnace, the NO_x emission rate in Figure 7.7 is calculated downstream of the point that would have represented the flue gas recycle point during oxy-fuel combustion with flue gas recycle. As the measurements during O_2/CO_2 combustion were carried out with a 27% O_2 and73% CO_2 mixture, the flue gas recycle rate of 73% by volume is considered for the calculation. The

NO_x emission rate, when compared with the corresponding air-blown combustion case as shown in Figure 7.7, is between 0.24 to 0.37 times lower. This is in agreement with most investigations carried out during oxy-coal combustion with flue gas recycle [And07, Cro00, Mon07, Yam06] and further confirms that the reduction of NO recycled back into the furnace is the most important factor resulting in lower NO_x emissions during oxy-coal combustion.

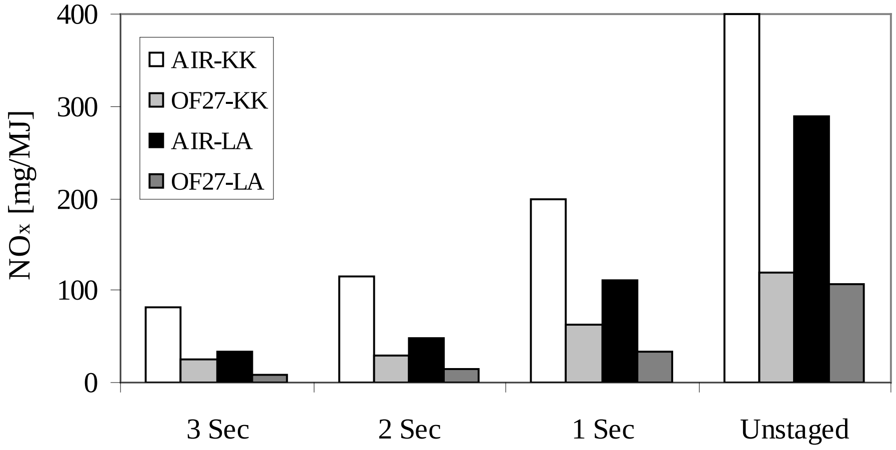


Figure 7.7: Comparison of NO_x emission rate during air-blown and oxy-coal combustion.

7.2. SUMMARY OF RESULTS

1. As indicated from the measurements with char of brown coal, recycled NO is prominently reduced by heterogeneous reactions in a fuel lean combustion condition. Recycled NO reduction of 41% was achieved with char, during OF27 combustion for an oxygen ratio of 1.15, whereas only a 15% reduction was achieved during natural gas combustion for similar combustion condition. However as oxygen availability decreases with a decrease in the burner oxygen ratio during staged combustion, homogeneous reactions (reactions with active hydrocarbon radicals) play a more

prominent role, as almost 90% reduction of recycled NO was achieved for a burner oxygen ratio of 0.75 and 0.85 during combustion of natural gas.

2. Increase in the concentration of recycled NO within the range of 1600 ppm showed no influence on the recycled NO reduction efficiency during char and coal combustion. This indicates that the reduction efficiency of recycle NO may remain unaffected with the increase in concentration of recycled NO.
3. The reduction of recycled NO during coal combustion for both air-blown and oxy-coal firing is entirely dependent on the prevailing combustion conditions (the burner oxygen ratio and the residence time in the reduction zone). When NO was injected via the burner, recycled NO reduction of almost 100% was achieved during staged combustion with a burner oxygen ratio of 0.75, and approximately 50% reduction was achieved during un-staged combustion. Similarly, a longer residence time in the reduction zone during staged combustion has a positive influence on recycled NO reduction, when NO is introduced via the burner.
4. The combustion media has a little influence on the recycled NO reduction when oxygen availability is low or when homogeneous reactions are prominent, as the reduction efficiency of recycled NO was very similar during air-blown and O_2/CO_2 combustion for a burner oxygen ratio of 0.75. However, as oxygen availability increases with an increase in the burner oxygen ratio, and as heterogeneous reactions become prominent, reduction efficiency of recycled NO is higher in a CO_2 media. This is most probably due to the presence of the higher CO concentrations during oxy-coal combustion, which are known to enhance NO reduction via heterogeneous reactions.
5. The reduction efficiency of recycled NO is also dependent on the location of NO injection, as the reduction of recycled NO when injected via the over-fire port is much lower than when introduced via the burner. However, the fraction of NO entering the furnace via the over-fire port when compared to the fraction entering the furnace via

the burner is small, and will therefore have a negligible influence on final NO concentration in the furnace. Furthermore, when compared to the bituminous coal, results demonstrate that the reduction efficiency of recycled NO introduced via the over-fire port is between 2 to 3 times lower for the pre-dried brown coal. It is suggested to be because of very few active carbon sites remaining, by the time the ash particles of the reactive coals like brown coals reaches the location of NO injection via the over-fire port. This further illustrates the importance of heterogeneous reactions by active carbon sites in an oxygen rich environment.

6. The NO_x emission rate, calculated by assuming the flue gas recycle of 73 vol. % and considering the measured overall reduction of recycled NO and the final stable NO concentration thus achieved, is between 0.24 to 0.37 times lower than air-blown combustion. This is in agreement with most investigations carried out during oxy-coal combustion with flue gas recycle and further confirms that reduction of NO recycled back into the furnace is the most important factor that results in lower NO_x emission rate during oxy-coal combustion.

CHAPTER 8

FATE OF SULPHUR DURING OXY-COAL COMBUSTION

Apart from the emissions of CO_2, NO_x, CO, etc., the combustion of coal is also associated with the conversion of sulphur in the coal into gaseous compounds such as SO_2, SO_3, H_2S and COS. The in-furnace SO_2 concentration has been reported to increase by a factor of 2-3, during O_2/RFG combustion [Cro01, Mön07, Yam06]. The presence of sulphur in the fuel is associated with high temperature corrosion at the furnace walls and the superheater sections, and low temperature corrosion through the condensation of sulphuric acid in the economiser or air heater. An investigation carried out by Yamada et al. [Yam06] report about 3 times higher SO_3 concentration during O_2/RFG combustion and this increase is seen to be proportional to the increase in SO_2 concentration. However, literatures describing the formation of H_2S (responsible for high temperature corrosion in the oxygen deficient radiative section) under oxy-coal combustion are very limited. Primary emphasis of this investigation is therefore to study the impact of the combustion media and recycled SO_2 on the formation of gaseous sulphur components (SO_2 and H_2S) within the furnace. The SO_2 retention capacity of a suite of coals (ash) in the radiative and convective section of a furnace for different combustion conditions is also investigated.

8.1. RESULTS

The furnace exit SO_2 concentration has been reported to be 2-3 times higher during O_2/RFG combustion due to the accumulation of SO_2 from recycled flue gas. As this investigation was carried out in a once through furnace, the SO_2 concentration in the furnace during O_2/CO_2 combustion will not represent the SO_2 concentrations of an oxy-coal plant with flue gas recirculation, as there was no accumulation of SO_2 in the furnace. With the primary focus of this study being investigation of sulphur chemistry in an oxy-coal environment, along with the measurements performed for different combustion conditions such as the burner oxygen ratio and combustion media (CO_2 or N_2), SO_2 was also injected in the furnace to simulate oxy-coal combustion with recycled flue gas. The term 'SO_2 injected' used throughout this section is the concentration of SO_2 measured at the furnace exit when SO_2 is injected via the burner, without any combustion of the fuel. The injection of SO_2 was increased in steps, in order to investigate its behaviour in the radiative section and the convective/flue gas path. It is therefore noted that, for some of experimental cases involving SO_2 injection, the concentration of SO_2 may not be representative of an O_2/RFG combustion condition. For such experimental cases, the theoretically calculated SO_2 concentration that represents an O_2/RFG furnace are also included in the figures, and discussed where relevant. Such theoretically calculated SO_2 concentration is referred as the maximum SO_2 during O_2/RFG combustion and its calculation method is included in Appendix A, section A.8. It is further noted that all the investigations in a CO_2 environment were carried out in 27% O_2/73% CO_2 environment.

8.1.1. Behaviour of Injected SO_2 in the Radiative Section of the Furnace

Due to flue gas recirculation during oxy-coal combustion, pollutants like NO_x and SO_2 are also re-circulated back into the furnace. Depending on the combustion condition, 40-90% of NO_x re-circulated back into the furnace is destroyed [Cro01, Liu05]. SO_2 re-circulated back has however been reported to accumulate in the furnace [Cro01, Mön07, Yam06]. Measurements, especially during O_2/RFG combustion also report a lower conversion of sulphur to SO_2 [Cro01, Kiga97, Woy95]. As mentioned earlier, it may be due to a higher retention of SO_2 in the ash, increased conversion of SO_2 to SO_3 or removal of SO_2 and SO_3 with the condensates during dry recycling. The retention of sulphur in the ash may be in the radiative section of the furnace or in the convective section of the furnace. Due to the unstable state of sulphates at temperatures above 1000°C, retention of sulphur within the ash in the radiative section of air-blown furnace has been reported to be unlikely [Fol04]. Although possibly unlikely in a CO_2 environment as well, investigations on the retention of sulphur by the ash during O_2/CO_2 combustion in the high temperature radiative section of the furnace were unavailable in open literatures.

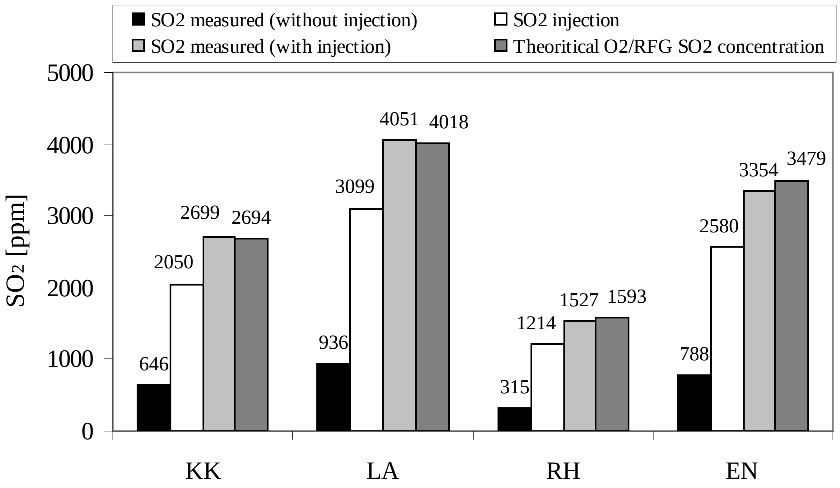


Figure 8.1: SO_2 concentrations at the furnace exit with and without SO_2 injection during OF27 combustion.

With the aim to determine if any sulphur is retained in the radiative section during O_2/CO_2 combustion, when the in-furnace SO_2 concentration are high, the SO_2 concentration measurements at the end of the radiative section (at 2.5 m from the burner) were carried out for all 4 coals. SO_2 concentration in the furnace was increased in steps by injecting a known concentration of SO_2. Although, the SO_2 injection in the furnace was gradually increased in steps, only the cases where the in-furnace SO_2 concentration during OF27 combustion is almost equal to the theoretical maximum SO_2 concentration during O_2/RFG [refer to Appendix A, section A.8] are represented in Figure 8.1. As shown by Figure 8.1, the difference between SO_2 measured (with injection) and SO_2-injection are almost equal to the SO_2 measured during coal combustion without SO_2 injection [SO_2 measured (without injection) in Figure 8.1], for all 4 coals investigated. This indicates that there is no retention of SO_2 in the radiative section of the furnace (wall temperature =1300°C) in a CO_2 media as well, even when the in-furnace SO_2 concentrations are approximately 4-5 times higher than the baseline cases without SO_2 injection. It may therefore be implied that the sulphates are not formed or stable at high temperature radiative section of the furnace, in a CO_2 environment as well.

8.1.2. Behaviour of Injected SO_2 in the Convective Section/Flue Gas Path of the Furnace

As previously indicated by the results represented by Figure 8.1, SO_2 is not retained in the ash of the investigated coals within the radiative section of the furnace. This is thought to be due to the temperature of the reactor being higher than the temperature at which the products of most sulphate forming alkaline earth metals (Ca, Mg) and alkali metals (Na, K) in the ash can remain stable. However, the operation temperature of the convective section of a furnace as well as the flue gas recirculation path may offer a potential for SO_2 retention by such elements in the ash. For the determination of the SO_2 retention potential by the ash constituents in the convective section/flue gas path, SO_2 measurements were carried out at the end of the flue gas path, just before the candle filter [refer to Figure 4.1]. The SO_2 concentration in the furnace was increased in steps by injecting a known concentration of SO_2. The flue gas temperature at the end of the radiative section was around 1050°C and the temperature at the SO_2 measurement point in the flue gas path before the candle filter was around 450°C.

To evaluate the influence of the combustion media on SO_2 retention in the flue gas path, Figure 8.2 illustrates the results of SO_2 retained at the end of the flue gas path, for all four coals, during air-blown and OF27 combustion. The SO_2 retained at the end of flue gas path is calculated from the difference in SO_2 measured at the end of the radiative section (2.5 m level) and the SO_2 measured at the end of the flue gas path, before the candle filter.

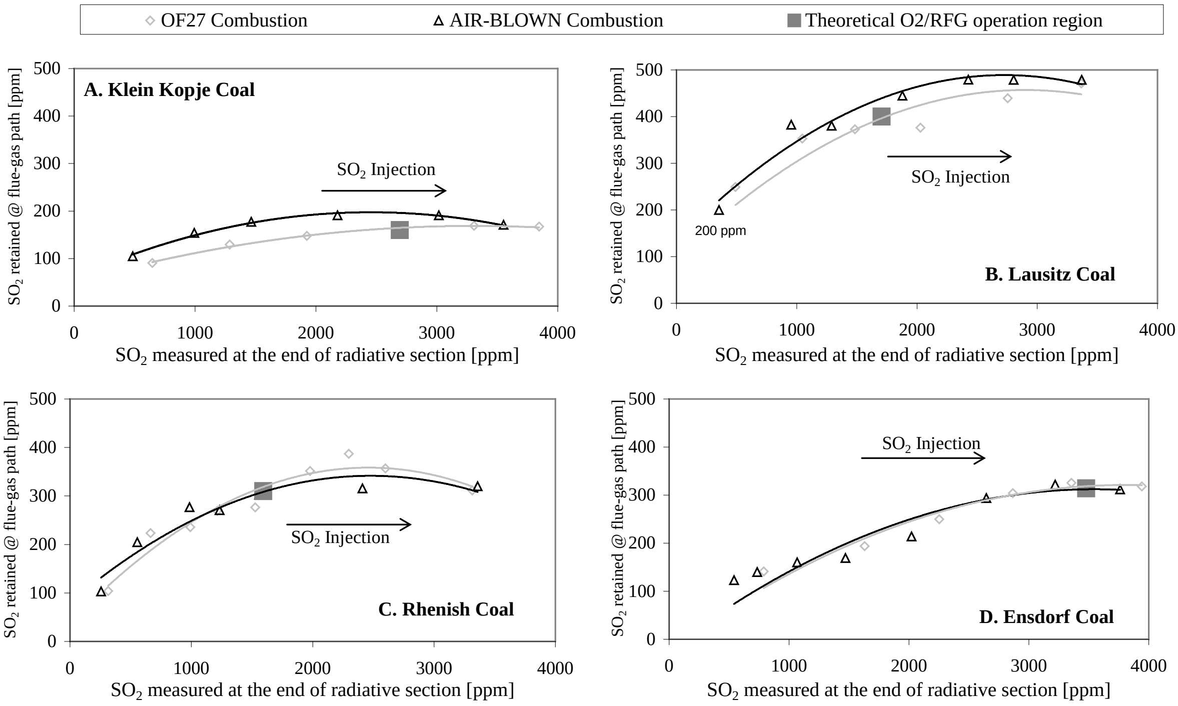


Figure 8.2: Influence of media on SO_2 retention in the convective section/flue gas path for (A) Klein Kopje coal, (B) Lausitz brown coal (S=0.35 %, wf), (C) Rhenish brown coal and (D) Ensdorf coal.

As seen from Figure 8.2, SO_2 retained in the flue gas path increases with an increase in SO_2 concentration at the end of the radiative section, for air-blown and OF27 combustion. However, a plateau is attained after a certain concentration of SO_2 at the end of the radiative section for all 4 coals, giving the indication of an optimum SO_2 retention capacity (it is noted that for some measurements, a slight decrease in sulphur retention is seen at high SO_2 injection rates and is attributed to measurement errors). Even though the residence time available for the interaction between SO_2 in the flue gas and sulphate forming elements within the ash is brief within the flue gas path, approximately 20% of SO_2 was retained for the Lausitz brown coal (approximately 500 ppm SO_2 retained when SO_2 concentration is 2500 ppm). This gives an indication of the potential of SO_2 retention in the convective section and the flue gas path, if a suitable coal and a suitable temperature gradient are available. The combustion media however displays a little influence on the desulphurisation efficiency, as for a particular Ca:S molar ratio, the SO_2 retained in the flue gas path is slightly lower for OF27 combustion.

The results from the present investigation however differs to that of tests conducted in a fixed bed reactor [Liu00] and for a thermo-gravimetric analysis [Haj88, Sno88], using $CaCO_3$ as a sorbent. The literatures [Haj88, Sno88, Liu00] report that direct sulphation (which occurs when the CO_2 partial pressure is high) enables a higher degree of sulphation than those observed in CaO-SO_2 sulphation. This is suggested to be due to the counter diffusion of CO_2 during direct sulphation, resulting in a porous product layer, which offers less resistance to diffusion of SO_2. It is however noted that the temperature and the residence time available within a fixed bed reactor in comparison to pulverised fuel firing is significantly different. During pulverised coal combustion, due to high temperature, the porosity of sulphate forming elements within the ash may have been destroyed. Even if the porosity is not destroyed, they may not have a sufficient residence time for complete sulphation reaction. This may be the reason for a negligible difference in desulphurisation efficiency during air-blown and O_2/CO_2 combustion for the present investigation.

SO_2 retention capacity of a coal ash has been reported to be a function of the concentration of alkaline earth elements and alkali metals (most prominently Ca) relative to the sulphur content, and the modes of occurrence of these elements [Fol04]. To investigate the influence of the alkaline elements concentration in retention of SO_2 from the flue gas path, measurements were carried out with 2 samples of Lausitz brown coals having a sulphur content of 0.36 and 0.85 [%, waf]. The concentrations of the alkaline elements in the ash of the coal samples were almost similar. This results in a Ca:S molar ratio of 3.17 for the coal with S=0.36%, and Ca:S ratio of 1.39 for the coal with S=0.85%. As seen from Figure 8.3, the sulphur content in the coal (or the difference in Ca:S molar ratio) has a weak dependency on the SO_2 retained in the flue gas path. This could be due to a short residence time in the flue gas path resulting in incomplete utilisation of sulphate forming elements for retention of SO_2.

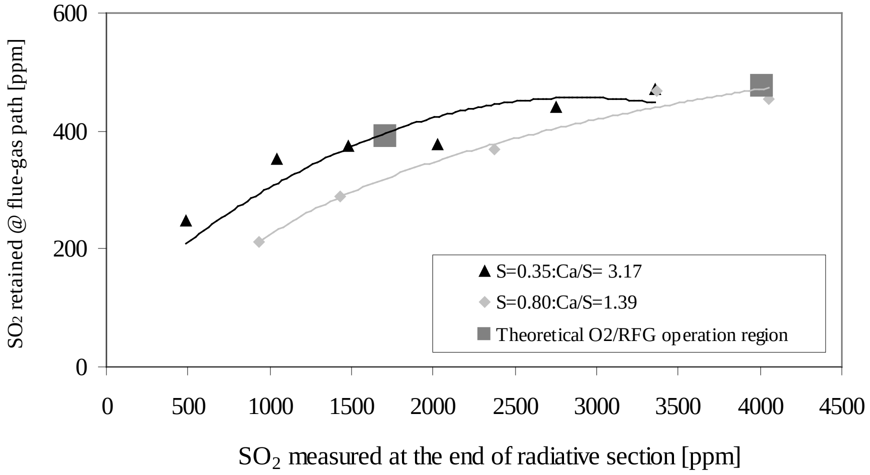
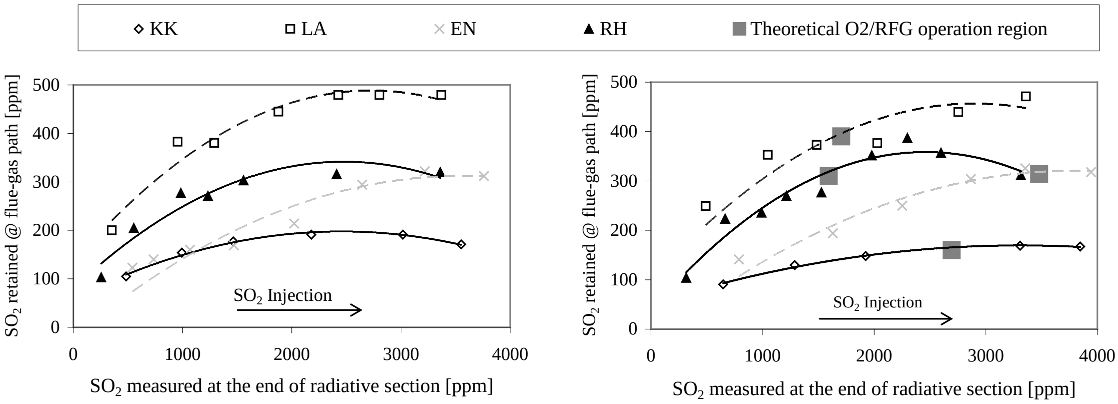


Figure 8.3: Influence of sulphur content in the coal on SO_2 retained in the flue gas path during OF27 combustion.

A weak dependency on the Ca:S molar ratio on SO_2 retention within the flue gas path is further evident from Figure 8.4, where the Ca:S molar ratio (refer to embedded table) is highest for the Rhenish brown coal and lowest for the Ensdorf coal. SO_2 retained in the flue gas path is however highest for the Lausitz brown coal and lowest for the Klein Kopje coal. This indicates that the form of calcium or minerals present in the ash may also play an important role on SO_2 retention. High ash coals like Klein Kopje normally contain a high amount of external impurities like silicates (SiO_2 = 46.1 mass % for Klein Kopje coal) and clay. Calcium, which is thought to play a dominant role on SO_2 retention, has been known to be less active when present in clay and silicate minerals. On the other hand, coals with lower ash fraction normally contain lower amount of external impurities, and the calcium in the ash is most probably present as carbonate minerals or organically bound calcium. Carbonate minerals like calcite ($CaCO_3$) and organically bound calcium are considered most active for sulphur retention. This could be the reason for coals with low ash content (Lausitz, Rhenish and Ensdorf) retaining more SO_2 than the coal with high ash content (Klein Kopje). Furthermore, the percentage of calcium relative to the ash for lower ash coals may be higher. However, further investigation on the form of calcium present within the ash is required to fully understand the retention of SO_2 by the ash. Also, Rhenish brown coal with the highest Ca:S molar ratio shows a lower retention capacity than the Lausitz brown coal. This could be due to the larger particle size distribution of Rhenish brown coal, as heterogeneous reaction of Ca and SO_2 have been reported to be dependant on the available surface area of a solid [Lev93]. Therefore, small particle size, high porosity and internal area are desirable.



A. Air-Blown Combustion, n=1.15

B. OF27 Combustion, n=1.15

Coal	Ash [wf, mass%]	CaO [wf, mass%]	S in fuel [wf, mass%]	Ca:S molar ratio
Klein Kopje (KK)	19.29	7.8	0.58	2.98
Ensdorf (EN)	7.29	10.50	0.77	1.03
Lausitz (LA)	4.79	23.78	0.35	3.17
Rhenish (RH)	4.07	35.10	0.34	3.96

Figure 8.4: Influence of coal property on SO_2 retained in the convective section/flue gas path during (A) air-blown combustion and (B) OF27 combustion (embedded table illustrating coal properties).

However, regardless of the combustion media (CO_2 or N_2), if the concentrations of sulphate forming elements in the ash are high and active, then SO_2 retained by the ash increases with an increase in SO_2 concentration, up to certain concentration of SO_2 in the flue gas. On the other hand, the sulphur content in the ash collected at the candle-filter [Figure 8.5] also increases with an increase in SO_2 concentration in the flue gas, and is in agreement with the drop in SO_2 concentration in the flue gas path. It is however noted that the SO_2 concentration in an air-blown furnace will be lower than that of an oxy-coal furnace with flue gas recycle. As shown by the theoretical O_2/RFG operation region in Figure 8.4.B, it may therefore be concluded that the sulphur retained in the convective section and flue gas recirculation path will be higher during oxy-coal combustion. Furthermore, higher concentration of SO_2 retained by the ash could be one of the most prominent reasons for lower conversion of fuel-S to SO_2 in an oxy-coal plant with flue gas recirculation.

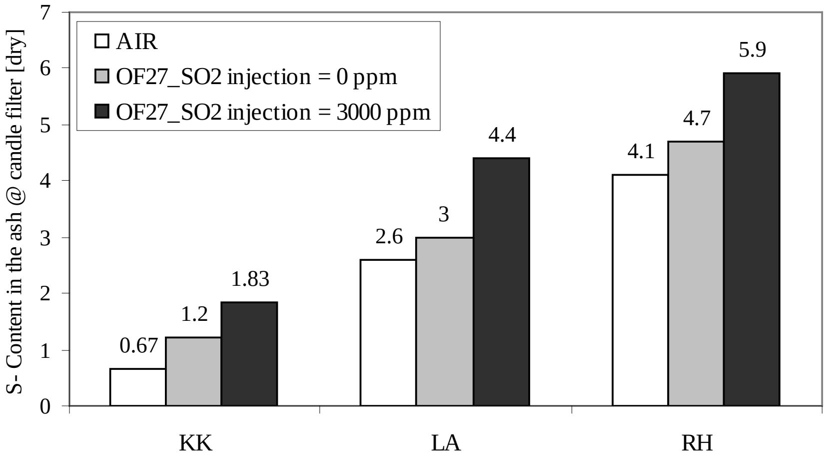


Figure 8.5: Sulphur content in the ash collected at the candle filter demonstrating the influence of SO_2 concentration on SO_2 retention.

The most important information that may be drawn from these results is that, if the coal being used has a high concentration of active sulphate forming elements, the opportunity of retaining maximum possible SO_2 in the convective section and flue gas recirculation path leading to decreased SO_2 accumulation must be considered, when designing a cost effective oxy-coal plant. Furthermore, SO_2 reduction by the injection of sulphate forming compounds like lime may be another viable option.

8.1.3. SO_2 and H_2S Formation Mechanism in O_2/CO_2 Environment

To investigate the H_2S formation mechanism in a CO_2 environment, axial in-furnace profile measurements were carried out during air-blown and OF27 combustion. Figure 8.6 demonstrates the result of such axial emission profile measurements for the Lausitz brown coal and a high volatile bituminous coal, Ensdorf. These measurements were performed during oxidant-staged combustion (air-blown and OF27 combustion) with a burner oxygen ratio of 0.75 and a residence time in the reduction zone of 3 seconds.

As seen from Figure 8.6, a peak of SO_2 is formed around 0.5 m in the oxidant-fuel mixing region, and then reduces rapidly in the reduction zone along with the drop in oxygen concentration. The mixing zone where O_2 is not fully consumed even during fuel-rich combustion is a region where most of coal mass and coal sulphur are devolatilised. A peak of H_2S is formed approximately between 0.9-1.10 m from the burner, a location where the SO_2 concentration is minimum. When a comparison between the sum of SO_2 and H_2S measured is made to the calculated sum of H_2S and SO_2 (Grey Square at 0.9 m), it seems the majority of the sulphur exists as SO_2 and H_2S in the reduction zone during air-blown and O_2/CO_2 combustion. The sum of H_2S and SO_2 has been calculated from the difference between the maximum theoretical SO_2 possible i.e. $(SO_2+H_2S)_{max}$ and SO_2 not released in the gas phase due to sulphur remaining in the char/ash collected at 0.9 m (refer to Appendix A, section A.9). Overall, it may be concluded that the SO_2/H_2S formation and destruction mechanisms are fundamentally similar in O_2/N_2 and O_2/CO_2 environment. The major difference observed from these measurements however is the difference in volumetric ratio between SO_2 and H_2S at the location of the peak of H_2S, and will be discussed later.

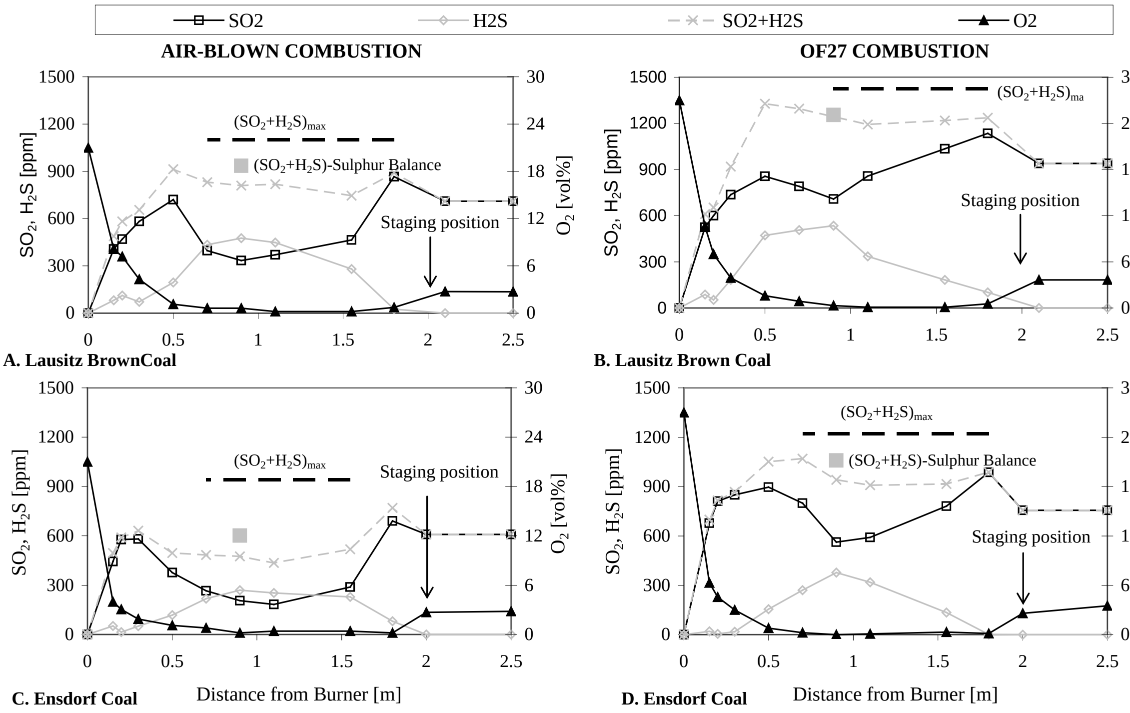


Figure 8.6: SO_2 and H_2S formation mechanism during staged combustion with n_1= 0.75 and τ_1~3 seconds for (A) Lausitz brown coal/ air-blown, (B) Lausitz brown coal/OF27, (C) Ensdorf HVB coal/air-blown and (D) Ensdorf HVB coal/OF27.

To evaluate the influence of the coal property on H_2S and SO_2 formation mechanism in O_2/N_2 and O_2/CO_2 environment, Figure 8.7.A and 8.7.B illustrates the axial concentration profile of SO_2 and H_2S for a medium volatile bituminous coal, Klein Kopje (volatile = 27.76 %, waf), a high volatile bituminous coal, Ensdorf (volatile = 37.21 %, waf) and the Lausitz brown coal (volatile = 57.36 %, waf) for air-blown and OF27 combustion with a burner oxygen ratio of 0.75.

As mentioned earlier, a peak of SO_2 is formed in the oxidant/fuel mixing region, where the oxygen concentration is still high. As the oxygen concentration drops and becomes negligible, the SO_2 concentration begins to drops as well, and reaches a minimum value in the fuel rich sub-stoichiometric region. The concentration of H_2S on the other hand reaches a peak at the location where SO_2 reaches a minimum value. However, the quantitative drop in the SO_2 level and increase in the H_2S level in the sub-stoichiometric region shows a strong relationship to the volatile content of the coal. High volatile coals, Ensdorf and Lausitz show a stronger drop in the SO_2 level with a higher H_2S peak, whereas a medium volatile coal, Klein Kopje shows only a small drop in the SO_2 level and a lower H_2S peak, during air-blown and O_2/CO_2 combustion. This could be due to the fact that coals with higher volatile content are more reactive, therefore consumes oxygen faster resulting in a deeper degree of staging and consequently produces a higher peak of H_2S.

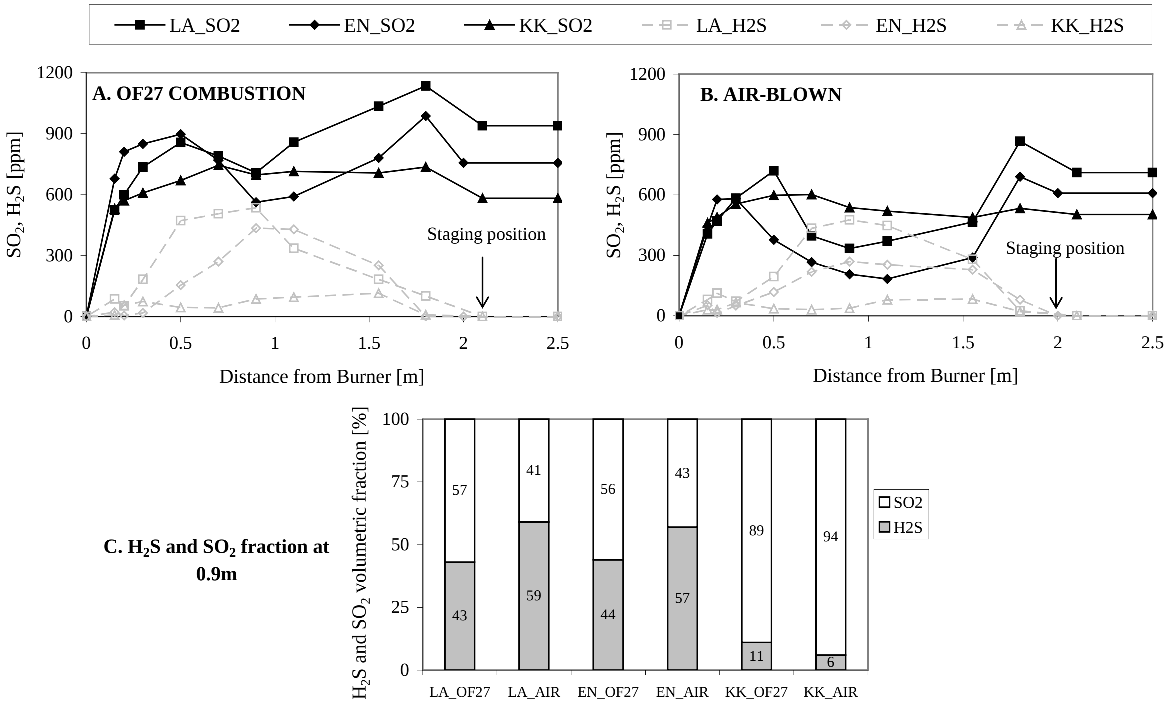


Figure 8.7: Influence of coal property on SO_2 and H_2S formation (A) during OF27 combustion, (B) during air-blown combustion and on (C) H_2S and SO_2 fraction.

Furthermore, the influence of the volatile content of a coal on the formation of SO_2 and H_2S as shown by Figure 8.7.A and 8.7.B, demonstrate similarities to the formation mechanism of NO, HCN and NH_3. As discussed previously in Chapter 6, the rate of reduction of NO and the formation of HCN and NH_3 within a fuel rich combustion environment are higher for high volatile coals. Similarly, the rate of reduction of SO_2 and the formation of H_2S is also higher for high volatile coals. The HCN and NH_3 are converted to N_2 in the absence of oxygen. The sulphur species, H_2S is unable to be converted to anything stable, apart from SO_2 and shown to be the case when H_2S enters the burnout region. The results therefore suggests that, higher the volatile content of a coal, the more is the yield of hydrocarbon radicals, which are able to reduce the SO_2 formed in the oxidant/fuel mixing region to H_2S in the fuel rich sub-stoichiometric zone.

As mentioned earlier, the major difference between a N_2 and a CO_2 environment observed from the measurement was the difference in volumetric ratio between SO_2 and H_2S at the location of the peak of H_2S (Figure 8.7.C). As seen from the Figure, the volumetric fraction of H_2S with respect to SO_2 in general, is higher for air-blown combustion. As discussed in previous chapters, the CO concentration in the near flame zone in a CO_2 environment is higher than in a N_2 environment (air-blown combustion). This has been suggested to be due to the enhanced production of CO by reaction of CO_2 with carbon, and consumption of H_2 to produce CO by the water-gas reaction as given by reactions R3.19 and R3.20. With the enhanced consumption of H_2 in a CO_2 environment to produce CO, the reaction rate of sulphur and hydrogen molecules required to produce H_2S may well be suppressed in a CO_2 environment, resulting in a lower fraction of H_2S within a CO_2 environment. The measured hydrogen concentration during pyrolysis in a CO_2 environment is also lower than in a N_2 environment for Lausitz and Klein Kopje coal [Al09] further adding support to this postulation.

8.1.4. SO_2 and H_2S Formation Mechanism in O_2/RFG Environment

Although the H_2S and SO_2 formation mechanism discussed earlier provides a sound understanding on the fate of sulphur in a CO_2 environment, it may not be representative of oxy-coal fired furnaces with flue gas recycle, as the concentration of SO_2 in the furnace during O_2/RFG has been reported to be much higher than air-blown combustion [Cro01, Mön07, Yam06]. To study the H_2S and SO_2 formation mechanism that closely represents practical oxy-coal furnaces, approximately 3000 ppm of SO_2 was also injected into the furnace so that the SO_2 concentration in the furnace achieves a level close to the O_2/RFG condition.

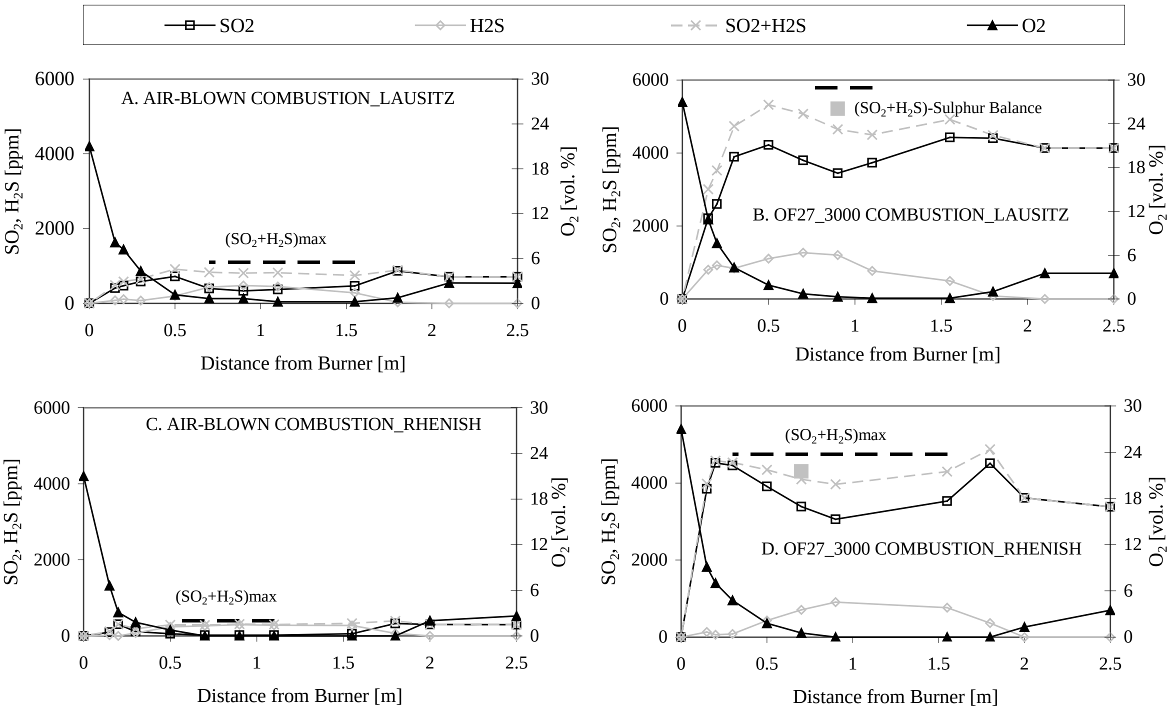


Figure 8.8: SO_2 and H_2S formation mechanism during staged combustion with n_1= 0.75 and τ_1~3 seconds for (A) Lausitz brown coal/ air-blown, (B) Lausitz brown coal/OF27_3000, (C) Rhenish brown coal/air-blown and (D) Rhenish brown coal/OF27_3000.

Figure 8.8 demonstrates the result of such axial gaseous concentration profile measurements for Lausitz and Rhenish brown coals, for oxidant staged combustion with a burner oxygen ratio of 0.75 and a residence time in the reduction zone of 3 seconds, during air-blown and OF27 combustion.

As seen from Figure 8.8, the in furnace concentration of both H_2S and SO_2 are much higher during OF27 combustion with 3000 ppm SO_2 injection, although the mechanisms of formation of SO_2 and H_2S in the oxygen deficient region is seen to be similar to air-blown combustion (refer to Figure 8.6 for clearer SO_2/H_2S profile for air-blown combustion). When a comparison between the sum of SO_2 and H_2S measured is made to the calculated sum of H_2S and SO_2 (Grey Square at 0.9 m), it seems that majority of sulphur in the gas-phase exists as SO_2 and H_2S in the reduction zone for O_2/RFG scenario as well. Calculation method for the sum of H_2S and SO_2 is included in Appendix A, section A.9.

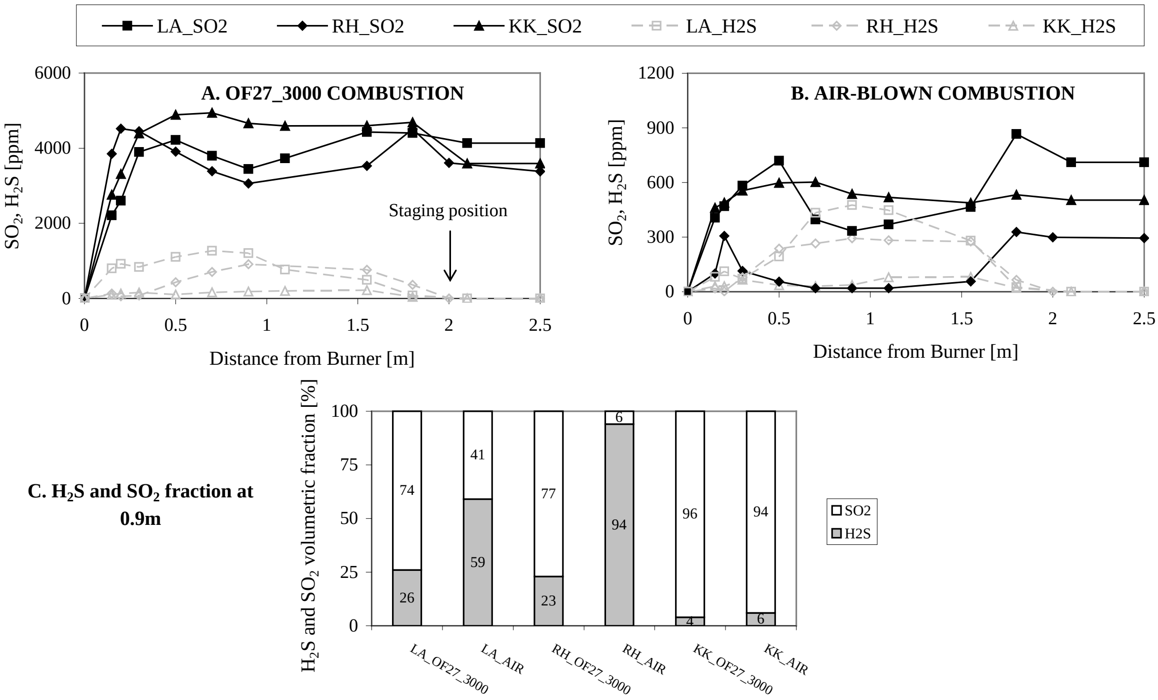


Figure 8.9: Influence of coal property on SO_2 and H_2S formation (A) during OF27_3000 combustion, (B) during air-blown combustion and on (C) H_2S and SO_2 fraction.

As seen from Figure 8.9.A and 8.9.B, the coals with higher volatile content demonstrate more reduction of SO_2 in the sub-stoichiometric region and a higher concentration of H_2S, for air-blown and OF27 combustion (with 3000 ppm SO_2 injection). This indicates that the influence of the coal property on the SO_2 and H_2S formation mechanism are similar for air-blown and O_2/RFG combustion. The volumetric fraction of H_2S in an O_2/RFG combustion scenario, as illustrated in Figure 8.9.C is observer to be much lower than air-blown combustion and O_2/CO_2 combustion. This is due to a much higher in furnace SO_2 concentration during O_2/RFG combustion, thereby resulting in a lower H_2S fraction, as H_2S fraction is the ratio of H_2S measured with respect to the sum of the H_2S and SO_2 measured.

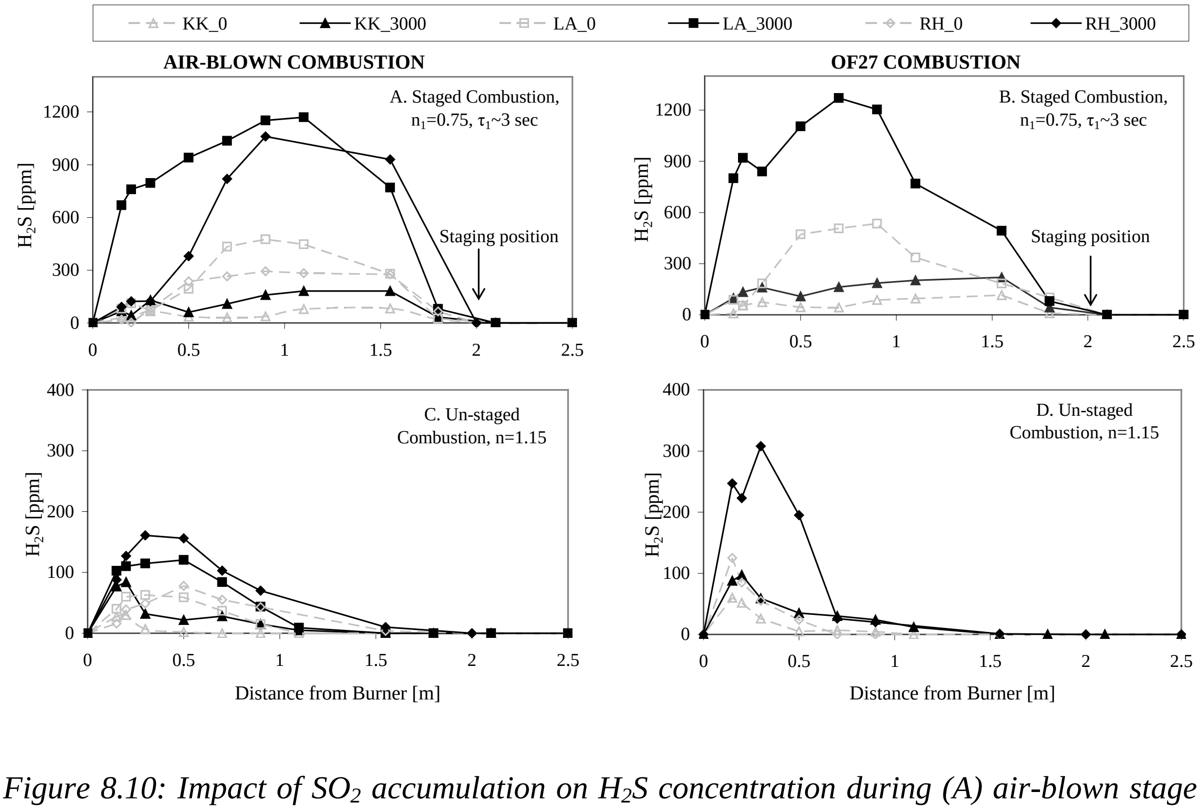


Figure 8.10: Impact of SO_2 accumulation on H_2S concentration during (A) air-blown staged combustion, (B) OF27 staged combustion, (C) air-blown un-staged combustion and (D) OF27 un-staged combustion.

However, as seen from Figure 8.10, the concentration of H_2S is approximately 2-3 times higher during OF27 combustion (with 3000 ppm SO_2 injection representing O_2/RFG combustion) when compared to air-blown combustion and O_2/CO_2 combustion (OF27, without injection of SO_2) in the near flame region, during staged as well as un-staged combustion. The concentration of H_2S during air-blown combustion with 3000 ppm SO_2 injection is also approximately 2-3 times higher than normal air-blown combustion. It is therefore suggested that, regardless of the combustion media, when the in-furnace SO_2 concentrations are high, the concentration of H_2S will also be high. It is however noted that air-blown combustion with 3000 ppm SO_2 injection has no practical relevance.

As H_2S is associated with high temperature corrosion in the radiative section of a furnace, it is therefore recommended to carefully consider the issue of corrosion during material selection of a furnace to be operated under oxy-coal combustion. This issue needs to be considered even more carefully for low rank, high sulphur containing coals, as the results from Figure 8.9.C and 8.10 clearly show a much higher volumetric fraction and concentration of H_2S for low rank brown coals, when compared to a medium volatile bituminous coal, Klein Kopje.

8.2. SUMMARY OF RESULTS

1. It is well understood that under air firing, sulphur is not retained in the high temperature radiative section of the furnace due to unstable state of sulphates formed at temperatures above 1000°C. This was seen to be the case during oxy-coal combustion as well.
2. A lower temperature window in the convective and recirculation path before ESP may offer a potential for SO_2 retention by sulphate forming elements in the ash. Regardless of the combustion media (CO_2 or N_2), if the concentration of sulphate forming

elements in the ash are high and sufficiently active, then SO_2 retained by the ash increases with an increase in SO_2 concentration, up to a certain concentration of SO_2 in the flue gas. As the SO_2 concentration is much higher during O_2/RFG combustion, the SO_2 retained by the sulphate forming elements in the ash will also be higher. The most important information that may be drawn from these results is that, if the coal being used has high concentration of active sulphate forming elements, the opportunity of retaining maximum possible SO_2 in the convective section and flue gas recirculation path leading to decreased SO_2 accumulation must be considered, when designing a cost effective oxy-coal plant. Furthermore, SO_2 reduction by the injection of sulphate forming compounds like lime may be another viable option.

3. The H_2S/SO_2 formation mechanism in a CO_2 environment is seen to be basically similar to the H_2S/SO_2 formation mechanism in a N_2 environment. However, the fraction of H_2S with respect to SO_2 is lower in a CO_2 environment and in O_2/RFG environment (OF27 with 3000 ppm injection of SO_2), when compared to air-blown combustion. This may be due to the enhanced consumption of H_2 to produce CO, resulting in a lower reaction rate of sulphur and hydrogen molecules to form H_2S. The concentration of H_2S in O_2/RFG scenario, on the other hand is much higher than air-blown combustion due to high in furnace SO_2 concentration. Therefore, it is recommended that careful attention needs to given to oxy-coal operated furnaces from corrosion point of view. This issue needs to be considered even more carefully for low rank (high volatile), high sulphur containing coals, as H_2S fraction and concentration for low rank coals is seen to be much higher than a medium volatile bituminous coal, Klein Kopje.

CHAPTER 9

SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

The main objective of this study was to experimentally investigate the combustion and emission behaviour during O_2/CO_2 conditions. A 20 kW electrically heated once through furnace was used for this investigation, which enabled highly flexible parametric studies as well as reliable and repeatable measurements. To simulate an oxy-coal combustion environment, almost pure O_2 and CO_2 supplied from the tanks was mixed in a highly flexible mixing station and supplied to the furnace via three different streams of the burner. Parametric studies were also performed during air-blown combustion to compare the combustion and emission behaviour in O_2/N_2 and O_2/CO_2 mixture. In addition, measurements with a simulated O_2/RFG (dry recirculation) scenario was conducted to investigate the behaviour of recycled flue gas species i.e. the behaviour of recycled NO and SO_2 by injecting a known concentration of synthetic NO and SO_2 into the furnace along with a mixture of O_2/CO_2. Four coals (ranging from medium volatile bituminous coal to pre-dried brown coal), natural gas and char were used for various parametric studies.

9.1. SUMMARY OF ACCOMPLISHED TASKS

As the initial application of oxy-coal combustion technology will most likely be a retrofit in existing pulverised coal furnaces, modifications are required to match the flame and heat transfer characteristics of air-blown furnaces. An investigation was therefore commenced with detailed in-flame and furnace exit measurements during un-staged combustion, using two bituminous coals (Klein Kopje and Ensdorf) and two pre-dried brown coals (Lausitz and Rhenish). Emission and combustion behaviour were investigated at different O_2/CO_2 concentrations by volume i.e. 21% O_2/ 79% CO_2 (OF21), 27% O_2/ 73% CO_2 (OF27) and 35%

O_2/ 65% CO_2 (OF35). To further establish the emission and combustion behaviour during oxy-coal combustion, investigation in explicitly gas-phase using natural gas was also performed. This investigation was able to develop a further understanding of the combustion behaviour of volatiles in O_2/CO_2 environment, whilst avoiding the influence of particles. This is thought to aid in improved prediction of homogeneous reactions taking place during oxy-coal combustion for scale-up and modelling purpose.

As the purity requirement of CO_2 for storage is still uncertain, it is rational to minimise impurities in the furnace when possible. The next focus of this investigation was therefore on the reduction of nitric oxide by oxidant staging during oxy-coal combustion. Detailed investigation of NO_x formation mechanisms during oxidant staged combustion in a CO_2 (27% O_2/73% CO_2 by volume) and N_2 (air-blown) environment was conducted by firing two pre-dried brown coals (Lausitz and Rhenish) and two bituminous coals (Klein Kopje and Ensdorf). Investigations of oxidant staged combustion in a CO_2 environment of 27% O_2/73% CO_2 was carried out as the initial results during un-staged combustion indicated that the combustion and emission behaviour for OF27 combustion was comparable to air-blown combustion. It is however noted that as the technology matures, future applications will be with reduced flue gas recycle rate resulting in higher combustion temperature. Gaseous concentration profile measurements for different burner oxygen ratios and residence time in the reduction zone were conducted. Measurement of in-flame HCN and NH_3, using a FTIR was also performed to determine the NO_x formation mechanisms during O_2/CO_2 combustion. This investigation not only aided in understanding the NO_x reduction potential during O_2/CO_2 combustion but also provided design features required for a low NO_x oxy-coal burner.

Oxy-coal combustion also requires recirculation of the flue gas to moderate the furnace temperature. Apart from CO_2 and water vapour, the recycled flue gas also contains pollutants from coal combustion and the impact of such pollutants recycled back into the furnace needs to be evaluated for successful application of oxy-fuel process. The next focus of this investigation was therefore the determination of the fate of nitrogen oxide recycled back into the furnace. Fate of NO recycle back into the furnace was determined by injecting a known concentration of pure NO via the burner or the over-fire port, along with air or O_2/CO_2 mixture, depending upon the investigation being carried out. A medium volatile bituminous coal (Klein Kopje) and a brown coal (Lausitz) were used for this investigation. Homogeneous and heterogeneous reduction of recycled NO was also determined by firing natural gas and char of a brown coal. Investigations were carried out during OF27 and air-blown combustion, with and without oxidant staging. This investigation has not only enhanced the understanding of NO_x re-burning mechanism during oxy-coal combustion, but may also provide the design features of low NO_x oxy-coal burner and assess the requirements of flue gas clean-up devices.

Besides the emission of CO_2, NO_x, CO, etc., the combustion of coal is also associated with the conversion of fuel sulphur into compounds such as SO_2, SO_3, H_2S, etc. The presence of sulphur components, especially H_2S and SO_3 are associated with high temperature corrosion at the furnace walls and super heater sections, and low temperature corrosion through the condensation of sulphuric acid in the economiser or air heater. Primary emphasis of the next investigation was therefore to assess the impact of combustion media (N_2 or CO_2) and recycled SO_2 on the formation of gaseous sulphur components in the furnace (SO_2 and H_2S). The SO_2 retention capacities of coals (ash) in the radiative and convective section of the furnace were also investigated. Investigations were carried out during air-blown and OF27 combustion, with and without staging. The impact of recycled SO_2 was investigated by injecting a known concentration of synthetic SO_2 through the secondary stream of the burner. This investigation not only assisted in assessing the risk of corrosion during oxy-coal combustion, but also aided in understanding the SO_2 retention capacity of different coals in the low temperature convective section of the furnace and the flue gas recycled path.

9.2. CONCLUSIONS

Extensive studies on the combustion and emission behaviour during O_2/CO_2 combustion using different ranks of coals, char and natural gas at different input oxygen concentrations (representing different recycle rates), different combustion conditions (staged and un-staged combustion) and simulation of different recycle flue gas species by injecting known concentrations of NO and SO_2 were successfully conducted. Major results and conclusions drawn from this study can be summarised as:

1. For an equivalent oxygen concentration, O_2/CO_2 combustion demonstrates a delay in combustion due to the higher heat capacity of CO_2. Measures such as higher input oxygen concentration and improved mixing are therefore required to match the combustion performance of an air-fired furnace. Similar flame temperature profile and gaseous concentration profile along the length of the reactor was observed for coals as well as natural gas firing during OF27 and air-blown combustion. The ash/char composition collected along the reactor length during coal firing was also observed to be similar for OF27 and air-blown combustion. This indicates that approximately 27 vol. % oxygen will be required during O_2/CO_2 combustion (representing oxy-coal combustion with dry flue gas recirculation) to achieve similar combustion performance of air-blown pulverised coal furnaces. The result further reinforces the findings from previous authors that oxygen concentration if properly adjusted gives the heat transfer and flame character similar to air-fired furnaces.
2. The conversion of fuel-N to NO at the furnace exit for all 4 coals tested during staged and un-staged combustion is seen to be lower in a CO_2 environment. When a comparison of the NO emission rate and fuel nitrogen conversion rate for different coals during un-staged OF27 combustion is made, a trend typical to conventional air-

fired, fuel lean combustion scenario was observed. That is, the higher the fuel-N content (for coals with comparable volatile content), the greater the NO emission, and the higher the volatile content (for coals with comparable fuel-N content), the greater the conversion of fuel-N to NO. It is however noted that the tests were conducted in a once through furnace without flue gas recirculation.

3. The carbon content in the ash and the NCV loss during air-blown and OF27 combustion, giving an indication of burnout and combustion efficiency of a combustion process, is in general lower during OF27 firing for staged as well as un-staged combustion. This indicates that ash arising out of oxy-coal combustion process may be a marketable product.
4. Oxidant staging for NO_x reduction is equally or even more effective for O_2/CO_2 combustion in terms of NO_x reduction potential, as the conversion of fuel-N to NO and NO_x emission rate is lower than corresponding air-blown combustion. Furthermore, fuel NO_x formation mechanism in a fuel rich environment during O_2/CO_2 combustion, as demonstrated by the formation and destruction of HCN and NH_3 is similar to air-blown combustion. The NO formed in the mixing zone reacts with hydrocarbon radicals to produce HCN or NH_3 which are converted to N_2 in the oxygen deficient reduction zone for both cases. As with conventional air-blown combustion, the formation of HCN and NH_3 is dependant on the coal rank as only HCN was detected for a medium volatile bituminous coal (Klein Kopje) while both HCN and NH_3 were detected for the Lausitz brown coal.
5. Reduction rate of NO formed in the fuel-oxidant mixing zone is in general higher for OF27 combustion and is most likely due to the higher concentration of hydrocarbon radicals in the flame. Higher concentration of HCN and NH_3 measured during OF27 firing further indicates more reduction of NO formed in the mixing zone to HCN and NH_3. The influence of burner oxygen ratio on the amount of HCN and NH_3 formed is

however similar for air-blown and OF27 combustion, i.e. the lower the burner oxygen ratio, higher the concentration of HCN and NH_3. In other words, lower the burner oxygen ratio, greater the reduction of NO formed in the mixing zone to HCN and NH_3, which is further converted to N_2. This is consistent with lower NO emission at the furnace exit during combustion with lower burner oxygen ratio. As with conventional air-blown combustion, the reduction of NO is proportional to the partitioning of fuel-N into the gas-phase. This may be considered an encouraging result from oxy-coal combustion perspective as the amount of fuel-N partitioned into the gas-phase is a function of temperature, and manipulation of local temperature is considered to be simpler during oxy-coal combustion. Direct injection of O_2 into the flame in order to increase the devolatilisation rate without affecting the overall heat transfer performance could be one viable option that can take advantage of existing infrastructure of an oxy-fuel plant for further reduction of NO.

6. By considering the overall reduction of recycled NO, the NO_x emission rate is between 0.24 to 0.37 times lower during oxy-coal combustion with 73 vol. % flue gas recycle. This is in agreement with historical investigations carried out during oxy-coal combustion with flue gas recycle, further confirming that the reduction of NO recycled back into the furnace is the most important factor resulting in lower NO_x emissions rate during oxy-coal combustion.
7. Reduction of recycled NO during coal combustion for both air-blown and O_2/CO_2 combustion is seen to be entirely dependent on the combustion conditions such as the burner oxygen ratio and the residence time in the reduction zone. Recycled NO reduction of almost 100% was achieved during staged combustion with a burner oxygen ratio of 0.75, and approximately 50% reduction was achieved during un-staged combustion. Similarly, a longer residence time in the reduction zone during staged combustion has a positive influence on recycled NO reduction when NO is introduced

via the burner. The reduction of recycled NO, at a burner oxygen ratio of 0.75 is almost similar for air-blown and oxy-coal combustion, indicating that the combustion media has little influence on recycled NO reduction when oxygen availability is low or when homogeneous reactions are prominent. However, as oxygen availability increases with increase in burner oxygen ratio (or when heterogeneous reactions are dominant), reduction of recycled NO is higher in a CO_2 media. This is most probably due to the presence of higher in-flame CO concentrations during oxy-coal combustion, which is known to enhance NO reduction via heterogeneous reactions. Furthermore, concentration of recycled NO within the range of 1200 ppm showed no influence on recycled NO reduction efficiency indicating that reduction efficiency will be unaffected with an increase in the concentration of recycled NO.

8. Reduction efficiency of recycled NO is also seen to be dependent on the location of NO injection as reduction of recycled NO when injected via the over-fire port is much lower than when it is introduced via the burner. Results demonstrate that the reduction efficiency of recycled NO introduced via the over-fire port is 2 to 3 times lower for pre-dried brown coal when compared to bituminous coal. This is thought to be due to fewer active carbon sites remaining in the ash of reactive coals like brown coals by the time they reach the location of the NO injection (over-fire port). This further illustrates the importance of heterogeneous reactions by active carbon sites in oxygen rich surroundings. However, the fraction of NO entering the furnace via the over-fire port during staged combustion is small when compared to the fraction entering the furnace via the burner, and therefore will have a minor influence on the final NO concentration.
9. Reduction of recycled NO by heterogeneous reaction with active carbon sites (as indicated by measurements with char of brown coal) is seen to be prominent when oxygen is in excess. 41% reduction was achieved with char during OF27 combustion

with a burner oxygen ratio of 1.15, whereas only around 15% reduction was achieved for natural gas combustion for a similar burner oxygen ratio. However, as oxygen availability decreases with a decrease in burner oxygen ratio during staged combustion, homogeneous reactions (reactions with active hydrocarbon radicals) becomes prominent, as approximately 90% reduction of recycled NO was achieved for a burner oxygen ratio of 0.75 and 0.85 during combustion with natural gas.

10. The CO emission at the furnace exit during staged as well as un-staged combustion for air-blown and O_2/CO_2 combustion cases are below 100 ppm indicating that the control of CO emission should not be any more challenging than during conventional air-blown combustion. However, higher CO peak was observed in the flame zone during O_2/CO_2 firing and could be due to enhanced CO_2 shift and water gas shift reactions in CO_2 environment.
11. The H_2S/SO_2 formation mechanism in CO_2 and N_2 environment are basically similar. However, the fraction of H_2S with respect to SO_2 is lower in CO_2 and O_2/RFG environment when compared to air-blown combustion. It is suggested that this may be due to enhanced consumption of H_2 to produce CO by the water shift reaction, resulting in lower reaction rate of sulphur and hydrogen compounds to form H_2S. The concentration of H_2S in O_2/RFG environment on the other hand is much higher than during air-blown combustion. This is due to the presence of high in furnace SO_2 concentration in O_2/RFG environment. Therefore, from a corrosion perspective, special attention may be required for oxy-coal operated furnaces. Low rank (high volatile), high sulphur coals might require even more attention, as both H_2S fraction and the concentrations are seen to be much higher than for medium volatile bituminous coal.
12. As expected, SO_2 is not retained in the high temperature radiative section of a furnace during oxy-coal combustion due to the un-stable state of sulphates formed at

temperatures above 1000°C. However, a lower temperature window in the convective and flue gas recirculation path before the ESP offers a potential for SO_2 retention by sulphate forming elements in the ash. Regardless of the combustion media (CO_2 or N_2), if the concentrations of sulphate forming elements in the ash are high and active, then SO_2 retained by the ash increases with an increase in SO_2 concentration, up to certain concentration of SO_2 in the flue gas. As the SO_2 concentration is much higher during O_2/RFG concentration, the SO_2 retained by the sulphate forming elements in the ash will also be higher. The most important information from these results is that, if the coal being used has high concentration of active sulphate forming elements, the opportunity of retaining maximum possible SO_2 in the convective section and flue gas recirculation path leading to decreased SO_2 accumulation needs to be considered, when designing a cost effective oxy-coal plant. Furthermore, SO_2 reduction by the injection of sulphate forming compounds like lime may be another viable option.

9.3. LIMITATIONS AND RECOMMENDATIONS

This study offered a unique opportunity to investigate the emission and combustion behaviour of a series of fuels (bituminous coals, brown coals, char and natural gas) during O_2/CO_2 combustion. The results not only confirm with much of what has been reported in previous studies, but the current knowledge has been improved in many aspects. However, not all issues regarding the process have been answered. The limitations within this study and recommendations for future investigations are proposed herewith:

1. All of oxy-coal combustion studies were conducted in a mixture of O_2/CO_2. Parametric study in a mixture of $O_2/CO_2/H_2O$ is therefore highly recommended to further understand oxy-coal combustion representing wet flue gas recirculation.

2. In-flame H_2S measurements have indicated that oxy-coal combustion with flue gas recirculation has much more corrosive environment than air-blown combustion. However, the presence of corrosive species will have little impact if they cannot reach the furnace wall. As the measurements for this investigations were conducted along the central axis of the furnace, measurements along the furnace wall to investigate the presence of corrosive species is recommended. Detailed investigation on slagging and fouling behaviour in oxy-coal operated furnace wall is also recommended. Furthermore, investigation on the formation of SO_3 and dew point corrosion during oxy-coal combustion is also recommended.
3. Proper burner design is capable of not only reducing the fuel and recycled NO, but could be effective in avoiding the in-furnace corrosive species from reaching the furnace wall and hence minimise high temperature corrosion. As this study was conducted with a single burner set-up, detailed investigations with different burner setups (swirl, direct O_2 injection etc) to determine the optimum burner set-up for oxy-coal combustion are recommended.
4. High in-furnace SO_2 concentration, an inherent characteristic of oxy-coal combustion process, could be responsible for high temperature corrosion due to higher concentration of H_2S thus formed. On the other hand, measurements conducted in the flue gas path shows a potential of retaining SO_2 by sulphate forming elements in the ash. Detailed investigation on SO_2 retention by injecting sulphate forming elements in the convective section of the furnace and the flue gas path is therefore highly recommended.
5. Although, a broad range of coals was covered, behaviour of low volatile coals (volatile content less than 20%) during oxy-coal combustion was not investigated within this study. Therefore investigation with low volatile coals during oxy-coal combustion is also recommended.

6. Issues not previously investigated like the performance of dust clean-up devices like ESP, bag-filter, etc., during oxy-coal combustion is also recommended. Similarly, investigation on the performance of flue gas clean up devices like SCR and FGD is recommended.
7. Detail investigation on the radiative and convective heat transfer behaviour during oxy-coal combustion is also recommended.
8. Although the carbon in ash during OF27 combustion is similar to air-blown combustion, detailed ash characterisation from the perspective of utilisation is also highly recommended.
9. Impact of oxy-coal combustion on mercury formation and capture is also recommended.
10. Investigations on the fate of recycled NO and SO_2 were conducted by injecting pure NO or SO_2 via the secondary stream of the burner. Investigation by injecting NO and SO_2 via all three streams of the burner, therefore representing more closely the oxy-coal combustion process with flue gas recirculation is suggested. Furthermore, study on the interaction of these recycled species by injecting NO and SO_2 into the furnace simultaneously is suggested.
11. A more detailed characterisation of the coals, especially the forms of calcium present, inorder to understand the mechanisms associated with the retention of SO_2 by the ash are also recommended.

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APPENDIX A

DEFINATION OF UNIQUE TERMS

The characteristic terms used within this study to evaluate, assess and compare the experimental results are explained in this section.

A.1. Oxygen Ratio (n)

Oxygen ratio is defined as the ratio of actual oxygen requirement to stoichiometric oxygen requirement and the correlation between the oxygen ratio and the inlet oxygen concentration is:

$$n = \frac{y_{O_2,d,inlet} + (\alpha - 1) y_{O_2,d,excess}}{y_{O_2,d,inlet} - y_{O_2,d,excess}} \qquad \text{[E A.1]}$$

Where,

$y_{O_2,d,inlet}$ = inlet oxygen concentration in a dry basis [vol. %]

$y_{O_2,d,excess}$ = oxygen concentration in the flue gas in a dry basis [vol. %]

$$\alpha = \frac{V_{G0,d}}{V_{O0,d}}$$

Where,

$V_{G0,D}$ = dry stoichiometric flue gas volume [m^3/kg]

$V_{O0,d}$ = dry stoichiometric oxidant volume [m^3/kg]

The oxygen ratio was calculated assuming an ideal gas condition with similar molar volume resulting in α=1 and leading to a simplified formula:

$$n = \frac{y_{O_2,d,inlet}}{y_{O_2,d,inlet} - y_{O_2,d,excess}} \qquad \text{[E A.2]}$$

It is noted that, unlike air-blown combustion, where the inlet oxygen concentration is normally 21 vol. %, the inlet oxygen concentration during oxy-fuel combustion depends on the recycle ratio. As can be seen from Table A.1, for an oxygen ratio of 1.15, the O_2 excess in dry basis will be 2.74, 3.52 and 4.57 vol. % during combustion with inlet oxygen concentration of 21 (Air, OF21), 27 (OF27) and 35 (OF35) vol. % respectively. Therefore, for oxy-fuel combustion besides the concentration of oxygen in the flue gas, concentration of oxygen in the combustion media is also required to define oxygen ratio.

Table A.1: Influence of inlet oxygen concentration on oxygen ratio.

	O_2 Excess [vol. %]			
Oxygen Ratio	Air	OF21	OF27	OF35
1	0.00	0.00	0.00	0.00
1.05	1.00	1.00	1.29	1.67
1.1	1.91	1.91	2.45	3.18
1.15	2.74	2.74	3.52	4.57
1.2	3.50	3.50	4.50	5.83
1.25	4.20	4.20	5.40	7.00

A.2. Emission Rate

To ensure similar flame shape and similar residence time inside the reactor, the total volumetric flow of oxidants through the burner was kept constant for all experimental cases. However, the coal feeding rate was increased for oxy-coal combustion with higher oxygen concentration to maintain the same oxygen ratio. Although the coal feeding rate was changed, its impact on the overall combustion is negligible as most of the heat in the test facility is provided from the electrical heaters.

Comparison of emission in concentration is however inadequate if the purpose is to compare emissions between air and oxy-coal combustion. An expression that takes into account the difference in energy input is required. Emission rate, which is defined here as the mass of species emitted per energy input is a neutral way of expressing pollutant emissions and is given by the expression:

$$\varphi_k = y_{k,d} \cdot \rho_{n,k} \cdot \frac{V_{G,d}}{H_u} \qquad \text{[E A.3]}$$

$$\rho_{nk} = \frac{M_k}{V_{mn,k}} \qquad \text{[E A.4]}$$

Where,

φ_k = emissions in the flue gas of the species k related to energy input [mg/MJ]

$y_{k,d}$ = volume fraction of species k in dry flue gas [ppmv]

$\rho_{n,k}$ = density of species k at STP conditions [kg/m^3]

$V_{G,d}$ = dry flue gas volume related to fuel mass at STP [m^3/kg]

M_k = molecular weight of species k [kg/kmol]

$V_{mn,k}$ = standard molar volume of species k [m^3/kmol]

H_u = net calorific value of the fuel [MJ/kg]

As the measurements for this study were conducted in a once through furnace, the dry flue gas volume is calculated by considering the total flue gas volume (positon A in Figure A.1) unless otherwise stated. However, most of the emission rate cited in literatures, during oxy-coal combustion with flue gas recycle are calculated by considering dry flue gas volume downstream of flue gas recycle point (position B in Figure A.1). The calculated emission rates in this study are therefore not directly comparable with those mentioned in literatures with flue gas recycle.

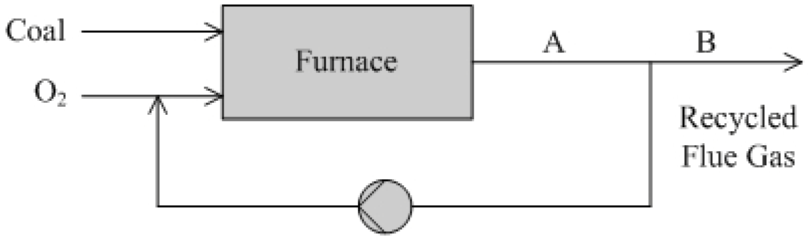

Figure A.1: Schematic illustrating the position of flue gas volume calculation for this study and cited literatures with recycled flue gas.

A.3. Conversion of Fuel-N to NO and Fuel-S to SO_2

The percentage conversion of the fuel-N to NO, and fuel-S to SO_2 is given by the equation:

$$\eta_k = \frac{100 \cdot y_{k,d}}{y_{k,\max,d}} \qquad \text{[E A.5]}$$

Where,

η_k = conversion of fuel-N to NO or fuel-S to SO_2 [%]

$y_{k,d}$ = measured volume fraction of species k (NO or SO_2) in dry flue gas [ppmv]

$y_{k,\max,d}$ = maximum possible volumetric concentration of species k (NO or SO_2) in dry flue gas if all of fuel-N or fuel-S are converted to NO or SO_2 [ppmv]

And,

$$y_{k,max,d} = \frac{V_{k,max,d} \cdot 1000000}{V_{G,d}} \qquad \text{[E A.6]}$$

Where,

$V_{k,max,d}$ = maximum possible volume of species k (NO, SO_2) related to dry flue gas mass if all of fuel-N or fuel-S are converted to NO or SO_2 [m^3/kg]

$V_{G,d}$ = dry flue gas volume related to fuel mass at STP [m^3/kg]

And,

$$V_{k,max,d} = \frac{M_k}{M_i} \cdot \frac{\gamma_i}{\rho_{n,k}} \qquad \text{[E A.7]}$$

Where,

M_k = Molar mass of species k (NO or SO_2) [kg/kmol]

M_i = Molar mass of substance i (N or S) [kg/kmol]

γ_i = fuel mass fraction of substance i (N or S)

$\rho_{n,k}$ = density of species k (NO or SO_2) at STP conditions [kg/m^3]

A.4. NCV Loss

Although carbon in ash gives an indication of efficiency of a combustion system, it does not take into account the ash content of a fuel and therefore might be misleading, especially when comparing different fuels. NCV loss gives efficiency loss of a combustion system due to incomplete combustion by taking into account the ash content of the fuel and is given by:

$$v_f = \gamma_A \cdot \frac{\gamma_{C,A}}{100 - \gamma_{C,A}} \cdot \frac{H_c}{H_u} \qquad \text{[E A.8]}$$

Where,

v_f = NCV loss [%]

γ_A = Ash content of the fuel [%]

$\gamma_{C,A}$ = Carbon content in the ash [%]

H_c = CV of char [33.82 MJ/kg]

H_u = NCV of fuel [MJ/kg]

A.5. Percentage Reduction of Recycled NO

During O_2/RFG combustion, as illustrated in Figure A.2, NO in the flue-gas is from two sources, namely nitrogen in the fuel and NO recycled back into the furnace. NO formed from the fuel can be defined as NO measured when recycled-NO is zero or when there is no injection of NO. Contribution of NO in the flue gas from recycled NO can then be defined as:

$$y_{NO,r} = y_{NO,\,wi} - y_{NO,woi} \qquad \text{[E A.9]}$$

Where,

$y_{NO,woi}$ = NO_{fuel} = Measured NO (dry) during combustion of fuel without NO injection [ppmv]

$y_{NO,wi}$ = $NO_{measured}$ = Measured NO (dry) during combustion of fuel with NO injection [ppmv]

$y_{NO,r}$ = NO_{rec} = Contribution of NO in dry flue gas from recycled (injected) NO [ppmv]

With the definition of $y_{NO,r}$, analysis of experimental results for the fate of recycle NO during oxy-coal combustion was carried out by introducing the term 'percentage reduction of recycled NO' given by:

$$\beta_{NO} = \frac{y_{NO,inj} - y_{NO,r}}{y_{NO,inj}} \cdot 100 \qquad \text{[E A.10]}$$

Where,

$y_{NO,inj}$ = Volumetric concentration of injected NO (dry) as measured at the furnace end without combustion of fuel [ppmv]

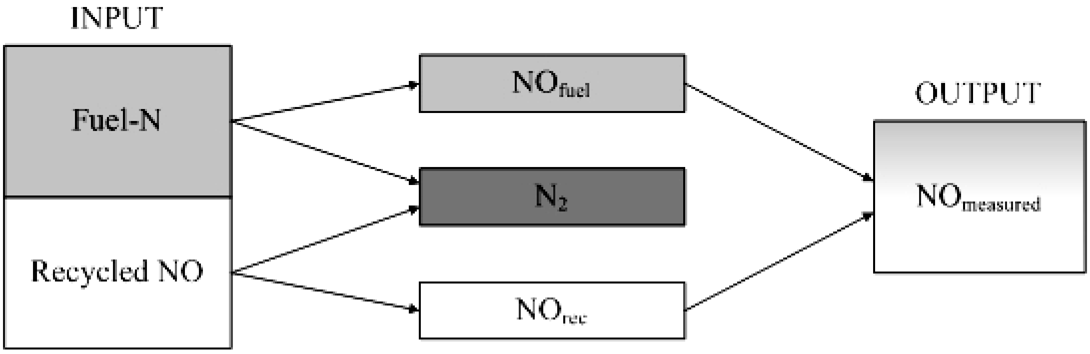

Figure A.2: Source of NO during oxy-coal combustion with recycled flue-gas.

A.6. Overall Percentage Reduction of Recycled NO

Measurements for the investigation of fate of recycle NO during oxy-coal combustion were conducted by injecting NO via the burner and via the over-fire port separately. The overall percentage reduction of recycled NO during staged combustion is therefore dependant on the fraction of recycled NO through the burner and the over-fire port and can be written as:

$$\beta_{NO,overall} = \frac{(\dot{V}_{O,bur} \cdot \beta_{NO.bur}) + (\dot{V}_{O,OFP} \cdot \beta_{NO.OFP})}{\dot{V}_{O,bur} + \dot{V}_{O,OFP}} \qquad \text{[E A.11]}$$

Where,

$\dot{V}_{O,bur}$ = Volumetric flow of oxidant (O_2/CO_2 or air) through the burner at STP [m^3/h]

$\dot{V}_{O,OFP}$ = Volumetric flow of oxidant (O_2/CO_2 or air) through the over-fire port at STP [m^3/h]

$\beta_{NO.bur}$ = Reduction of recycled NO introduced via the burner [%]

$\beta_{NO.OFD}$ = Reduction of recycled NO introduced via the over-fire port [%]

A.7. Stable or Equilibrium NO Concentration

Similarly, method used for calculation of stable-NO concentration or equilibrium NO concentration in the furnace after accumulation of recycled NO and can be written as:

$$y_{NO,s} = \frac{y_{NO,woi}}{1-(1-y_{O_2,d})(1-\frac{\beta_{NO,overall}}{100})} \qquad \text{[E A.12]}$$

Where,

$y_{NO,s}$ = stable or equilibrium NO concentration in dry flue gas [ppmv]

$y_{NO,woi}$ = NO from fuel-N or measured NO during combustion of fuel without NO injection [ppmv]

$\beta_{NO,overall}$ = overall percentage reduction of recycle NO as calculated using equation E A.11 [%]

And,

$$1 - y_{O_2,d} = \frac{\dot{V}_{rec,d}}{\dot{V}_{O,d}} \qquad \text{[E A.13]}$$

Where,

$\dot{V}_{rec,d}$ = volumetric flow of recycled flue gas (dry) at STP [m^3/h]

$\dot{V}_{O,d}$ = volumetric flow of recycled flue gas after addition of oxygen (dry) at STP [m^3/h]

A.8. Maximum SO_2 Concentration during O_2/RFG Combustion

The theoretical maximum SO_2 concentration in the furnace during O_2/RFG combustion due to the accumulation of SO_2 can be approximated by considering combustion in pure oxygen [Sche08] and using the expression:

$$y_{SO_2,max,d} = \frac{V_{SO_2,max,d} \cdot 1000000}{V_{G,PO,d}} \qquad \text{[E A.14]}$$

Where,

$y_{SO_2,max,d}$ = maximum possible volumetric concentration of SO_2 in dry flue gas if all of fuel-S is converted to SO_2 [ppmv]

$V_{SO_2,max,d}$ = maximum possible volume of SO_2 related to dry flue gas mass if all of fuel-S is converted to SO_2 [m^3/kg]

$V_{G,PO,d}$ = dry flue gas volume related to fuel mass at STP during combustion with pure oxygen [m^3/kg]

And,

$$V_{SO_2,\max,d} = \frac{M_{SO_2}}{M_S} \cdot \frac{\gamma_S}{\rho_{n,SO_2}} \qquad \text{[E A.15]}$$

Where,

M_{SO_2} = Molar mass of SO_2 [kg/kmol]

M_S = Molar mass of S [kg/kmol]

γ_S = fuel mass fraction of S

ρ_{n,SO_2} = density of SO_2 at STP conditions [kg/m^3]

A.9. (SO_2+H_2S)-Sulphur Balance

The sum of SO_2 and H_2S is calculated from the difference between maximum theoretical concentration of sulphur containing species (SO_2 and H_2S) in the gas phase and concentration of SO_2 not released in the gas phase due to sulphur remaining in the char collected and is given by the expression:

$$y_{SO_2+H_2S,MB,d} = y_{SO_2+H_2S,\max,d} - y_{SO_2+H_2S,A,d} \qquad \text{[E A.16]}$$

Where,

$y_{SO_2+H_2S,\max,d}$ = maximum possible volumetric concentration of sulphur containing species (SO_2 and H_2S) in dry flue gas if all of fuel-S is converted to SO_2 and H_2S [ppmv]

$y_{SO_2+H_2S,A,d}$ = maximum possible concentration of SO_2 in dry flue gas if all of sulphur retained in the ash is converted to SO_2 and H_2S [ppmv]

APPENDIX B

CROSS SENSITIVITY OF THE ANALYSERS USED

Careful attention needs to be given to the analysers for oxy-coal combustion measurements, as the CO_2 concentration is much higher in the flue-gas. NO_x analyser based on chemiluminescence principle has a quenching effect in a CO_2 environment, therefore NO_x calibration gas in a CO_2 background was used for the calibration of NO_x analyser for oxy-fuel combustion measurements.

Similarly, the cross- sensitivity of CO and CO_2 in oxy-fuel environment for CO analysers based on NDIR principle also needs to be checked and corrected appropriately. As seen from Figure B.1, the CO analyser based on NDIR principle measures CO in an O_2/CO_2 environment although there is no presence of CO in the synthesis gas and therefore the CO readings need to be corrected accordingly.

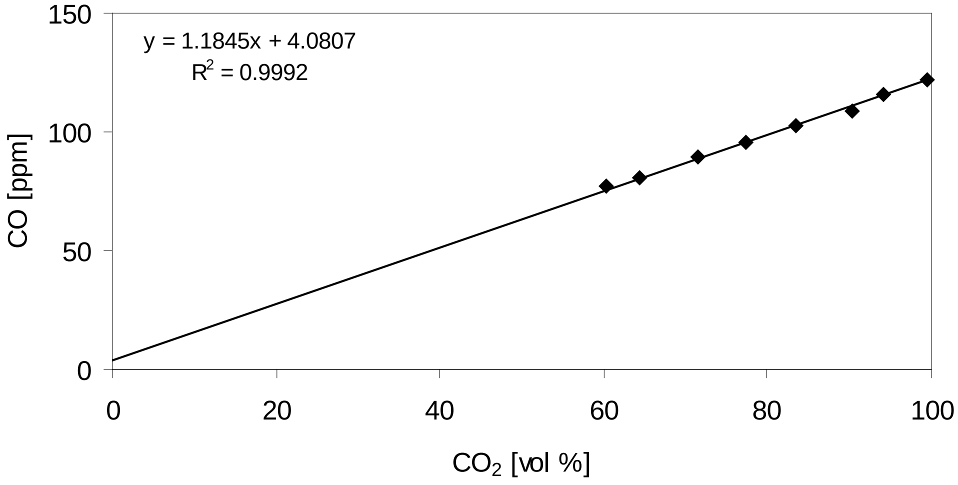

Figure B.1: Cross sensitivity of CO analyser in CO_2 environment.

Details on avoiding cross sensitivity and interference from different species present in the flue-gas during measurements with FTIR is included in the dissertation from Benöhr

[Ben03]. Similarly, the cross sensitivity on H_2S analyser used for this investigation (from Western Research from Canada, model 921CE) was checked with different species that might be present in the flue-gas i.e. CO_2, NO, SO_2 and H_2. As seen from Figure B.2 and B.3, the analyser displayed cross sensitivity effect from NO and SO_2 and therefore the H_2S readings were corrected accordingly.

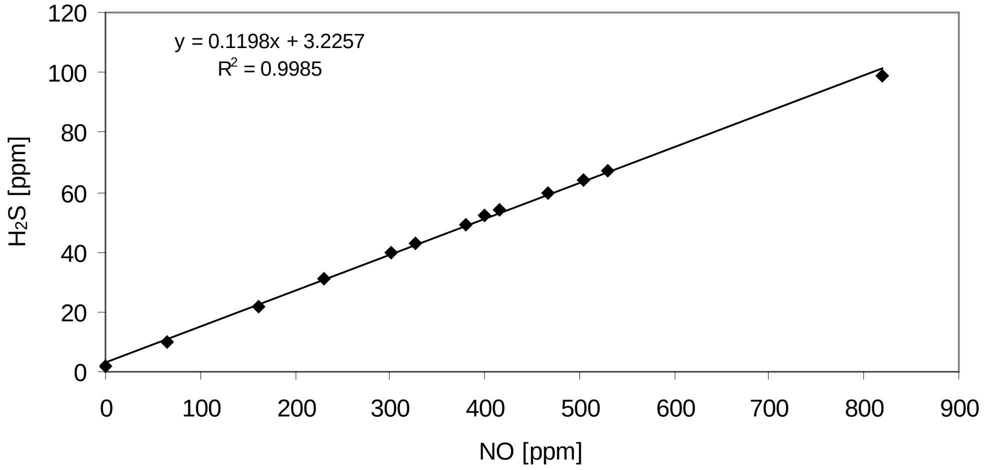

Figure B.2: Cross sensitivity of H_2S analyser with NO.

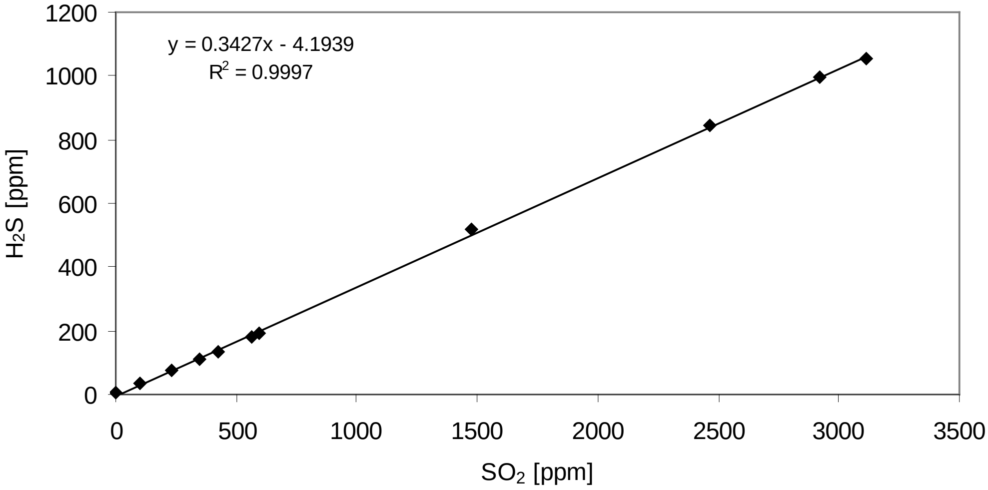

Figure B.3: Cross sensitivity of H_2S analyser with SO_2.