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A Study of the Behaviour of Coal Injected into the Blast Furnace

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The manufacture of metallurgical coke is a major cost component in the manufacture of steel by the traditional blast furnace – BOS route that still dominates the industry worldwide. Coke oven capital and maintenance costs are high, whilst prime coking coals are increasingly expensive; with limited options for replacement with blends of poorer quality coals. Reduction of the metallurgical coke requirement for producing molten iron in the blast furnace thus remains a key aim of the steel industry.

Traditional furnace practice has relied upon metallurgical coke as the sole carbon source, however, as the price of coke has risen, alternatives have been actively sought. In the limit, coke is only necessary as a porous burden support; the provision of carbon for heat generation, and for chemical reduction of iron oxides, can be supplied by injecting oil, gas or coal into the base of the blast furnace. Modern practice now includes coal injection at rates of up to 180 – 200 kg per tonne hot metal. This level of carbon substitution is still short of the ultimate limit dictated by burden support criteria, suggesting that further gains may be possible. However, operational difficulties have appeared when higher injection rates have been attempted; these include blockage by fines of the coke bed and carbon carry-over from the furnace top. Bed blockage is a potentially serious problem, since it is difficult to reverse and furnace campaigns are based on years of continuous operation.

Study of the behaviour of coal under blast furnace injection conditions had been the subject of a 1999-start ECSC research project, co-ordinated by Corus (UK) Limited, and involving Imperial College London, TKS and CSM. Imperial had used a wire-mesh reactor to attempt a laboratory simulation of the conditions experienced by coal in the tuyeres and raceway zones of a modern blast furnace. Simulation of these conditions is very difficult, since it is necessary to expose coal to oxygen-enriched air (typically 25% O\textsubscript{2}), for very short residence times (tens of ms), at high temperature (up to 2000ºC) and at elevated pressure (up to 0.5 MPa). This short-pulse oxidation must then be followed directly by CO\textsubscript{2} gasification of the surviving coal char. The project was partially successful in simulating the desired conditions. A short-pulse oxygen injection system was developed and much useful data produced. However, the maximum temperature achieved was 1500ºC, and operation was limited to near atmospheric pressure. Never-the-less, the project produced an interesting overall conclusion; the fate of injected coal depends primarily on carbon dioxide gasification in the raceway, not direct combustion by oxygen, due to the short time available.

The encouraging progress made in this ECSC project lead to the formulation of the current BCURA project. Here the objective has been to further modify the wire-mesh reactor to more closely simulate the real conditions in the raceway and coke bed of a blast furnace, operating with coal injection. The project has aimed to achieve temperatures up to 2000ºC and pressures up to 5 MPa. Information has again been sought on the separate extents of coal weight loss caused by initial pyrolysis, short-pulse oxygen exposure and, finally, CO\textsubscript{2} gasification. Specific objectives are listed as follows:

1. Laboratory-scale investigation of the fundamental devolatilisation behaviour of selected blast furnace coals, under conditions prevailing in tuyere and raceway regions of the blast furnace.
2. Investigation of relationships between pyrolysis/combustion conditions (in the tuyere and raceway regions of the blast furnace) and the combustion reactivity of chars formed under these conditions.
3. Design of a new short pulse oxygen injection system for the wire-mesh reactor and definition of its operation limits.
4. Evaluation of the relative combustion and CO₂-gasification reactivity of chars with respect to the degree of burnout in the coal plume.
5. Investigation of char combustion kinetics and estimation of kinetic coefficients based on the wire-mesh experiments.
6. Provide collaborating institutions with estimates of the behaviour and eventual fate of coal particles injected into the hot blast, as a function of original coal properties and plume conditions based on those determined in larger scale experiments.

Achievement of the more realistic simulation sought has required a fundamental re-design of the short-pulse oxygen injection system and its application to the high-pressure version of the wire-mesh reactor. This re-design has proved to be time-consuming, but has resulted in a significant improvement in the accuracy of control of injected oxygen. The exact quantity of oxygen; the timing and sharpness of the injected spike; the flowrate control and minimization of pressure fluctuation have all been improved. Furthermore, operating pressures representative of those in commercial blast furnaces, up to about 0.5 MPa, have been achieved for the first time. Unfortunately, excessive oxidation of the molybdenum mesh, used to support the coal sample, has proved to be an unsurmountable obstacle to the attainment of the most extreme operating conditions hoped for at the outset. Great effort has been expended in defining the limits of operation [temperature, pressure, residence time, oxygen concentration] with the new system; with a significant study of molybdenum chemistry as an unplanned addition.

Despite these limitations, it has been possible to conduct pyrolysis experiments up to the desired maximum operating temperature, 2000 °C, and at pressures up to 1.0 MPa. Short-pulse oxidation experiments have had to be limited to 3% oxygen at 1500 °C under representative pressures, and 20% oxygen at 1300 °C, also under representative pressure. However, the data derived have enabled some kinetics to be derived and suggest that above about 1400 °C, the char oxidation becomes mass transfer, rather than chemistry, i.e. temperature, controlled. The measured extents of combustion are always less than 10%, suggesting that the conclusions of the earlier ECSC project were correct, i.e. that char consumption depends on gasification rather than short-pulse combustion. Successful completion of CO₂ gasification experiments, under pressure, have re-affirmed the earlier conclusion that about 10s of gasification time is needed to completely consume the residual char. To put this into the context of blast furnace operation, typically, char particles are expected to remain in the high temperature, oxidising regions of the furnace for around 20-100 ms.

An extensive investigation of char reactivity has also been conducted by TGA, yielding valuable data on pyrolysis and combustion char reactivity as a function of rank and formation condition, e.g. peak temperature, pressure, oxygen exposure. In addition, kinetic coefficients have been estimated for the coal combustion process under blast-furnace conditions.

In total, a large body of new data, including process trends, has been generated during the project. These are intended to provide improved estimates of the likely behaviour, and eventual fate, of coal particles injected into the base of a blast furnace. The inclusion of high pressure operation represents a significant advance over the previous work, as does the achievement of
2000 °C pyrolysis temperature. The initial objectives of the project have thus been achieved in the main; subject only to the physical limitations imposed on the short-pulse combustion experiments by molybdenum mesh oxidation.

The key commercial implications may be listed as follows:

i). The pyrolysis weight loss increases with temperatures up to 2000 °C, although losses above 1500 °C are due to mineral matter volatilisation; in addition, the char reactivity decreases with the exposure temperature. The short-pulse oxidation studies show that char oxidation is controlled by external diffusion of oxygen above about 1400 °C. Thus the combustion rate will not be improved by further increasing temperature; improved exposure of the coal to oxygen is required to improve burn-out. However, increasing the temperature in the blast furnace raceway will increase the char gasification reactivity, thereby shortening the time for the destruction of residual char.

ii). The type of coal injected into the blast furnace is another important factor. Coals with higher volatile matter contents normally achieve higher weight loss during pyrolysis. However, this is not necessarily true during char combustion inside the raceway. Although, coals with higher volatile matter content produce more reactive chars during pyrolysis, the difference diminishes with increasing temperature. Coals with high volatile matter content are more likely to have a negative physical impact on the raceway performance due to the higher blast momentum produced.

iii). Although coal devolatilisation can be accomplished in a short period of time at high temperatures, the 20 ms, or so, available inside the blast furnace tuyere and raceway are unlikely to be sufficient to ensure complete volatile release in the coal plume. Therefore, increasing the coal particle residence time would increase the weight loss during pyrolysis. It would also increase the degree of char burnout and the extent of CO\textsubscript{2} gasification inside the raceway. Increasing the O\textsubscript{2} concentration will also increase the extent of combustion and improve the reactivity of the surviving char. The coal particle residence time could be increased by (1) increasing the distance between the coal injection lance and the tuyere nose, or (2) inducing more coal/air mixing through improved coal injection lance design. Increasing the O\textsubscript{2} concentrations in the blast could achieve higher burnout inside the raceway, subject to the constraints of increased oxygen supply costs and blast main temperature limits.

iv). There appears to be little benefit in further increasing the blast pressure. Although the extent of combustion increases slightly with pressure, up to 0.5 Mpa, this small gain is offset by a slight decrease in pyrolysis yield. The rate of CO\textsubscript{2} gasification of residual char is not sensitive to pressure below 1.0 Mpa.

v). The technical data produced in the project have immediate use in two current blast furnace research projects being pursued by Corus UK Limited; the EC RFCS project entitled “Minimising environmental emissions by optimised reductant utilisation” [MEORU] and the €80 M Pan-European project entitled “Ultra low carbon dioxide steel making” [ULCOS].
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1. INTRODUCTION

The operation of large batteries of coke ovens is a major cost component in the manufacture of steel by the traditional blast furnace – BOS route that still dominates the industry worldwide. The long coal residence time necessary in these batch ovens means that both productivity and energy efficiency are low. Furthermore, coke oven capital and maintenance costs are high and environmental emission standards are not easily met. In addition, prime coking coals are increasingly scarce, therefore expensive, and options for their partial replacement in ovens by blends of poorer quality coals are limited.

Minimisation of the amount of metallurgical coke needed to reduce iron ore to molten iron in the blast furnace thus remains a crucial issue in the manufacture of steel. Traditional furnace practice has relied upon metallurgical coke as the sole carbon source, however, as the price of coke has risen, alternatives have been actively sought. In the limit, coke is only necessary as a porous burden support; the provision of carbon for heat generation, and for chemical reduction of iron oxides, can be supplied by injecting oil, gas or coal into the base of the blast furnace. Modern practice now includes coal injection as the most economic method of coke substitution and injection rates of up to 180 – 200 kg per tonne hot metal are regularly achieved. This level of carbon substitution is still some way short of the ultimate limit dictated by burden support criteria, suggesting that further gains may be possible. However, operational difficulties have appeared when higher injection rates have been attempted; these include blockage by fines of the coke bed and carbon carry-over from the furnace top.

Replacement coal is injected through a lance into the preheated air blast as it passes, at high velocity, towards the tuyere and thence into the raceway region at the base of the furnace shaft\(^1\). The raceways are high temperature fluidized reaction zones formed at the locations where the air blast meets the base of the coke bed; there may be 20 or more individual tuyeres, each with an associated raceway, around the circumference of a large furnace. The principal reactions are the release of the coal volatiles by pyrolysis; the combustion of the volatiles and partial combustion of the residual char by oxygen; and, finally, the gasification of residual char by CO\(_2\). If the latter processes are not completed within the raceway region, residual char fines will be carried into cooler regions of the furnace where coke bed blockage will occur. In addition, the carbon content of the dust collected in the blast furnace gas conditioning plant will increase, due to char and soot carry-over with the top-gas.

A single tuyere pilot plant has been developed by Corus (U.K.) Limited; this has been used to carry out coal combustion studies. The results\(^2\) indicate that the furnace operation problems under high injection rates are due to a combination of increased blast activity, resulting from gasification of the coal within the tuyere, and the production of uncombusted coal char. Furthermore, several European operators have taken drilled core
samples from commercial furnaces, at the tuyere level, from which they have confirmed the presence of uncombusted char in the vicinity of the raceway at high injection rates. A significant increase in dust and slag production has also been observed at injection rates, above 200 kg/thm. In addition, there is an increase in the carbon content of the carryover material in the gas released from the top of the furnace. It can be concluded, therefore, that the behaviour and eventual fate of injected coal, and the resultant char properties, are considered to be a major factor affecting furnace operation.

Bed blockage is a potentially serious problem because the pathways for molten iron and slag flows are impeded and the effective working cross-section of the furnace is progressively reduced, thereby limiting productivity. Furthermore, once a volume within the furnace has become blocked it is very difficult to recover the lost porosity. Given that furnace campaigns usually exceed ten years of continuous operation, any mid-campaign loss of productivity will carry severe long-term cost implications.

The nature of the behaviour of coal under blast furnace injection conditions had been the subject of a 1999-start ECSC research project involving Imperial College London, Corus (UK) Limited, TKS and CSM. The Imperial College London contribution normally on laboratory simulation, using a wire mesh reactor, of the conditions experienced by coal in the tuyeres and raceway zone of a modern blast furnace. Simulation of these conditions is difficult, since it is necessary to expose coal to oxygen-enriched air (typically 25% O_2), for very short residence times (tens of ms), at high temperature (up to 2000ºC) and at elevated pressure (of a few bar). This short-pulse oxidation should then be followed directly by CO_2 gasification of the surviving coal char. The project successfully developed an air injection system that was able to inject short pulses of air/enriched air (lasting between 20 and 200 ms) through the wire mesh reactor. This could be followed by a longer controlled period in CO_2 if desired. However, because of equipment limitations it was not possible to achieve the very high temperature (2000ºC) of the raceway; instead a maximum temperature of 1500ºC had to be accepted. Nor was it possible to achieve the operating pressure of the raceway, because of limitations of the valves available.

The behaviour of a range of coals was investigated during the project. In a typical test, a coal with Proximate Analysis Volatile Matter content of 30% was observed to lose around 30% volatiles during the heat-up period (at 1000 K/s under pyrolysis conditions) to the peak temperature used, 1500ºC. However, a 50 ms exposure of the residual pyrolysis char to 25% O_2 (in N_2) only increased this weight loss by a few extra percent. Subsequent char gasification at 1500ºC, under a CO_2-rich atmosphere, proceeded at a rate approximately 1/50th of the oxidation rate, thereby requiring tens of seconds to achieve complete char consumption. Thus the general conclusion was that, contrary to initial expectations, the fate of injected coal is more dependent on the relatively slow CO_2 gasification of residual, post-oxidation chars in the bed of the furnace, rather than on coal consumption in the O_2-enriched air during its rapid passage through the furnace raceway. This conclusion implies that carbon carry-over will occur if the residual char formed in the raceway is swept rapidly upwards to cooler regions of the furnace, before it can be fully gasified by CO_2. Mathematical modelling work, conducted in parallel, suggests that pyrolysis char oxidation during the short air pulse is limited by mass transfer processes.
The objective of the current BCURA project has been to further modify the wire mesh reactor in order to gain detailed information under conditions more closely simulating those in the raceway and coke bed of a blast furnace, operating with coal injection. The project has aimed to achieve temperatures up to 2000°C and pressures up to 5 bar. Information has been sought on the extents of reaction (combustion, pyrolysis and gasification), as before.

A final component of the project had been an intended study of blast furnace dust samples supplied by Corus (UK) Ltd. These dusts, recovered from the gas cleaning system of commercial blast furnaces, will contain carbon derived from coke fines, coal char, soot and pyrolytic carbon, in addition to refractory fragments, fluxes and ferruginous materials. Means of rapid estimation of the coal-derived carbon contents of these dusts would provide a useful tool for furnace operation. The Size Exclusion Chromatography [SEC] technique promises to provide valuable information here, following on from preliminary work in the earlier ECSC project3. However, a new EU:RFS research project4, again co-ordinated by Corus [UK] Limited, is now running in parallel with the BCURA project and the application of SEC and also FT-Raman Spectroscopy to these dusts is the principal aim here. Dust analysis work has been omitted from the BCURA study, therefore, since the EU RFCS results will be available in the public domain.

The main objectives of this BCURA project may be listed as follows:

1. Laboratory-scale investigation of the fundamental devolatilisation behaviour of selected blast furnace coals, under conditions prevailing in tuyere and raceway regions of the blast furnace.
2. Investigation of relationships between pyrolysis/combustion conditions (in the tuyere and raceway regions of the blast furnace) and the combustion reactivity of chars formed under these conditions.
3. Design of a new short pulse oxygen injection system for the wire-mesh reactor and definition of its operation limits.
4. Evaluation of the relative combustion and CO₂-gasification reactivity of chars with respect to the degree of burnout in the coal plume.
5. Investigation of char combustion kinetics and estimation of kinetic coefficients based on the wire-mesh experiments.
6. Provide collaborating institutions with estimates of the behaviour and eventual fate of coal particles injected into the hot blast, as a function of original coal properties and plume conditions based on those determined in larger scale experiments.
2. EXPERIMENTAL

2.1 EXPERIMENTAL METHODOLOGY

The main objective of this BCURA project has been further development of our understanding of the reactions that occur in the tuyere, raceway and coke bed of a blast furnace, when operating with coal injection. Physical simulation of the operating conditions in a working blast furnace has been attempted using an electrically heated wire-mesh reactor [WMR]. The reactor, first developed by Howard et al. has been used extensively over many years in these laboratories for a wide range of coal pyrolysis and gasification [in carbon dioxide, steam, hydrogen] studies. The high pressure version of the wire-mesh reactor had been extensively modified in the previous ECSC project in order to permit short-pulse oxygen injection, possibly followed by carbon dioxide injection, for post-combustion gasification studies of residual chars.

None-the-less, because of limitations in the initial modifications, it has been necessary to expend considerable effort on further technique development during the current project, in order to refine the oxygen injection system. The heart of the wire-mesh reactor technique is a small strip of folded molybdenum mesh in which a monolayer of coal particles is trapped. A charge of between 1 and 6 mg of coal has been used, ground to 150 – 212µm [the size determined by the mesh size available]. The mesh plus coal strip is stretched [with tension provided by a spring] between water-cooled electrodes. An alternating current is then passed through the mesh to provide very accurately controlled time-temperature history. Temperature of the particles is measured directly by ultra-fine thermocouples located within the mesh. The mesh is continuously swept by gas during experiments; nitrogen being supplied during pyrolysis experiments. The current project then requires virtually instantaneous substitution of nitrogen by an oxygen-containing gas stream, at a critical point in the heating cycle. This gives simulation of the short exposure to oxygen experienced by coal injected into the blast furnace. The facility to swap this oxygen-containing flow, after a very short time interval, for either nitrogen or carbon dioxide, for gasification measurements, is a further exacting requirement.

Experiments with the modified wire-mesh reactor thus aim to determine rates of particle mass loss over the range of conditions that are likely to exist within a coal plume. Pyrolysis, combustion and CO₂-gasification reactivity measurements are carried out using time-temperature histories similar to those undergone by coal particles in the tuyere, raceway and stack of the blast furnace. The information gained should make a significant contribution to the understanding of how, and where, volatiles are released and whether chars will be completely gasified within the coal plume. The work also aims to provide some high quality data on the fate of injected coal particles for the development of accurate predictive computer codes. In addition, TGA (thermogravimetric analysis) will be used to determine the reactivity of the char samples recovered from the wire-mesh reactor.

The real conditions experienced by coal in the tuyere and raceway are severe. Injected particles are heated very rapidly [at above \(10^4\, ^\circ\text{C}/\text{s}\)] to a temperature about 1700° C in an
An air stream [enriched to 24% oxygen by volume, typically] at elevated pressure, up to about 5bar. The first attempt to simulate these conditions was made by S. Pipatmanomai in the 1999-start ECSC project. She equipped the WMR with two 3-way solenoid valves to achieve the control of short-pulse air injection. Although this project provided interesting data, conditions were limited to a temperature of 1500°C and the pressure to a little above atmospheric. Furthermore, subsequent analysis has shown that the control of the gas flow rate is not precise enough to deliver accurately reproducible pulses of oxygen.

Detailed description of the electrically heated wire-mesh reactor, and the modifications made during this project, follow in the ensuing sections.

2.2 ELECTRICALLY-HEATED WIRE-MESH REACTOR

An overview of the development of wire-mesh reactors has been reported before. In this laboratory, research on the construction of a wire-mesh reactor began in the early 1980’s. Gibbins built the first reactor that has since served as the basic configuration. The apparatus has been modified by subsequent workers, and these have been reviewed by Pipatmanomai in her PhD thesis.

The reactor has been modified more recently by Peralta. Operation has been achieved at temperatures up to 2000 °C, and pressures in excess of 3 Mpa, under inert conditions. Figure 1 shows a typical temperature-time history profile conducted under these extreme conditions. The figure also shows the values of computer-controlled input voltages. Figure 2 exhibits the schematic diagram of the high-pressure wire-mesh reactor used in this study. Detailed descriptions of the equipment are presented elsewhere. Briefly, a folded molybdenum mesh is used to contain a monolayer of coal sample and to act as an electrical resistance heater, whilst held between two water-cooled electrodes. One of the electrodes is spring-loaded to compensate for thermal expansion of the mesh at high temperatures. Two pairs of type D thermocouples are used to monitor the temperature across the reaction zone of the mesh (97% tungsten with 3% rhenium, positive pole; 75% tungsten with 25% rhenium, negative pole). Type D thermocouples can be used at temperature up to 2400 °C in a neutral atmosphere and have been proven to work successfully in an oxidizing atmosphere for a short period of time. The material is known to harden at high temperature, but this did not cause any problems during the short runs in this work. However, fresh thermocouple wires are required for each test.

A wound corrugated metal tube and two sinter discs are used to distribute the gas flow beneath the mesh. During operation, a stream of cold gas flows through the base of the reactor where it provides the required gaseous environment and sweeps newly released volatiles away from the mesh. An insulating sheet made of alumina is used to prevent the mesh from contacting the support plate and avoid a short circuit. The molybdenum mesh sample holder has proven to be sufficiently durable under these extreme conditions during pyrolysis. However, in O2 or CO2, the mesh becomes very brittle by 1600 °C, particularly at high pressure, and the rates of molybdenum oxidation...
become unacceptably high. Consequently, under these circumstances, the upper temperature must be limited to 1500 °C. Pipatmanomai was the first to use this reactor to study coal combustion behaviour. Her operating conditions were limited to a maximum of 1500 °C under atmospheric pressure.

Experiments are normally undertaken with around 5-6 mg of coal sample (except for combustion tests, where amounts down to 1mg have been used). The amount of char yield depends upon the coal type and experimental conditions. Great care had to be employed to ensure consistent, reproducible results with these tiny coal samples.

2.3 MODIFICATION OF THE WMR FOR SHORT-PULSE O₂ INJECTION

The proposed experimental procedure during the combustion tests is shown in Figure 3. In the procedure, the coal sample was heated up in N₂ to the desired peak temperature, and then exposed to a short pulse of reactive gas, with a set oxygen concentration diluted by N₂, for a desired length of time. This is followed by the rest of the holding time plus the cooling period under N₂. Careful design of the gas controlling system is necessary and several criteria need to be strictly fulfilled.

First, the arrival time of the oxygen pulse at the sample [and thus the sample temperature] must be controlled precisely, for the char combustion may be strongly affected by the temperature. Also, it is expected that the char reactivity will decline with increase of holding time in the inert atmosphere, so with different oxygen injection points during the holding stage under otherwise identical conditions, the extent of combustion could be different. Secondly, the reactive gas pulse should be terminated immediately after the sample has been exposed to oxygen for a desired length of time (for example, 20ms). Also, the gas flow should be laminar and mixing of the O₂-containing pulse with the normal N₂ sweep gas should be minimized. These criteria require the use of computer-controlled fast-acting solenoid valves in the system. Moreover, during the period of sample exposure to oxygen, the gas flow rates and pressure must be kept constant, because these two factors might influence the local diffusion of oxygen towards the sample particles. Unfortunately, increasing the flow rate and pressure of the reactive gas aggravates the oxidation of molybdenum mesh, producing more molybdenum oxides (MoO₂, MoO₃ etc.) thereby reducing the effective O₂ concentration available to the coal. Therefore, sensitive needle valves and pressure gauges with high accuracy need to be applied in the controlling system.

The modified system developed during this BCURA project is illustrated in Figure 4. The schematic diagram of the valve system using three solenoid valves with low flow resistance (SV-1401, OMEGA Company, cᵥ = 0.13) is shown in Figure 5. During an experiment, the three solenoid valves are activated simultaneously. Before valve activation, all the N.O. ports (normally open ports) are open allowing nitrogen to pass through the valve system. Once the valves are activated, the N.O. ports are closed and all the N.C. ports (normally closed ports) are opened immediately, thus pushing the O₂/N₂ mixture stored in the tubing between valve A and valve B into the wire-mesh reactor. The
amount of oxygen charged into the tubing between valves A and B prior to the experiment can be controlled accurately. The injection pulse is timed so that oxygen just reaches the sample holder at the very instant the sample has reached the desired peak temperature. No second valve switching is necessary now, since the gas flow automatically returned to nitrogen once the oxygen pulse had passed through the system. The duration of the pulse could be varied by changing the length of tubing, hence amount of oxygen trapped, between valves A and B. The relationship between the variable length of tubing, gas flow rates and the pulse duration is shown in Figure 6. The amount of trapped oxygen is a function of pressure, gas flow rate, oxygen concentration in the mixing gas, and the length of the loop between valves A and B. In addition, a gas-mixing system has been installed to permit adjustment of the oxygen concentration in the injection gas loop. The modified oxygen injection system exhibits some outstanding advantages:

1. The gas flow rate can be controlled precisely and is continuous.
2. The controlled pressure can be much above the 0.15 MPa used previously (up to 1.1 MPa), which is well above the highest operating pressure in a commercial blast furnace.
3. The residence time of diluted oxygen pulse over the coal sample at a given flow rate can be varied by using different lengths of tubing between valve A and valve B.
4. Alternatively, with the same residence time and oxygen concentration, under the same pressure, the amount of oxygen injected can be varied by adjusting the flow rate [the rotameter located at the outlet of the wire-mesh reactor measures the flow rate controlled by needle valves in the system].
5. The oxygen concentration in the mixed gas can be adjusted accurately.

To remove the temperature limitation (1500 °C) of the type K thermocouples, W-W/Re thermocouples (Type “D”) have been commissioned to monitor the temperature during experiments. It has been proven that these thermocouples work successfully at temperature up to 2000 °C, even under the short-pulse combustion conditions used in this study (20-200 ms).

2.4 THERMOGRAVIMETRIC ANALYSIS OF CHARS

TGA equipment has been widely used in the study of pyrolysis and gasification of coals and coal chars. The main advantage of this technique is the continuous record of the weight loss, which can be applied for determining reaction kinetics. In this study, the TGA served to measure the relative combustion reactivity of char by a non-isothermal method. It has also been used to derive the intrinsic reactivity of char from BS2 coal, under isothermal conditions.

A Perkin-Elmer Thermogravimetric analyzer (TGA 7) has been used in this study. The schematic diagram of the instrument is given in Figure 7. A flow of helium is used to keep the balance mechanism under a stable, inert atmosphere and free from exposure to any gaseous products. Nitrogen or air is used to purge the sample, and the flow rates are each set at 40 ml min⁻¹. All gases are passed through moisture and oxygen traps (except
The TGA has a sensitivity of ±1 µg, a maximum heating rate of 200 °C min⁻¹ and a maximum operating temperature of 1000 °C.

A non-isothermal method has been used to study combustion reactivity of chars recovered from the wire-mesh experiments. The weight loss with time is measured; the indicator of reactivity is the half-life (the time required for 50% of the initial sample mass, on a dry ash free basis, to be lost). Longer reaction times indicated less reactive samples. Char samples are initially placed in the balance pan at 50 °C for 5 min for weight stabilization in a nitrogen atmosphere. The furnace is then heated at 50 °C min⁻¹ to 400 °C and again kept at this temperature for 5 min for weight stabilization. After this period, nitrogen is replaced with air to start the combustion process. The furnace is then heated at 15 °C min⁻¹ to 900 °C and kept at this temperature for 5 min to ensure the complete combustion of the sample. The test is stopped at the time when the sample has been completely consumed. The results are reported as a plot of sample weight versus time, from the time of switching from nitrogen to air. Figure 8 exhibits a typical non-isothermal TGA profile, showing the percentage of sample weight versus temperature as a function of time.

The intrinsic reactivity of a char may conveniently be measured at low temperature, where mass transfer limitations are not an issue. Many combustion kinetic measurements of chars have been obtained using thermogravimetric analysis. In this study, to compare the results derived from the experiments conducted on the wire-mesh reactor, an isothermal TGA method has been used to determine the intrinsic reactivity [<600 °C] of coal chars. To begin the isothermal stage, the system is heated up at 25 °C min⁻¹ to the desired temperature [in this study, four temperatures were selected: 500 °C, 525 °C, 550 °C and 575 °C] and held for about 5 minutes to get a uniform temperature within the sample. The inert gas inlet is then manually switched to air for the reaction with O₂. The temperature is kept for an interval of time, depending on the char reactivity. Before finishing the test, the temperature is raised to 900 °C and held for 30 minutes to achieve complete reaction. To calculate the combustion rate coefficient k, a global one step kinetic chemical reaction model has been used:

\[ \frac{da}{dt} = k (1-a) \]

where \( a=(1-W/W_0) \) is the fractional weight conversion, \( W \) is sample weight, \( W_0 \) the original sample weight, and \( t \) is the time interval. Solution of this differential equation via integration, subject to the initial condition \( a = 0, t = 0 \) yields:

\[ -\ln(1-a) = k t \]

Hence \( k \) may be determined from the slope of a plot of \(-\ln(1-a)\) versus \( t \). Subsequently, values of the Arrhenius activation energy \( E \), and pre-exponential factor \( A \), may be estimated from the slope and intercept of a plot of \( \ln k \) versus \( 1/T \), where \( T \) is the isothermal temperature.
2.5 COAL AND CHAR SAMPLES

Pyrolysis and combustion experiments have been carried out on three blast furnace coals, code-named BS2, EC2287LV and EC2288HV. Details of their analysis are given in Table 1, including Volatile Matter content, ash content and Ultimate Analysis. The Ultimate Analyses show the composition of C, H, N, S and O (by difference). CY dust from the single tuyere pilot plant [of Corus (UK) Limited] has been used in the CO2 gasification tests. The dust, which contains 0.2% [d.b.] volatile matter and 40.9% [d.b.] ash, has been chosen as representative of post-oxidation char from a commercial blast furnace. The particle size of all the samples was in the range of 150 – 212 µm which is governed by the aperture size of the wire-mesh sample holder (∼140 µm × 140 µm).

2.6 MOLYBDENUM MESH OXIDATION STUDIES

The literature shows that molybdenum is reactive under conditions simulating the environment in the raceway of a blast furnace. It reacts with O2 rapidly at temperatures above 500 °C, with formation of volatile MoO3. In turn, MoO3 can be easily reduced to MoO2; it is also possible for MoO2 to be formed directly. Several researchers have calculated the Gibbs standard reaction energies of the reaction “Mo(s) + O2 ↔ MoO2” and pointed out that the formation of MoO2 is endothermic. Thus, as temperature increases, the energy required for the reaction decreases. However, the dissociation of MoO2 also becomes significant at elevated temperatures. In this BCURA project, it has been necessary to identify conditions under which the oxidation of the molybdenum mesh is both limited and reproducibly quantifiable. Otherwise the impact of mesh oxidation cannot be corrected for, when attempting to evaluate the extent of coal conversion from experimental data.

Molybdenum mesh oxidation behaviour has been studied extensively in this project in order to refine the extent of coal combustion data. Pipatmanomai calculated the coal combustion yield by correcting for the mesh weight gain she observed from a set of blank tests without a coal sample. However, in the current project, when attempts were made to increase the temperature above 1600 °C, or the pressure above 0.3 MPa, with high oxygen concentrations, experiments failed to show reasonable results when using the same calculation method. Thus it became necessary to develop understanding of the mesh oxidation behaviour under these more extreme conditions and to develop a revised calculation method.

It has become apparent that oxidation of molybdenum may produce either solid oxides, which coat the mesh directly, or vaporized products. The latter are evidenced by the formation of white and yellowish powder which has condensed on cooler surfaces inside the wire-mesh reactor. The observed effects are dependent on the conditions used, being sensitive to temperature and the mass of available O2 (caused by increasing oxygen concentration, pressure, air flow rate and/or exposure time). Temperature affects the rate of reaction, whereas pressure and flow rate affect the mass of O2 passing through mesh.
At temperatures below 1600 °C, at pressures up to 0.3 MPa and with low oxygen concentrations, the mesh becomes discoloured (dark blue/purple) on exposure to O\textsubscript{2} and the weight increases. However, under more intense conditions, the mesh becomes less discoloured and shows a weight loss.

A theoretical study has also been made, using the MTDATA code produced by the National Physics Laboratory, Teddington, UK. This programme uses the Gibbs free energy minimisation method to calculate the concentration, and phase, of species present at thermodynamic equilibrium, as a function of temperature and pressure. Simulation of the experimental conditions used in the current project has shown that it is possible to form a wide range of molybdenum oxides, at temperatures up to 2000 °C. As indicated in Figure 9, the formation of solid MoO\textsubscript{2} is favoured at temperatures below about 1500 °C; however this oxide disappears gradually with further increase of temperature. It is evident, from Figure 10, that vapour phase species, mainly MoO\textsubscript{3}, become dominant above 1600 °C. These species also include gaseous MoO\textsubscript{2}. Furthermore, doubling the amount of oxygen present is predicted to produce higher molybdenum oxides, as either solid or vapour phase species (Figure 11 and Figure 12).

XRD analysis of the discoloured mesh, produced when the temperature was limited to 1500 °C in the presence of oxygen, showed that solid MoO\textsubscript{2} has been formed (Figure 13). At the highest temperature tested (2000 °C, under pyrolysis conditions), only Mo metal was detected on the mesh surface after a test. An SEM investigation of the oxidized 1500 °C mesh revealed deposits on the surface of the mesh, which were assumed to be MoO\textsubscript{2} (Figure 14). At more extreme conditions (either higher temperature or a greater mass flow of O\textsubscript{2}), less discolouration occurred and a white/yellow deposit was formed on the cooler parts of the equipment downstream from the wire-mesh reactor. XRD analysis of these deposits showed that it comprised of two different forms of MoO\textsubscript{3} (Figure 15).

Under conditions where volatile oxides had been produced, the mesh weight gain is lower than under the solid-only oxide formation conditions. Furthermore, the processes of solid oxide formation, leading to mesh weight gain, and vapour oxide formation, leading to mesh weight loss, run in parallel and in competition. Under the more extreme conditions tested the net effect is an overall mesh weight loss. Thus it is evident that there is a transition region in which the formation of the solid dioxide declines and formation of the vapour phase trioxide increases. The existence of these two competing processes makes the mesh weight change impossible to predict accurately in coal oxidation experiments. Unfortunately, this transition region occurs below the maximum temperature (about 1700°C) desired in the current study, particularly at the elevated pressures, in oxygen-enriched air, pertaining in commercial blast furnace practice.
3. RESULTS AND DISCUSSION

3.1 MOLYBDENUM OXIDATION

As explained in the previous section, the formation of molybdenum oxides has complicated the measurement of the weight change during the tests, and also reduced the amount of O\(_2\) available to combust the coal sample. Preliminary attempts to measure the extent of combustion in air, and enriched air, at temperatures above 1600 °C, or pressures above 0.5 MPa, failed to yield sensible results. This failure led to a detailed study of the oxidation behaviour of bare mesh, under a range of conditions, with a view to determine the operating limits of the technique. Figure 16 shows the mesh weight change as a function of temperature, at 0.3 MPa, using oxygen-enriched air (25% O\(_2\)). The data show that up to 1600 °C, the mesh weight increases with the temperature. However, above this temperature, the weight falls due to the formation of molybdenum oxide vapour. The effect of pressure on the mesh weight change is shown in Figure 17. Here again, at higher pressure, there is clear evidence of volatile molybdenum oxides forming at the expense of solid. Figure 18 shows the effect of air residence time. Initially, the mesh weight is seen to increase with time (due to solid MoO\(_2\) formation) but, after a certain point, the solid molybdenum oxide coated on the mesh is removed by further oxidation (presumably by gaseous MoO\(_3\) formation). Figure 19 shows the effect of sweep gas flow rates. Here, the mesh weight loss increases at the higher gas flow rates tested.

It is apparent that at least four reactions contributed to the oxidation behaviour of the mesh:

\[
\begin{align*}
(1) \quad Mo + O_2 & \rightarrow MoO_2(s) \\
(2) \quad 2Mo + 3O_2 & \rightarrow 2MoO_3(g) \\
(3) \quad 2MoO_2(s) + O_2 & \rightarrow 2MoO_3(g) \\
(4) \quad MoO_2(s) & \rightarrow MoO_2(g)
\end{align*}
\]

The first three are chemical reactions whilst the fourth is a phase change. Up to a certain threshold of temperature, pressure and gas flow rate, it seems that reaction (1) predominates over the other three. This leads to a reproducible weight gain of the mesh; potentially permitting reliable measurement of extent of combustion, provided that there is sufficient O\(_2\) remaining in the gas phase. Under more severe conditions, a combination of solid and vapour formation occurs, making the weight change behaviour very variable and the remaining O\(_2\) concentration unpredictable.

During each combustion test, the gas flow rate and the time for valve activation are set so that the instant peak temperature is reached, the injected oxygen pulse starts to pass through the bottom layer of mesh, where it produces solid or gaseous molybdenum oxides. This reduces the oxygen concentration that reaches the coal sample. The concentration of the injected oxygen must therefore be corrected for the losses to the lower layer of mesh to reveal the oxygen concentration that is available for reaction with the coal sample. Any losses to the upper layer are not important, as they could not influence the extent of coal combustion.
A series of tests have been done, with a single layer of mesh (and no sample) to measure the weight change of the mesh when exposed to O\(_2\) under a range of conditions. The observed changes have then been used to revise the inlet O\(_2\) concentration for reaction with the mesh. At high temperatures (above 1300 °C), the injected O\(_2\) concentration has been reduced to 5% (by volume) in order to limit the potential for mesh oxidation to MoO\(_3\) (vapour), since previous tests have shown that O\(_2\) concentration is an important factor in promoting volatile molybdenum oxide formation. Figure 20 and Figure 21 show the oxygen concentrations escaping the bottom layer of mesh, as a function of peak temperature and injected oxygen concentration, respectively. The total amount of injected oxygen, and the amount of oxygen reacting with the mesh, are also shown in the Figures. The calculations are based on the assumption that solid MoO\(_2\) is the only species forming when the mesh weight increases during a test. When the mesh weight is seen to fall from its peak weight at more extreme conditions, it is assumed that MoO\(_2\) is converting to MoO\(_3\) vapour. Figure 20 suggests that, above 1600 °C, the amount of oxygen reacting with the molybdenum mesh increases enormously, even with the low injected O\(_2\) concentration. It becomes impossible to obtain meaningful coal combustion data under these conditions.

Calculations show that an injected oxygen concentration of 5% corresponds to an actual oxygen concentration for the coal of around 3 %, at temperatures between 1100 and 1600 °C. However, Figure 21 suggests that if the temperature is reduced to 1300 °C, nearly 80% of the inlet oxygen is able to pass through the mesh without reaction, even under 25% O\(_2\) at pressures up to 0.3 Mpa. Figure 22 shows the corrected oxygen concentration as a function of pressure between 0.3 and 0.5 Mpa, but using a lower test temperature of 1300 °C; the oxygen availability to the coal sample is seen to increase slightly with pressure.

Figure 23 shows a plot of the extent of combustion and the weight of O\(_2\) actually reacted with the char (calculated from the extent of combustion) as a function of the initial coal sample weight. This shows that the extent of combustion (at 1500 °C, 0.3 MPa, 25% oxygen injected for 105ms) decreases linearly with increasing sample size. Under these conditions the oxygen availability to the coal sample is clearly inadequate as only 0.3 mg has reacted (compared with an inlet weight of 3.75 mg), irrespective of coal sample weight. This small amount of surviving oxygen is immediately mopped up by the coal sample; the smaller the sample size the bigger the apparent extent of combustion. These measurements must be constrained by the limited oxygen availability; even the highest extent (from the smallest sample) does not necessarily represent the true extent in unlimited oxygen.

A series of tests was then conducted using less extreme conditions. The inlet O\(_2\) concentration was controlled at 5% when the temperature went up to 1600 °C, and the temperature was limited below 1300°C when 25% of inlet O\(_2\) was used. The results are shown in Figure 24 and Figure 25, respectively. The O\(_2\) consumed by the bottom layer of the mesh has been estimated in the way that has already been described. The O\(_2\) reacting with the sample is estimated from the extent of combustion and the excess O\(_2\) is
calculated as the difference between this value and the inlet value. The data show that there is an excess of O\textsubscript{2} during these tests. Therefore, under these conditions, the extent of combustion is not limited by the availability of O\textsubscript{2} and real effects on coal conversion can be studied.

3.2 COAL PYROLYSIS

A study of the effect of pyrolysis conditions on the total volatile yield has been carried out on three coal samples using the high-pressure wire-mesh reactor. Factors influencing the weight loss behaviour of coal, including coal rank, peak temperature, pressure, and heating rate, have been studied. The effect of holding time at peak temperatures has been investigated previously by Pipatmanomai\textsuperscript{7}, who pointed out that the maximum level of volatile release was achieved within 1 s, at a holding temperature of 1000 °C. When the peak temperature was set at 1500 °C, the maximum volatile release was obtained at zero hold-time, i.e. by the time the peak temperature was reached. Therefore, in this study, a holding time of 1 second has been applied for all pyrolysis tests.

3.2.1 Effect of heating rate

In the blast furnace tuyere and raceway, the heating rate of the injectant coal is normally above $10^4$ °C s\textsuperscript{-1}, depending on the velocity of the air blast and the rate of coal injection. However, the highest heating rates that can be achieved successfully in the wire-mesh reactor is 7500 °C s\textsuperscript{-1}, because the high heat capacity of the molybdenum mesh causes a lag in temperature control. Li et al.\textsuperscript{18} observed an increase of pyrolysis yield when coals are heated to 700 °C at 1000 °C s\textsuperscript{-1}, compared to heating at 1 °C s\textsuperscript{-1}. They also noticed that the greater volatile evolution observed at higher heating rates consisted mostly of additional tar release. One likely explanation is that greater tar survival should be possible due to the rapid expulsion of tars and tar precursors; slow heating would allow more time for the repolymerisation of tar precursors. However, Cai\textsuperscript{9} suggested that tar and total volatile yields during pyrolysis are not sensitive to heating rate above 1000 °C s\textsuperscript{-1}. This has been confirmed subsequently by Pipatmanomai\textsuperscript{7}, who studied the effect of heating rate between 1000 and 5000 °C s\textsuperscript{-1}, at a peak temperature of 1000 °C with zero holding time.

As a further check, some tests have been done under the current BCURA contract. Heating rates of 1000 °C s\textsuperscript{-1} and 5000 °C s\textsuperscript{-1} have been tested at a peak temperature of 1500 °C, with a 1 second hold-time, under 0.3 MPa pressure. The data indicate, Figure 26, that the total volatile yield at the higher heating rate is essentially the same as that at 1000 °C s\textsuperscript{-1}, within experimental error. Thus, even at 5000 °C s\textsuperscript{-1} heating rate, the residence time of 1 second appears sufficient to allow pyrolysis to go to completion at 1500 °C.
3.2.2 Effect of peak temperature

Temperatures inside the blast furnace raceway can reach above 1700 °C, although temperatures as high as 2200 °C have been measured in the adjacent coke bed. Pyrolysis experiments have been conducted on three coal samples to investigate the effect of the peak temperature, under a pressure of 0.3 Mpa. The variation of total volatile yield with peak temperature is shown in Figure 27 to 29. A temperature of 2000 °C was reached for BS2 coal, while 1700 °C was the maximum achieved for the other two samples. A trend of increasing total volatile yield with increasing peak temperature is apparent.

In the previous ECSC project, Pipatmanomai\textsuperscript{7} had studied pyrolysis behaviour between 500 and 1500 °C, at atmospheric pressure. She noted a rapid increase in total volatile yield between 500 °C and 900 °C; however, the yield increase thereafter was minor. This observation has been confirmed by Peralta et al.\textsuperscript{8}, in these laboratories. A modified high-pressure wire-mesh reactor was used to study coal pyrolysis up to 2000 °C. However, although there was a general levelling of yield between about 1000°C and 1500 °C, some further volatile yield was observed at the highest temperatures studied. Since the pyrolysis of the organic volatiles in coal is known to be complete within 1 s at temperatures above 1000 °C, this high temperature loss must be attributable to another mechanism. Volatilisation of a portion of the inorganic mineral material is the likely candidate.

3.2.3 Effect of pressure

Pressure inside the blast furnace raceway is a function of furnace design; the normal range is between 0.3 and 0.6 MPa. Measured pyrolysis yields as a function of pressure are shown in Figure 30 and Figure 31. The apparent trend is for the total volatile yield, at 1500 °C, to decrease with pressure over the whole range tested, from 0.15 to 0.5 MPa. This trend is consistent with the observations of Guell\textsuperscript{10} and Messenboch\textsuperscript{5} who used a wire-mesh reactor to investigate the effect of pressure over a much wider pressure range; from atmospheric to 15 MPa. These researchers noted an initial sharp reduction of volatile yields as the pressure was increased up to about 1.0 MPa. This reduction may be explained by the greater resistance exerted by the sweep gas on the escaping volatiles, as pressure increases. The volatiles experience an increase in residence time within the particles, facilitating some re-polymerization with carbon being reincorporated into the forming char\textsuperscript{8}. Some differences in pressure sensitivity between the coals tested are apparent. Figures 30 and 31 also suggest that elevated pressure has more impact on the higher volatile matter coal EC2288HV coal (36.6 %db) compared to BS2 coal (volatile matter: 13.2 %db).

3.2.4 Effect of coal rank

The three coal samples investigated show some variation in coal rank, and thus Proximate Analysis Volatile Matter content (see Table 1). Pyrolysis experiments have been carried
out at a heating rate of 1000 °C s\(^{-1}\) to 1500 °C, with 1 second hold-time, under a pressure of 0.3 MPa. The measured total volatile yields, together with the associated Volatile Matter and carbon contents, are shown in Table 2. As expected from previous studies\(^{19}\), the total volatile yield is seen to decrease with increasing coal rank.

### 3.3 SHORT-PULSE OXIDATION

It has been necessary to set the short-pulse oxygen exposure time at 105 ms in all combustion experiments. This is to ensure that the extent of combustion can be measured without a limit in oxygen supply. This time is a little longer than that likely to be experienced by particles in a real furnace, where 20-40ms might be more typical. The sample weight losses, including coal pyrolysis and char combustion, have been determined by measuring the weight of the sample before, and after, each test. Coal pyrolysis has been done separately for each experimental condition; thereafter a short-pulse oxidation experiment has been conducted under the same conditions. The extent of combustion is determined by subtraction of the two resultant weight changes. Extents of combustion have been measured as a function of peak temperature, pressure and \(O_2\) concentration, for two coals (BS2 and EC2287LV).

#### 3.3.1 Extent of combustion as a function of peak temperature

The observed extent of combustion, within a specific reaction time, reflects the burning rate of a char. The functional variation in burning rate with temperature is used to infer whether the char combustion is controlled by the chemical rate (Zone I), the combined effects of chemistry and pore diffusion (Zone II), or bulk diffusion (Zone III). In this study, a series of tests have been done at temperature between 1200 °C and 1600 °C. The pressure has been maintained at 0.3 MPa and the reactive gas has been limited to an oxygen content of 3 % \(O_2\) (by volume).

Figure 32 presents the measured extents of combustion as a function of peak temperatures for both coal samples. The data indicate that the extent of combustion of BS2 coal is only 3 ~ 4 %, even at 1600 °C. This implies that the degree of char combustion is insignificant in the central region of the coal plume, where oxygen concentrations are low. The data also indicate that the extent of combustion increases with increasing temperature up to 1400 °C, but level off thereafter. This suggests a transition from one combustion zone to another.

Mitchell\(^{20}\) concluded from entrained flow reactor studies that the transition to Zone III conditions may occur at temperatures as low as 1450 °C. Young et al.\(^{21}\) measured the combustion rates of an Australia brown coal char over the temperature range 670 – 1150 °C. They concluded that their char particles were burning under Zone II conditions. Wells et al.\(^{22}\) investigated char combustion in a drop-tube furnace over the temperature range from 1030 °C to 1430 °C; they observed an increase in external and pore diffusional resistances as the temperature increased. A more recent study\(^{23}\) suggests that mass
Transport limitations in char combustion become evident at temperatures as low as 600 ~ 700 °C. These earlier observations all suggest that under the conditions studied here, i.e., temperatures above 1400 ~ 1500 °C, the char combustion is probably occurring under Zone III, or in the transition region between Zone II to Zone III.

The extents of combustion of EC2287LV coal at two temperatures (1300 °C and 1500 °C) are almost identical (see Figure 32) with those of BS2 coal; the deviations being within the experimental error. Pipatmanomai took a set of SEM photographs of chars prepared from several coal samples (all pyrolysed at 1500 °C, with zero holding time). She observed that the morphologies of the residual chars were markedly different. This could result in different reactivities if the chars are burnt under zone II conditions. However, Hurt has indicated that differences in reactivity diminish at high temperatures. In this current BCURA study, the combustion results can be explained as follows: (1) for short reaction times, the penetration depth of oxygen into the char particle is limited; (2) the char particles are burnt at such high temperatures that the reactions are probably controlled by bulk diffusion (Zone III) and the differences of char morphologies are negligible.

3.3.2 Extent of combustion as a function of pressure

In this study, the effect of total pressure on the extents of char combustion was investigated at two oxygen concentrations: 3 % and 6 %, respectively. The experiments were carried out using BS2 coal. The temperature was maintained at 1300 °C and reaction time was kept at 105 ms. Figure 33 and Figure 34 show a slight increase of the extent of combustion with pressures up to 0.5 MPa.

There is general agreement on the main effects of pressure on char combustion. Previous studies at fixed gas composition have shown two trends: (1) in kinetic-limited combustion, increasing system pressure produces a rise in oxygen partial pressure, thereby accelerating the chemical rate; whereas, (2) in diffusion-limited combustion there is no effect of pressure. In the latter case, the higher oxygen partial pressure is counterbalanced by a lower oxygen diffusion coefficient. Essenhigh calculated diffusion rate kinetics and indicated that the influence of total pressure on the diffusion rate depended only on the product of gas density and oxygen diffusion coefficient. However, since the oxygen diffusion coefficient is inversely proportional to pressure whilst density is proportional to pressure, their product is essentially independent of total pressure. However, Essenhigh also acknowledged a second-order pressure dependence due to adsorption. This effect may be apparent in the measurements reported here.

3.3.3 Extent of combustion as a function of oxygen concentrations

A series of combustion tests have been conducted under a pressure of 0.3 MPa, at 1300 °C, with the O₂ concentrations varying from 3 to 20 %; the extents of combustion measured for BS2 coal are shown in Figure 35. The data indicate that the O₂
concentration supplied plays a dominant role in controlling the extent of the char combustion.

Theoretically, the char combustion rate is proportional to the $n^{th}$ power of $O_2$ partial pressure$^{29,30}$, where $n$ stands for the reaction order. As mentioned above, at 1300 °C, char burns under pore diffusion control (Zone II), so that the combustion rate is largely dependent upon the diffusivity of $O_2$. Slattery et al.$^{31}$ developed a model to calculate the diffusivities of some binary gas mixtures at a given temperature and pressure; pointing out that diffusivity increases with increasing partial pressure of the reactive gas. In an earlier study, Field$^{32}$ measured the char burn-off in a laminar flow reactor, using two oxygen concentrations (5 and 10 %) at temperatures above 1100 °C. The measured burn-off was 3 ~ 4 times higher at 10 % oxygen concentration than at 5 %. In the earlier ECSC project, Pipatmanomai$^8$ studied the effect of $O_2$ partial pressure on the extent of combustion over the range 21 to 75 % $O_2$ at 1500 °C. She also noted a trend of increasing char burn-off with increasing oxygen concentrations.

In addition to increasing the mass transfer of oxygen to the char, an increase of $O_2$ partial pressure may offer a further, indirect, benefit to char combustion. Using a pressurized entrained-flow reactor, Reichelt et al.$^{33}$ observed that, at constant system pressure, the particle temperature increased with increasing $O_2$ concentrations. This resulted in an increased char combustion rate. This difference between the particle surface temperature and gas temperature has been also been observed by Field$^{32}$. He found that the surface temperature is always higher than the gas temperature, with the difference becoming greater with increasing oxygen concentration.

### 3.4 CARBON DIOXIDE GASIFICATION

In the blast furnace, the devolatilisation of the injected coal normally takes place in the tuyere or the front of the raceway. However, as the oxygen supply is depleted rapidly in front of the tuyere nose, the main reaction at the end of the raceway, and along the furnace shaft, is $CO_2$ gasification of the char produced by pyrolysis of the injected coal. However, if the extent of coal combustion in the raceway is limited to a few percent, as the current project suggests, the destruction of char will largely dependent upon $CO_2$ gasification. In order to ascertain likely gasification rates under simulated furnace conditions, a representative char was needed. In this study, CY dust from the single tuyere pilot plant [Teesside Technology Centre, Corus (UK) Limited] has been taken as the best available post-oxidation char. CY dust (see Table 1 for composition) has been gasified in an 18% $CO_2$ / 82 % $N_2$ mixture in the wire-mesh reactor over a range of temperatures, pressures, and holding times. This particular mixture has been taken as typical of normal furnace raceway conditions. The experiments have been carried out at 0.3 MPa, which is also representative of commercial blast furnace practice.

#### 3.4.1 Effect of $CO_2$ gasification temperature

The extent of gasification (%, dry ash free) has been determined by subtracting the small weight loss due to pyrolysis from the gasification weight loss, measured under otherwise similar conditions. The data shown in Figure 36 reveal that the extent of gasification
increases with increasing peak temperature up to the maximum tested, 1500 °C. These results are in a good agreement with those obtained by Pipatmanomai, who examined the effect of gasification temperature at atmospheric pressure. She found that the extent of gasification increased significantly between 1300 °C and 1500 °C.

3.4.2 Effect of holding time

Figure 37 shows the extent of gasification as a function of holding time. Here, the dust sample has been gasified at 1500 °C, in 18 % CO\textsubscript{2} at 0.3 MPa, with experiments performed at three different holding times, 1 s, 4 s, and 10 s. The extent of gasification is seen to increase over the range of holding times studied, and complete conversion is achieved by 10 s. In previous studies\textsuperscript{6,8}, using coal chars produced in the wire-mesh reactor, the instantaneous rate of gasification, which is calculated from the weight change within each period of holding time, had been found to drop sharply with the gasification holding time. However, in the present study, this effect is not so significant (the decline being from 11.2 % (daf) s\textsuperscript{-1} during 1 – 4 s period to 9.2 % (daf) s\textsuperscript{-1} during 4 – 10 s period). This difference is probably due to the CY dust having been more fully annealed after the longer exposure to high temperature in the pilot plant furnace. The decrease of gasification reactivity with increasing holding time is probably due to the continuous decrease in carbon content of the dust as gasification proceeds.

3.4.3 Effect of \textit{CO}_2 gasification pressure

The variation in the extent of gasification with pressure is shown in Figure 38; for a peak temperature of 1500 °C, with 1 s holding time, and a \textit{CO}_2 concentration of 18 %. The data indicate that the effect of pressure on the extent of gasification is negligible below 0.7 MPa. This may be explained by the enhanced reactivity of \textit{CO}_2, created by elevated pressure, being compensated by the increased deposition of less reactive secondary char. However, in a previous study by Messenboch, using the same reactor, the gasification reactivity was seen to pass through a minimum as the pressure increased; with reactivity dropping in the pressure range of the current study. This normally might be explained in terms of the higher volatile matter content of the coal used by Messenboch, or by differences in the reactivities of the secondary chars produced.

3.4.4 Effect of \textit{CO}_2 concentration

The gasification of CY dust has also been studied as a function of \textit{CO}_2 concentration. This dust sample has been exposed to a range of \textit{CO}_2/N\textsubscript{2} gas mixtures, with \textit{CO}_2 concentration varying between 0 – 18 %. In all cases the peak temperature has been 1500 °C, with 1 s holding time, at an operating pressure of 0.3 MPa. The results are shown in Figure 39. It is clear that the extent of gasification increases proportionally with increasing \textit{CO}_2 concentration. This observation suggests that the gasification reaction is probably first order, under the test conditions.
3.5 THERMOGRAVIMETRIC ANALYSIS

3.5.1 Effect of pyrolysis conditions on the reactivity of the residual chars

A study of the effect of pyrolysis conditions on the relative reactivity of the pyrolysis chars has been conducted. The relative combustion reactivity of the residual chars has been measured in a standard TGA, operated non-isothermally, in air, from 400 °C to 900 °C, with a heating rate of 15 °C/min. The measured half-life of the char has been taken as an index of char reactivity; the half-life being defined as the time required to combust half of the organic material in the char. This non-isothermal method can achieve complete char conversion in a shorter period of time (approximately < 1 h) than the isothermal method. The dependence of char reactivity on a range of parameters has been investigated here, i.e. pyrolysis peak temperature, pressure, heating rate and coal properties.

Figure 40 and Figure 41 show non-isothermal TGA data of two residual chars, EC2287LV and EC2299HV, respectively. Chars prepared under three different pyrolysis peak temperatures are shown, i.e. 1000 °C, 1500 °C and 1700 °C. The corresponding half-lives are shown in Table 3. These data show that the half-life increases with pyrolysis temperature, i.e., the char becomes less reactive. This must be caused by thermal annealing, which occurs when chars are exposed to high temperatures. This trend is in consistent with that obtained from a previous study using the same non-isothermal method. In addition, Pipatmanomai, using an isothermal method, also noticed a large reduction of char reactivity with increasing pyrolysis peak temperature, up to the maximum studied, 1500 °C.

Figure 42 is derived from Table 3, with the reactivity of the char samples of the two coals produced at three different pyrolysis temperatures. The results show that EC2288HV coal, with lower rank and higher volatile matter content, gives more reactive char. However, the discrepancy between the coals diminishes at higher pyrolysis peak temperatures. This is in consistent with previous observations.

The effect of pressure on char reactivity has been measured at 1500 °C; the TGA profiles are shown in Figure 43. It appears that pressure had a mild impact on the char reactivity. Peralta et al. also observed the deactivation of chars with increasing pressure up to 2 Mpa at 1000 °C. However, they pointed out that this effect was less significant than the effect of temperature and became negligible when peak temperature reached 2000 °C.

Pipatmanomai studied the effect of heating rate on the char reactivity at 1000 °C, with zero holding time. She observed some differences in char reactivity between 1000 and 5000 °C s⁻¹ and the effect of heating rate was dependent on the coal type. In this study, the pyrolysis temperature has been increased to 1500 °C, close to the temperature inside the blast furnace raceway, and a holding time of one second has been applied at this peak
temperature. Two non-isothermal TGA profiles are presented in Figure 44, with heating rates of 1000 and 5000 °C s\(^{-1}\), respectively. The results show that the effect of heating rate is negligible in this range, probably due to rapid annealing at the high temperature.

3.5.2 Effect of combustion conditions on the reactivity of the residual chars

The effect of short-pulse oxidation on the reactivity of residual chars from the wire-mesh reactor has been investigated also; using the TGA under the same non-isothermal mode. Figures 45 and 46 show the non-isothermal TGA profiles of BS2 chars produced in the wire-mesh reactor under 0.3 and 0.5 MPa pressure, respectively. These Figures enable char reactivity to be compared as a function of O\(_2\) concentration during the short-pulse exposure; the corresponding half-lives being shown in Table 4. The data show that the combustion-derived chars are more reactive than the pyrolysis-derived chars, obtained from experiments without O\(_2\) injection under otherwise similar conditions. It is also evident that the half-life decreases with increasing O\(_2\) concentration, i.e. the char became more reactive. This observation may be associated with the higher degree of burnout experienced by chars at higher O\(_2\) concentrations. In the previous study, Pipatmanomai\(^7\) found that the char had higher burnout, and became more reactive, when it was exposed to longer air-pulse length. Both trends might be explained by: (1) the burn-off of the secondary (less reactive) carbon deposited on the char surface; and (2) the increase in the surface area (by creation or widening of the char pores) during combustion\(^{34}\). The results are in a good agreement with those observed by Aarna and Suuberg\(^{35}\), who examined the changes in reactive surface area and porosity during char oxidation. They found that specific surface area usually passed through a maximum at some intermediate level of burn-out, where the rate of formation of new area was offset by the rate of destruction of the initial area. They also noted the same surface area development, irrespective of whether char oxidation occurred under Zone I or Zone II reaction regime.

4. CONCLUSIONS

4.1 Pyrolysis experiments

- The total volatile yield of all three coals tested increases with peak temperature up to 1500 °C; this is consistent with the observations of Pipatmanomai\(^7\). Above 1500 °C, partial vaporization of some constituents of the inorganic mineral material in the coals begins to contribute to the weight loss during pyrolysis, this additional loss may be significant at the highest temperature used in this study, 2000 °C.

- TGA analysis reveals that pyrolysis char reactivity decreases with increasing peak temperature used in formation.
• During pyrolysis below 1500 °C, total volatile yields increase with decreasing coal carbon content and increasing Proximate Analysis Volatile Matter content [i.e. with decreasing rank].

• Pyrolysis char reactivity is higher for low rank, high Volatile Matter coals. However, the effect of rank on reactivity diminishes with increasing peak temperature.

• Over the pressure range studied (0.15 to 0.5 Mpa), increasing pressure has a negative, although minor effect on the pyrolysis yields. The study suggests that the effect of pressure is dependent on coal type.

• TGA analysis indicates that pyrolysis char reactivity decreases slightly with increasing pressure.

• For pyrolysis runs with 1s hold-time, neither pyrolysis weight loss nor char reactivity vary significantly with heating rate, for rates above 1000 °C s⁻¹.

4.2 Combustion experiments

• The degree of oxidation, at 1600 °C, of pyrolysis chars in 3% O₂ / 97% N₂ is small, even at an exposure time of 105 ms; being less than 5% (daf) typically. Even when the O₂ concentration is increased to 20 %, at 1300 °C, the extent of combustion at a residence time of 105 ms is still below 5% (daf).

• Char burning rate is dependent upon the combustion temperature. Generally, the extent of combustion increases with increases of temperature. However, study of the kinetics implies that above about 1400 °C, the char burns in Zone III or in the transition region between Zone II and Zone III. Here, mass transfer processes begin to dominate so that further increases of temperature will not increase the extent of combustion significantly.

• The extents of combustion of two different coal samples are almost identical at temperatures above 1300 °C. This is further evidence to suggest that char is burning under Zone III conditions at blast furnace raceway temperatures (at least 1700 °C).

• Increasing the O₂ concentration, at a fixed total pressure and at 1300°C, increased the extent of combustion of coal. Furthermore, the combustion reactivity of the residual char increases with exposure to higher O₂ concentrations in the sweep gas.

• Increasing the total pressure, at a fixed O₂ concentration, enhances the extent of combustion slightly.
4.3 CO2-gasification experiments

- In an atmosphere simulating the blast furnace raceway [18% CO\textsubscript{2}/N\textsubscript{2} at 1500 °C, under 0.3 MPa pressure] post-oxidation char is seen to be consumed completely after about 10s, i.e. the extent of gasification becomes close to 100% (daf, of the char mass). This suggests that char must remain in the raceway for around 10 s, if it is to be completely consumed.

- Char gasification reactivity increases significantly with formation temperature up to 1500 °C, especially between 1300 and 1500 °C.

- The extent of gasification increased with increasing of CO\textsubscript{2} concentration in the sweep gas.

- Pressures below 0.7 Mpa have a negligible effect on extent of gasification, for a given CO\textsubscript{2} concentration. The extent of gasification then increases slightly, i.e. by 4-5% (daf), as the pressure is increased from 0.7 Mpa up to 1.0 Mpa. Pressure is thus unlikely to be a significant factor in char gasification at the modest pressures used in commercial furnaces (up to about 0.5 Mpa).

5. ACHIEVEMENTS IN RELATION TO OBJECTIVES

The intended laboratory-scale investigation of the fundamental devolatilisation and combustion/gasification behaviour of selected blast furnace coals, under conditions prevailing in tuyere and raceway regions of the blast furnace, has been completed successfully. This has required the re-design of a new short pulse oxygen injection system for the wire-mesh reactor. This re-design has produced more accurate control of the oxygen injection system and the attainment of operating pressures representative of those in commercial blast furnaces, up to about 0.5 MPa, for the first time. The limits [temperature, pressure, residence time, oxygen concentration] have been carefully mapped and the new operating limits defined.

Unfortunately, excessive oxidation of the molybdenum mesh used to support the coal sample has limited operation to below those hoped for at the outset. Never-the-less, pyrolysis experiments have been conducted up to the desired maximum operating temperature, 2000 °C, and at representative furnace pressures. Short-pulse oxidation experiments have been limited to 3% oxygen at 1500 °C under representative pressures, and 20% oxygen at 1300 °C, also under representative pressure. The data derived have enabled some kinetics to be derived and suggest that above about 1400 °C, the char oxidation becomes mass transfer, rather than chemistry, i.e temperature, controlled. The
measured extents of combustion are always less than 10%, suggesting that the conclusions of the earlier ECSC project were correct, i.e. that char consumption depends on gasification rather than short-pulse combustion. Successful completion of CO\textsubscript{2} gasification experiments, under pressure, re-affirm the earlier conclusion that about 10s of gasification time is needed to completely consume the residual char.

An extensive investigation of char reactivity has been conducted by TGA, yielding valuable data on pyrolysis and combustion char reactivity as a function of rank and formation condition, e.g. peak temperature, pressure, oxygen exposure. In addition, kinetic coefficients have been estimated for the coal combustion process under blast-furnace conditions.

The body of data, and process trends, developed during the project is intended to provide improved estimates of the likely behaviour, and eventual fate, of coal particles injected into the base of a blast furnace. The inclusion of high pressure operation represents a significant advance over the previous work, as does the achievement of 2000 °C pyrolysis conditions. The initial objectives of the projects have thus been achieved in the main; subject only to the physical limitations imposed on the short-pulse combustion experiments by molybdenum mesh oxidation.

6. COMMERCIAL IMPLICATIONS

- The present study indicates that during pyrolysis, the weight loss of injected coal increases with temperatures up to 2000 °C, although little occurs above 1500 °C; the char reactivity decreases with the exposure temperature. The short-pulse oxidation studies shows that char oxidation is controlled by external diffusion of oxygen above about 1400 °C. Thus the combustion rate will not be improved by further increasing temperature. Improved exposure of the coal to oxygen is required to improve burn-out. However, increasing the temperature in the blast furnace raceway will increase the char gasification reactivity, thereby shortening the time for the destruction of residual char.

- The type of coal injected into the blast furnace is another important factor. Coals with higher volatile matter contents normally achieve higher weight loss during pyrolysis. However, this is not necessarily true during char combustion inside the raceway. Although, coals with higher volatile matter content produce more reactive chars during pyrolysis, the difference diminishes with increasing temperature. Coals with high volatile matter content are more likely to have a negative physical impact on the raceway performance due the higher blast momentum produced.

- Although coal devolatilisation can be accomplished in a short period of time at high temperatures, the 20 ms, or so, available inside the blast furnace tuyere and raceway are unlikely to be sufficient to ensure complete volatile release in the coal plume.
Therefore, increasing the coal particle residence time would increase the weight loss during pyrolysis. It would also increase the degree of char burnout and the extent of CO₂ gasification inside the raceway. Increasing coal particle residence time could be achieved by (1) increasing the distance between the coal injection lance and the tuyere nose, or (2) using a high-turbulence lance (for example, increasing the outer diameter of the injection pipe or making coal particles swirl in the plume).

- The present study suggests that increasing O₂ concentrations will increase the extent of combustion under the conditions inside the blast furnace raceway. Also, the combustion reactivity of the residues is higher when the char is burnt at higher O₂ concentrations. Therefore, increasing O₂ concentrations in the blast could achieve higher burnout inside the raceway. Additionally, improving particle/gas mixing or enhancing the flow turbulence inside the tuyere and raceway is also recommended.

- It has been found in this study that pyrolysis yield decreases slightly with increasing pressure. However, this may be off-set by the extent of combustion increasing slightly with pressure, up to 0.5 MPa. The rate of CO₂ gasification of residual char is not sensitive to pressure below 1.0 MPa [which exceeds current furnace operating pressures]. Thus it may be concluded that overall effect of pressure on the coal reactions occurring inside the blast furnace raceway is negligible.

7. RECOMMENDATIONS FOR FUTURE WORK

- In the present study, the combustion behaviour of only two blast furnace coals has been investigated, using the high-pressure wire-mesh reactor equipped with the newly-developed short-pulse oxygen injection system. More experiments need to be done with a wider range of coal samples in order to aid the selection of injectant coals.

- Excessive oxidation of the molybdenum mesh, used to support the coal sample, has limited the range of combustion conditions that could be studied reliably in the wire-mesh reactor. There may be some benefit in testing other refractory metals, such as tungsten or tantalum, to see if they can tolerate more extreme conditions than molybdenum. However, the supply of these metals in suitable mesh format may be problematic.

- Further development of our understanding of the behaviour of coal injected into the blast furnace will require improved theoretical analysis. Computation fluid dynamics (CFD) modelling, using the experimental data from the wire-mesh reactor, seems an obvious way forward.
8. ACKNOWLEDGEMENTS

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### Table 1 Coal sample analyses

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### Table 2 Effect of coal rank and volatile matter content on the pyrolysis yields.

Experiments were carried out at 1500 °C under pressure of 0.3 MPa with heating rate of 1000 °C s⁻¹

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### Table 3 Thermogravimetric half-life of EC2288HV and EC2287LV pyrolysis chars

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<td>O₂ concentration (°C)</td>
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![Figure 23]

Figure 24. Availability of O₂ during tests. Conditions: 0.3 MPa of pressure, 5% O₂ and 105 ms residence time

![Figure 24]
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14. PUBLICATIONS

