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Citation for final published version:

Steer, Julian Mark , Marsh, Richard , Sexton, D and Greenslade, M. 2018. A comparison of partially burnt coal chars and the implications of their properties on the blast furnace process. *Fuel Processing Technology* 176 , pp. 230-239. 10.1016/j.fuproc.2018.03.027

Publishers page: <http://dx.doi.org/10.1016/j.fuproc.2018.03.027>

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A comparison of partially burnt coal chars and the implications of their properties on the blast furnace process

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Abstract: Blast furnace coal injection is a vital part of modern ironmaking, reducing the amount of coke reductant required in the process and increasing its efficiency. However the injection of different coals or their blends, into the raceway formed by the hot blast, has technical issues due to the very short particle residence times and the limited availability of oxygen in this region. This makes complete burnout difficult and limits the range of coals suitable for this application, leading to partially burnt chars being carried out of the raceway into the blast furnace shaft and potentially into the off-gas system.

This paper explores the fate of these chars, from a range of different coals, looking at how this influences the selection for injection and the implication of these on the blast furnace. In particular, we have looked beyond the limitations of selecting coals based on proximate analysis alone by examining in more detail other physical and chemical properties and their potential effect on the process. A drop tube furnace (DTF) has been used to synthesise chars in a high heating rate environment, and although burnout and volatile loss values suggest suitability of some coals for blast furnace injection, additional problematic effects have been identified and measured such as char swelling and agglomeration which may impact the gas permeability of the furnace. A TGA/DSC has been used to measure the gasification of chars by the Boudouard reaction and compare the thermal impact of more reactive samples.

Whilst other studies have concentrated on the combustion of injection coals to determine their suitability, this one focuses on the implications of the partially burnt chars formed by incomplete reaction in the raceway.

Keywords: Coal injection; XPS; Blast furnace, Char reactivity, Drop tube furnace.

1. INTRODUCTION

The blast furnace ironmaking process uses carbon based reductants such as coke and coal in the process of reducing iron ore to iron. Coal is injected into the hot air blast which is directed into the furnace through tuyeres and plays a vital role in the process by reducing the reliance on expensive coking coals; improving the yield of iron per tonne of raw materials; and reducing environmental emissions associated with the coking process [1].

However, oxygen is rapidly consumed in the 'raceway' region, formed where the hot blast and coal are injected into the furnace. This limits the opportunity for coal to combust completely, which can result in limited burnout of the injected coals leading to partially burnt chars being carried into other regions of the furnace or out of the top as dust emissions in the off gas system where they can impact gas permeability through the coke and iron ore burden and thermal stability [2, 3]. Much research work has concentrated on the importance of coal burnout reactivity but with respect to combustion [4, 5], specifically Kalkreuth et al explained how higher volatile matter coals produce more reactive chars [6]. Work has also been carried out on the effect of those volatiles, by Ross et al [7] and Hayhurst et al [8], who showed how the reaction environment and conditions influence the fuel particle devolatilisation behaviour especially under oxidizing conditions

In addition to the reactivity of the coals, the physical structure and properties of the partially burnt coal chars affects the utilisation of these and is likely to impact the thermal stability of the furnace, which in turn will affect the production and cost of iron. Stubbington et al described how devolatilisation can be accompanied by swelling, shrinking and fragmentation of the particles all of which will affect the behaviour and utilisation of the chars [9].

In particular, this paper looks specifically at the fate of partially burnt coal chars with respect to a blast furnace. The raceway is characterised by short residence times, high temperatures and high heating rates and these conditions influence the burnout and physical properties of the chars. This paper aims to look at the variation in these properties and the reactivity of these partially burnt chars, examining changes in the surface chemistry, investigating and considering the ways it might adversely affect the process; and to show the importance of the char gasification reaction, via the reverse Boudouard reaction, which occurs further up the shaft of the furnace.

67

68 2. MATERIALS AND METHODS

69 2.1 Materials

70 A range of coals, indicative of the type that might find themselves in blends for injection, were
 71 chosen ranging from the high rank semi-anthracitic LV1 to the lower rank high volatile bituminous
 72 HV1. Three particle size classifications were chosen, a typical granulated specification, $100\% \leq$
 73 $1000\mu\text{m}$ with $50\% \leq 250\mu\text{m}$; a pulverised coal specification $100\% \leq 106\mu\text{m}$ and an intermediate size
 74 classification of $100\% \leq 500\mu\text{m}$. The samples were milled to this specification using a TEMA™ disc
 75 mill and classified by dry sieving using the standard BS1016-109:1995.

76

77 Table 1. Analysis of coal samples dried (size classification = $100\% \leq 1000\mu\text{m}$ with $50\% \leq 250\mu\text{m}$)

Coal type	Volatile matter content (% wt)	Ash content (% wt)	Fixed carbon content (% wt)	Vitrinite (% vol)	Liptinite (% vol)	Inertinite (% vol)	Mineral matter (% vol)
LV1	8.2	5.8	86.0	83	1	14	2
LV2	12.5	8.6	78.9	60	0	39	1
LV3	14.4	4.7	80.9	78	1	18	3
MV1	24.4	7.8	67.8	52	1	46	1
MV3	20.3	7.8	71.9	78	1	20	1
MV4	17.6	5.2	77.2	72	6	20	2
HV1	33.0	6.9	60.1	71	10	17	2

78

79 2.2 Methods

80 The classified samples were dried at 105°C using BS11722:2013 until a constant weight and the
 81 volatile matter content was measured using standard BS15148:2005. Ash contents were carried out
 82 using the standard method BS 1171:2010.

83

84 A drop tube furnace (DTF) was used to characterise the devolatilisation and burnout behaviour of
 85 the coal samples at 1100°C in air for residence times at 35 ms to 700 ms as detailed by the authors
 86 in previous publications [10, 11]. Particles were fed into the top at feed rates of 30 g/hr, entrained in
 87 a laminar air flow at 20 L/min and collected at the bottom by means of a cyclone collector. The

88 particle residence time was controlled by altering the distance of a moveable water cooled collection
89 probe feeder. The ash tracer method was used to calculate the burnout of the coals, sometimes
90 referred to as the combustion efficiency.

91
92 The petrographic maceral analysis was carried out in accordance with ISO7404 by preparing a
93 polished particulate block and carrying out a point count under reflected light microscopy to identify
94 the different macerals present. Particle size analysis work was carried out using a Malvern
95 Mastersizer 3000 laser diffraction particle analyser, capable of measuring between 0.01 - 3500 μm ,
96 using a wet cell accessory with obscuration levels between 4-8%.

97
98 The gasification reactivity was determined by the reverse Boudouard reaction where the carbon in
99 the char is reacted with carbon dioxide gasifying it to carbon monoxide. A Mettler-Toledo TGA/DSC
100 3+ was used to monitor the weight loss by first heating to 900°C in nitrogen and holding for 7mins to
101 devolatilise the sample then switching to a CO₂ flow rate of 100ml/min until complete conversion was
102 obtained. The gasification metric used to compare the reactivity of the samples was defined as $t_{0.5}$,
103 the time taken in minutes to achieve 50% conversion of the sample.

104
105 A Kratos Axis Ultra DLD system was used to obtain XPS spectra using monochromatic Al X-ray source
106 operating at 144 W. Pass energies of 160 eV were used to collect data for survey spectra, and 40
107 eV for the high resolution scans. The system was operated in the hybrid mode, which utilises a
108 combination of magnetic immersion and electrostatic lenses and acquired over an area approximately
109 300 x 700 μm . A magnetically confined charge compensation system was used to minimize charging
110 of the sample surface, and all spectra were taken with a 90° take off angle. A base pressure of ~
111 1×10^{-9} Torr (0.133 μPa) was maintained during collection of the spectra. In all cases a binding energy
112 of 284.5 eV was used for the C 1s peak to account for peak shifts due to differences in sample
113 charging.

3. RESULTS AND DISCUSSION

3.1 Variation in the gasification reactivity of chars obtained from different coals

Different types of coal have been shown to vary in the reactivity of the partially burnt char formed when the coal is not completely combusted [2, 12, 13]. As there is limited scope for complete combustion in the raceway region of a blast furnace, it is important to consider both the burnout and the gasification reactivity that takes place further up the shaft, as the char residue could be very important to utilisation of the injected reductant and the furnace performance.

Most coals used for blast furnace injection are milled to a pulverised size classification [14] and it is well understood that the increases in the surface area can lead to improvements in combustion reactivity and therefore utilisation of the coal in the raceway region of the furnace [15-17]. However, due to the extra cost, energy and wear on grinding equipment some ironmakers use larger granulated classifications that require less milling [18-20].

In a previous paper [10] the authors described how the process of grinding the coals affected the physical properties of the residual char, and in particular the surface chemistry, and that in terms of burnout the two effects might counteract each another to give burnouts in larger classifications of coals similar to smaller particle size classifications with higher surface areas.

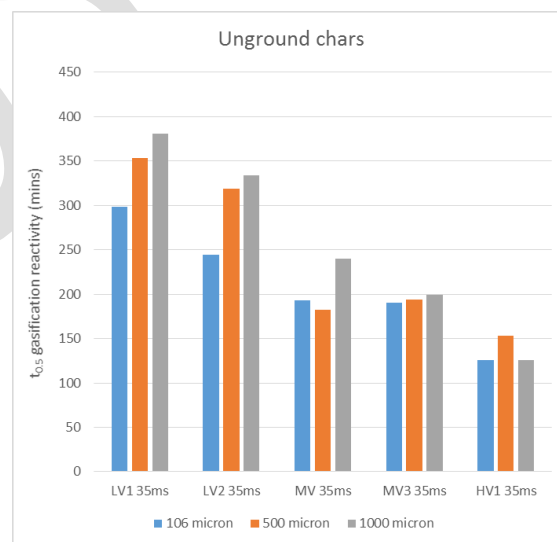
Potentially large quantities of partially burnt coal chars could arise from the incomplete burnout of coal and their physical properties could have a detrimental effect on the ironmaking process. If lower reactivity chars are retained in the furnace by the burden then this could result in the accumulation of these chars in different parts of the shaft which impact the furnace thermal stability and the efficiency of iron production.

A drop tube furnace (DTF) was used to produce chars with similar properties as chars exiting the raceway in a blast furnace, so that the suitability and impact of coals with different particle size classifications could be compared to establish the impact of grinding. The high temperature and dynamic raceway environment cannot be replicated easily, but the DTF technique has been used by many researchers to mimic the short residence times, high temperatures and high heating rates as closely as possible in the laboratory environment; Li et al compared it to a pulverised coal injection rig

147 and found the high particle heating rate conditions (10^4 K/s) are comparable and useful to compare
148 with this environment [2, 21, 22].
149

150 Figure 1 compares the gasification reactivity of chars formed from different coals classified to three
151 different sizes after a 35ms residence time in a drop tube furnace at 1100°C. It is evident from the
152 results that the coal rank impacts on the char reactivity. The higher rank LV1 and LV2 coals formed
153 less reactive chars (longer $t_{0.5}$ reaction times) and for these coals in particular there is a bigger
154 difference in the reactivity between the small and large size classifications. Gibbins et al described
155 how coal petrography affects the thermal annealing, showing that high vitrinite coals tend to exhibit
156 thermo-deactivation on heat treatment more than those with high inertinite content [23]. However,
157 despite this LV2 had one of the lowest vitrinite contents, but a lower gasification reactivity than many
158 of the coals tested and illustrates the difficulty assigning relationships that cover all coals. In
159 comparison, for the lower rank coals the gasification reactivity is much higher (shorter $t_{0.5}$ reaction
160 times) and the particle size classification has less influence on the reactivity.
161

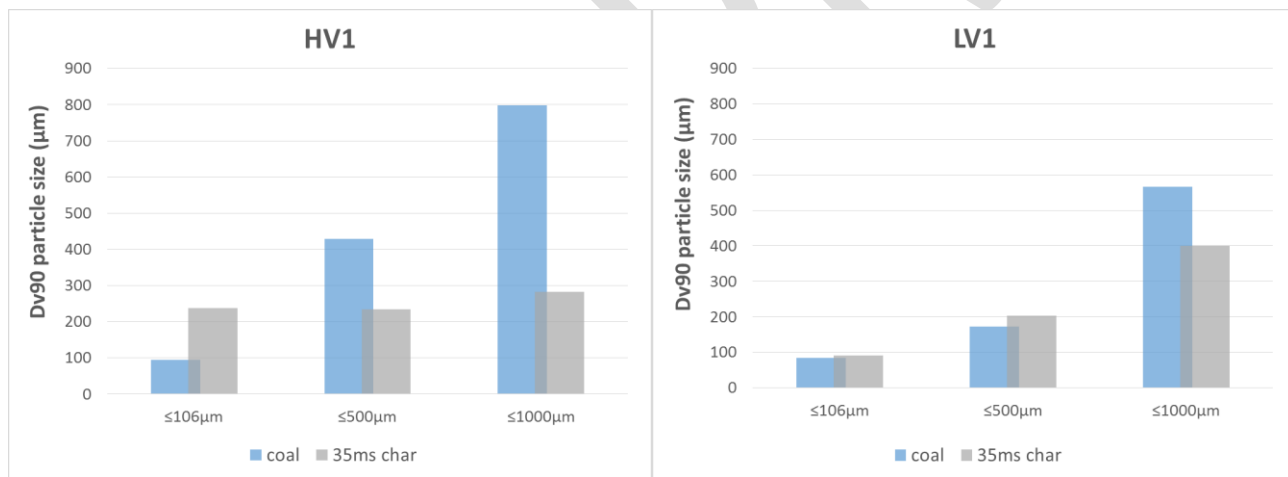
162 This has important potential implications for two reasons, the first is the effect on the reactivity of
163 partially burnt char entering the upper furnace, as the rate of consumption of less reactive material
164 will be slower; the second is the physical size of the particles, whose upward flow will be restricted
165 through the furnace and might potentially block the pores and permeability of the coke burden. In
166 turn, this could impact the distribution of heat, descent of the burden and overall stability of the
167 process.



169 Figure 1. $t_{0.5}$ gasification times for unground chars of different coal size classifications post drop tube
170 furnace.
171

172 It has been shown in other research that the size classification of the ground coals has important
173 effects on the physical properties of the chars formed in the DTF conditions, and that these vary
174 depending on the coal type [21, 24]. Smaller classifications often show particle swelling, especially
175 higher volatile matter coals and caking coals exhibiting plasticity; while larger particles fragment when
176 they are exposed to the high heating environments [21, 22].
177

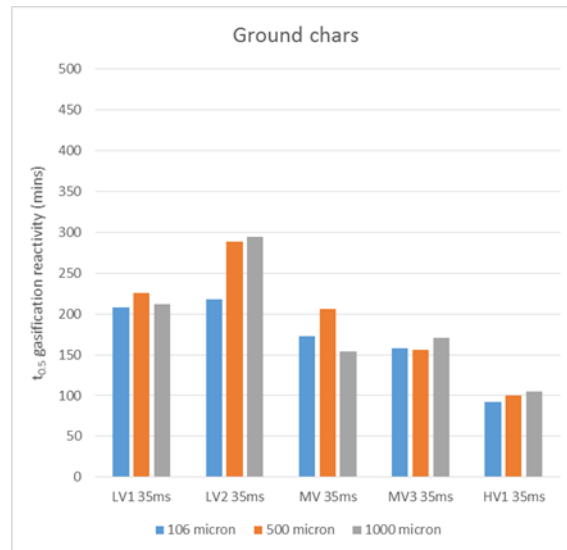
178 Examples of this effect on the D_{v90} particle size are shown for two coals in Figure 2, where different
179 initial coal size classifications of the lower rank high volatile matter content HV1, formed chars with
180 similar D_{v90} for the particle size distributions post DTF. In comparison, the higher rank lower
181 volatile LV1 shows a wider spread of char size distributions which is an additional contributing factor
182 to the greater variation in gasification reactivity for LV1 compared to HV1.
183



184 Figure 2. D_{v90} particle size for initial coal classification and char after 35ms at 1100°C.
185
186

187 Many papers have discussed the effect of heating rate on the reactivity of the chars formed, and
188 that the chemistry of the parent coal, or char formed, can have an important effect on its reactivity [25,
189 26]. For that reason, and because of the swelling/fragmentation effects noted with different coals,
190 the intrinsic gasification reactivities were compared on an equivalent basis by grinding the chars to
191 the same particle size, as shown in Figure 3. As expected after grinding to smaller particle sizes,
192 due to the increased surface area the gasification times were shorter than the unground post DTF
193 samples. The improvement is particularly relevant for the higher rank/less reactive LV1 chars where

194 the difference in reactivity between the initial coal size classifications is reduced. The results in
195 Figure 3 suggest that the initial coal size classification does not show a strong correlation with the
196 intrinsic gasification reactivity, but that the coal type is important, with higher rank coals exhibiting
197 lower reactivity and the lower rank coals with higher reactivity.
198



199 Figure 3. $t_{0.5}$ gasification times for chars of different coal size classifications in a drop tube furnace
200 post grinding.
201
202

203 The effect of mass transfer at the gas solid interface is an important parameter for char reactivity
204 and the mass diffusion of gases at the surface can be limited by low porosity through the char
205 network. Results in Table 2 compare the difference in porosity for some of the coals where the
206 smaller size classifications exhibit swelling forming higher porosity chars, in comparison the larger
207 coal sizes fragment in the high heating rate of the drop tube furnace and have correspondingly lower
208 porosities. However, no direct correlation between porosity and gasification reactivity was observed,
209 in fact the most porous char (MV3 106 μm 35ms) exhibited the lowest reactivity, this has been
210 previously observed in other studies [27]. The results also show that any link between reactivity and
211 porosity is coal dependant, as the chars derived from the smaller coal specification all show
212 improvements in the porosity, but both MV3 and HV1 showed little or no improvement in char
213 reactivity compared to MV4 which exhibited a large improvement.
214
215

Table 2. Porosity and gasification reactivity of unground chars formed after 35ms

	Porosity (m ² /g)			Gasification time (mins)		
	MV3	MV4	HV1	MV3	MV4	HV1
COAL	CHAR					
1mm 35ms	28.3	10.0	16.6	199	197	126
106µm 35ms	90.2	40.3	59.7	190	98	126

3.2 The relationship between burnout and gasification reactivities

Other papers have shown how coal burnout varies considerably in the raceway region of the furnace due to the short particle residence time, coal reactivity and the limited oxygen available for combustion [5, 28]. Because of this, it is probable that considerable quantities of partially burnt coal chars make their way into the furnace shaft potentially altering the gas flow through the burden and contributing to other competing reactions which will have an important effect on the process. In addition, the gas composition varies through the furnace and conversion of the partially burnt solid chars to gas will continue to happen due to gasification by thermal pyrolysis and also by the reverse Boudouard reaction where carbon reacts with carbon dioxide and is converted into carbon monoxide, as takes place with the coke burden.

For this reason the type of coal and the raceway conditions are not only important to how much of the injected coal is consumed and utilised by combustion in this region, but also very important to the properties of the partially burnt coal chars produced. These properties will affect where chars are deposited further up the shaft and where they are consumed in the furnace.

This balance between the consumption of coal in the raceway by combustion, or as a char further up the shaft by gasification has important implications on the selection of suitable coals and blends for injection. To investigate this balance, the gasification reactivity of partially burnt coal char has been compared to the coal burnout for chars formed after a short residence time of 35ms through the DTF as shown in Figure 4. There is a trend for those coals with the highest burnout to form chars with higher gasification reactivity (lowest $t_{0.5}$ time).

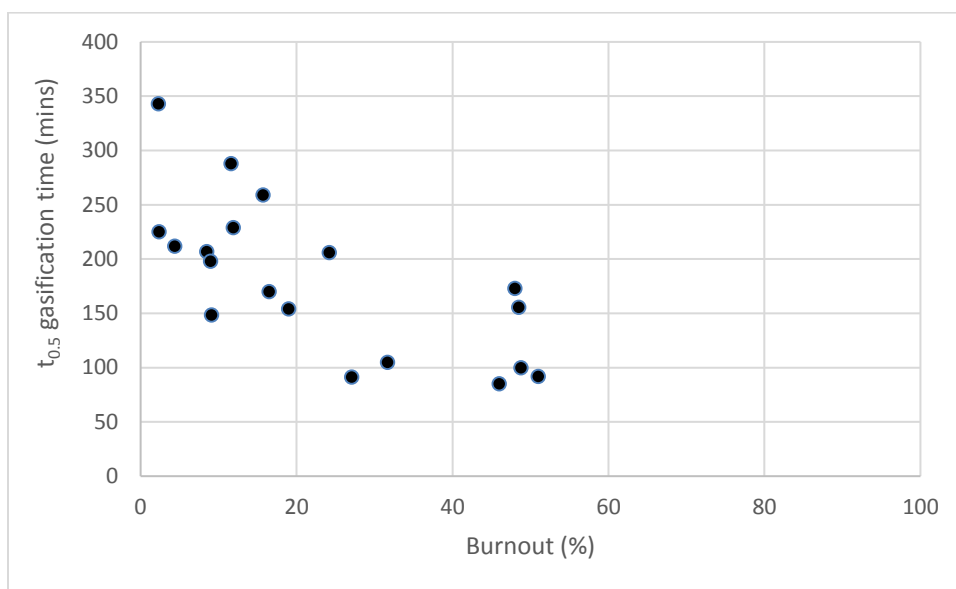


Figure 4. Relationship between $t_{0.5}$ gasification times and burnout for DTF chars at 35ms residence time.

The raceway formed by the hot blast is characterised by short particle residence times due to the high blast velocities in the order of 180m/s, and research suggests that residence times are typically in the region of 20-50ms [5, 28, 29]. But it has also been pointed out by other researchers that the gas flow may be very turbulent in this region, and in certain circumstances this could contribute to particle circulation and longer residence times [30]. Because of the possibility of longer residence times the gasification times were also measured for DTF chars formed after 700ms, shown in Figure 5, and they also indicate an increasing trend for gasification reactivity with higher burnout for the char.

It is clear from the results that the particle residence time has an important effect on the properties of the chars formed, but that the coal type has a greater effect. However, no absolute correlation for burnout and gasification was observed between different coals, as there is considerable difference between the gasification reactivity for chars formed after a short residence compared to a longer residence time. For example, those chars formed after 50% burnout of the parent coal at 700ms, have a much lower gasification reactivity ($t_{0.5} > 300$ mins) than those formed after 50% burnout at 35ms ($t_{0.5} < 170$ mins). It is not burnout per se that determines the char reactivity, but the coal from which it is derived and the char it subsequently forms. The individual coals show decreasing gasification reactivity at higher burnout conversions as the more reactive components of that coal are consumed and its properties change. Also, it appears from the porosity results that other additional factors are also important to the reactivity of chars; mineral catalysis or deactivation; structural

ordering and different functional chemical groups are all possibilities identified by other studies [25, 31, 32].

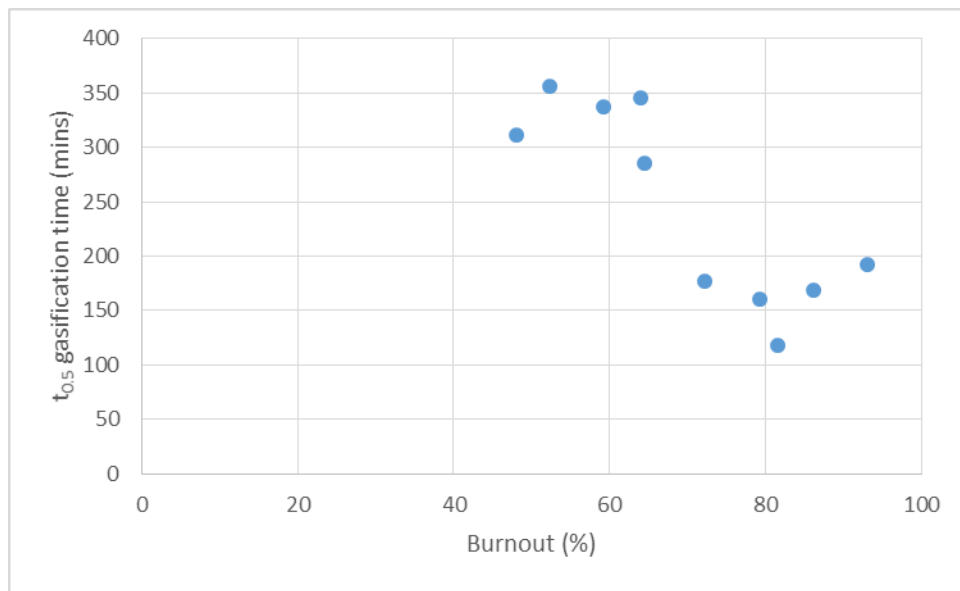


Figure 5. Relationship between $t_{0.5}$ gasification times and burnout for DTF chars at 700s residence time.

3.3 The relationship between the char properties and reactivity with residence time

Variations in the blast furnace process parameters and conditions, as mentioned in the previous section, could alter the residence time of the particles in the raceway region which will not only affect the burnout of the coal but also the properties and reactivity of the partially burnt chars which are carried into the furnace as noted by previous research [33, 34]. Feng et al described this thermal deactivation as associated with loss of active sites for subsequent oxidation [35] and consistent with Radovic who also described the importance of the concept of active sites in gasification reactions [36]. As shown in Figure 6, the chars formed at longer residence times are less reactive while those formed at shorter times are more reactive. Senneca et al related the loss of gasification reactivity to higher heat treatment temperature, longer heat treatment time leading to thermal annealing [37].

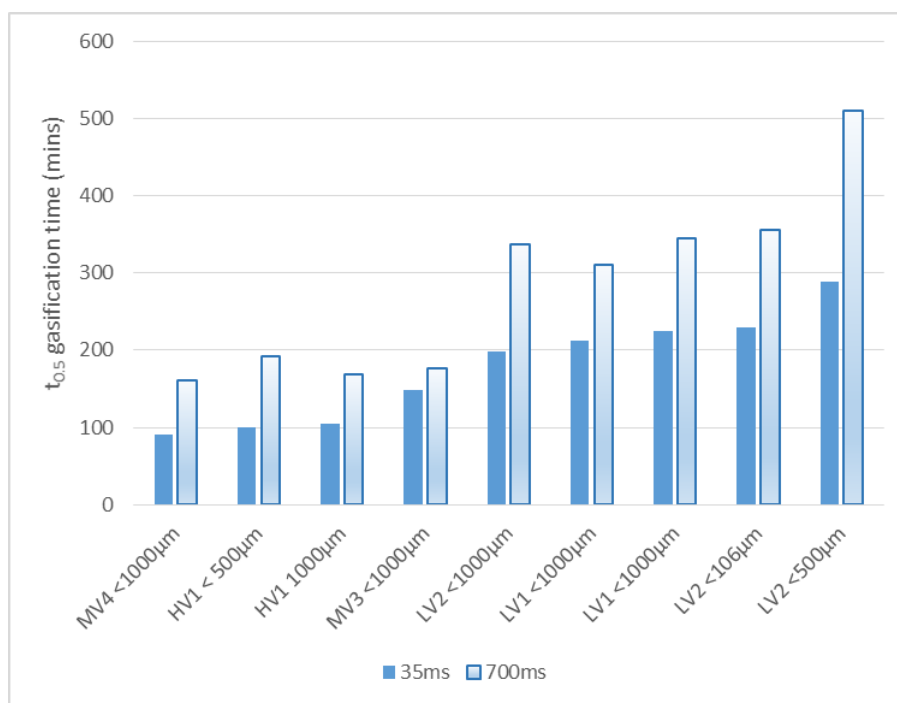


Figure 6. Relationship between residence time and gasification time for a range of DTF chars.

Bulk analytical chemistry techniques give useful information to relate to reactivity, but the gasification reaction occurs at the solid-gas interface on the char surface. X-ray Photo Electron Spectroscopy (XPS) is a valuable analysis technique used to examine the surface chemistry to a depth of circa 10nm [38] and has been used to look more closely at the role of the surface chemistry in relation with the properties and reactivity.

The results in Figure 7 indicate higher atomic surface oxygen concentration for the chars formed in the DTF at longer residence times compared to shorter ones due to increased coordination with reactive groups on the surface. It is observed that the surface oxygen content increases at the 700ms residence time with respect to each individual coal, and as we saw in Figure 4 there is a corresponding decrease in gasification reactivity also observed at the same time for the respective coal chars. However, the results suggest no direct relationship between the absolute atomic concentration of surface oxygen and the gasification reactivity for different coals. The results indicate a consistent pattern of increased surface oxygen at higher residence times, but show variation in the concentration between samples.

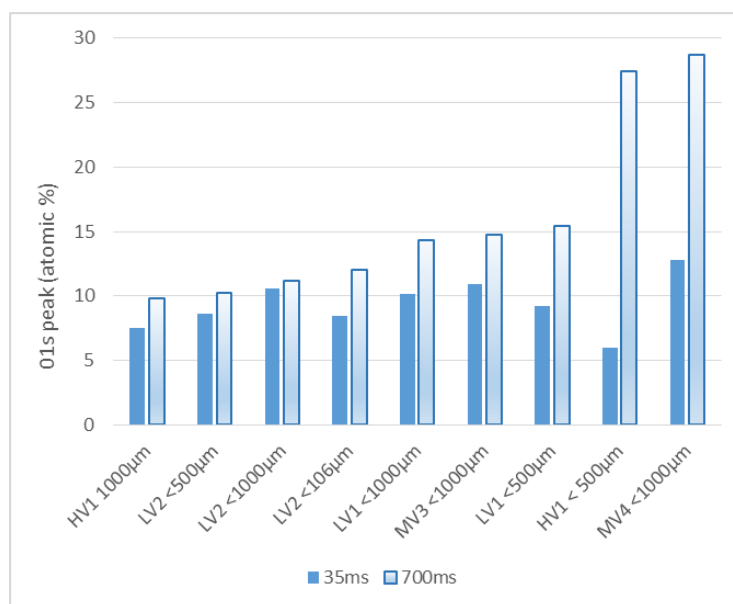


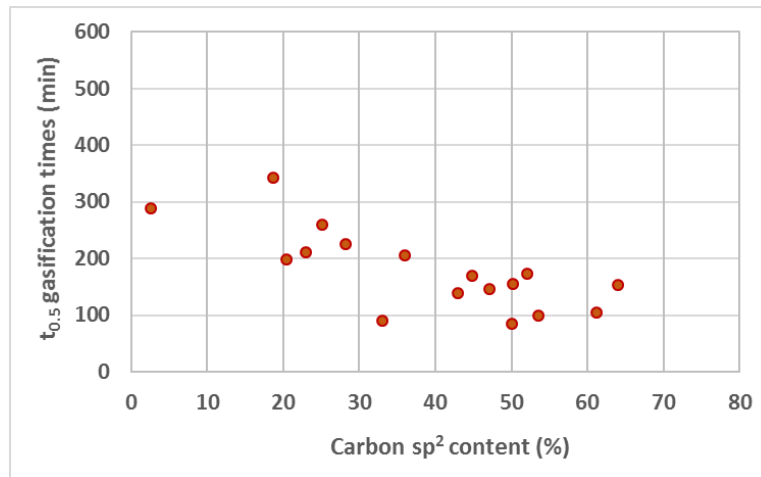
Figure 7. Change in surface oxygen for 35ms and 700ms DTF chars

Carbon is the most abundant element on the surface of the partially burnt coal chars samples and XPS analysis has shown it is present either bonded to itself or to other elements to form the basis of different functional chemical groups. The type of bonding present affects both the physical properties and the chemical reactivity of the carbon but as can be seen in graphite and diamond, the type of bonding plays an important role on properties.

Because of the close peak overlap between sp^2 and sp^3 bonding in the carbon C1s peak the most widely adopted method using the XPS technique is use the carbon auger peak to determine the change in the proportion of sp^2 hybridisation bonding of the carbon on the surface. Carbon sp^2 bonding is associated with graphitic type ordered forms of carbon and has been linked by many authors to a reduced char reactivity [4, 39, 40].

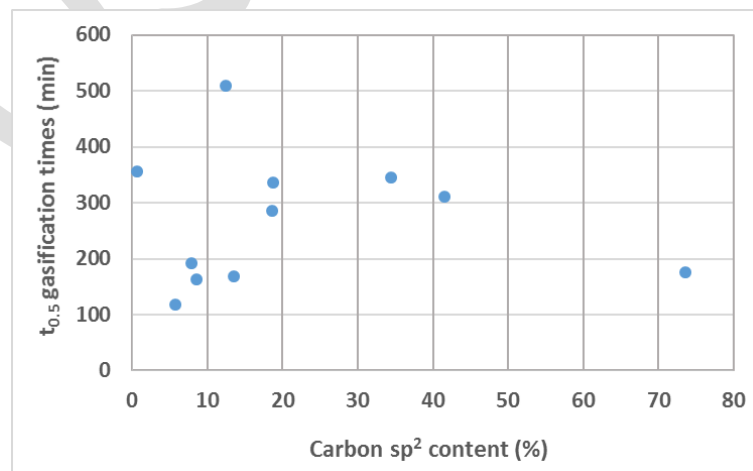
The results shown in Figure 8, suggest a relationship between the reactivity and the sp^2 content for the chars formed at the lower residence times of 35ms in the DTF, whereas the results in Figure 9 for the 700ms chars are more random in nature. For the 35ms residence time, the coals which produce chars with higher sp^2 content were found to have better gasification reactivity (lower $t_{0.5}$ times) suggesting initial structural mobility in terms of bond rearrangement of the surface carbons during the formation of chars in the DTF. This is consistent with the formation of the metaplast and would be facilitated by the loss of low molecular weight functional groups and hydrogen on the coal

322 surface during the thermal devolatilisation which could result in the formation of new reactive sites
323 and increase the gasification reactivity.
324



325
326
327 Figure 8. Relationship between gasification and surface carbon bonding for 35ms DTF chars.
328

329 However, any initial structural mobility or reactive sites produced at the lower residence times are
330 likely to be very short lived. In Figure 9 at the longer residence time of 700ms there was no such
331 obvious trend, in general the degree of carbon sp² bonding is much less and the gasification reactivity
332 is much lower (indicated by higher t_{0.5} gasification times). However the longer residence time shows
333 variability and there are exceptions with some chars showing high sp² value and high gasification
334 reactivity.
335
336



337
338

339 Figure 9. Relationship between gasification and surface carbon bonding for 700ms DTF chars.
340

341 Previously Figure 6 compared the difference in gasification reactivity for specific coal chars and
342 showed that longer residence times gave lower gasification reactivity. Investigating this further,
343 Figure 10 compares the change in sp^2 bonding for the chars formed from coals at different residence
344 times and shows a much less predictable relationship. At longer residence times some coal chars
345 show an increase in the sp^2 nature of the surface carbon, while others decrease. The increase is
346 consistent with other research theory of a reduced reactivity for the more ordered graphitic carbon
347 while some others show the opposite effect and exhibit a decrease in the sp^2 ordering [25, 39, 40]. In
348 this respect, much of the research work carried out by other authors on char reactivity has focussed
349 more on those formed and consumed in combustion conditions typical of a power generation context
350 and using bulk analysis techniques. However, this study investigated more specifically the role of
351 the surface chemistry and in conditions that relate to a blast furnace where particles experience very
352 short residence times; rapidly diminishing oxygen concentrations; and char reactions with carbon
353 dioxide. This may go some way to explain the variation between research findings with respect to
354 the graphitic nature of carbon.
355

356 It is noted that for the lower rank HV1 and MV4 coals the reduction in sp^2 bonding at higher
357 residence times corresponds with observations of swelling behaviour and agglomeration effects in
358 these chars. Previous studies by Bar-Ziv et al attributed differences in reactivity to thermal
359 annealing of the carbon in the char [41], and in this case the plasticity and reactivity of these coals
360 contributes to less ordered chars with lower sp^2 type carbon which is then consistent with the higher
361 burnout and gasification reactivity measured for them.
362

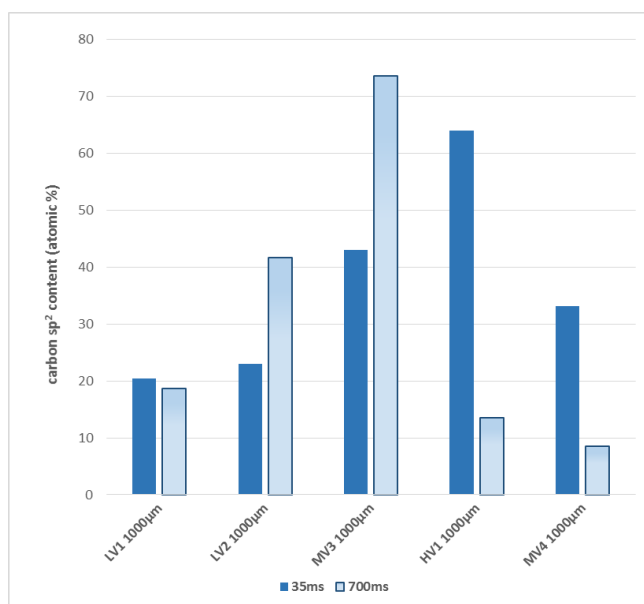


Figure 10. The sp^2 carbon content of chars formed at 35ms and 700ms in a DTF.

The importance of the carbon-carbon bonding in relation to the gasification reactivity of the char is clear, but the results indicate a role for other variables. XPS is particularly useful to investigate detailed chemical bonding information for the carbon (C1s peak) with oxygen and the high resolution analysis spectra can be deconvoluted using a peak fitting technique to determine the carbon-oxygen bonding due to shifts in electron binding energy due to the chemical environment surrounding the carbons [42].

The deconvoluted C1s spectra for the coal and char samples shown in Figure 11 for MV3 and Figure 12 for MV4 show higher binding energy asymmetry due to carbon-oxygen bonding. In particular, the char samples exhibit further carbon-oxygen peak broadening due to the combustion environment, but in contrast to this there was less at the lower DTF O:C ratio. The peaks were fitted into five respective components relating to the type of bonding for sp^2 type carbon bonding (peak I BE=284.3-284.5 eV); sp^3 type carbon bonding (peak II BE=285.1-285.5 eV); carbon present in alcohol or ether groups (peak III BE=285.6-286.5 eV); carbonyl groups (peak IV BE=287.0-287.8 eV); and carboxyl or ester functions (peak V 288.1-288.8 eV). Satellite peaks at higher binding energies are attributed to aromatic $\pi-\pi^*$ shake up effects above 290eV and plasmon loss effects occur at lower energies below 284eV [43-45].

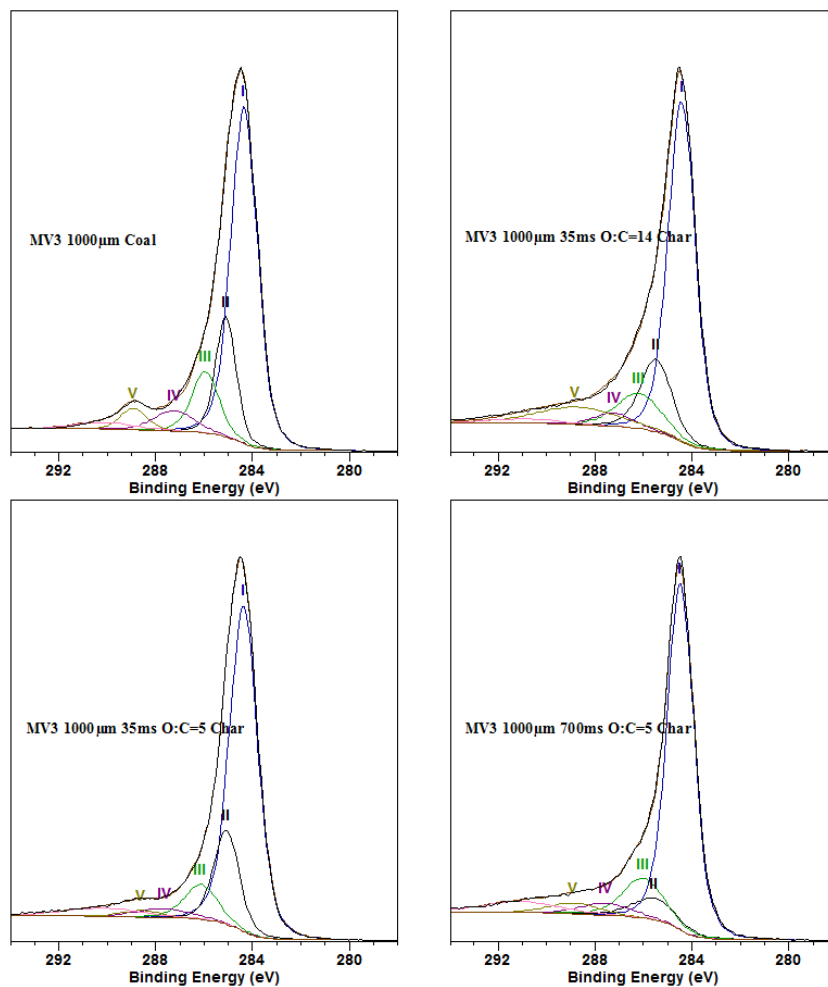


Figure 11. XPS deconvoluted C1s spectra for MV3 coal and char samples

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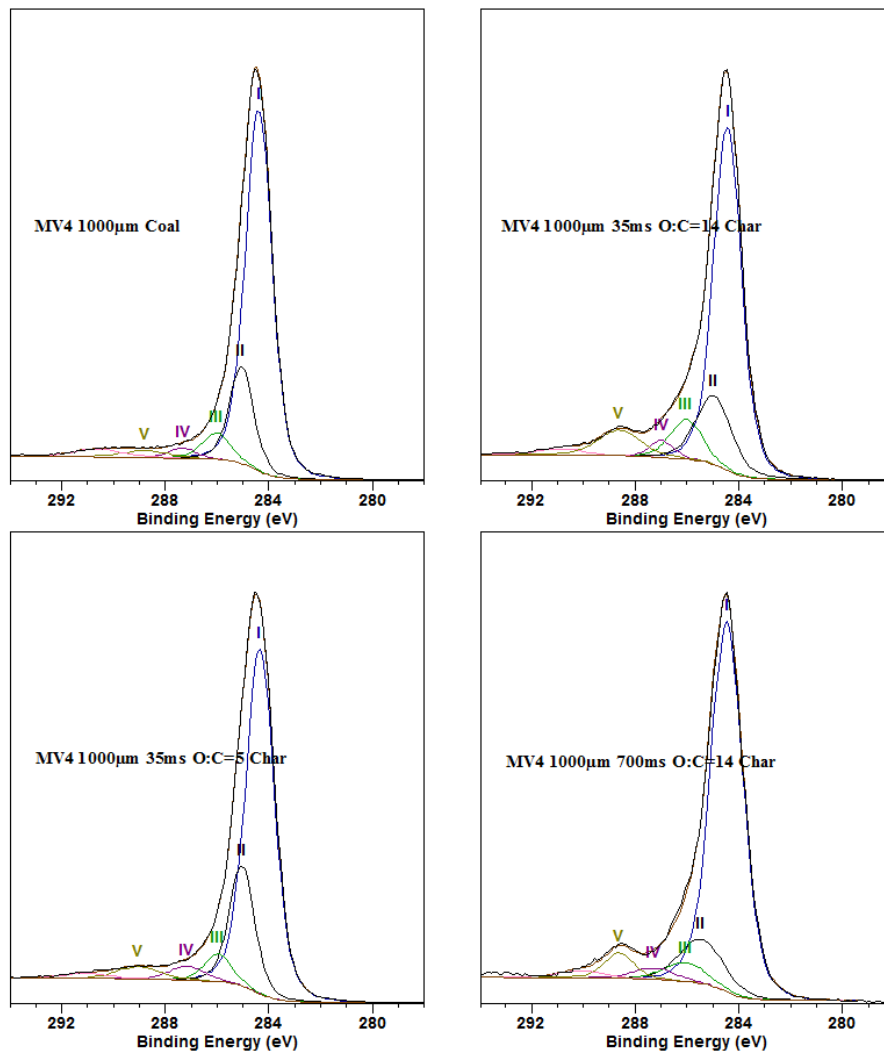


Figure 12. XPS deconvoluted C1s spectra for MV4 coal and char samples

The figures shown in Table 3 quantify the peak fitted components for the coal and coal char samples as absolute atomic percentages of the carbon on the surface. The predominant form of carbon bonding with oxygen in the coal samples was as hydroxyl or ether groups and this was also the case in the chars after 35ms through the DTF. However, when combusted at this short residence time both the MV3 and MV4 coal chars showed an increase in the carboxyl/ester type functional groups formed through surface oxidation.

In comparison, the chars formed at the lower O:C ratio in the drop tube furnace showed reduced surface oxidation compared to those at the higher ratio. Interestingly, for the MV3 the total carbon bonded to the oxygen at the lower ratio was 11.3% which was less than the 16.2% for the original coal indicating that the surface was less reactive to oxidation compared to the MV4.

404
405
406
407

Table 3. Absolute atomic % of deconvoluted high resolution XPS C1s spectra

Peak	I	II	III	IV	V	Satellite π - π^* peaks	C1 s	Total carbon- oxygen bonding (%)
Binding energy range (eV)	284.3 - 284.5	285.1 – 285.5	285.6 – 286.5	287.0 – 287.8	288.1 – 288.8	289.4 – 293.9	284.5	
MV3 Coal 1000 μm	48.3	13.2	8.9	4.3	3.0	2.2	79.9	16.2
MV3 Char O:C=14 1000μm 35ms	50.8	12.4	8.5	2.8	7.7	1.5	83.6	19.0
MV3 Char O:C=5 1000μm 35ms	54.6	14.1	6.9	2.8	1.6	3.8	83.7	11.3
MV4 Coal 1000 μm	61.0	14.9	4.7	1.6	2.0	2.4	86.6	8.3
MV4 Char O:C=14 1000 μm 35ms	53.6	13.6	7.1	2.3	6.1	1.5	84.2	15.5
MV4 Char O:C=5 1000 μm 35ms	60.7	18.8	4.6	3.0	3.3	1.6	92.0	10.9

408
409

In the blast furnace raceway, the concentration of oxygen in the hot blast rapidly decreases as it is consumed during combustion of the coal and coke in this region. To investigate the effect of this reduction of available oxygen on the reactivity and surface chemistry of the chars, the oxygen:carbon ratio of the feed gas was varied by diluting the flow of air through the DTF with nitrogen. The results in Table 4 indicate a reduction in the burnout of the coals at lower oxygen concentration, and the partially burnt coal chars formed in these conditions also show a reduction in the gasification reactivity (as indicated by the increase in $t_{0.5}$ gasification time).

417
418
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420

The role of surface association of oxygen with carbon has been widely discussed in terms of reactivity by other authors, but more with respect to combustion or the purity of graphene rather than the gasification by the Boudouard reaction [46, 47]. Haynes et al discussed how carbons form

421 significant quantities of stable surface complexes with oxygen, however the amount of surface oxide
 422 formed due to the reaction with carbon monoxide (from partial combustion of carbon at lower O:C
 423 ratios) is approximately one tenth of that formed with oxygen. They also pointed out that the oxide
 424 complexes arising from reaction with oxygen are very different from those believed to occur in the
 425 Boudouard reaction [46].

426
 427 For the chars shown in Table 4, formed at 35ms in the DTF, the higher coal burnouts give partially
 428 burnt chars with higher gasification reactivity. It is expected that at the higher O:C ratio and burnouts
 429 the particles reach higher temperatures due to the 'high temperature rapid combustion field' of
 430 volatile matter noted by other authors [5, 48, 49]. In turn the difference in the environment
 431 surrounding the particles leads to differences in the type of carbon-oxygen bonding described in
 432 Table 4, carbon sp² content and higher gasification reactivities. In these DTF conditions at a shorter
 433 residence time, the chars with higher gasification reactivity had higher sp² content and although the
 434 smaller particle sizes give higher burnouts, the difference in the gasification reactivity was not great.

435
 436 Table 4. Variation in DTF burnout and gasification reactivities at
 437 different oxygen:carbon ratios at 35ms residence time

	Burnout (%)	Gasification t_{0.5} (mins)	Carbon sp² content (%)	Total carbon-oxygen bonding (%)
MV4<1mm 35ms O:C = 14	27	91	39	15.5
MV4<1mm 35ms O:C = 5	12	139	15	10.9
MV4<106µm 35ms O:C = 14	46	85	57	15.2
MV4<106µm 35ms O:C = 5	16	140	51	13.8
MV3 <1mm 35ms O:C = 14	9	149	51	19.0
MV3 <1mm 35ms O:C = 5	5	180	27	11.3
MV3<106µm 35ms O:C = 14	49	156	57	16.3
MV3<106µm 35ms O:C = 5	25	213	39	13.2

438

439

440 Whilst it is evident from the variation in the gasification reactivities of chars shown previously in Figure
441 1, that the coal type from which they are derived is very important, the results shown in Table 4
442 indicate that at a fixed residence time the coal burnout also plays an important role in the reactivity of
443 the char produced. At a higher O:C ratio the burnout is higher and the results suggest that the
444 combustion of the volatiles leads to a higher particle temperature rise compared to the lower ratio
445 which facilitates additional structural mobility, thermal annealing and higher carbon sp² content. At
446 the lower oxygen content the burnouts were lower and the reduced extent of coal combustion results
447 in lower particle temperature rise which in turn appears to produce a less reactive char. Work by
448 Shim et al described a higher propensity for annealing in higher reactivity coals and that char
449 reactivity is more sensitive to peak temperature than residence time [50].
450
451

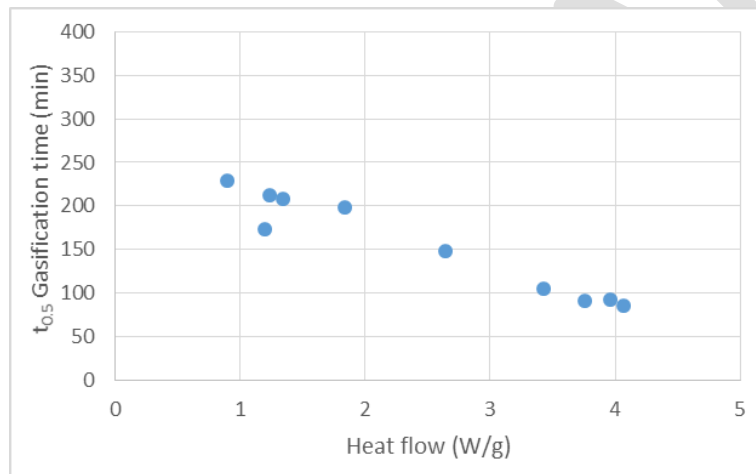
452 **3.4 The potential impact of char properties and gasification reactivity on the blast furnace** 453 **process**

454 While it is clear that there are a range of property changes which are occurring on the surface, what is
455 most important is how these might affect the blast furnace. Although partially burnt coal char will
456 contribute to dust in the off gas, a great deal is also likely to be retained in the furnace burden after
457 exiting the raceway were it will react in the same way that the coke does.
458

459 Whilst a higher gasification reactivity will help consume the partially burnt char quickly and prevent its
460 accumulation higher in the furnace, there are important thermal implications for more reactive chars.
461 To maximise the efficiency of the blast furnace the process requires to be balanced thermally so that
462 the reduction of iron ore occurs evenly throughout the furnace, reducing the chance of localised hot
463 spots and uneven burden descent.
464

465 In the raceway, coal is consumed by combustion with oxygen in the hot blast but the availability of
466 oxygen decreases rapidly and higher up the furnace thermal pyrolysis and gasification via the reverse
467 Boudouard reaction are the predominant reactions. Both are endothermic processes and will
468 contribute to temperature loss in the upper regions which will contribute to uneven thermal profiles
469 through the furnace, ultimately limiting the quantity of injected coal.
470

471 Using a TGA-DSC, the heat flow required for the gasification reaction has been used to investigate
472 the potential negative impact of different chars. The higher the heat flow the more thermal loss due
473 to the endothermic reaction in the blast furnace. The results indicate a strong trend showing how the
474 heat flow (W/g) increases as the gasification reactivity increases. This suggests that partially burnt
475 chars exiting the raceway with a lower gasification reactivity (larger $t_{0.5}$ gasification time), will have a
476 lower thermal impact on the blast furnace. For the 35ms chars shown in Figure 13, the chars with the
477 highest reactivity have 4.5 times more thermal requirement compared to those with the lowest
478 gasification reactivity.
479



480
481 Figure 13. Heat flow for 35ms DTF char gasification
482

483 In comparison, the heat flow results for the char formed at 700ms in the DTF shown in Figure 14, also
484 show an increasing heat flow trend as the gasification reactivity increases. However, the maximum
485 heat flow for chars with the highest gasification reactivity was 1.82 W/g for 700ms chars compared to
486 4.1 W/g for the 35ms chars.
487

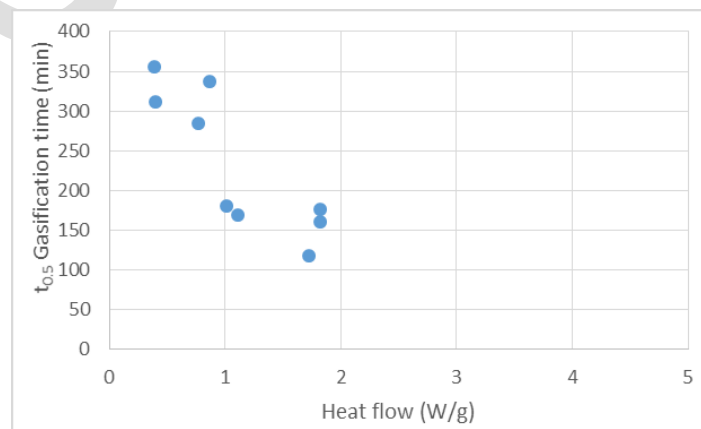


Figure 14. Heat flow for 700ms DTF char gasification

In terms of blast furnace injection the results suggest that coals producing lower gasification reactivity chars are more preferable, as the partially burnt chars ascending the furnace have a lower heat requirement for the endothermic reaction than those with a higher gasification reactivity, and that this in turn will have less localised cooling effect and better heat distribution in the furnace.

Blast furnace operators seek to maximise the burnout of coal in the raceway region where the hot blast enters the furnace. These findings illustrate the potential negative impact of these chars in the furnace and Figure 15 shows the variation in heat flows for the different chars formed after 35ms and 700ms in the drop tube furnace.

At low residence times, higher burnout coals form chars with high heat flows that could have a negative effect higher up the furnace. It is therefore imperative that the utilisation of these type of high burnout coals, which are typically higher volatile content, is maximised in the raceway region using process options such as oxygen enrichment, higher raceway temperatures or increased raceway length. At higher residence times those coals showing the highest burnout produce chars which are less likely to have such a negative effect in the upper furnace.

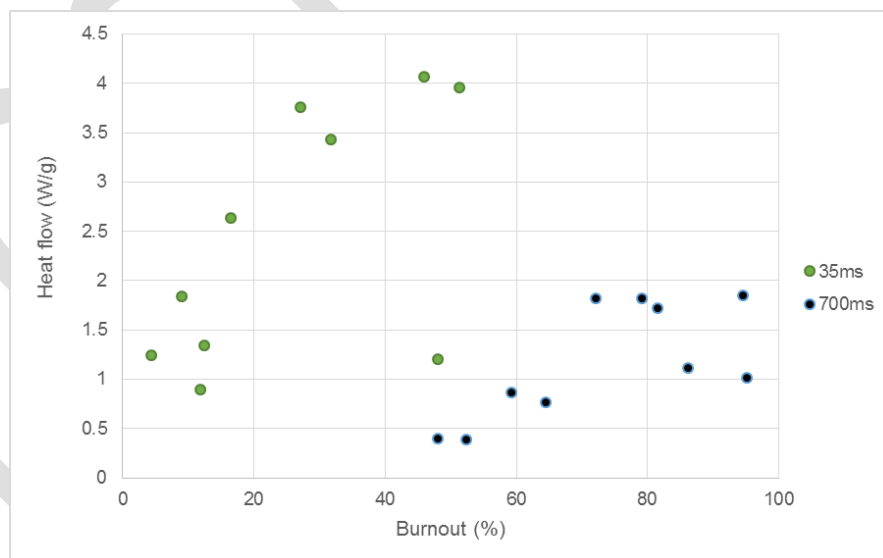


Figure 15. Heat flow variation for chars formed at different levels of burnout

511 There is a wide variation in temperature in a blast furnace ranging from peak temperatures around
512 2000°C in the raceway to 100°C at the top where raw materials are charged. Because the
513 endothermic heat requirement for the char gasification reaction varies depending on the temperature,
514 the heatflow was tested at three temperatures. The results shown in Table 5 indicate an increasing
515 heat flow requirement for the reaction as the temperature increases, which means that partially burnt
516 chars will have a greater cooling effect and thus impact the temperature stability in the hotter regions
517 of the furnace.

518
519 It is also noticeable, that there is less of a difference between the heatflow for chars from different
520 coals at 1100°C compared to 900°C. It will be very important how far the chars ascend the furnace
521 before they are retained by the burden and chars such as those formed from MV4, which exhibit
522 agglomeration effects, are more likely to be retained lower in the furnace causing issues in this
523 region. Other coals showing less swelling or agglomeration are more likely to ascend further up the
524 furnace where they will have a proportionately smaller effect on the furnace.

525
526 Table 5. Variation in Heat flow with temperature for chars from coals classified to <1000µm

Temperature (°C)	900	1000	1100
	Heat flow (W/g)		
MV4	3.8	10.4	27.3
HV1	3.4	7.6	31.1
MV3	2.6	6.3	22.8
LV2	1.8	5.2	18.6
LV1	1.2	6.2	21.1

527 528 529 **4. CONCLUSIONS**

530 Blast furnace coal injection plays an important role in the efficiency of the ironmaking process but
531 there is considerable variability in the coals and process conditions in a blast furnace. Much work
532 have been carried out on the importance of combustion burnout in the raceway region where coals
533 are injected, but far less information is available on the fate of partially burnt coal chars that have not
534 been completed utilised in this region.

535

536 It is evident from this work that there are some important reactivity and property considerations
537 which could have a potential effect on the stability of the process. In particular, higher volatile,
538 higher burnout coals give chars which are more reactive; but if these coal types are not utilised as
539 much as possible in the raceway region then their chars have higher gasification reactivity which
540 could have greater potential thermal impact further up the furnace compared to less reactive chars.

541

542 In relation to production costs, where larger granulated coal size specifications are to be utilised by
543 iron makers, to reduce the cost and energy associated with milling to smaller sizes, choosing coal
544 types which exhibit a high degree of fragmentation could be more beneficial as these produce chars
545 with a smaller size.

546

547 Close examination of the surface chemistry shows a range of relationships with reactivity, but above
548 all when looking at these results and comparing them with other research, it is evident how important
549 it is to look at the specific properties of the coal selected for incorporation in the blast furnace, as the
550 char it produces is very dependent on the context and conditions it is used in.

551

552

553 **Acknowledgements**

554 I would very much like to acknowledge and thank both the Sêr Cymru National Research Network in
555 Advanced Engineering and Materials, and TATA Steel UK, for their funding and support for this work.

556

557

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