COAL AGGLOMERATION IN BLAST FURNACE INJECTION COALS

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DANE SEXTON

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DECLARATION AND STATEMENTS

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ABSTRACT

In order to reduce expensive coke usage, blast furnace operators inject coal to replace a portion of the coke. However, the use of some injection coals can result in blast furnace instability and lowered permeability.

This thesis is concerned with the injection of coal under entrained flow, high heating rate (10^4-10^6 °C/s) blast furnace conditions, namely the possibility of coal particle agglomeration via the use of caking coals. Methods of mitigating agglomeration via blending and pre-oxidation are tested, whilst the resultant performance implications of agglomerated coal chars are considered and analysed.

A drop tube furnace (DTF) was used to experimentally test coal injection under conditions that are applicable to the blast furnace 'hot blast' region. Relatable DTF parameters include an operating temperature of 1100°C, and heating rate of 10^4 °C/s. Four industrial injection coals with varying volatile matter and caking properties were tested at both granulated and pulverised particle size specifications.

It was found that coals defined as 'caking coals' showed consistent agglomeration during DTF injection, a potentially problematic effect regarding blast furnace injection. Agglomeration percentages (as defined by sieve classification) for the industrially problematic MV4 coal were 11% and 23% for the granulated and pulverised samples respectively. Blending of whole coals was effective in reducing the amount of agglomerated material in the char, as was sample pre-oxidation prior to injection. Regarding performance, agglomerated chars had greater combustion performance and gasification reactivity than the non-agglomerated samples.

With agglomeration shown to be present under high heating rate conditions at temperatures akin to the blast furnace hot blast, it is concluded that agglomeration is a possibility during blast furnace injection. However, due to differing feed systems between the DTF and blast furnace, the precise form and extent of agglomeration in the blast furnace remains uncertain. Based on char combustion and gasification analysis, chars characterised by fine agglomerated material are not likely to be problematic for blast furnace operators relative to 'standard' injection coals.

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NOMENCLATURE AND ABBREVIATIONS

GCI: Granulated Coal Injection

PCI: Pulverised Coal Injection

VM: Volatile Matter

tHM: Tonne of hot metal

RAFT: Raceway Adiabatic Flame Temperature

TGA: Thermogravimetric Analysis

DSC: Differential Scanning Calorimeter

DTF: Drop Tube Furnace

BF: Blast Furnace

EFR: Entrained Flow Reactor

DDPM: Dial Divisions Per Minute

FSI: Free Swelling Index

CI: Caking Index

XPS: X-ray Photoelectron Spectroscopy

AFT: Ash Fusion Test

GC/MS: Gas Chromatography/Mass Spectrometry

SSA: Specific Surface Area

M_0: Initial char mass

M: Instantaneous char mass

M_{ash}: Mass of ash within the char

A_0: Initial coal ash content (pre-DTF)

A_1: Char ash content (post-DTF)

C_0: <1mm char material

C_1: >1mm char material

r : Pearson’s correlation coefficient

r_s : Spearman’s rank correlation coefficient

$t_{0.5}$ – Time taken for coal char to reach 50% conversion (by mass) during gasification

Chapter 1: Introduction

1.1 Background

1.1.1 Coal formation

Throughout history coal has been one of the most dominant sources of energy across the globe (Speight, 2012). Today its main use is in the production of electricity, alongside use in industrial processes, including refining metals. It is often preferred to other fossil fuels due to relatively low cost ($15-90 per tonne as bought from mine) and large reserves with 2015 estimates of 1.1 trillion tonnes of recoverable coal worldwide (EIA, 2018) . As a result of concerns regarding climate change caused by global CO_2 emissions, there are increasingly tight emission regulations that restrict carbon emissions in industry. They are designed to promote interest and investment in cleaner coal technologies and push industry to increase the efficiency of many processes that involve the use of coal (IEA CCC, 2017). Research into improving the process utilisation of carbon fossil fuels is of particular importance for European steelmakers who face a range of global challenges.

Coal is formed by the burial of plant matter and remains (e.g. roots, bark, leaf matter, resins etc.) that are compacted as a result of pressure and chemically altered by heat in a process called coalification (Crelling and Rimmer, 2015). The plant matter, usually the remains of a low-lying forest, is gradually inundated by the deposition of silt layers and other inorganic sediments which compress it and protect it from oxidation and biodegradation. As more layers are deposited, temperature and pressures increase which, over geological time periods, convert the dead vegetation into peat, and eventually coal via chemical and physical processes including graphitisation and dehydrogenation.

There are generally considered to be four main ranks of coal which differ due to them being subjected to heat and pressure for different amounts of time

(Berkowitz, 1979). Speight (2012) classifies coal into four main types which typically contain properties within a certain range for each coal type as detailed below. The earliest stage of coal development is into lignite, a low rank, young coal with low fixed carbon content (31% w/w). It has a relatively low heating value (>5,800 kcal/kg) and a high moisture content (39% w/w). With further coalification lignite becomes darker, harder, and progresses into sub-bituminous coal. Sub-bituminous coals still have a relatively low heating range though generally contain less moisture and more carbon than lignite. Following sub-bituminous is the bituminous category, again a darker coal that can be classified further dependent on its vitrinite reflectance. It contains greater amount of fixed carbon (~45-80% w/w), low moisture (2-16% w/w), greater heating value (>8400 kcal/kg), and is the coal rank on which this investigation is based. Anthracite is the final classification, used when the coal has reached ultimate maturation. It contains the largest percentage of fixed carbon (as high as 86%) and is typically hard, with a high lustre, and jet black appearance. Other variations occur in coal properties as a result of the parent plant matter that makes up the coal. These factors influence volatile matter contents, mineral components, and maceral compositions, all of which impact coal performance.

1.1.2 Coal usage

It is reported that global coal reserves are currently sufficient to meet 153 years of global production, approximately three times the ratio for oil and gas (British Petroleum, 2017). From 2005-2015 coal has composed around 28-29% of global energy sources, second only to oil (World Energy Council, 2016). Meanwhile, coal remains the dominant choice of fuel globally regarding electricity production, accounting for around 41% of the global electricity mix (IEA, 2017a).

However, due to growing concerns over the environmental impact of carbon emissions, the energy industry is trending towards producing cleaner, renewable forms of energy and electricity production with a projected growth in renewable-derived electricity of 43% by 2022 (Carbon Brief, 2017). It is forecast that increased solar power developments in China and India will make up a pronounced portion of this increase. As shown by Figure 1, in 2016, renewables saw a greater increase in net capacity growth than both coal and gas that saw reductions on 2015.

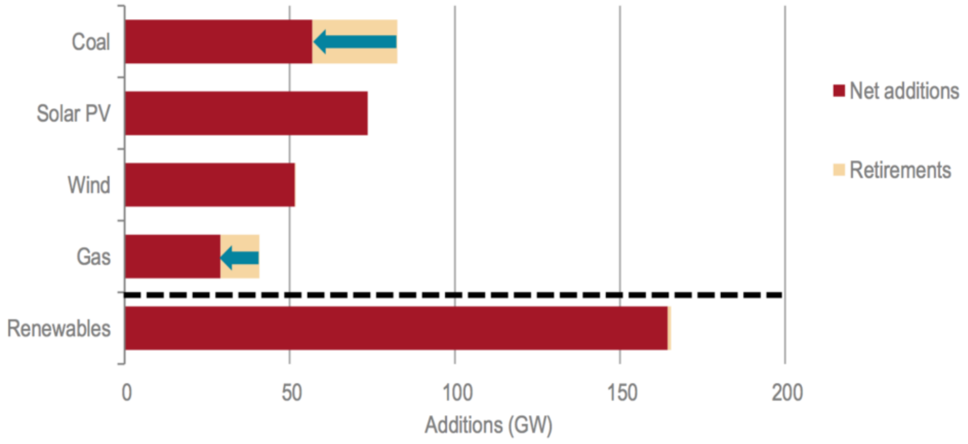


Figure 1: Electricity additions to global net capacity in 2016 showing decline in coal and gas additions and large increase in renewables (Carbon Brief, 2017)

Regarding energy, the most recent coal marketing report produced by the International Energy Agency in late 2017 discusses a second successive year of reduced global coal demand in 2016 with a drop of 1.9% and a total reduction of 4.2% since 2014 (IEA 2017b). The report details this as being due to lower gas prices and the surging popularity of renewable energy resulting in decreased coal consumption.

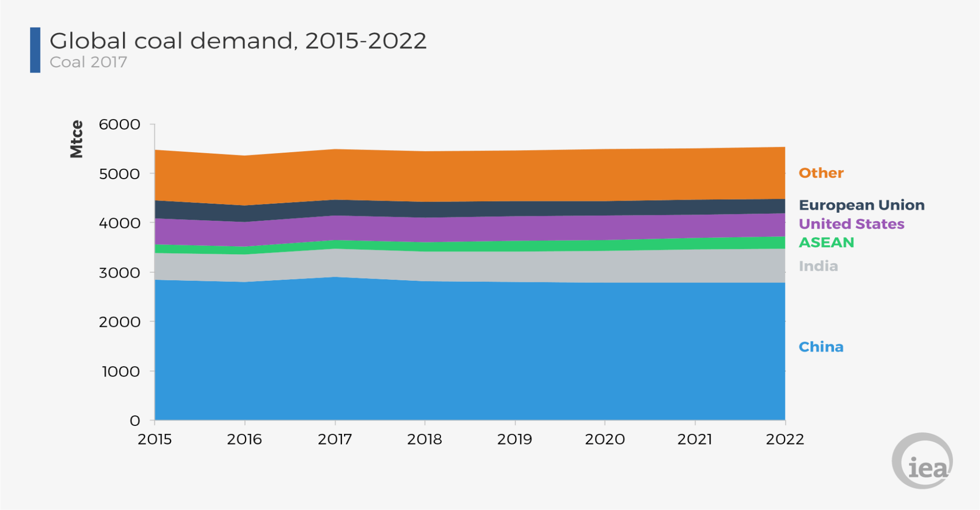


Figure 2: Predicted global coal demand in Mtce (metric tons carbon equivalent) for 2015-2022 (IEA, 2017b)

It is predicted in Figure 2 that coal's share in the global energy mix will decline from 27% in 2016 to 26% in 2022 based on less demand and poor growth relative to alternative fuels/technologies that are receiving more investment. Growth through to 2022 is likely to be concentrated in India and Southeast Asia, while coal demand in Europe, Canada, and the United States is predicted to decline (IEA, 2017b). This decline in demand is also predicted in China due to reduced use in both industrial and residential sectors in a bid to improve air quality (IEA, 2017b). Noticeable efforts to provide alternative means of energy and electricity generation are present in the UK with BBC News (2018) reporting that Britain went three days without generating electricity from coal, being replaced with both non-renewables and renewable alternatives including gas and wind power. Additionally, some power stations are utilising increasing amounts of gas and biomass at the expense of coal, with Drax "looking at opportunities for a coal-free future" (Vaughan, 2017).

There are concerted efforts for both governments and corporations to provide sustainable energy. The World Energy Council (2018) defines energy sustainability as based on three core dimensions – energy security, energy equity/cost, and environmental impact. These three factors constitute the energy trilemma, the framework for which sustainable energy is founded. Although coal use is desirable due to its often low cost relative to renewable energy (particularly to Less Economically Developed Countries/LEDCs), it is problematic regarding fulfilling environmental requirements when used for traditional combustion purposes. However, alternative coal technologies are being developed to counter this issue with techniques such as gasification and carbon capture and storage (CCS) providing means of meeting the more environmentally conscious criteria of the trilemma (Rao and Padke, 2017). Additionally, consideration of the non-energy/electricity generation uses of coal are becoming more prevalent such as in utilising coal for chemical products (tars, gasification products, rare earth elements, activated carbon, and use in agriculture [Kolker et al., 2017; Reid, 2018]).

1.1.3 Steel industry challenges

The most common method of steelmaking across the globe is the integrated route, typically utilising a blast furnace (BF) to reduce iron ore, followed by basic oxygen steelmaking to form steel. As noted in Figure 3, the integrated route constitutes almost 75% of global steelmaking with this method requiring large amounts of coal relative to the alternative electric arc method (World Coal Association, 2018).

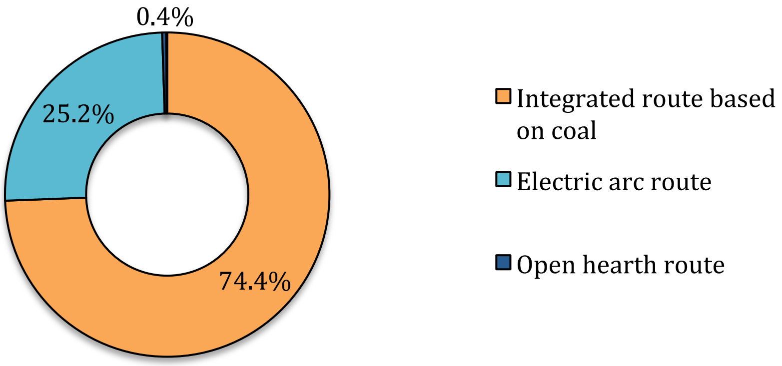


Figure 3: Crude steel production by process (World Coal Association, 2018)

The typical integrated route has high coal requirements (~770kg per tonne of steel) due to the use of metallurgical coal in producing coke, one of the key components of the blast furnace iron making process (World Coal Association, 2018). In addition to large quantities of coal used in cokemaking, coal is injected into the blast furnace in pulverised or granulated format as an alternative reductant. An alternative reductant is a part substitute for coke with regards to providing reducing gases for reduction of iron ore. However, alternative reductants cannot replace coke entirely due to its use in forming a permeable bed. Coal injection is desirable due to expensive coking costs, with injected coal allowing for the replacement of a portion of the required coke.

At present, the European steelmaking industry is facing a range of challenges. Following the financial crisis in 2007-08 and the recession that followed, demand for steel in Europe has fallen and not yet recovered to pre-financial crisis levels (fall from 200 million tpa in 2007, to 155 million tpa in 2016, Pooler, 2017). The reduced demand was also impacted by China, the largest steel producer globally. As construction demand in China fell, large quantities of surplus steel entered the global market, thus reducing the value of steel further (Greenwood, 2017). Additionally, the US recently announced a 25% tax on import steel from the EU, likely damaging steel exports (Mayeda et al., 2018). Alongside these unfavourable market conditions, European steelmakers believe that European Union (EU) environmental policies and emissions requirements put them at a further disadvantage globally with increased taxes and unsustainable industrial emissions targets (de Lusignan, 2017; Pooler, 2018). For example, under EU reforms, steelmakers in Europe would pay $32 per tonne of emitted carbon, whilst (as of 2017) foreign producers selling steel in the EU would not pay for their carbon emissions (The Economist, 2017).

Global steel demand is set to increase marginally in 2018 (1.8%) and 2019 (0.7%) (Angel, 2018), with the European Commission (2018) continuing to take steps against Chinese dumping. However, despite market improvements the industry is still being forced to improve and reduce production costs wherever possible. As a result, research into all aspects of steelmaking is required in order to optimise the process and improve efficiency.

This investigation aims to study the processing of coal injected into the blast furnace as an alternative reductant to coke. Improving the coal injection process will have a range of benefits and improve sustainability. Firstly, more effective coal injection can allow for desirable higher coal injection rates (>200 Kg/tHM), resulting in lower coke demands (as low as 300 Kg/tHM) – thus reducing cokemaking emissions and reducing costs. Additionally, coke oven lifespan may be extended due to lower coke production requirements. This is an important factor as many coke ovens are reaching the end of their life, with significant investment required to replace them. New coke ovens would also be required to meet stringent environmental standards, increasing costs further (Carpenter, 2006). Also, by optimising the coal injection process it is possible that less coal will leave the blast furnace unreacted as wasted carbon. This work is one example of the desired process improvements currently being researched by integrated steelmakers.

1.2 Thesis Aims and Objectives

As mentioned previously, high coke costs are encouraging iron makers to maximise blast furnace coal injection as a means of cost saving whilst simultaneously improving furnace operability. Upon injection, various coals are prone to a range of physical and chemical effects including swelling, fragmentation, fluidity, mineral effects, and more. One effect akin to these is agglomeration – an effect that has had little regarding in depth research concerning injection in the blast furnace, hence the reason for this work. It is possible that char agglomeration could result in char accumulation in the burden and blockages in injection lances and deeper in the furnace. These are issues that can go on to impact operations and furnace permeability (already an issue with coal injection). Occurrences of coal agglomeration will likely result in a net increase of particle size, possibly negating some of the positive effects gained by grinding. This may then go on to impact coal combustion performance in the raceway region, resulting in increased coal carryover deep into the furnace. In this carbon-rich environment, gasification reactivity is the driving mechanism for coal conversion where an agglomerated char structure may create a problematic, unreactive particle due to suspected reduced particle surface areas.

The specific aim of this thesis is to investigate the agglomeration of blast furnace injection coals and the possibility of agglomeration occurring in the blast furnace. The coal properties responsible for agglomeration will be established in order to provide an industrial means of predicting agglomeration. The likely performance implications of agglomerated char in the blast furnace are also considered. Additionally, options regarding the mitigation of agglomeration for the industrial sponsor will be provided. As a result, the main objectives of the work are to:

- Test injection coals on a laboratory scale for signs of agglomeration.
- Relate laboratory experimental results to the blast furnace process.
- Link caking properties of the injection coals with occurrences of agglomeration via means of a caking test.
- Evaluate the effects of agglomeration on coal performance by experimentally testing coal combustibility and char gasification reactivity.
- Test the effectiveness of a number of possible methods of mitigating coal agglomeration.

The scientific hypotheses tested in this thesis are as follows:

1. 'Coals have the potential to agglomerate during blast furnace coal injection conditions, dependent on their inherent caking properties'.

2. 'Agglomerated chars will likely be problematic in the blast furnace as a result of poor combustion and gasification performance'.

1.3 Thesis Structure

Chapter 1 - Provides a background into coal formation and the present global picture regarding coal usage in energy and electricity generation. It provides insight into the various challenges faced by European steelmakers, driving research into process improvements. Thesis aims and objectives are also stated.

Chapter 2 - Reviews literature relating to blast furnace steelmaking, coal injection, coal agglomeration, caking properties, combustion, and gasification reactivity under blast furnace conditions.

Chapter 3 - Reviews the experimental techniques and test rigs utilised in order to investigate coal agglomeration and the analysis methods used in order to assess coal and char performance criteria. Also details procedural information.

Chapter 4 – Details experimental testing of coal injection via the use of a drop tube furnace. The agglomeration of injection coals is the focus of this experimental testing. Due to key similarities between the DTF and BF, the results from laboratory injection are used to make inferences regarding the blast furnace process. The occurrence of agglomeration within experimental chars is quantified in order to establish the propensity of the range of tested coals to agglomerate. Also assesses coal chemical and rheological properties and their relationship with agglomeration in the drop tube furnace.

Chapter 5 – Studies the impact of pre-oxidation on coal properties and agglomeration in order to gain further insight into the relevant properties and effects of agglomeration on char combustion and gasification performance. Also provides industrial options regarding mitigation of agglomeration.

Chapter 6 – Details experimental results investigating the effects of agglomeration on coal performance including combustion, resultant char structure, and gasification reactivity.

Chapter 7 – Provides real-world relevance and implications for the industrial process as a result of this thesis.

Chapter 8 – Discusses the conclusions of this work and the directions of future research.

Chapter 9 – A bibliography of studies referenced in this work.

Chapter 10 – Additional material relating to this thesis.

Chapter 2: Literature Review

2.1 Introduction

Coal injection technology is utilised in blast furnace iron making in order to reduce costs by replacing a portion of the coke required to operate the furnace (Geerdes et al., 2009). Coke is expensive to produce due to high coking coal costs (current average of $185/tonne [Leotaud, 2018]) and process energy requirements relative to blast furnace coal injection. The injection of coal into the blast furnace provides a range of challenges for furnace operators with a number of particle effects possible upon injection. One of these potential particle effects, agglomeration, is assessed in this work due to the relative scarcity of publications in this area. This chapter will detail technical information on the blast furnace and coal injection, in addition to information on the agglomeration of coal in the wider literature. The potential impacts of agglomeration are considered alongside the likely responsible coal properties. The performance of injected coal in the blast furnace is also discussed with regards to combustion and gasification of coal particles.

2.2 Blast Furnace and Coal Injection

2.2.1 Blast furnace iron making overview

The blast furnace's primary purpose is to reduce iron ore (using coke and coal) to produce liquid/pig iron (Geerdes et al., 2009). The furnace is continuously charged from the top with alternating loads of iron ore (in the form of lump, pellets, and sinter), coke, and flux (limestone or lime), whilst a blast of oxygen-enriched heated air and ground coal are added near the base as the driving mechanism for the furnace. This creates a counter current moving bed reactor with the burden (material charged into the top of the furnace) moving down the shaft of the furnace whilst gases formed lower down ascend through the burden.

The amount of time taken for gases to ascend up through and exit the furnace is in the region of 3 seconds. As shown in Figure 4, the blast furnace has a varying temperature profile dependent on depth into the furnace. The blast furnace can be broadly separated into three key areas of interest (Peacey et al., 1979):

The stack - the top of the furnace into which the burden is charged, followed by heating and the beginning of iron reduction.

The bosh – reduction of the charge is completed here and the ore is melted.

The hearth – the base of the furnace where the molten metal and slag are collected and then drained from.

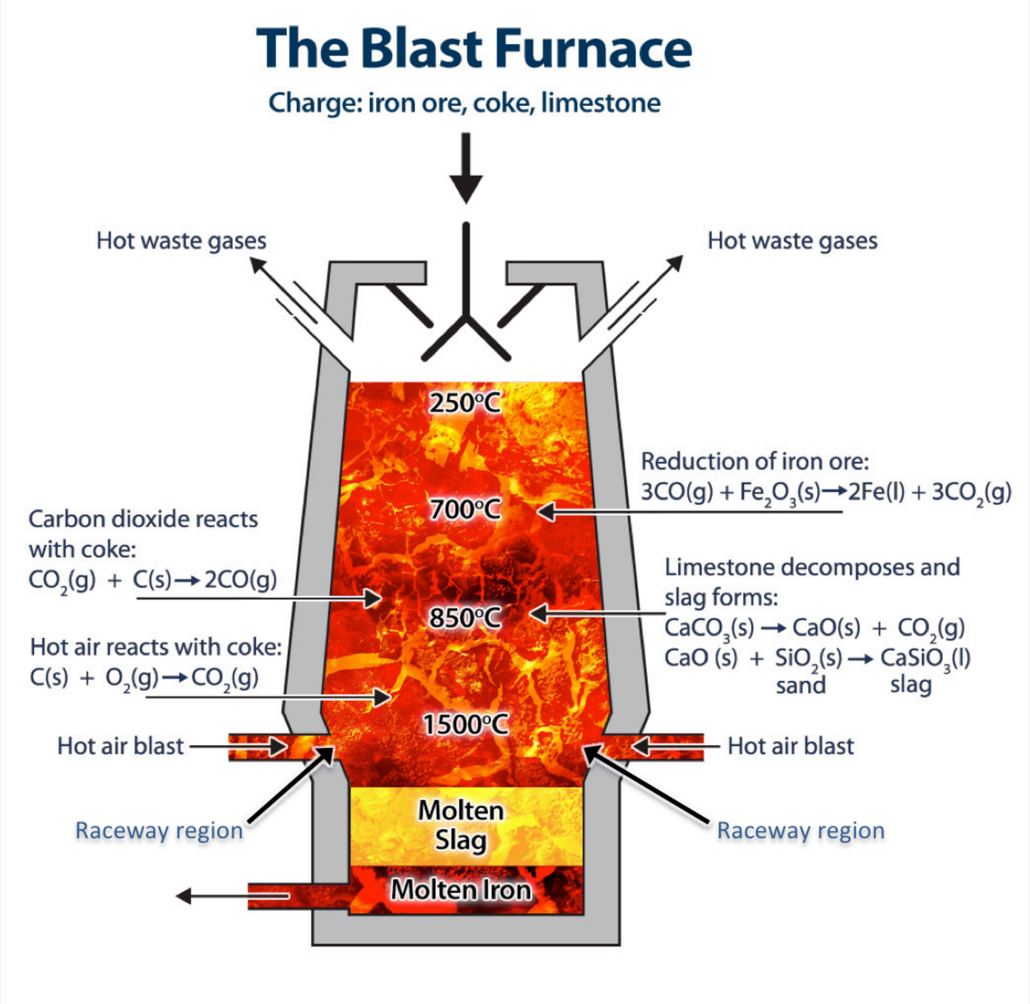


Figure 4: Blast furnace schematic showing the various temperature regions in the blast furnace alongside the key reactions occurring at each level (UKCSMA, 2018)

As the charge descends it is first dried and preheated by gases leaving the furnace (~150-250°C). With continued descent it is heated further to approximately 900°C before the start of reduction of the iron ore by the rising reduction gases carbon monoxide (CO) and hydrogen (H_2) (Geerdes et al., 2009). Further down the furnace the burden starts to soften and deform at around 1100°C in the cohesive zone. Reduction continues as the temperature increases to 1400°C whilst the burden begins to melt at this point before reaching the fluid zone containing temperatures of around 1500°C. As the hot blast is injected it creates an area called the raceway, the hottest part of the furnace with typical temperatures of 2200°C (Carpenter, 2006). Tuyeres inject a combination of hot air and pulverised coal into this region which generates both reducing gases and the heat necessary to melt the iron ore. Following this the molten iron and slag pass to the furnace base where they are then drained through the tap hole before the slag is skimmed from the molten iron.

2.2.2 Blast furnace coal injection

Coke is a crucial ingredient in blast furnace operation, used as a principal source of both fuel, and reducing agent in smelting iron ore (Peacey et al., 1979). Initially, blast furnaces were heavily dependent on coke for reducing gases. However, it was discovered that in order to reduce costs, alternative carbon sources could be injected into blast furnaces in order to reduce coke usage and thus cut down expensive coke costs. These auxiliary injectants could not replace the expensive coke entirely as it is necessary in order to provide a permeable bed in the furnace. They can however reduce the amount of coke needed by providing an alternative source of reductants. In the 1960s, oil was the injectant of choice until rising oil prices meant that by the 1980s it had been replaced by coal as the most common auxiliary injectant. At present, roughly 30 to 40% of early coke requirements have been replaced by injection of coal and in some cases, oil and natural gas (Geerdes et al., 2009).

Prior to injection the coal is either pulverised (approx. 75μm) or granulated (usual top size of 2-3mm) as it goes through the drying, grinding, and milling process before it is stored and pneumatically transported to the blast furnace ready for injection (Geerdes et al., 2009). As shown in the blast furnace tuyere schematic in Figure 5, coal is injected alongside a blast of hot air into the furnace through the tuyeres. Injection lances are used to inject the coal through the blowpipe and into the tuyeres. Upon reaching the tuyere the coal particles are rapidly heated where the devolatilisation and combustion process begins before leaving the raceway region where there is risk of unburnt char build up (Carpenter, 2006). The combustion process can be split into a number of steps, some of which occur simultaneously. With temperatures of approximately 1200°C the hot blast rapidly heats the injected coal particles at a rate of around 10^4-10^6 °C/s depending on operating conditions of the blast furnace in question (Bortz, 1983; Ishii, 2000). Following this, the coal undergoes thermal decomposition with the loss of volatiles in the form of tar, and light gases (namely CO, CO_2, H_2O, and low-molecular weight hydrocarbons). The devolatilisation stage has a large effect on the coal both chemically and physically with particle softening, swelling, fragmentation, potential agglomeration, and re-solidification seen alongside the evolution of volatile matter (McCarthy, 1980; Chen et al., 2007; Steer et al., 2015b). This process leaves a coal residue; char, made up largely of carbon and minerals. The char particle remains and undergoes combustion in the raceway, and gasification, mostly outside of the raceway.

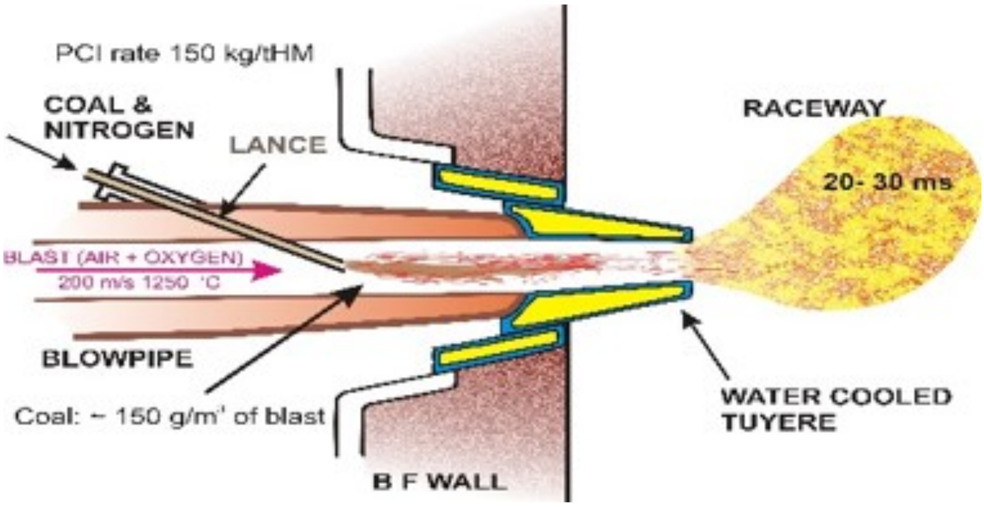


Figure 5: PCI schematic showing coal injection lances, tuyere region and resultant raceway shape (ERNW, 2017)

Coal injection in the blast furnace provides a range of both economic and operational benefits as discussed below (Danieli Corus, 2009; Worrell et al., 2010):

- Cost savings resulting from a lower coke injection rate. With high coke prices ($185/tonne [Leotaud, 2018]) it is beneficial to utilise as much of the cheaper injection coals as possible and have as high a coke replacement ratio (RR) as the process will allow (dependent on coke and coal quality, furnace geometry, and operational parameters.
- Higher blast furnace productivity with regards to the amount of hot metal produced per day in conjunction with greater operability.
- Higher blast furnace operability through the option to control coal injection e.g. it is possible to make thermal changes to the furnace quicker by altering coal injection as opposed to adjusting the burden charge at the top of the furnace.
- Reduced emissions for the steel plant. This is due to the reduced coke requirements that mean the coke oven operations can be reduced. As such, there are less emissions from this process.

- An extension of coke oven life with lower coke production requirements.

However, the addition of injected coal into the blast furnace process does cause a number of changes to furnace operations, many of which become issues at high coal injection rates such as 200kg/thm (Bennett and Fukushima, 2003; Xu et al., 2005). For example, the injected coal results in lowered flame temperatures (80-220°C per 100kg/thm) that in turn slow the melting rate of iron ore causing instabilities in furnace operations (Babich et al., 2002; Ghosh and Chatterjee, 2008). Operations can also become unstable as a result of an accumulation of unburnt coal chars that can lower permeability (Ichida et al., 1992; Akiyama and Kajiwara, 2000; Dong et al., 2003) and disrupt gas flows in the furnace e.g. potentially resulting in peripheral gas flows causing increased heat load on the walls, shortening their life span (Lu et al., 2010). The furnace slag is also impacted with the coal bringing additional minerals into the system (e.g. sulphur) with some coals increasing slag volumes (US DOE, 2000a). With too high an injection rate many of these issues are exacerbated as far as to make high rate injection detrimental. However it is in the interest of the furnace operators to have as high an injection rate as possible (ideally >200kg/thm) without negatively affecting operations in order to maximise the coke replacement ratio and thus reduce costs. As a result of this, a number of countermeasures have been developed to increase injection rates as noted by Deno and Okuno (2000). These include:

- Increasing hot blast oxygen content to improve coal combustion and reduce unburnt char build-ups. This should allow for greater coal consumption in the raceway, reducing the amount of issues present deeper in the blast furnace e.g. cohesive zone and stack.
- Alterations to burden distribution and charging.

- Changing coal injection systems/lance positioning. For example, use of double lance systems and coaxial lances with mixing chambers have been attributed to reductions in unburned char.

An additional countermeasure is to change the properties/types of coke, iron ore, and, most commonly, the coal being used. For example, a more reactive coal may improve coal combustion/gasification reactivity and thus reduce unburned char accumulation, whilst varied coke physical properties may allow for greater burden porosity and less accumulation.

2.2.3 Injection coal requirements

A good injection coal must satisfy a number of criteria, primarily coal handleability, economic benefits, and blast furnace operability. Handleability involves the costs and technical issues revolving around the transportation and milling of the coal, excluding the costs of the coal itself. Economic benefits mainly consist of monetary savings as a result of the coal price and partial replacement of expensive coke with the cheaper coal injection. The parameter used for evaluating this saving is the coke replacement ratio (RR), defined as the mass in kilograms, of coke replaced per kilogram of coal injected. The RR will vary with the amount of coal that can be injected, the costs of that coal, and the properties of the coal. It has been reported by Hutny et al. (1990, cited in Coaltech, 2005) that there is a general increase in RR with increase in the C/H ratio of the coal whilst Brouwer and Toxopeus (1991, cited in Coaltech, 2005) found that increases in coal RR correlate with increases in coal rank. These findings can be seen amongst others in Figure 6 showing a range of modelled and actual blast furnace performance results.

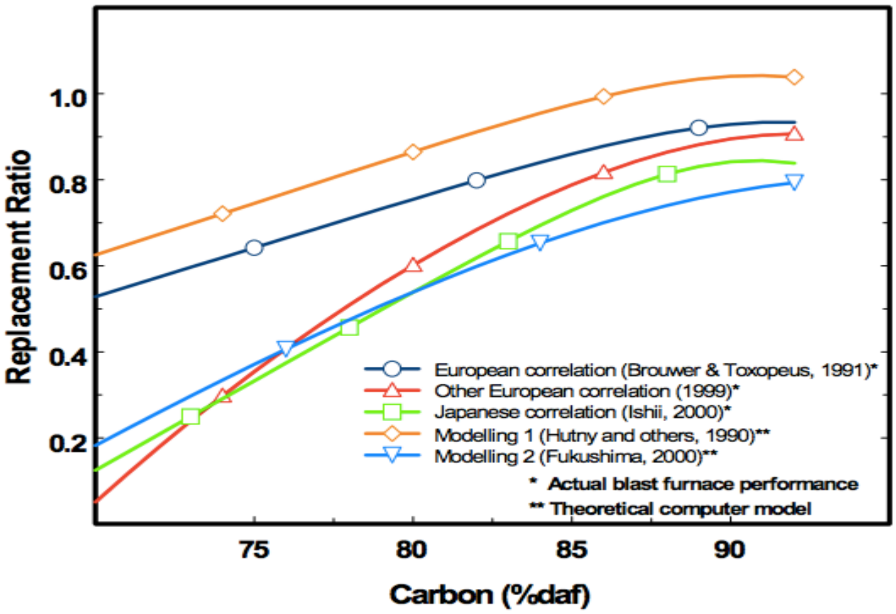


Figure 6: Variation of replacement ratio with injection coal carbon % (on daf – dry ash free basis) (Coaltech, 2005)

Of the parameters affecting coal choice, the direct performance of the coal is perhaps the most important and will be the focus of this investigation. Many steel makers look at the proximate analysis of potential coals in order to select a suitable coal for operations (M Greenslade, 2014, personal communication, 5 November). The material described as the volatile matter is often used as an indicator towards the coal's performance with high volatile matter coals generally considered as having greater combustion efficiency and burnout (Kalkreuth et al., 2005). The use of proximate analysis in predicting coal performance may not be suitable in many cases, where the rheological effects of the coal can induce plasticity and impact devolatilisation and char formation/structure. A coal should have as little moisture as possible as this will increase costs not only with regards to handleability but also the BF process with higher moisture contents being linked to a lower raceway adiabatic flame temperature (RAFT) meaning drying is often necessary (Carpenter, 2006). An injected coal should ideally have mineral matter of less than 10% as the minerals can cause high wear on pulverisers and increase slag volumes (Chatterjee, 1999). Certain elements in the coal (e.g. aluminium, chlorine, phosphorus, sulphur, silicon) are kept to a minimum as a result of their negative impact on either furnace performance or operation costs (Carpenter, 2006). There are differences in opinion regarding the optimal size of the coal particles being injected (e.g. granulated/pulverised). For example, in the UK the coal is often granulated before injection, a cheaper process than pulverising it. The debate surrounding this issue is whether the increased costs of the pulverising process are negated by improved performance in the blast furnace (US DOE, 2000b). It is likely that grinding the coal to the finer, pulverised size will improve combustion and gasification performance in the blast furnace on account of the greater surface area available for reaction. However this is more expensive than granulating coal, and assessing the value of the improved performance on the blast furnace is complex.

It is evident that there are a number of variables involved in the performance of a blast furnace injection coal, with many coals requiring trade-offs not just in process performance, but also economically and with regards to handling and preparation. In an attempt to combat this, most steelmakers have developed coal blends as a way of utilising some of the more favourable coal properties in tandem with one another. A popular blend technique is a high volatile matter coal with a low volatile matter one which attempts to optimise the respective strengths of the two coal types. The combustion performance of blends is more complex than with singular coals with combustion and burnouts taking place at differing rates and temperatures with the potential for one of the coal's characteristics to become dominant. For example, Kunitomo et al., (2004) found that a high volatile coal produces a high temperature combustion field that promotes combustion of the low volatile matter portion of the blend, whilst Artos and Scaroni (1993) found minimal impact of blending on combustion in a DTF or TGA (both cited in Steer et al., 2015a).

2.2.4 Coal agglomeration and potential operational issues

Under certain conditions, coal is prone to physical changes including swelling, fragmentation, and agglomeration (McCarthy, 1980 and 1981; Chen et al., 2007; Steer et al., 2015b) all of which will go on to influence char performance. During heating, some coals are prone to undergoing a thermo-plastic phase of coal development wherein the particles becomes viscous and potentially adhesive to one another. As a result, particle agglomeration can occur where a number of particles combine and resolidify into larger particles called agglomerates (Chen et al., 2007). Although Shampine et al. (1995) determine that agglomeration has little effect on performance in “typical utility combustors”; no such strong conclusions have been drawn regarding the effects in the blast furnace. Potential issues include blocked injection lances (Nightingale et al., 2003; Atkinson, 2006, as cited in Carpenter, 2006) and lower coal combustibility, thus increasing unburnt char that is prone to accumulating, causes blockages and permeability issues (Ichida et al., 1992; Akiyama and Kajiwara, 2000; Dong et al., 2003; Nogami, et al., 2005). Additionally, the gasification reactivity of the char particles may be lower, another cause of lowered blast furnace permeability (Schott, 2015). However, due to a lack of investigation into coal agglomeration in the blast furnace, it is currently uncertain whether or not agglomeration will occur, and also what the likely impacts will be. As a result of the relative lack of information in this area, coal agglomeration under blast furnace conditions will be investigated and assessed, whilst the potential issues will be discussed in more detail in Section 2.3.3.

2.3 Coal Agglomeration

In general terms, agglomeration can be defined as the action or process of gathering particulate solids together into a conglomerate (Pietsch, 2002). An agglomerating coal is one that, “during a volatile matter determination, produces either an agglomerate button capable of supporting a 500g weight without pulverising, or a button showing swelling or cell structure”, as defined by the USGS (1981). Agglomeration in coal can be limited to two individual particles fusing together, to larger, multi-particle agglomerates being formed (Chen et al., 2007). In combustion, coal agglomerates can form in two main circumstances, during the devolatilisation/plastic stage of coal heating, and also as a result of ash fusion. This thesis will be investigating the potential agglomeration of coal particles during initial heating (during plasticity and devolatilisation) rather than mineral/ash fusion.

2.3.1 Agglomerate formation: mechanism

Though the exact mechanism of coal plasticity is not completely understood, it is generally agreed that the process occurs in part as a result of the production of volatile matter content, in particular the liberation of hydrogen-rich liquid tars from the the caking coal (Speight, 2012). The liberation of these liquid hydrocarbons generates a metaplast and results in a caking coals’ plastic stage that can result in individual particles joining together (Schobert, 1990). The contribution of thermoplasticity is that it provides fluidity and an adhesive nature to the particle surface, creating the mechanism for the initial particle agglomeration. As the coal particles continue to be heated, they will reach resolidification temperatures that end the plastic phase. Upon this temperature the particles will solidify in their newly formed structure, with two or more particles having combined forming an agglomerate structure (Chen et al., 2007).

Figure 7 has been created in order to provide clarity on the formation of agglomerates, with examples of two particle and multi-particle agglomerates shown. The initial connection is formed due to an adhesive bridge provided by the coal metaplast. Upon resolidification temperatures, the connection between the two particles becomes a solid bridge and results in the newly formed agglomerated particle.

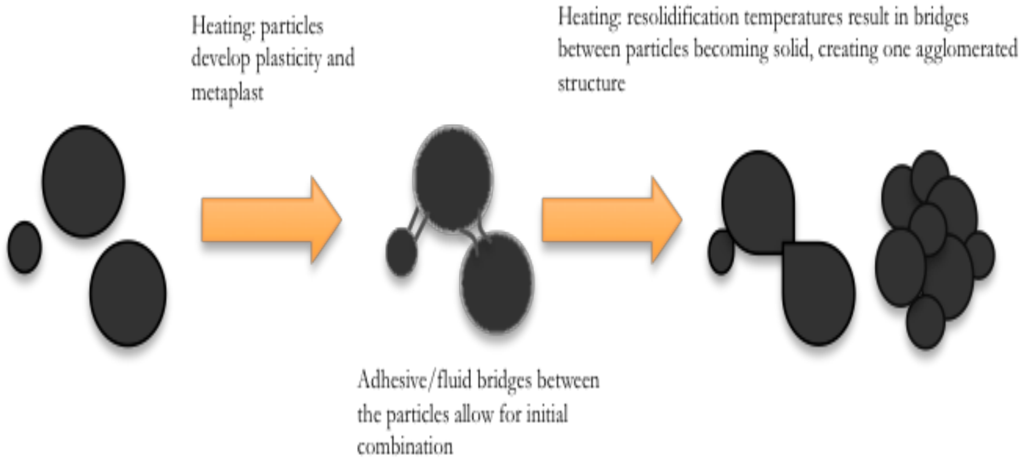


Figure 7: Process of coal particle agglomeration during heating

2.3.2 Coal agglomeration in the literature

The majority of the literature making up the field of coal agglomeration is limited to the study of coking coals and their agglomeration as the basis of cokemaking. The study of plasticity and agglomeration in high heating rate (10^4°C/s) and high temperature (>1000°C) applications is less well established, particularly with regards to the impacts of agglomeration. This relative scarcity of publications is even more apparent when considering the issue of agglomeration in terms of coal injection for the blast furnace with little information readily available. The following publications consider the agglomeration of coal under generally high heating rate, non-cokemaking conditions.

There is no currently well-known standard with regards to measuring or testing agglomeration in coal, with the majority of publications tailoring the methods to their particular requirements, often with industrial relevance in mind.

McCarthy (1980 and 1981) measured the amount of agglomeration occurring in an entrained flow reactor (EFR) with three pulverised coal samples under pyrolysis conditions. Links were found between agglomeration and coal caking properties. McCarthy used a sieve classification (>160μm) method to screen larger particles that were characterised as agglomeration. It should however be noted that the swelling of particles (Gao et al., 1997; Wall et al., 2002; Yu et al., 2003b; Steer et al., 2015b) may result in inaccuracies in the results. Hence, due to the raw coal sample size and the agglomeration sieve size, it is feasible that the >160μm particles are not 100% agglomerated material, but in part individual swollen particles. The experimental method used by McCarthy is not suitable for relating agglomeration to the blast furnace due to the low temperatures used (500-700°C) being lower than those found in the blast furnace, and the nitrogen atmosphere not replicating the chemical reactions found in the furnace hot blast/raceway. Despite the relatively low temperatures used, these publications show that agglomeration in an entrained flow under high heating rate conditions can occur.

The agglomeration of lump coal was investigated by Campbell et al. (2010) by using a tube furnace. The publication is useful in assessing the role of macerals in agglomeration (e.g. greater quantities of liptinite and vitrinite found to increase agglomeration). However, the experimental procedure used is not suitable with regards to blast furnace coal injection (lump coal, no entrained flow, samples held together in holder to promote agglomeration, inert atmosphere). The maximum temperature used of 1000°C is similar to those under hot blast conditions with agglomeration remaining at this temperature. However, the inert atmosphere means that no oxidation of the sample took place and thus is less relatable to coal injection.

Although the experimental procedure used in Reddy and Mahapatra (1999) does not reflect that found in the blast furnace due to use of a fluidised bed combustor, the coal factors relating to agglomeration that were assessed are relevant. With the authors considering the caking properties of the coals, it was found that more plastic coals were prone to agglomeration in the combustor. Additionally, agglomeration was exacerbated in the finer particle size coals, due to a greater surface area.

It is work by Chen et al. (2007) that most accurately replicates blast furnace coal injection with the presence of agglomerates found within the chars of two coals. The work utilises a drop tube furnace to create chars at a range of temperatures (1000-1400°C) with a residence time of 500ms. These conditions are suitable in replicating blast furnace coal injection due to the high heating rate used, although a shorter residence time would be more representative of the raceway region. However, the testing was carried out under a nitrogen flow rate of 2l/m. Reaction under an inert environment does not take into account the sample oxidation that will occur in the blast furnace hot blast, with the relatively low flow rate constituting a weakly entrained particle flow that is not representative of the blast furnace coal stream. The coal feed rate was also not disclosed preventing the consideration of differences between the experimental and industrial processes. Despite this, the method is somewhat suitable in assessing agglomeration in the blast furnace due to the high temperature and high heating rate used. The author provides evidence of agglomeration by SEM and particle size classification and finds that agglomeration is mostly prevalent in the finer of the two pulverised size specifications used. SEM images showing the most prominent examples of agglomerated char particles are provided in Figure 8.

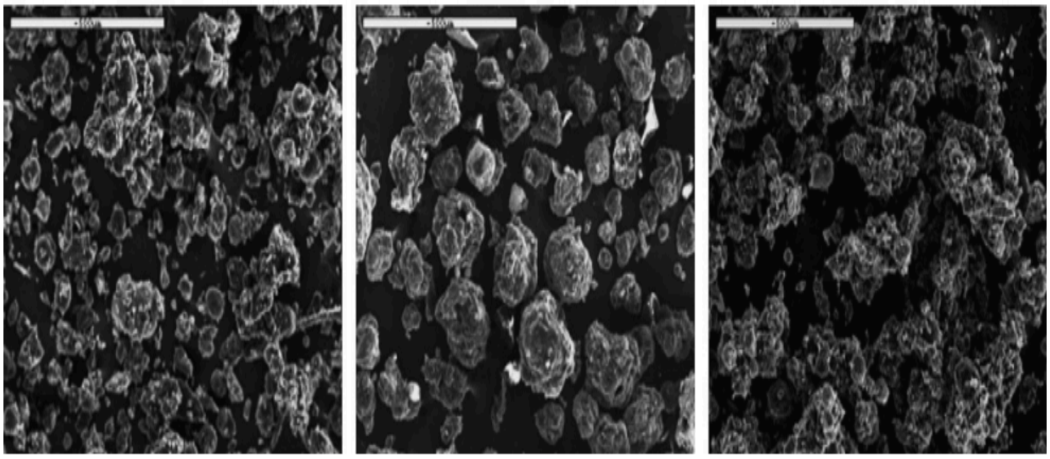


Figure 8: SEM images in Chen et al. (2007) showing agglomerated char particles in the finer coal particle size (74-44μm). Differing images of the same sample. 500μm scale bar.

With regards to computer modelling of coal agglomeration, Kang et al. (1991) developed a high heating rate model that utilised the metaplast theory of coal plasticity (Fitzgerald, 1956; Chermin & van Krevelen, 1957). The model found that agglomeration is less likely to occur under high heating rate conditions due to the competition between adhesive force of the particles and the centrifugal force generated by volatile gas release during flash pyrolysis. However, the model is designed to consider the likelihood of coal agglomeration in a coal combustor rather than the differing and complex blast furnace injection environment.

Most of the previously discussed studies have been focussed on the occurrence of agglomeration in various scenarios with little consideration and testing regarding the resultant impacts of agglomeration. Shampine et al. (1995) mention this and attempt to address it using a plug-flow model of a pulverised coal combustor. A range of coal parameters and particle sizes are used with a coal burnout figure used to assess the impact of agglomeration on combustion. The study concludes that, in a conventional combustor, the agglomeration of pulverised coal will have little impact on combustion with the authors stating, “Results from this model provide a solid theoretical basis for the assumption that agglomeration can be ignored”. This may explain the relative scarcity of investigations in coal agglomeration, though it is important to consider that the blast furnace is not a typical combustor and has limitations regarding oxygen availability. As such experimental simulations of the blast furnace are challenging due to the dynamic, fluctuating blast furnace environment.

With regards to the resultant impact of agglomeration in the blast furnace, Chen et al. (2007) discuss the char gasification performance of two chars that contain agglomerated material. However, they do not make any conclusions on the impact of agglomerated material in the resultant chars with the work focussing on char vs. soot reactivity. The study does not investigate the impact of agglomeration on coal combustion performance (relevant in the blast furnace raceway), likely due to the inert atmosphere used in the method meaning minimal sample oxidation took place.

After studying the literature regarding coal agglomeration, it is clear that there is a scarcity of coal research measuring the potential for agglomeration under blast furnace injection conditions, despite confirmation that agglomeration (referred to as coking) of coal particles has occurred in blast furnace injection lances (Atkinson, 2006, cited in Carpenter, 2006). The most suitable study (Chen et al., 2007) uses a DTF method with a number of operational parameters that could be tailored to improve replication of blast furnace conditions. For example, the use of an air atmosphere as opposed to nitrogen would allow more replicable sample combustion that is more relatable to the blast furnace. Additionally an increased flow rate/stronger entrained flow would create a more replicable ‘coal stream’ as is found in the blast furnace. With regards to the potential impacts of agglomeration on the blast furnace, there is scope for assessing both the combustion and gasification of agglomerated chars in order to ascertain performance in the raceway region and burden environment of the blast furnace.

2.3.3 Potential impacts of agglomeration in the blast furnace

As mentioned previously, due to the lack of literature available on this specific area, there are no strong conclusions regarding the potential operational impacts of agglomeration on the blast furnace. However, it is useful to consider that an agglomerate is a large char particle and as a result, will share a number of process implications with problems that arise from standard chars. The impacts of larger char agglomeration may result in more severe forms of these issues than char fines, dependent on the size and extent of the agglomeration.

When contemplating the impact an agglomerating coal could have on the blast furnace, it is beneficial to consider the process affecting the coal as it travels through the furnace. Upon injection the coal particles are rapidly heated in the injection lance and hot blast at temperatures of circa 1300°C before reaching the raceway with temperatures upwards of 2000°C. During this initial injection phase, the coal will be subject to flash devolatilisation, particle plasticity (coal dependent), combustion, and gasification. It is thought to be beneficial to the blast furnace process for as much coal to be consumed within this region as possible, as this allows a higher coal injection rate and cost savings. When the coal char leaves this region unburnt, as is common (discussed below), the char particles enter a lower temperature, carbon rich environment where the much slower gasification reactions take place. It is in this region where char can accumulate and be problematic.

One of the most common issues arising from coal injection is lowered furnace permeability – an important factor in maintaining stable blast furnace operations (Raygan et al., 2010). As the blast furnace is a counter-current reactor, effective permeability is dependent on sufficient gas ascension, and burden descent (Ishii, 2000). Coal chars (and agglomerates) that are not fully reacted in the raceway will leave the region unburnt with a majority swept upwards where they are prone to accumulate in the furnace, affecting permeability (Ichida et al., 1992; Akiyama and Kajiwara, 2000; Dong et al., 2003). Alongside operational difficulties, uneven permeability may introduce furnace longevity concerns with improper gas flow/gas blockages causing heat and pressure build-up spots on furnace walls (Hutny et al., 1991; Lu, et al., 2010). Whilst too high an injection rate is often given as the cause for lowered permeability (Bennett & Fukushima, 2003; Xu et al., 2005), Schott (2015) claims that a key factor in permeability issues is inefficient gasification of char particles. As a result, the gasification performance of the agglomerated chars must be investigated to determine the risk to furnace permeability.

Another potential impact of agglomerated chars is interactions with liquid metal. Lüngen and Poos (1996) state that char fines react very little with the liquid metal and slag, as they cannot penetrate into the liquids provided that they maintained their pulverised form. However, they state that if chars are agglomerated into larger particles, they can carburise the metal to saturation, a factor that would require addressing in post blast furnace processing.

Unreacted char particles that do not accumulate pass up through the cohesive zone to the furnace stack and, if still unreacted, are emitted in the offgas as waste (Carpenter, 2006). However, Carpenter suggests that the majority of chars are consumed within the furnace as a result of studies by Lüngen and Poos, (1996), Okochi et al (2000), and England et al (2001) wherein offgas char percentages vary little with injection rates. Additionally, it is likely that larger agglomerates are more likely to accumulate than standard char due to their size.

Additionally, agglomeration may result in plugged injection lances. Nightingale et al. (2003 as cited in Carpenter, 2006) state that injecting medium and high volatile coals that have some caking properties could lead to lance blockages (most likely due to particle agglomeration), whilst Inland Steel assess coal caking properties when evaluating lance plugging propensity (Chaubal et al., 1996). Carpenter states that lance blockages at Scunthorpe blast furnaces have been attributed in part to the coal partially coking during injection whilst in hot injection lances (Atkinson, 2006, as cited in Carpenter, 2006). This “partial coking” can be considered as agglomeration as coking typically refers to the industrial process of agglomeration of coal particles. Additionally, Mathieson et al. (2004) states that many cases of coking of pulverised coal in test rig injection lances were found. They note that this was due to the amount of lance that was exposed to the blast temperatures (presumably increasing internal lance temperatures, inducing plasticity, which results in coking/agglomeration). As a result, it is feasible that the injection of an agglomerating coal may result in blocked injection lances, dependent on the blast furnace set-up.

2.4 Coal Caking Properties

The formation of agglomerated material discussed in Section 2.3.1 depends heavily on the coal particle developing an adhesive surface during the plastic phase of heating. Coals that undergo this phase are often defined as caking coals. Caking is the softening or plastic properties of the coal that cause particles to melt or sinter together to form larger particles/agglomerates. (van Dyk et al., 2001). Caking coals are typically bituminous coals that undergo a phase of softening, plasticity, and often swelling, prior to resolidification upon reaching a certain coal specific temperature (Berkowitz, 1979; Speight, 2012).. Caking coals are used during cokemaking with the principle of agglomeration central to the process. As a result of the plasticity attained by the caking coals, individual particles can combine to form a coherent mass, either intentionally as during cokemaking, or unintentionally, as in certain combustors and potentially during blast furnace injection.

Common factors of a caking coal are thermoplasticity, swelling, cell development, and particle strength, with varying degrees of these occurrences being used to define weak to strong caking coals (Fieldner and Selvig, 1951). The most important property in a caking coal is the development of thermoplasticity, with other factors such as swelling and cell development often occurring as a result of the plastic phase.

In order to link the agglomeration of coals in experimental testing to the responsible properties, it is necessary to consider the factors behind coal caking and plasticity.

2.4.1 Plasticity and influencing factors

The onset of coal plastic properties during heating is a complex phenomenon with a range of contributions from various coal properties. Initially, the plastic properties of coal were interpreted via the metaplast theory (discussed in Fitzgerald, 1956; Solomon et al., 1992; van Krevelen, 1993). Over time the importance of transferable hydrogen on fluidity was also considered (Neavel, 1982; Clemens and Matheson, 1992).

The onset of plasticity appears to be related to molecules (sometimes referred to as “extractables”) that become detached from the coal macromolecule, while still remaining partly bound to the particle (Kandiyoti et al., 2006). These extractables are constituted of the hydroaromatic portion of the coal, the pre-cursors to tar. These materials become the metaplast portion of the coal particle that introduce fluidity to the coal surface. The hydroaromatic constituents also serve to prolong plasticity by means of hydrogen donation. Smith et al. (1994) state that transferable hydrogen produced by the coal effectively stabilises free radicals produced during heating, combining them with the available donor hydrogen. This serves to prevent the free radicals from recombining with the coal macromolecule (resolidifying), resulting in prolonged fluidity. As temperatures continue to increase, the resolidification process begins (generally above 400-500°C). The hydroaromatic portion of the coal undergoes cracking, leading to its release as tar and gases. Additionally, higher temperature results in an increase in the production of free radicals. At this stage, the loss of the hydroaromatic material and the donor hydrogen it contains means that free radical generation exceeds the capability of the coal to provide donor hydrogen to occupy the free radicals. As a result, free radicals recombine with the coal macromolecule forming a char residue.

The heating of coal particles in the blast furnace takes place under very high heating rates (10^4-10^6 °C/s). Due to the majority of the research in the field of coal plasticity relating to cokemaking, much of the current understanding is at relatively slow heating rates (1-3 °C/s). Kidena et al. (1998) found that increases in heating rate were effective in increasing coal plasticity. However, the heating rates tested were not replicable of the blast furnace (3 and 30 K/min). In order to test higher heating rates, Fong et al., (1986) developed a rapid heating plastometer and found that the softening temperature was insensitive to heating rate variations alongside minimal changes in apparent viscosity. However, Solomon et al. (1990) found that some coals that do not exhibit fluidity at conventional heating rates can develop fluidity under rapid heating, likely due to reduced chemical cross-linking. As a result, the effect of heating rate when considering caking and plasticity under blast furnace conditions cannot be definitively stated.

After establishing the general mechanism for coal plasticity, the broad coal properties that can impact plasticity are briefly assessed.

2.4.1.1 Elemental Properties

Regarding plasticity, Speight (2012) mentions that a coal's elemental composition will impact plasticity with a greater hydrogen content increasing plasticity, and a greater oxygen content decreasing plasticity.

As discussed previously, hydrogen rich compounds are heavily linked with plasticity due to them being partly liberated from the coal during heating, often forming a fluid metaplast phase (Kandiyoti et al., 2006). Additionally, the presence of these compounds as hydrogen donors also plays a role in stabilising free radicals and promoting plasticity (Neavel, 1982).

Regarding oxygen content, it appears that the impacts of oxygen on plasticity relate to oxygen functional groups and cross-linking reactions. Neavel (1982) considers that cross-linking occurs due to the formation of oxygen functional groups that occur during heating. Wachowska et al. (1974) reported that oxygen groups such as ethers form free radicals during cracking, a factor in reduced plasticity. These free radicals stabilise by bonding, initially with donor hydrogen (if available), followed by the formation of mobility-retarding cross-links with the coal macromolecule when free radical production exceeds available hydrogen (Marsh and Walker, 1979).

2.4.1.2 Proximate Properties

The plasticity of a coal is governed to some extent by the total volatile matter, with coals in the 25-35% VM range typically having greatest plasticity (Speight, 2012). This increase in plastic properties with volatile matter content is due to the increase in tar-bearing constituents in the coal that compose a portion of the volatile matter content. When predicting a coal's plasticity/caking performance, Loison et al. (1963, cited in Schlosberg, 1985) state that volatile matter content does not provide as much correlation with plasticity as coal rank.

It has been reported that the impact of mineral matter on coal plasticity is that typically the greater amount of total minerals in a coal, the less plasticity. This is due to mineral matter undergoing minimal physical change at the relevant plastic temperatures meaning it can be largely considered as inert. It will negate plasticity by not reacting and remaining in a solid physical state, increasing the amount of material that needs to be incorporated into the plastic phase, whilst not contributing towards increased plasticity (Ryan et al., 1997). Price et al. (1992) found that as little as a 1% addition of mineral matter to a coal can result in a decrease in maximum fluidity of 36%. It should however be noted that although minerals generally reduce plastic properties, some compounds such as quartz and kaolinite can cause minor increase in fluidity (Price et al., 1992).

2.4.1.3 Petrographic Properties

The macerals make up the organic component of a coal and are composed of various decayed organic matter, with different plant origins making up the three main maceral groups, vitrinite, liptinite, and inertinite that are then composed of a variety of sub-maceral groups. (Crelling and Rimmer, 2015).

The vitrinites are generally the most abundant maceral group and are formed from coalified woody tissues (roots, bark, tree trunks). Whilst generally the most sparse group the liptinite macerals are derived from waxy and resinous matter such as spores cuticles and resins. They are considered to be particularly hydrogen rich (Taylor et al., 1998). Inertinite macerals are composed of plant matter that has been strongly altered and degraded during formation, often through oxidation (for example, fossilised charcoal derived from peat fires, thermally matured peat, and various fungi [Scott, 1989]). As suggested by the name, the inertinites are considered to undergo less reactions and change relative to vitrinite and liptinite during heating.

Variations in the type of macerals that constitute a coal's organic matter will influence the elemental analysis of the coal and affect plasticity. Speight (2012) states that difficulties in the isolation of macerals for testing means that no definitive conclusions have been drawn, whilst the maceral groups themselves see large variation within themselves. For example, Price and Gransden (1987) suggest that vitrinite within eastern US coals contains more elemental hydrogen than in western Canadian coals.

There are numerous reports of maceral behaviour during heating and how they impact coal plasticity. A generalisation provided by Ryan et al. (1997) mentions how fluidity is controlled by the proportion of reactive components (liptinite and vitrinite) relative to inert components (inertinite and minerals), with the reactive components becoming plastic and viscous during heating. Zhuo et al. (2000) demonstrated that vitrinite melts and swells whereas inertinite does not melt. Meanwhile, liptinite was found to melt, but not swell or agglomerate.

In practice, it is considered that the plasticity of the vitrinite portion of the coal will have the greatest impact on coal plasticity, largely due to the greater relative quantities of vitrinite in coal. It is generally found to have intermediate-strong plastic properties (Maroto-Valer et al., 1998; Kidena et al., 2002). Liptinite, though considered highly plastic (Gray, 1989) is often of less relevance due to lower relative quantities (typically 5-15% of total maceral content). Inertinite macerals meanwhile tend to produce little plasticity due to their hard and friable nature (Maroto-Valer et al., 1998; Kidena et al., 2002). However, as mentioned, strong conclusions between maceral group behaviour and plasticity are not readily available, for example, Yoshida et al. (2000) found limited correlation of fluidity and maceral content when studying a wide range of coals via Gieseler plastometer.

2.4.2 Impact of oxidation on caking properties

In some applications it may be desirable to remove the caking properties of a coal. Dependent on the likely impact of agglomerated material on the blast furnace, it is possible that ironmakers may seek to remove coal caking properties in a bid to reduce agglomeration. Although solvent extraction can be used to reduce coal plasticity (Pierron and Rees, 1960), alternative methods may be more suitable for industrial applications.

A more practical method of potentially reducing agglomeration in industry is through oxidation prior to heating. It is well established that periods of weathering at low temperatures effectively reduces the thermoplastic properties of coals via oxidation (Maloney et al., 1982; Cox and Nelson, 1984; Wu et al., 1988; Alvarez et al., 1998; Jha et al., 2014; Miroschnichenko et al., 2017). By reducing the thermoplastic properties, there is potential to reduce agglomeration (provided agglomeration is a product of caking properties). McCarthy (1981) tested the pre-oxidation of both strong and weak caking coals at 400°C with a residence time of 2 seconds which was found to reduce agglomeration of all samples.

McCarthy contends that oxidation dehydrogenates the coal surface. This can limit plasticity, as there are less hydrogen-rich groups to create metaplast and provide donor hydrogen. Additionally, oxygen functional groups may cross-link hydroaromatic ring structures together which serves to reduce and potentially eliminate the plastic phase (Wachowska et al., 1974; Marsh and Walker, 1979; Neavel, 1982).

It is clear that the pre-oxidation of coal samples has proven effective in mitigating agglomeration in some applications, with further investigation required to study the effects on agglomeration under heating conditions representative of blast furnace coal injection. This will have the additional benefit of providing a potential option for industrial operators.

2.5 Injection Coal Reactions in the Blast Furnace

The differing performances of coals in the blast furnace provide a range of both positive effects, and operational challenges. It is generally considered that a faster reacting coal is desirable due to the possibility of a higher coal injection rate and thus an improved coke replacement ratio (Carpenter, 2006).

Upon injection, coal particles are initially heated either in the injection lance or oxygen-enriched hot blast, followed by the raceway region where they are devolatilised, producing non-condensable volatiles (gases), condensable volatiles (tar), and a carbonaceous char (Hutny et al., 1991; Yeh et al., 2002). The volatile matter produced is ignited and combusted to produce CO_2 and H_2O, taking a matter of milliseconds (Wu, 2005). Following this, the residual char is partly combusted in the raceway region whilst oxygen is available, though this is a much slower process than the volatile matter combustion (Carpenter, 2006). Once the char passes to a carbon rich environment, char gasification takes place. This is the slowest coal/char reaction and takes place mostly outside the raceway.

When considering the effects of these reactions on blast furnace performance, it is likely that the slower reactions, combustion and gasification, have more potential to create operational problems with potential for char build up and blockages.

2.5.1 Combustion performance

Coal combustion in the raceway region is an important factor to consider as it affects the amount of the coal that can be injected into the blast furnace and the amount that leaves the raceway. Combustion of injected coal provides heat and carbon for reducing gases necessary for the ironmaking process. Initial hot blast temperatures are approximately 1300°C (Bortz, 1983) rising to upwards of 2000°C in the raceway (Ishii, 2000). Coal combustion and the products vary dependent on the availability of oxygen with combustion reaction mentioned by Kamijou and Shimizu (2000) shown in Equation 1:

$$C(s) + \frac{1}{2}O_2(g) = CO(g)$$

Equation 1: Partial coal combustion reaction

Kamijou and Shimizu (2000) discuss how gas composition in the injection region varies in the Kakagawa blast furnace, producing Figure 9 that displays coal reactions in the raceway. It is shown that most of the available oxygen is consumed near the nose of the tuyere, with CO_2 and CO rich atmospheres produced in the middle and end of the raceway respectively. This suggests that combustion of injected coal particles takes place in a very short period at the start of the raceway and is quickly replaced by the much slower gasification reactions (solution loss reaction zone).

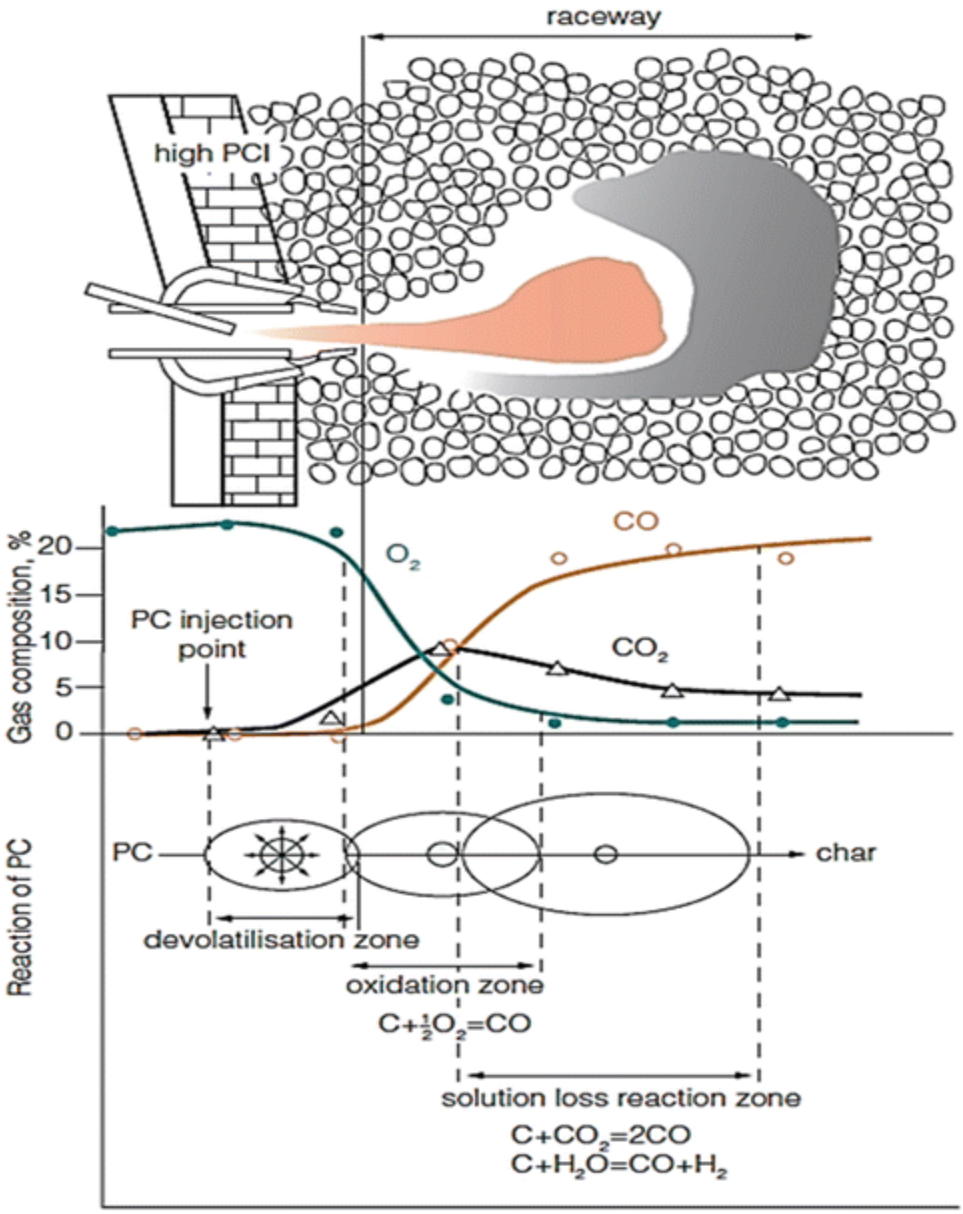


Figure 9: Pulverised coal reactions in the raceway region alongside variations in gas composition (Kamijou and Shimizu, 2000)

Coal/char oxidation mechanisms vary dependent on the temperature of the environment with three zones or regimes commonly quoted in the literature (Essenhigh, 1981; Prado et al., 1987; Wu, 2005; Wall et al., 2009). Figure 10 shows the three regimes and the resultant reactivity of them alongside the dominant reaction mechanism.

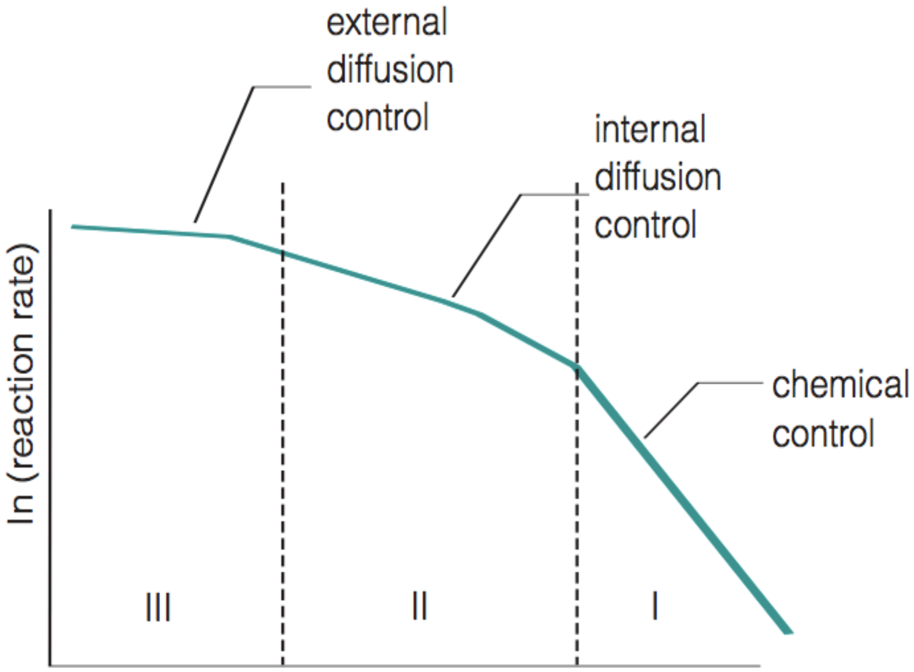


Figure 10: Reaction zones of char oxidation and the reaction rates present (x-axis shows reaction regimes as detailed below) (Wu, 2005)

Char oxidation under raceway conditions is controlled by Regime III – external diffusion (of oxygen) to the particle due to the high temperatures found in the raceway (Essenhigh, 1981; Prado et al., 1987). Due to the temperatures involved, all the oxygen transported to the coal surface is consumed (Wu, 2005) meaning char combustion in the raceway is mainly bulk diffusion controlled. As a result, the surface area of the injected coal particles is integral with the greater surface area of finer coals often providing greater combustion (Xiumin et al., 2002; Barranco et al., 2006; Du et al., 2010). Regarding agglomeration, it is possible that the agglomeration of particles during combustion will reduce combustion performance by reducing the surface area available for reaction. Although Shampine et al. (1995) state that agglomeration is not likely to be detrimental to coal combustion in typical combustors, the oxygen concentrations and oxidation residence times are greater than those blast furnace injected coals are exposed to. Du et al. (2010) found that combustion efficiency could not be improved further with grinding as a result of increased instances of agglomeration in finer coal, implying that agglomerated particles are problematic regarding combustion.

Generally, coals with high volatile matter content have greater combustion performance when tested under blast furnace simulated conditions (Kalkreuth et al., 2005; Steer et al., 2015a) whilst mineral matter can both promote, and inhibit combustion (Zhang et al., 2009). The maceral content of the coal also contributes with Suarez-Ruiz and Crelling (2008) stating that the combustibility (temperature of combustion) of the coal macerals is considered to be liptinite < vitrinite < inertinite.

2.5.2 Gasification performance

The gasification performance of the char produced via initial oxidation is believed to be an important factor in blast furnace performance. Due to the minimal time available for oxidation in the raceway (~35ms), and the limitations in oxygen supply to the particle surface, Pipatmanomai et al. (2003) state that a significant proportion of char will be carried out of the raceway region not fully reacted. As the more desirable high injection rates are reached (>200kg/thm), combustibility declines further resulting in greater unburnt char production (Carpenter, 2006). The char particles are distributed across the blast furnace, accumulating at the back of the raceway and under the cohesive zone with fines collecting near the walls where they can disrupt gas flows and reduce furnace permeability (Dong et al., 2003). The char will also be entrained into the gas flow and enter the stack where burden permeability is affected prior to potentially being emitted in the offgas (Ichida et al., 1992; Akiyama and Kajiwara, 2000). As previously mentioned, Schott (2015) states that inefficient gasification of char particles is a key factor in permeability issues, and hence can impact furnace stability. Additionally, unburnt char will compete with coke and be preferentially gasified (Akiyama and Kajiwara, 2000), consequently decreasing coke degradation.

Although char gasification begins at the end of the raceway region (as marked by solution loss reaction in Figure 9), the residence time is likely too short for any significant reaction to take place resulting in gasification mostly occurring in the cohesive zone and furnace shaft. The gasification reactions taking place occur between char carbon and CO_2, and char carbon and H_2O as detailed in the following equations.

$$C(s) + CO_2(\mathrm{g}) \rightleftharpoons 2CO(g)$$

Equation 2: Boudouard reaction

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$$

Equation 3: Char gasification with steam

Both these gasification reactions provide the reducing gases (CO and H_2) that reduce iron ore and are integral for replacing coke in the blast furnace.

As discussed in Section 2.5.1, the relevant reaction mechanism varies with temperature in the blast furnace. With the gasification reactions generally taking place in the stack, temperatures are lower at 1000-600°C down to 110°C for the top gas (Geerdes et al., 2009). At these higher temperatures, char reactivity will be diffusion controlled by Regime II – internal pore diffusion (Essenhigh, 1981; Prado et al., 1987) with relatively slow reactivity due to lower temperatures (compared with reactivity and temperatures in the raceway region). Prior to leaving the blast furnace, gasification will take place under Regime I – chemical control, though smaller quantities of char will reach this stage and likely be less problematic than those deeper in the furnace. When discussing char gasification in CO_2, Irfan et al. (2011) claim that the rate of gasification of a char particle in a high carbon environment is governed by the accessibility of the reactant gas to the active sites located on the internal surface of the char. It is claimed by Hippo and Walker Jr (1975) that low reactivity will arise when a particle has a relative lack of larger “feeder pores”, thus resulting in gas diffusion into (and product desorption out of) the particle being driven through micro-pores as opposed to macro feeder pores. As a result, diffusion into and out of the particle is believed to be key, with particle porosity an important factor.

The physical structure of the char is strongly dependent on the initial heating and combustion of the particle. The combustion efficiency of the sample will also impact the resultant char with more reacted particles likely having increased porosity. These effects will go on to influence char reactivity based on the diffusion ability of the particle. As a result, it would be expected that coal agglomeration would result in decreased char reactivity based on increase in particle size with a loss of exposed surfaces where gases can diffuse into the particle. This would of course be dependent on the physical development and porosity of agglomerated particles. As stated by Schott (2015), the gasification reactivity of the char is a factor in blast furnace permeability and stability amongst other things. It is currently uncertain as to the impact of agglomerated material on char reactivity, and as a result should be investigated further to provide some insight into the potential performance implications of injecting coals that agglomerate.

2.6 Chapter Summary

This chapter has reviewed previous studies relating to blast furnace injection, coal agglomeration, thermoplasticity, and coal performance in blast furnace environments. To summarise, the following conclusions are drawn.

As a result of plasticity developing in caking coals under low-heating rate conditions, certain coal particles can agglomerate. The use of caking (and likely agglomerating) coals has been linked with blocked injection lances in the blast furnace (Carpenter, 2006), and may affect the blast furnace via accumulation of char (Dong et al., 2003). This would lower blast furnace permeability (Ichida et al., 1992; Akiyama and Kajiwara, 2000), causing instability. Additionally, agglomerated particles may carburise the liquid metal (Lüngen and Poos, 1996). However, the possibility of coal agglomerating under blast furnace high heating rate conditions in an entrained laminar flow is currently not known. As a result, this is an area that this thesis aims to provide clarification on.

Whilst coal caking properties are linked heavily to the plastic stage of coal heating, coal oxidation has been found to effectively reduce plastic development in a coal, and also coal agglomeration in an experimental pyrolyser (McCarthy, 1981).

Regarding coal performance in the blast furnace, combustion takes place primarily in the raceway region for a duration of approximately 35ms (Kamijou and Shimizu, 2000). As a result, it is likely that char will leave the region partly unreacted. Unburnt char is reacted in the blast furnace stack via gasification in CO_2 and H_2O, with reports stating that gasification reactivity is controlled via pore diffusion (Irfan et al., 2001), suggesting that char physical structure is integral to gasification reactivity (Hippo and Walker Jr, 1975). Although the impacts of agglomeration on char gasification reactivity are not known, it is believed that it will most likely have a negative impact due to agglomeration materials likely increasing char particle size and surface area.

Potential areas of investigation based on uncertainties and gaps in the literature are the possibility of agglomerate formation under blast furnace heating conditions, responsible coal properties, and agglomeration behaviour during coal blending. Additionally, the performance implications of agglomerated chars should be considered with regards to combustion and gasification.

Chapter 3: Experimental Rigs and Methodology

3.1 Introduction

This chapter discusses the experimental design, detailing the various techniques used whilst providing the rationale behind the use of the chosen tests. This contains justification for injecting coals into a drop tube furnace and relating the results to the blast furnace. Following this, information on the materials used, experimental equipment, and the procedural methods used to complete this work are provided.

3.2 Design of Experiment

The research undertaken in this body of work was concerned with providing insight into the possibility of coal agglomeration during injection in the blast furnace. Coal agglomeration under conditions akin to blast furnace injection was tested, alongside an assessment of the responsible coal properties. Methods of mitigating agglomeration were also assessed. Additionally, the likely performance implications of agglomerated coal chars in the blast furnace were investigated via combustion and gasification analysis.

The above work was undertaken via an experimental study that can be identified as having three main sections:

- **Coal characterisation** – Used to provide information on the materials to be tested and investigate coal properties responsible for agglomeration.
- **Laboratory coal injection** – A drop tube furnace was used to test the injection of coal under high heating rate (10^4°C/s), high temperature (1100°C) conditions. Due to key similarities between the DTF and BF, the results from laboratory DTF injection were used to make inferences regarding agglomeration in the blast furnace process. Coal was injected into the DTF with the resultant char collected for analysis (note: the term

char used throughout this investigation refers to a partially-reacted residue).

- **Product char analysis –** The drop tube furnace chars were analysed for evidence of agglomeration and tested to infer the resultant performance implications on the blast furnace.

These sections and the experimental process are shown in Figure 11.

3.2.1 Coal characterisation

Coal characterisation was carried out on the coal samples following their preparation to injection coal size specifications.

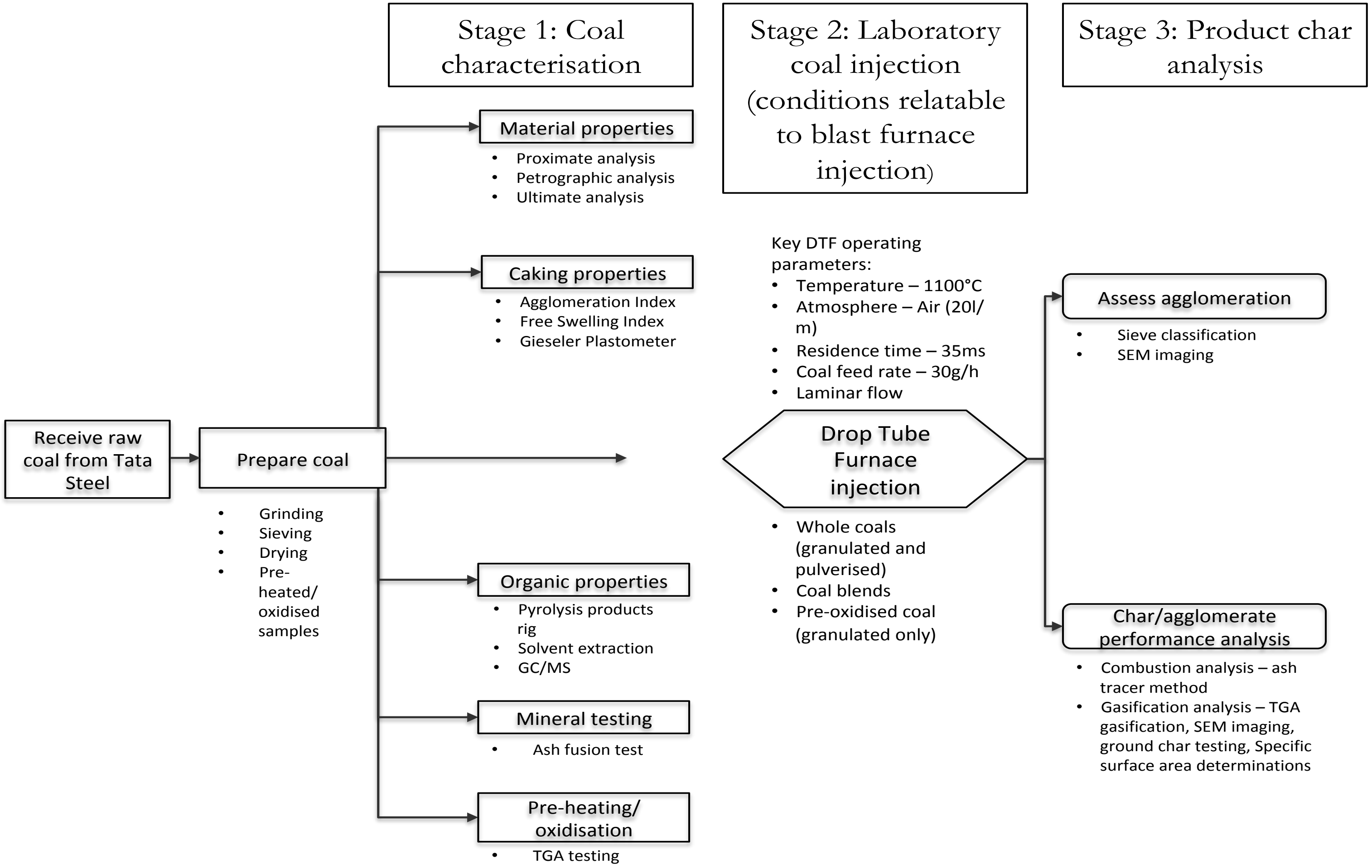
3.2.1.1 Material properties

The coal's properties were initially analysed by means of proximate, petrographic, and ultimate analysis to provide fixed carbon, ash, volatile matter, maceral contents, and elemental information. These tests were carried out due to the prevalence of their use in industry.

3.2.1.2 Caking properties

As discussed in Chapter 2, the caking and plastic properties of the coals are likely to be a factor in agglomeration during heating in the blast furnace and drop tube furnace. Typically, the caking properties of a coal are studied with regards to cokemaking and the coking properties of the coal. As a result, many of the industry standard tests are flawed with regards to the work of this thesis. This is due to the much lower heating rates used in cokemaking resulting in caking/plasticity tests also using low heating rates. With regards to this investigation, the caking properties of the coal will be generated upon rapid heating, 10^4°C (Li et al., 2014), in the DTF leaving a clear limitation in the suitability of some tests.

Figure 11: Investigation methods including three main areas of research: coal characterisation, laboratory coal injection, and product char analysis



Caking/agglomeration index

A caking test called the agglomeration index was used to provide an indication of general caking properties based on Fieldner and Selvig, 1951, and Speight, 2012). It should be noted for reasons of clarity that the title of the test – "agglomeration index", is not related to any instances of agglomeration found during DTF investigation. These are simply the terms used by the aforementioned references to define a coal that does or does not form a singular residue during the test procedure.

The test takes account of a range of caking criteria and was chosen due to its heating rate making it suitable for assessing caking performance in the blast furnace and drop tube furnace. Additionally, the test was used for pragmatic purposes as it was effective in analysing a large number of samples at different stages of the investigation without the need for outsourcing, as was the case with the alternative free swelling index. Although a potential limitation of the test is the area of subjectivity involved with interpretation of the test criteria, this was addressed by having the same person carry out and analyse the test residue for each sample. Although the test does not subscribe to a scientific standard, the residue is created by means of BS ISO 562:2010 resulting in a standardised test method for the production of the residue to be analysed.

Free swelling index

The aforementioned agglomeration index is limited in the range of possible scores for highly caking coals (with only 3 scores defined as caking coals). As a result the free swelling index was used to provide greater opportunity to distinguish between caking samples. The free swelling index also gives prominence to coal swelling thus providing additional information on coal physical change during the plastic phase of heating and is a standardised method of assessing coal swelling (BS ISO 501:2012). Additionally, carrying out the FSI allowed for the assessment of suitability of the FSI vs. agglomeration index with regards to predicting coal agglomeration – a matter of interest industrially as well as to this research work.

Gieseler Plastometry

Due to the likely role of plasticity with regards to caking and agglomeration, a Gieseler plastometer was selected to test the capability of each coal to attain thermoplasticity. It was then possible to link DTF agglomeration with the parent coal's plasticity and fluidity. However, due to the prevalence of cokemaking in coal plasticity research, the heating rate of the Gieseler test (3°C/m) is far below that of the DTF and blast furnace (10^4-10^6°C/s). This is something that must be considered when drawing strong conclusions from Gieseler plastometer results. Studies of the literature show that softening temperatures are unaffected by higher heating rates whilst impacts on maximum fluidity remain unclear with both increases and decreases with heating rate found (Loison et al., 1963, cited in Schlosberg, 1985; Fong et al., 1986; Oh et al., 1989; Gerjarusak et al., 1992). However, due to the heating rates in the blast furnace and drop tube furnace, the amount of time spent in the plastic state will be significantly lower than under Gieseler conditions.

3.2.1.3 Organic properties

After establishing a range of properties of the various coal samples (caking, swelling, plasticity), it was necessary to assess the coal components that result in these rheological, physical effects. Due to the involvement of the hydrocarbon portion (generally present as tar under heating) of coal in developing plastic properties, tests were designed in order to provide further insight into this area.

Pyrolysis products test rig

A pyrolysis test rig was constructed in order to assess the relative pyrolysis yields of the coal samples. The test produced three components: char, tar, and gases. By studying the relative yields of tar, it was possible to assess the impacts of condensable hydrocarbon materials and link them with the plastic and caking properties of the parent coal. Additionally, it was possible to link volatile gas yield with coal swelling. The main limitation of this testing is the lower heating rate available (approximately 15°C) than those in the drop tube furnace, with volatile matter yields generally increasing with higher heating rates (Fong et al., 1986; Solomon et al., 1987; Gibbins-Matham and Kandiyoti, 1988). However, the results of the test are useful to compare the coals relative to one another and find the relative quantities of each pyrolysis product (char, tar, gases).

Solvent extraction & Gas Chromatography/Mass Spectrometry

Solvent extraction followed by Gas Chromatography/Mass Spectrometry (GC/MS) on the extracted sample was used in order to provide additional detail on the organic constituents of the coals with particular interest given to hydroaromatic components. The test was used due to its ability to identify individual components in the coal and study the relative proportions of *n*-ring hydroaromatics in the coals. Due to the successful use of large *n*-ring hydroaromatics as caking additives (Koyano et al., 2010; Takanohashi et al., 2014; Sakimoto et al., 2014) the relative quantities of these components as well as total hydroaromatics was investigated.

3.2.1.4 Mineral testing

In order to determine how relevant the mineral portion of the coal is in influencing agglomeration (and establish that the agglomeration effect is not due to fused mineral matter), the various ash fusion temperatures were determined. If it was found that the DTF operating temperature were lower than the mineral softening temperatures it would be unlikely that the mineral component was involved in fusing and agglomerating.

However, the results from this test cannot be used to categorically dismiss ash as playing a role in agglomerate formation, with Stallmann & Neavel (1980) finding ash agglomeration occurring (in pilot gasification rigs) below the relevant ash fusion test temperatures. Due to this, the results from this test will be used alongside other methods including correlation of agglomeration with caking, and SEM imaging to make a determination regarding the role of ash in DTF char agglomeration.

3.2.1.5 Pre-heating/pre-oxidation

In order to develop knowledge on agglomeration and caking properties whilst establishing a means of reducing them, pre-heating of the raw, granulated MV4 coal was investigated. The MV4 was chosen as the sample to be tested due to its high caking score of 7 and high levels of agglomeration in the DTF. The aim of pre-heating was to reduce the caking properties of the coal and to clarify what effect this would have on agglomeration and other performance parameters. A pre-heating temperature of 300°C was chosen as it was high enough to sufficiently oxidise the sample whilst not being high enough to engage any plastic properties. The caking properties of the sample could potentially be altered via a number of means, both thermally, and due to oxidation. Thermal effects such as the loss of volatile matter content and hydrocarbons were possible, whilst oxidation may cause cross-linking of the hydroaromatic components of the sample due to increased oxygen functional groups occurring during oxidation. As a result of this number of potential explanations for reduced caking, the pre-heating of the MV4 sample was carried out in both oxidative and inert atmospheres using air and nitrogen respectively to isolate the effect of oxidation on caking properties.

Following creation of the pre-oxidised MV4 coal, the samples were injected into the DTF and studied for signs of agglomeration and analysed for the resultant performance implications.

3.2.2 Laboratory coal injection

An experimental drop tube furnace (detailed in Figure 16) was selected as a means of testing agglomeration under high heating rate conditions. The drop tube furnace shares a number of key characteristics with coal injection in the blast furnace. These shared conditions between the DTF and blast furnace allow for the resultant coal performance in the DTF to be related to that of the blast furnace. The key injection parameters between the two are noted below:

- High heating rate:
    - Blast furnace coal injection heating rate – 10^4-10^6 °C/s (Bortz, 1983; Ishii, 2000; Carpenter, 2006).
    - Drop tube furnace heating rate – 10^4 °C/s (Li et al., 2014).
    - The replicable heating rates between the two furnaces mean that the DTF coals will be subjected to flash devolatilisation and development of plasticity in a manner akin to in blast furnace heating. It is uncertain as to the precise development of caking properties under such heating rates, including whether the plastic phase will occur for sufficient duration for particle agglomeration to occur.
- Short residence time:
    - Blast furnace raceway residence time – 35-100ms (Carpenter, 2006; Geerdes et al., 2009; ERNW, 2017).

    - Drop tube furnace residence time – 35-700ms (adjustable)
    - Short residence time DTF collection allows insight into char formation at crucial stages of injection: following devolatilisation and plasticity developments, and prior to full reaction (35ms residence time used in this thesis).
- Hot blast temperature:
    - Blast furnace hot blast temperature – 900-1300°C, typically 1100-1200°C (Bortz, 1983; Ishii, 2000).
    - DTF temperature – 1100°C
    - As injection coal particles are initially heated when leaving the injection lance/entering the furnace hot blast, it is at this temperature that the coal initial heating and likely agglomeration. As a result, a DTF temperature of 1100°C is suitable for replicating the hot blast temperatures.

Following testing under these key experimental conditions, the coal char was collected prior to char analysis, the results of which are used to make inferences regarding the industrial process.

The drop tube furnace used in this body of work has been used previously in the study of coal for blast furnace injection as detailed in work by Steer et al. (2015a; 2015b; 2018). The use of a drop tube furnace in this field is well established with numerous groups utilising a DTF to assess coal performance in blast furnace environments (Lu et al., 2001; Yu et al., 2003a; Kalkreuth et al., 2005; Gupta et al., 2006; Borrego et al., 2008; Du et al., 2010; Pohlmann et al., 2010; Sahu et al., 2014). As to the effectiveness of a drop tube furnace in replicating blast furnace injection, Li et al. (2014) published a paper assessing the suitability of a DTF vs. a specifically designed pilot-scale pulverised coal injection rig. The work concluded that a drop tube furnace is capable of providing reasonable indications of coal combustion performance when compared with the pulverised coal injection rig, though the drop tube furnace has greater sensitivity to volatile matter content. With regards to the chars produced and their reactivity, both the drop tube furnace and pulverised coal injection rig produced chars with comparable reactivities.

The blast furnace coal injection blowpipe and raceway regions are highly dynamic, fluctuating environments with inconstant conditions, pressurised injection lances, and variable injected oxygen concentrations. It is acknowledged that these conditions cannot always be satisfied in the DTF. A common consideration in DTF injection relative to the blast furnace is the lower temperatures available – typically a maximum of around 1500°C compared to the raceway flame temperatures - upwards of 2000°C. However, as mentioned prior, the purpose of this study is to assess the possibility of agglomeration occurring. This is more likely to occur during initial heating (wherein the adhesive particle surface develops) in the hot blast in which significantly lower temperatures are typical (900-1300°C). As a result, the 1100°C DTF temperature of this study is suitable for replicating the desired blast environment where temperature is concerned. Although the following raceway flame temperatures are higher (>2000°C), it is accepted that char commonly leaves the raceway region partly unreacted (Ichida et al., 1992; Akiyama and Kajiwara, 2000; Dong et al., 2003). As a result, it is possible that agglomerated char will form in the lower temperature injection lance or blowpipe and remain in this physical state upon leaving the raceway and potentially go on to be problematic deeper in the furnace (e.g. cohesive zone and stack).

One limitation of the DTF when making links to the BF is that it cannot match the injection coal stream density to the same level as the blast furnace due to differing feed systems through the injection lances and size of the respective furnaces. The literature suggests coal may agglomerate around the tip of the injection lances, potentially causing blockages (Nightingale et al., 2003; Atkinson, 2006, as cited in Carpenter, 2006). Industrial visits to Tata Steel Port Talbot blast furnace no. 4 (10/02/2015) and Scunthorpe blast furnaces (20/10/16) have allowed the author to visibly assess the coal stream into the furnaces through viewing ports. The injected coal stream can be described as constant and dense. This is in contrast to the DTF through which a relatively dilute phase is injected at a given time. A dilute phase is necessary in the DTF in order to promote consistent, repeatable injection testing. As a result of this differing feed rate, the DTF is not capable of perfectly replicating the injection stream under heating. However, due to the relative differences, it would be likely that the occurrence of agglomeration in the DTF will mean that some agglomeration is likely to occur in the blast furnace environment due to the greater coal stream density.

3.2.3 Product char analysis

After coal injection into the DTF the product char was collected for analysis. As one of the objectives of this work was to study the possibility of coal injection in the blast furnace, the chars were first assessed for signs of agglomeration. Following this, the impact of coal agglomeration on char performance with regards to combustion and gasification was established.

3.2.3.1 Assessing char agglomeration

Sieve analysis

McCarthy (1980 and 1981) utilised a sieve screening approach to characterising agglomeration of pulverised coal during flash pyrolysis. A similar method was utilised in this thesis albeit with a larger 1mm sieve top size to take into account granulated particles. The aim of this sieve testing was to quantify the agglomeration of the injection coals relative to one another.

Upon char collection from the DTF, it was possible to visually inspect the 35ms char for signs of agglomeration with larger agglomerates visible to the naked eye. In order to determine the extent to which each coal sample agglomerates it was necessary to quantify agglomeration by calculating the amount of agglomerated material per char. This allowed an agglomeration figure to be assigned to each char.

A sieve size of 1mm was selected with char particles above this size denoted as agglomerated material. This was chosen as 1mm is the largest particle size that should be entering the DTF in the raw coal (due to the granulated coal top size of 1mm). Any particles leaving the DTF >1mm have increased in size during reaction. It is noted that this size classification results in the exclusion of numerous <1mm agglomerates, of which there are many (as found via SEM imaging). However, due to the broad raw coal particle size ranges and the potential for confusion between agglomerates and swollen particles, it is not possible to differentiate between fine agglomerated material and singular particles by size (e.g. two particles combined would be an agglomerate, yet particle size would remain fine). The impact of smaller agglomerates are considered in this work and studied via SEM imaging.

It should also be noted that the agglomeration figure given by sieve classification is used to study the agglomeration of the coals relative to one another, as it cannot be accurately determined what form or to what extent agglomeration will occur in the blast furnace with discrepancies between the DTF and blast furnace. As a result of uncertainty regarding the presence of larger agglomerates in the blast furnace, and issues with TGA crucible/balance size, the >1mm materials remained separate from the 35ms chars for the remaining tests including SEM analysis and char gasification reactivity. This allowed for the testing of finer agglomerated material that is more likely to be present in blast furnace chars. A comparison of the two char size fractions is discussed in Appendix B that highlights the similarities between the two which permitted their exclusion.

SEM imaging

Following collection of the DTF chars, scanning electron microscopy was used to produce images of the char. There were two main reasons for doing this. Firstly, these images allowed for inspection of the finer particles and importantly, finer agglomerates. As mentioned prior, “agglomerates” were defined as >1mm particles only for the purposes of quantification. It was acknowledged that there were numerous smaller-scale agglomerates present in the chars undetected by sieve analysis. SEM imaging provided a means of assessing the structure and prevalence of this finer agglomerated material. In addition to this, SEM images provided a means of linking DTF char/agglomerate structures to gasification reactivity in the TGA, allowing insight into the relevance of agglomerated materials when assessing gasification performance.

3.2.3.2 Char performance analysis

Combustion analysis – Ash tracer method

Coal combustion was measured by ash tracer analysis of the 35ms DTF chars. The ash tracer method is used to estimate the relative burnouts of the char samples and is well established in the field of coal pyrolysis and combustion (Gat et al., 1984; Osório, et al., 2006; Steer et al., 2015a; Steer et al., 2015b). As the DTF temperatures are lower than those found in the blast furnace raceway, it is the coal performance relative to one another and other coal parameters that are of most relevance, thus making the ash tracer method a useful tool for the purposes of this investigation.

The ash tracer method assumes that the coal ash is conserved in the char throughout the DTF process with no ash portion of the coal/char left uncollected or volatilised (Steer, 2015a). This assumption is an established limitation of the method. As Ried (1981, cited in Gat et al., 1984) states, the ash tracer method can be unreliable in coal combustion experiments where oxidation and volatilisation of minerals can result in loss of the tracer, potentially causing negative burnout. Additionally, Lester (1994) states that burnouts can be inaccurate due to the collected char sample failing to contain 100% of the original minerals with lighter fragments at risk of becoming lost in the gas flow. A laminar flow is utilised in the DTF in this work to negate this as much as possible. Lester also mentions how the selective loss of char/ash particles can occur in the collector probe as volatiles recondense on the interior surface of the probe resulting in build up as a tarry residue over time. He claims that ash particles may be prone to adhering to this sticky surface and thus be lost from the char. In this investigation, this occurrence was limited by ensuring the collector probe was cleaned thoroughly between each run.

Gasification analysis – TGA testing and specific surface area

In order to produce a carbon-rich environment and simultaneously measure the char reactions occurring, thermogravimetric analysis was used. The experiment was designed to replicate blast furnace conditions outside of the raceway region as the char enters the cohesive zone and stack. A CO_2 atmosphere was used to promote the Boudouard reaction whilst a temperature of 900°C is acceptable when replicating the stack temperature of the blast furnace. The use of thermogravimetry with CO_2 as a gasifying agent is well established when testing blast furnace gasification environments (Sahajwalla et al., 2004; Gupta et al., 2004; Hilding et al., 2005; Pohlmann, et al., 2010; Jayasekara et al., 2015; Rodero et al., 2015; Barbieri et al., 2016). However, it is noted that the TGA method cannot replicate alternate char reaction mechanisms such as interactions with the hot metal.

When assessing the gasification reactivity of a char, the physical structure is often cited as an important property (Hippo and Walker Jr, 1975; Irfan et al., 2011). As a result, it was believed that the agglomeration of char particles would prove impactful on the resultant gasification reactivity. To test this, the chars were gasified in both an unground and ground state with chars ground in a mortar and pestle. The aim was to remove the role of physical differences between the chars and test the relative inherent/chemical reactivities of the chars.

Additionally, the specific surface area of the unground chars was found in order to quantify the physical differences between the chars.

3.3 Materials

The industrial sponsor Tata Steel provided all coal samples used in this investigation, selecting a range of industrial injection coals. The coals provided were raw, unmilled coals sampled prior to industrial processing. It was necessary to select a variety of coals with a range of properties. Volatile matter content was chosen as the most important selection criteria due to prominent use by blast furnace operators when inferring coal performance (M Greenslade, 2014, personal communication, 5 November). As a result, four coals were chosen with one low volatile matter coal (LV1 – 9.1% [wt%]), two medium volatile coals (MV4 and MV3 – 17.6% and 20.2% respectively [wt%]), and one high volatile matter coal (HV1 – 34.5% [wt%]). The coal names have been replaced due to a commercial confidentiality agreement with the industrial sponsor. In order to accurately represent industrial coal injection, the coals were required to approximately meet industrial particle size specifications. The industrial sponsor Tata Steel injects coal into blast furnaces located both in South Wales - Port Talbot, and the Netherlands – IJmuiden. However the size specifications at these locations differ. At Port Talbot, coal is granulated prior to injection, whilst IJmuiden utilises pulverised coal, finer than the coarse granulated coal. In order to accurately select representative coal specifications, industrial data was used to assess the industrial particle size range. The resultant size specifications selected for the experimental work are detailed below as agreed upon for suitability with the industrial partner:

Granulated - 100% < 1mm, 50% <250μm

Pulverised - 100% < 300μm, 50% <75μm

A laboratory bowl mill was used to grind a subsection of the coal prior to dry hand sieving using international standard sieves. It was necessary to remove a subsection of the coal for grinding so as to allow a sample representative of the whole coal. For example, if a subsection was not taken, it is possible that harder coal macerals would remain unground and be sieved out resulting in an unrepresentative sample. The grinding and sieving method was done bearing this in mind in order to reduce unintended maceral selectivity.

Prior to experimental testing, the samples were oven-dried at 105°C for one hour. This temperature was chosen in order to replicate the coal drying temperature used by the industrial sponsor at Port Talbot, approximately 110-120°C (M Greenslade, 2014, personal communication, 5 November). In order to confirm that excessive oxidation of the samples does not occur under these drying conditions (due to the effects of oxidation on caking properties), the coal caking properties were tested pre-drying and post-drying (using agglomeration index method as detailed in Section 3.4.1.2). The results of these tests showed that caking properties were not reduced by the drying procedure with caking scores remaining unchanged after drying. Additionally, work by Burmistrz et al. (2005) has shown that there are no significant impacts on caking properties under heating in air at both 150°C and 210°C. This study, alongside caking testing suggests that the drying temperature used in this investigation does not alter the sample properties with regards to caking.

In order to create pre-oxidised samples, the MV4 coal was chosen as it consistently agglomerated during DTF injection with a view to establishing whether this continued after oxidation. The MV4 coal was oxidised in a muffle furnace at 300°C for 60 minutes to produce the pre-oxidised coal sample prior to DTF injection.

3.4 Experimental Procedures

3.4.1 Coal characterisation

3.4.1.1 Material properties

Proximate analysis (BS ISO 17246:2010)

The proximate analysis of the coal samples was carried out as per BS ISO 17246:2010 (on dried samples) where volatile matter and ash contents are calculated with fixed carbon calculated by difference. Prior to proximate analysis determinations, the samples were ground to pass through a 212μm sieve. Volatile matter content was calculated by means of weighing 1g of sample into an enclosed crucible and rapidly heating in a muffle furnace at 900°C for 7 minutes. After this, the mass loss was calculated to give a volatile matter percentage. Regarding ash content, 1g of sample was weighed into an open crucible and heated in an air environment muffle furnace to 500°C for one hour followed by 815°C for one hour. The residue in the crucible is the ash portion of the original 1g coal sample that can be given as a percentage. All proximate analysis testing was carried out in at least duplicate for the range of coals.

Petrographic analysis (BS ISO 7404:2009)

Due to lack of required equipment, specialist analytical service providers Minton Treharne and Davies carried out petrographic analysis. Block preparation and analysis was carried out in accordanlsce with BS ISO 7404. A polished particulate block was prepared from each sample with the maceral group compositions determined by carrying out a point count on each block under reflected light microscopy to identify the different macerals present.

Ultimate analysis

As a result of lack of required equipment, analytical service provider CE Instruments carried out ultimate analysis for the range of dried coal samples. A Thermo Scientific Flash 2000 CHNS/O was used with a HWD430 detector and cystine used for calibration purposes. The testing utilised chromatography with tube temperatures of 950°C and 1060°C and carrier flows of 140ml/min. For the CHNS data, the total run time was 850 seconds with the 2-3mg samples analysed with the addition of 10mg vanadium oxide to act as an oxidiser. The CHNS testing was run in either duplicate or quadruplicate, whilst all oxygen analysis was carried out in duplicate. The elemental variances between runs are low for H, N, S and O results ranging from 0.0001-0.04mg, with larger variances shown for C results ranging from 0.02-107mg.

3.4.1.2 Caking properties

Caking test – Agglomeration Index

The agglomeration index utilised a volatile matter residue button (generated via BS ISO 562:2010). One gram of coal was weighed into an enclosed crucible and heated at 900°C in a muffle furnace for 7 minutes. During this time, volatile matter gases were driven off resulting in the swelling of the viscous coal mass. Following creation, the button was inspected whilst referring to set criteria including strength, swelling, and lustre in order to assign a caking score as detailed in Table 1. In order to test the strength of the residue, a 500g weight was carefully lowered onto the button with different scores dependent on whether the residue withstood the weight without pulverising. The index can define coals as caking or non-caking coals depending on the caking score.

The test was carried out four times for each coal sample with the residue buttons analysed in order to provide a suitable average caking score, with a maximum variance of 1 caking score found.

Free Swelling Index (BS ISO 501:2012)

The free swelling index was carried out by SGS Nederland B.V. to the ISO 501:2012 standard. The procedure entails the heating of a 1g coal sample to 820°C in 2.5 minutes whilst in an enclosed crucible, producing a coke button. The coke button is then analysed with a 500g weight, then against the set of profiles shown in Figure 12 with various scores dependent on the profile of the button. The residue button was turned so as to compare the most swollen portion of the button to the profiles.

Table 1: Agglomeration index scoring criteria (Fieldner and Selvig, 1951; Speight, 2012)

Class	**Group**	**Appearance of residue from standard method volatile matter coal determination (BS ISO 562:2010)**	**Caking score**
Nonagglomerating – button shows no swelling or cell structure and will not support a 500 gram weight without pulverising	**NA** (nonagglomerate)	**NAa** – non coherent residue	1
		NAb – button shows no swelling or cell structure and after careful removal from the crucible will pulverise under a weight of 500 grams carefully lowered on button	2
Agglomerating – button shows swelling or cell structure or will support a 500 gram weight without pulverising	**A** (agglomerate) – button dull black and sintered, shows no swelling or cell structure; will support a 500 gram weight without pulverising	**Aw** (weak agglomerate) - buttons come out of crucible in more than one piece	3
		Af (firm agglomerate) - buttons come out of crucible in one piece	4
	C (caking) – buttons shows swelling or cell structures	**Cp** (poor caking) – button shows slight swelling with small cells, has slight grey lustre	5
		Cf (fair caking) – button shows medium swelling and good cell structure, has characteristic metallic lustre	6
		Cg (good caking) – button shows strong swelling and pronounced cell structure, with numerous large cells and cavities, has characteristic metallic lustre	7

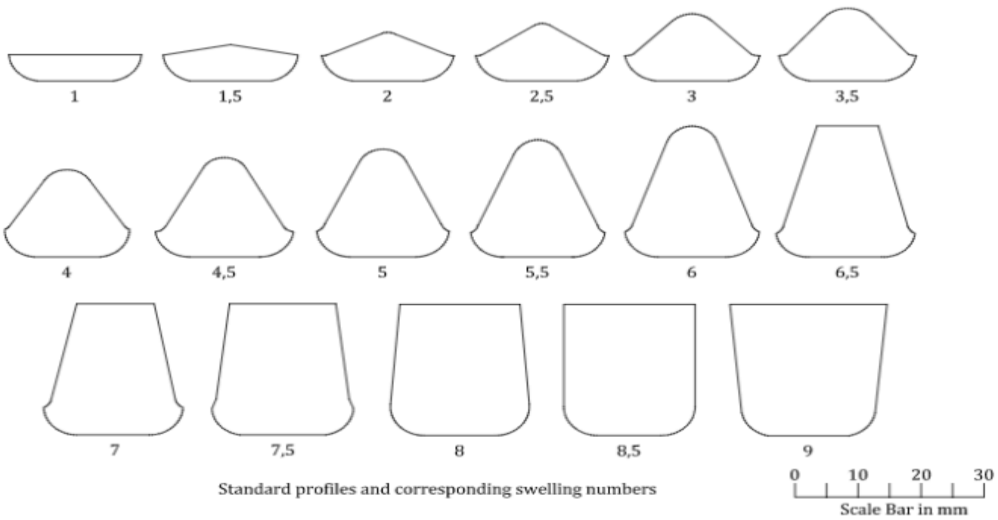


Figure 12: Free Swelling Index scoring criteria (BS ISO 501:2012)

Gieseler Plastometry (ASTM D2639, 2016)

The Gieseler plastometer is an instrument designed to measure the thermo-plastic behaviour of a coal sample by means of a torque stirrer. Due to the specific nature of the instrument, it was not possible to carry out the test personally. As a result, SGS Nederlands B.V. and the Materials Processing Institute in Teesside, carried out Gieseler tests on the range of coal samples with replicable results between both plastometers. The test procedure uses five grams of coal which is heated to the test start temperature of 350°C. It was then heated at a rate of 3°C per minute. Meanwhile, the stirrer revolves through the coal mass, measuring resistance and the dial divisions per minute (DDPM). The DDPM and stirrer speed change with coal fluidity before stopping when the coal mass heats to the resolidification temperature. Key temperatures are recorded including softening temperature, maximum fluidity temperature, and resolidification temperature in addition to maximum fluidity (measured in DDPM).

3.4.1.3 Organic matter

Pyrolysis products test rig

In order to attain the pyrolysis product yields for the coal samples, a pyrolysis rig (shown in Figure 13) was designed and used. A Carbolite tube furnace was used with a heating program running from ambient temperatures to 900°C at the highest heating rate allowed by the furnace – approximately 15°C/minute. With regards to the coal sample, all testing was carried out on granulated size specification coals with 10g sample used. In order to prevent combustion of the sample, a nitrogen flow rate of 2l/m was used. The condensable portion of the coal products were collected via means of an ice-cooled dewar filled with solid CO_2 and 300ml isopropanol. Placed inside the dewar was a glassware tar trap filled with 20ml isopropanol through which the furnace exit gases were directed. Due to the low temperature inside the dewar (approximately -35°C), condensable products (defined as tar by Smith et al., 1994; Miura et al., 2004) were captured within the dewar and weighed in order to quantify. Meanwhile, the gaseous products are not generally believed to condense at this temperature and therefore exit the dewar prior to ventilation. The remaining char is weighed relative to the starting coal with the weight of the tar and char products allowing for the quantification of the gaseous product by difference.

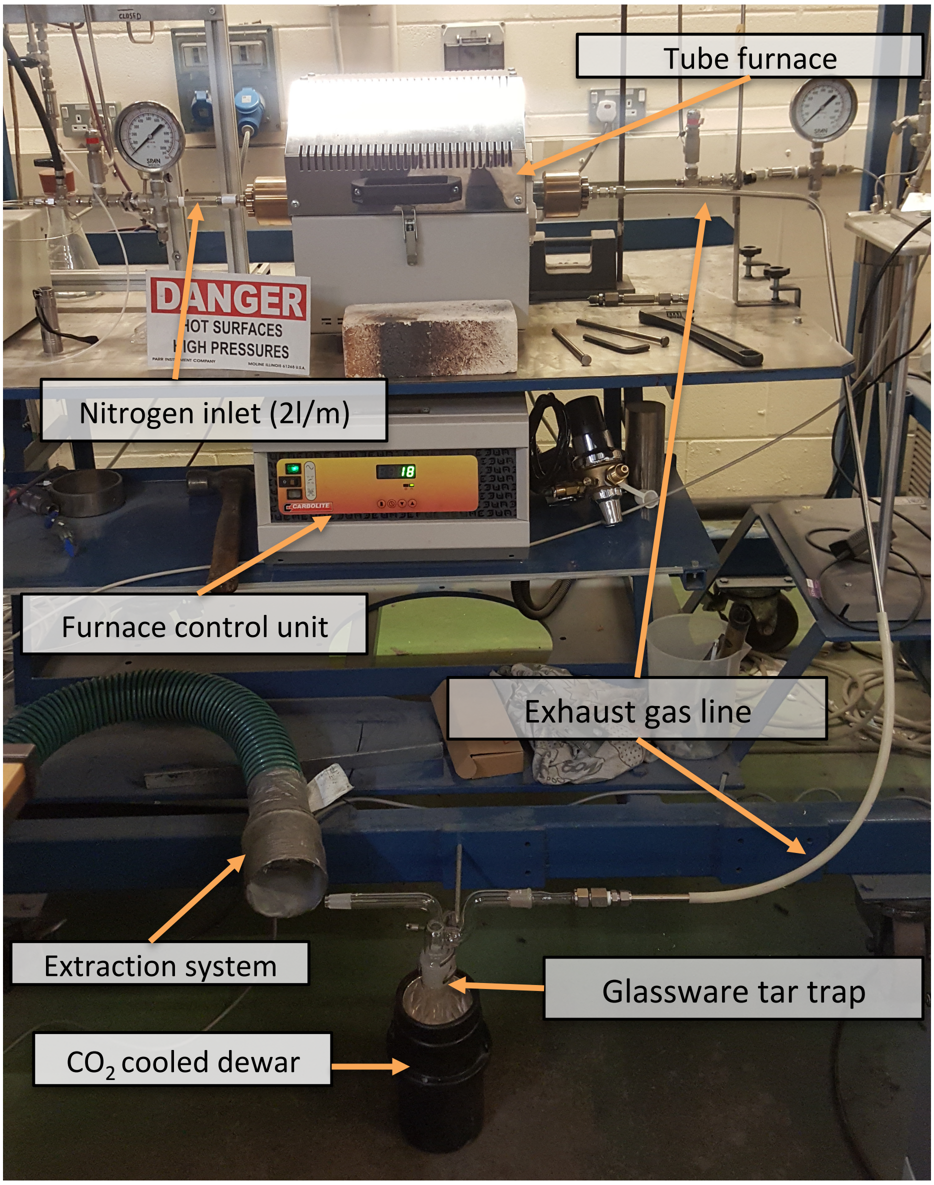


Figure 13: Pyrolysis products test rig showing tube furnace and exhaust gas line leading to tar collection system

Solvent extraction & Gas Chromatography/Mass Spectrometry

GC/MS analysis was carried out in order to assess the relative percentages of hydroaromatic components. Accelerated Solvent Extraction was used to extract the organic matter with a solvent mixture of CH_2Cl_2:Acetone at a 1:1 v/v. Diatomaceous Earth was used as the drying agent with a ratio of 4 parts coal, 1 part diatomaceous earth. Extraction was carried out at a temperature of 100°C and a static time of 5 minutes with the resultant solvent/organic products stored in glass containers (Figure 14).

Figure 14: Post solvent extraction products: (left to right) LV1, MV4, MV3, HV1)

Following extraction, 5 µl coal solvent/organic products were analysed by GC/MS. A Restek Rxi-5ms, 30m x 250µm column was used with the oven heating program as follows: Initial temperature: 75°C for 0.50 minutes, ramp rate 25°C/m to 245°C, ramp rate 4°C/min to 290°C, hold for 1 minute. A helium carrier gas was used with an injection temperature of 275°C. A solvent delay of 3 minutes was applied to the analysis with a scan range of 35 – 550 m/z. When analysing the experimental results, potentially uncertain compounds (highlighted by a Rev Match Factor <700) were not included due to lack of confidence in the result. In order to quantify the various groups, the sum of the spectral peaks for the individual components were totalled, providing information on relative quantities of n-ring hydrocarbons.

3.4.1.4 Mineral testing

In order to study how the mineral portion of the coal might influence agglomeration, ash fusion temperatures were determined. As a high temperature furnace with a suitable observation window was not available, the test was carried out using a muffle furnace with the ash samples removed at various temperatures and visually inspected for signs of softening, hemispherical shape, and flow. The MV4 granulated sample was selected to do this due to MV4 having the greatest occurrences of agglomeration in the DTF. The MV4 ash was created via BS ISO 17246:2010 (as detailed in Section 3.4.1.1) before being moulded into 5x5mm cubes with a drop of water used as the binder (cube shown in Figure 15). The cubes were then heated from room temperature to 1400°C in a muffle furnace, being checked every 50°C to allow the determination of the relevant temperatures when the cube edges begin to soften and alter. Due to the drop tube furnace reaching maximum temperatures of 1100°C, the test was most interested in establishing whether or not the relevant MV4 ash temperatures were above or below this threshold as this would provide insight into whether mineral matter in the coal was melting or softening during drop tube furnace injection.

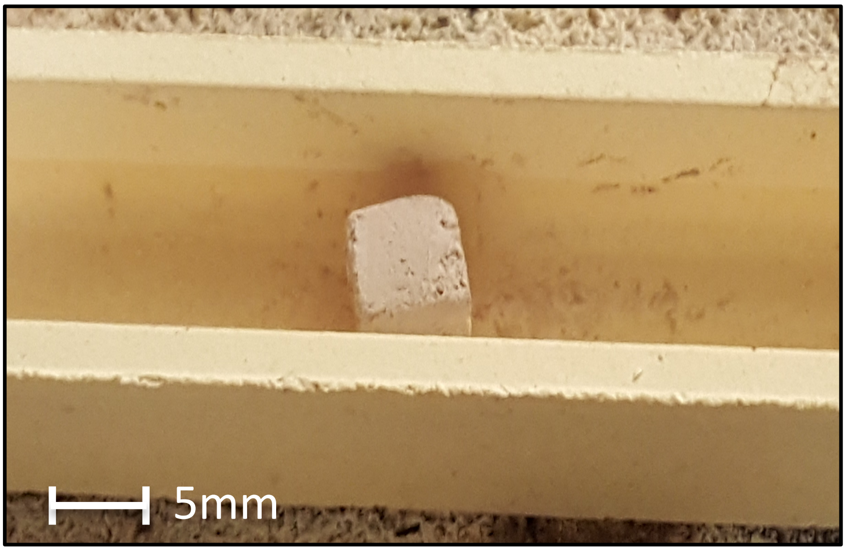


Figure 15: Ash fusion test cube. Ash from MV4 coal created via BS ISO 17246:2919

3.4.2 Laboratory coal injection – drop tube furnace

The DTF injection process is detailed in the following section. An image of the DTF is shown in Figure 16 with the collection probe inserted into the furnace alongside a DTF schematic.

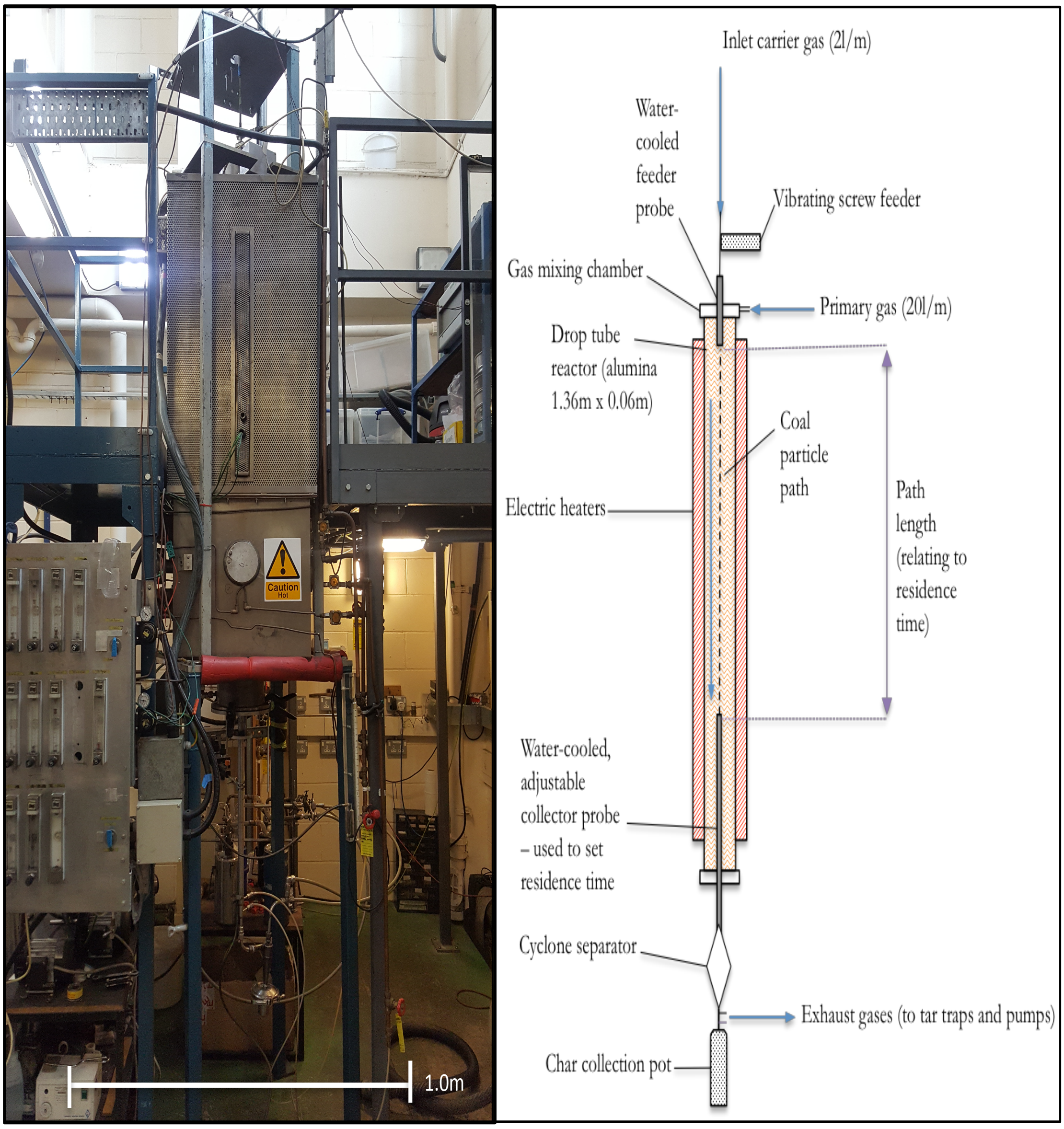


Figure 16: Image of drop tube furnace alongside schematic diagram. Diagram shows main inlet gases entering the top of the furnace with exhaust gases leaving through collector probe. Adjustable collector probe in order to set variable residence time

The key DTF operating specifications used in this work are listed below.

- DTF temperature: 1100°C
- Coal injection rate: 0.5g/min
- Particle residence time: 35ms
- Laminar gas flow: 20l/min, air

Prior to DTF injection, the coal sample was ground to size specification (granulated: 100% < 1mm, 50% <250μm, pulverised: 100% < 300μm, 50% <75μm) and dried. Each coal run of the DTF was timed to take 30 minutes for 15 grams of coal sample to pass through in order to maintain the same flow rate/flow density for each run. Runs that did not adhere to this time scale were abandoned with the feeder system adjusted to correct this. This was done in order to ensure the coal injection stream remained consistent for all coal samples. The coal particles were injected via a vibrating screw feeder at a rate of 0.5g/min, briefly passing into a nitrogen inlet carrier gas flow before travelling through the heated alumina work tube (1.36m x 0.06m) in an entrained laminar air flow of 20l/m. A particle residence time of 35ms was selected by means of altering the length of the water-cooled collector probe. This shortened the amount of time that the coal particles spent exposed to the heated furnace atmosphere. The water-cooled collector probe acted to quench the coal/char samples before leading to a cyclone trap whereupon the char was collected for analysis. The furnace exhaust gases were drawn via pumps through a system of 9 glass wool tar traps wherein a portion of the gas was directed to an O_2 analyser (Servomex Analyser Series 1400) that was used to confirm when combustion in the furnace was occurring. Each coal was injected into the drop tube furnace for at least two separate 30 minute runs between which the furnace probes were removed and cleaned. As a result, two char samples were created for each original coal sample, with the chars stored in airtight containers prior to further analysis.

The distance required to set a specific residence time is calculated by the velocity of the gas flow using Equation 4 where d = distance between injector probe and collector probe (cm), v = gas velocity (ms^{-1}), s = residence time (ms), whilst a correction factor of 5 was applied to allow for the mixing of inlet gases.

$$d = 5 + (vs)$$

Equation 4: Drop tube furnace residence time calculation wherein d = distance between injection and collector probes (cm), v = gas velocity (ms^{-1}), s = coal residence time (ms), and 5 = correction factor applied

3.4.3 Char analysis techniques

3.4.3.1 Assessing char agglomeration

Agglomerate quantification – sieve classification

In order to assess how much each coal sample had agglomerated during DTF injection, the agglomerated material within the char needed to be separated and quantified with sieve classification used to do this. A size of >1mm was used to denote a particle as an agglomerate (particles visually inspected to confirm) with a 1mm sieve used for this separation. After separation of the >1mm agglomerated material, the agglomerate mass as a percentage of the total char mass was calculated to give the final agglomeration percentages. Two chars were created for each coal sample with the average agglomeration figure of the two chars used to give the final agglomeration percentage. The equation used to assign an agglomeration percentage is shown below, with c_1 = >1mm char material (g), and c_0 = <1mm char material (g).

$$Agglomeration\,\% = \frac{c_1}{c_0}\,X\,100$$

Equation 5: Agglomeration percentage quantification

The DTF probes were removed and cleaned between runs with the chars analysed for agglomeration.

SEM imaging

In order to collect SEM images, the chars were first prepared by placement onto the required SEM stub with a black stickered backdrop used to hold the particles in place. Prior to SEM analysis, the samples were sputter coated in carbon that negated any electron charging in the SEM. An Agar Turbo Carbon Coater was used with carbon adhesive tab coating the sample under a vacuum of 10^{-4} mB. The SEM used was an FEI XL30 Environmental SEM. A range of SEM magnification and contrast parameters were used and constantly tailored in order to gain the clearest image for each particular sample with both back scattered and secondary electron images taken. The secondary electron detector is capable of resolutions of greater than 10nm. The final images submitted in this thesis were chosen as they were representative of the char studied under SEM.

3.4.3.2 Char performance analysis

Combustion analysis – Ash tracer method

In order to assess the combustion performance of the coals, an ash tracer technique was used (Equation 6). The method uses the initial raw coal ash content (A_0) and the ash content of the post-DTF 35ms char (A_1) to provide an estimation of the coal's burnout and combustion performance. The technique used to establish the ash contents was BS ISO 1171:2010 with 1g of sample heated at 500°C in air for one hour followed by one hour at 815°C.

$$Burnout\ \% = \frac{10^4\,(A_1 - A_0)}{A_1(100 - A_0)}$$

Equation 6: Ash tracer method equation used to denote char burnout % (Steer et al., 2015a)

Due to the uncertainties discussed in Section 3.2.3.2, the test was carried out twice per 35ms char in order to establish the repeatability of the method

Gasification analysis – TGA testing

Char gasification testing was undertaken using a Mettler Toledo TGA/D`SC 3+ (Figure 17) with a specifically designed heating program tailored to be as representative as possible to the relevant blast furnace conditions. The 35ms coal chars were prepared for gasification analysis by weighing 10.0-10.9 mg of each char sample into alumina crucibles. Ground chars differed only in that they were ground in a mortar and pestle prior to testing. Sieve analysis of the ground chars ensured they passed through a 50μm sieve. Grinding of the chars in this manner was done in order to remove as many physical differences between the various char samples as possible in order to test the inherent/chemical gasification reactivity of the chars rather than the macro physical structure.

After preparation, both the unground and ground chars were individually heated from ambient temperature to 900°C (heating rate of 20°C/min) and held under a 100ml/min flow of nitrogen. This was done in order to fully devolatilise the chars so as to only test the gasification reactivity of the remaining carbon/mineral structure of the chars. Following this stage the gas flow was switched to 100ml/min of CO_2 as the gasifying agent to commence the Boudouard reaction

($CO_2 + C \rightleftharpoons 2CO$) and gasify the chars. The chars were held at this temperature for 420 minutes whilst the TGA measured mass loss over time.

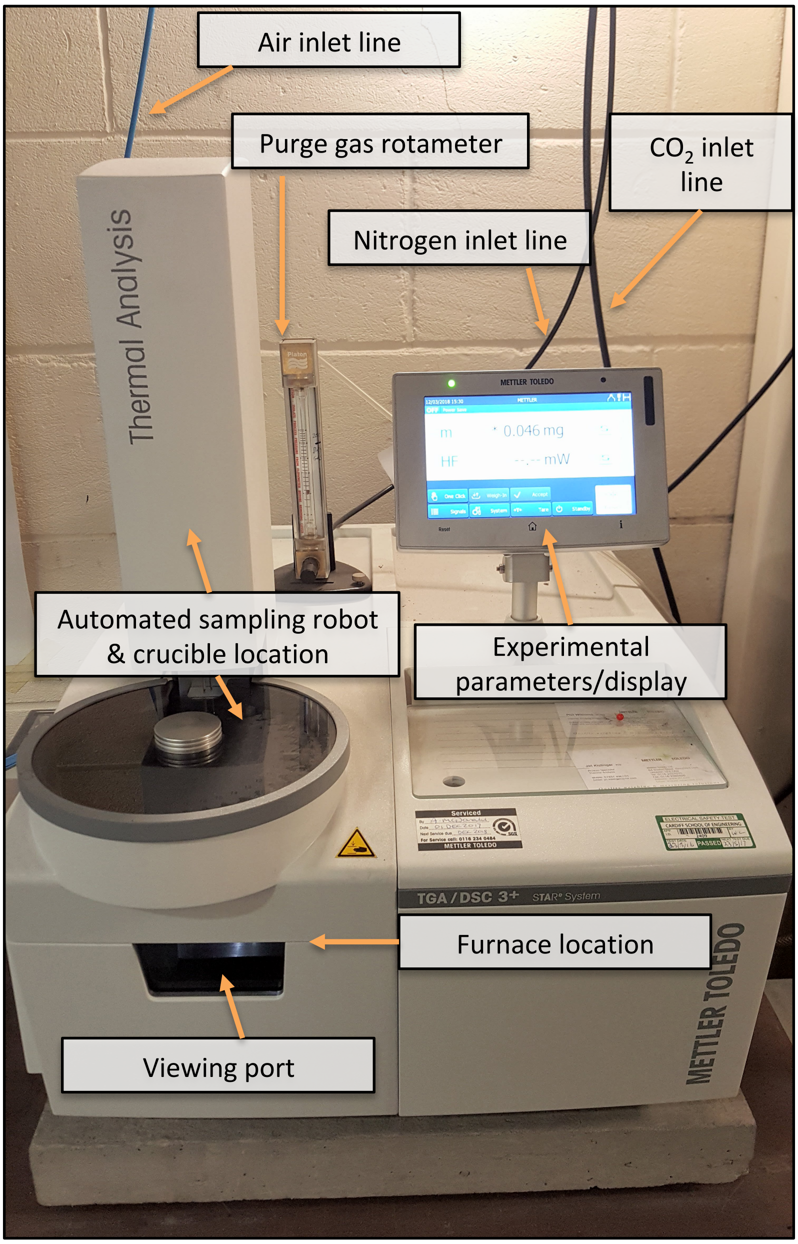


Figure 17: Mettler Toledo TGA/DSC 3 used for char gasification reactivity testing. 10mg char samples used at 900°C under a 100ml/m CO_2 flow

Following completion of the experimental testing, the resultant data was analysed in order to calculate a conversion figure for each char sample. Char conversion (denoted as x) was calculated using Equation 7 with initial mass (M_0), instantaneous mass (M) and mass of ash (M_{ash}) the data used.

$$x = \frac{M_0 - M}{M_0 - M_{ash}}$$

Equation 7: Conversion equation used to produce conversion data for the experimental TGA run

The conversion data was then used to calculate a reactivity indicator for each sample: $t_{0.5}$ – the time in minutes taken for the chars to reach 50% conversion (Zhou et al., 2012; Edreis and Yao, 2016; Cempa and Smoliński, 2017). The faster a char reaches this 50% conversion, the faster reacting/more reactive the char is. As a result, a lower $t_{0.5}$ number signifies a faster reacting and more reactive char sample.

The gasification method was carried out a minimum of twice per char with the average of these two experiments taken as the final indicator of gasification reactivity for that char.

Gasification analysis – specific surface area

Specific surface area determinations were carried out using a Quantachrome Nova 2200e Surface area and pore size analyser. 1g of the char sample was dried prior to vacuum degassing at 120°C for 3 hours. Following this the sample cells were analysed using Brunauer-Emmett-Teller (BET) theory with nitrogen as the adsorbate. 5 specific surface area readings were taken for each sample run and checked for consistency with the average used as the final surface area score and in m^2/g.

3.4.4 Pre-oxidation study

Initially, TGA testing was carried out to study the thermogravimetric changes and to select an effective amount of time to hold the sample at raised temperature for. As mentioned, the testing was carried out under both oxidative and inert atmospheres to allow for comparisons between the two. An isothermal TGA heating program was designed, running at 300°C for one hour with 10mg of dried MV4 used. After one hour the mass loss curves had begun to flatten suggesting that the sample reactions had slowed (shown in

in Section 5.2). As a result, one hour was chosen as the time period to continue pre-heating testing on a larger scale.

In order to produce pre-heated samples for DTF injection and other analysis, a muffle furnace was used at 300°C for one hour with both air and nitrogen atmospheres used to create two samples – pre-oxidised and pre-heated respectively. The dried MV4 coal was placed inside a shallow tray and stirred every 15 minutes to ensure the whole sample was heated/oxidised sufficiently.

Upon creation of the pre-heated samples they were subjected to DTF injection as discussed in Section 3.4.2 and agglomerate analysis using both sieve analysis and SEM imaging. Proximate analyses of the samples were also carried out as per Section 3.4.1.1 as was the caking/agglomeration index detailed in Section 3.4.1.2. The organic constituents of the pre-oxidised coal sample were investigated using the pyrolysis products rig as per Section 3.4.1.3.

X-ray photoelectron spectroscopy

The surface atomic oxygen percentages for the oxidised MV4 coal vs. the MV4 coal were found using x-ray photoelectron spectroscopy (XPS). The survey spectra for the samples were collected with the $O1_s$ peak intensity used to provide the surface oxygen contents. This was carried out using a Kratos Axis Ultra DLD system with a monochromatic Al X-ray source at 144 W; pass energy of 160 eV was used. A sample area of approximately 300 x 700 µm was studied with a magnetically confined charge compensation system used to minimise sample charging. A base pressure of approximately 1 x 10-9 Torr was used throughout spectra collection.

3.4.5 Statistical analysis

Two statistical methods were used to aid in the analysis of experimental results. The methods were used to test the linear relationship between two experimental variables by means of a correlation coefficient. Pearson's correlation (denoted as *r*) was used for the majority of statistical testing alongside graphical depictions of the data. Meanwhile, Spearman's Rank (r_s) was used when a nonparametric test was required as was the case with the ordinal caking data. The resultant correlation coefficients can range from -1.0 to 1.0 with 0 signifying no relationship between the variables and a figure closer to either -1.0 or 1.0 showing strong correlation (Statisticssolutions, 2018). The equations for Pearson's correlation coefficient and Spearman's Rank are shown in Equation 8 and Equation 9 respectively.

$$r = \frac{\sum(x-\bar{x})(y-\bar{y})}{\sqrt{\sum(x-\bar{x})^2 \sum(y-\bar{y})^2}}$$

Equation 8: Pearson's correlation coefficient

$$r_s = 1 - \frac{6\Sigma d^2}{n(n^2-1)}$$

Equation 9: Spearman's Rank correlation coefficient

3.5 Chapter Summary

This chapter provides details of the experimental methods used throughout this investigation in order to assess coal agglomeration under blast furnace heating conditions. Additionally, the relevant data analysis techniques are included. To summarise, the chapter details methods including:

- Sample preparation – from receipt of the coal sample through drying, grinding, and sieve classifications to attain the relevant industrial particle sizes.
- “General” coal analysis consisting of proximate, petrographic, and ultimate analysis.
- Testing of coal caking properties, predominantly the “agglomeration index” used to define general caking. Additionally, information on Gieseler analysis and the Free Swelling Index is provided.
- Coal organic constituents were investigated using a specifically designed pyrolysis rig with tar collection system. Additionally, solvent extraction and GC/MS analysis provided an alternative means of studying the organic materials.
- An integral part of this work is the creation of coal chars in a laboratory coal injection system that replicates aspects of the blast furnace injection system. A drop tube furnace was used to do this with a laminar airflow at 1100°C and a coal residence time of 35ms. These parameters allow parallels to be drawn between coal injection in the DTF and the blast furnace. The DTF used in this work and various other methods included in this thesis are published in Sexton et al. (2018).
- Char analysis to determine how much each sample has agglomerated was carried out using sieve analysis and SEM imaging.
- Analysis of char performance and impact of agglomerates was studied via means of char burnout calculations using an ash tracer method. In addition, char gasification performance was tested via a TGA heating program of 900°C for 420 minutes under a 100ml/m CO_2 reactant gas flow.

- The range of methods used in pre-oxidation are discussed, many of which are shared with other sections of this work.

Chapter 4: Results of Drop Tube Furnace Injection, Agglomeration, and Influencing Coal Parameters

4.1 Introduction

As discussed in Chapter 2, certain types of coals undergo a plastic phase through heating with a number of physical effects occurring as a result. One of the effects rarely considered is the agglomeration of coal particles, often thought to be of little importance in conventional combustors (Shampine et al., 1995).

The work in this chapter aims to investigate the experimental agglomeration of injection coals in a laboratory setting, before assessing whether coal agglomeration during blast furnace injection is a possibility, and furthermore, whether it occurs as a function of coal caking properties.

A drop tube furnace was used to test coal injection under key hot blast parameters with char residues analysed post injection for signs of agglomeration. Testing on a range of 32 samples was carried out in order to ascertain confidence and reliability in the DTF agglomeration method.

Following this, it was necessary to consider and test the coal properties that result in agglomeration, with the aim of establishing a consistent link between caking properties and DTF agglomeration. If agglomeration was believed to be a potential problem for blast furnace operators, a reliable test to predict the effect would be of particular value. A number of coal criteria including plasticity and organic components were also studied for links to coal caking properties.

Additionally, the possibility of agglomeration via mineral matter fusion (Basu, 1982; Carty et al., 1988) as opposed to caking was contemplated and studied.

4.2 Drop Tube Furnace Coal Injection

4.2.1 Agglomerate quantification

In order to assess the potential for agglomeration occurring during blast furnace injection conditions, it was important to utilise an experimental rig that satisfies a number of key criteria relevant to the industrial furnace; namely temperature, heating rate, and residence time. One appropriate technique is to use a drop tube furnace (DTF). With an operating temperature of 1100°C it is capable of subjecting injection coals to temperatures akin to those within the hot blast. In addition, short residence times of 35ms and high heating rates (10^4°C) are also comparable to blast furnace injection conditions. Following initial drying and grinding to size specification, a set of four coals was injected into the DTF at both granulated and pulverised size specification. The DTF reactant gas atmosphere was air whilst a residence time of 35ms was used. The ground coal was injected into the furnace at 0.5g/min with char collected in a water-cooled probe prior to further analysis. The agglomeration sieve classification technique detailed in Section 3.2.3.1 was used in order to quantify and assign an agglomeration percentage per coal. All DTF injections were carried out a minimum of two times per sample following a full furnace cleaning and refitting of collector probe between runs.

The following figure shows the agglomeration percentage for each coal sample that occurred during DTF injection.

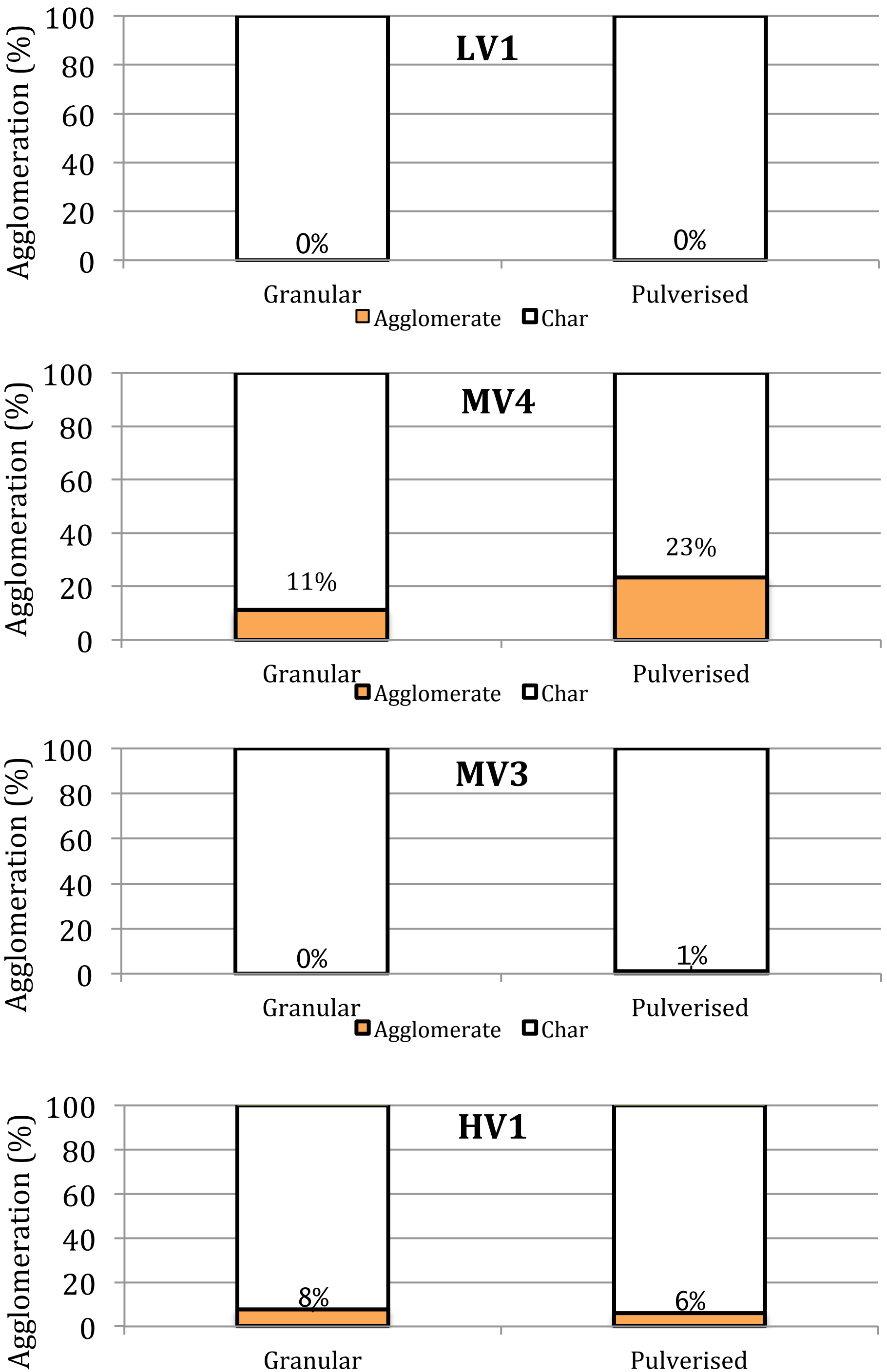


Figure 18: Char agglomeration percentages for drop tube furnace 35ms chars. Chars created under DTF conditions of 1100°C, 35ms residence time in an air atmosphere

As shown in Figure 18, there is significant variation in agglomeration dependent on the injection coal used. LV1 did not show any signs of agglomeration with

100% of the collected char being made up of particles below 1mm. This was the case for both the granulated and pulverised particle sizes meaning LV1 is considered a non-agglomerating coal in the DTF.

MV4 saw consistent levels of agglomeration at both particle sizes with the amount of agglomeration found in the pulverised char at 23%, whilst the granulated sample contained 11%. Following the completion of testing, MV4 proved to be the strongest agglomerating coal sample tested, often causing blockages in the DTF and resulting in numerous disrupted runs; a potential factor in its poor real-world/blast furnace performance.

Despite a volatile matter content similar to MV4, MV3 saw contrasting DTF performance with no agglomeration occurring in the granulated sample and minimal agglomeration of 1% found in the pulverised sample. This shows that volatile content (one of the most common parameters used in injection coal selection) cannot be used as an accurate indicator of a coal’s propensity to agglomerate.

The highest volatile matter content coal HV1 saw regular agglomeration to a lesser extent than MV4 with figures of 8% and 6% for granulated and pulverised samples respectively. The agglomerating coals (MV4 and HV1) caused a number of DTF processing issues including blockages in various locations and gas pressure build-ups. It is also noted that both the MV4 and HV1 chars show examples of finer agglomeration (<1mm) when studied under a SEM whilst LV1 and MV3 do not. These images are provided in Section 6.3.1 when discussing char reactivity.

It is clear that, with a DTF being a largely accepted method of testing blast furnace injection, there is the possibility that agglomeration of some form will occur in the blast furnace, particularly when considering the mechanism for agglomeration and the relatively dilute injection stream in the DTF when compared to the dense coal stream in the blast furnace. Although the extent of agglomeration in the blast furnace cannot be estimated, agglomeration on the scale seen in the DTF has the potential to be significantly detrimental to blast furnace operations, negating the positive impacts gained by grinding the coal prior to injection.

Occurrences of agglomeration in the blast furnace if present are likely to occur upon initial injection of the coal, forming in the vicinity of the injection lances and the early raceway. The presence of agglomerated material may result in greater instances of char accumulation and blockages (common issues regarding coal injection) due to the increased size of the agglomerated material when compared to non-agglomerated chars. Char blockages can result in gas flow issues that cause temperature and pressure build-ups, an overall reduction in furnace permeability, and increased instability, whilst blocked injection lances limit injection and furnace operability. Anecdotal evidence provided by blast furnace operators (personal communication between author and blast furnace technician) has shown MV4 to perform particularly poorly in the blast furnace, negatively impacting blockages, permeability, and furnace stability (M Greenslade, 2015, personal communication, 10 February). This correlates with the experience of injecting MV4 into the DTF, suggesting that agglomerating coals may be problematic when utilised in the blast furnace.

4.2.2 DTF blend agglomeration

To further test the reliability and consistency of DTF agglomeration, the previously injected coals were mixed to a variety of ratios with the most susceptible coal – MV4 being used in every blend. Blending coals is a common practice in the blast furnace (Du et al., 2010; Sahu et al., 2014) so the effects of blending on agglomeration are of much interest and relevance. The coal blend ratios selected were 1:3, 2:2, and 3:1, with the agglomeration figures for 100% coal calculated in the previous section. Due to sample shortages it was not possible to test a MV4:HV1 blend at the pulverised size specification. In order to establish additional confidence in the DTF method, theoretical blend agglomeration percentages were developed based on the agglomeration seen in the whole coals. The actual blend agglomeration was then tested and found to show strong correlation with the theoretical values (r=0.89) and relatively linear agglomeration performance as discussed in Section 4.5.

The agglomeration results for each blend tested are shown in Table 2. It is clear that the addition of MV4 to a blend results in an increase in the amount of DTF agglomeration. It appears that the granulated samples have a more predictable agglomeration behaviour when compared with the more variable results seen in the pulverised blends. This is not altogether unsurprising when considering the nature of the agglomeration effect being largely down to chance collision and particle adhesions. In addition, the pulverised coals consistently see higher levels of agglomeration than the larger granulated size specifications. This is not likely to be a chemical effect (due to precautions taken in the grinding method), rather an impact of the expected increased numbers of individual particles being injected at a specific time and greater total surface area available for agglomeration. Additionally, the violent fragmentation effect that occurs during injection of larger granulated coals (Steer et al., 2015a) will serve to separate individual particles during injection thus reducing the possibility of particle combinations. As a result, the chances of particle collisions and combination for pulverised samples are higher, raising the likelihood of agglomerates forming.

It is clear that MV4 will reliably agglomerate in the DTF in most coal blends. Only two coal blends containing MV4 saw no agglomeration – both MV4:LV1 at 1:3 ratio granulated and pulverised blends. It appears that only a blend with a strictly non-agglomerating coal will mitigate MV4 to the extent that no agglomeration occurs. The relatively linear agglomeration results as the blend percentages change further improve confidence in the consistency and repeatability of the DTF agglomeration method. They additionally provide further clarity on the consistency of agglomeration occurring in specific samples, reinforcing the previous testing regarding the possibility of blast furnace agglomeration.

Table 2: 35ms DTF agglomeration percentages for blended coal samples

Blend size	**Blend ratio**	**DTF agglomeration percentage values**				
		MV4 100%	MV4 75%	MV4 50%	MV4 25%	MV4 0%
Granulated Blends	HV1 0%	11	-	-	-	-
	HV1 25%	-	10	-	-	-
	HV1 50%	-	-	8	-	-
	HV1 75%	-	-	-	7	-
	HV1 100%	-	-	-	-	8
	MV3 0%	11	-	-	-	-
	MV3 25%	-	8	-	-	-
	MV3 50%	-	-	6	-	-
	MV3 75%	-	-	-	3	-
	MV3 100%	-	-	-	-	0
	LV1 0%	11	-	-	-	-

	LV1 25%	-	5	-	-	-
	LV1 50%	-	-	3	-	-
	LV1 75%	-	-	-	0	-
	LV1 100%	-	-	-	-	0
		MV4 100%	MV4 75%	MV4 50%	MV4 25%	MV4 0%
Pulverised Blends	MV3 0%	23	-	-	-	-
	MV3 25%	-	26	-	-	-
	MV3 50%	-	-	16	-	-
	MV3 75%	-	-	-	16	-
	MV3 100%	-	-	-	-	0
	LV1 0%	23	-	-	-	-
	LV1 25%	-	23	-	-	-
	LV1 50%	-	-	19	-	-
	LV1 75%	-	-	-	0	-
	LV1 100%	-	-	-	-	0

4.3 Caking Properties and effect on Agglomeration

After establishing consistent and measureable agglomeration during DTF injection, it is important to consider the relevant controlling properties resulting in the effect. Caking coals are often defined as those that will form a coherent solid residue upon heating (van Dyk et al., 2001). This is opposed to non-caking coals, which are more likely to remain as individual particles. Caking properties are an important factor in coking coal to the extent that almost all coking coals will undergo some degree of caking. Caking properties will be influenced by a number of alternative coal properties such as fluidity, swelling, and coal strength (Speight, 2012). Particle plasticity and fluidity is generally required for a caking coal to undergo physical changes during lower temperature heating.

When considering the effects of caking properties (combination of coal particles to a single residue), it may be that they are linked to the agglomeration found during DTF injection. A test of a coal's caking properties (referred to as the "caking test/agglomeration index" in Chapter 3) by Fieldner and Selvig (1951) was utilised to test the correlation between the results of DTF agglomeration and caking properties of coal. This particular test was selected due to it having a heating rate more relevant to injection than many of the slower heating rate alternatives designed with coking coal in mind. The test utilises a standard volatile matter test residue as produced in BS 562:2010 with the test operator analysing the residue button for evidence of set criteria including swelling, strength, and pore development. Based upon the presence of these criteria, a caking score can then be assigned to the coal. Coals with a score of 5,6, & 7 are defined by the test as caking coals.

The sample residue buttons following the heating procedure are shown in Figure 19 with clear differences between the residues. The resultant caking scores derived from the residues are detailed in Table 3.

Figure 19: Agglomeration Index residues by which caking scores are determined. Clockwise from top left: LV1 residue, MV3 residue, MV4 residue, HV1 residue

Table 3: Coal caking scores as determined by Figure 19 residues and caking index criteria as per Table 1. A low score indicates a coal with minimal or no caking properties, whilst a high scoring coal shows strong caking properties

Coal	**Caking score**	**Coal characteristics**
LV1	1 - NA, NAa	Non agglomerate, non coherent residue
MV3	4 - A, Af	Little swelling or cell structure
HV1	6 - C, Cf	Little swelling, strong lustre, good cell development
MV4	7 - C, Cg	Strong swelling and pronounced cell structure

As is evident in Figure 19, there are distinct differences between the four coal samples, resulting in their varied caking index scores (noted in Table 3). The

LV1 residue has not undergone any caking and has seen minimal physical changes. The residue has remained as a powder with no developments in physical structure. It can be described as a completely non-coherent residue. As a result of this, the lowest possible caking score was assigned to the coal – 1 (NA, NAa) meaning LV1 has no caking properties.

The MV3 coal as shown has seen little to no particle swelling and has no significantly developed cell structures. Rather the original coal powder has formed largely into one solid residue, capable of supporting a 500g weight without pulverising. However, the aforementioned lack of swelling in addition to the dull, black lustre means the MV3 is scored a 4 (A, Af) – a mid-range score though not high enough to define MV3 as a caking coal.

The next highest scoring coal is HV1. The residue button has seen minimal swelling though has good cell development, whilst having a strong lustre and supporting a 500g weight. Ultimately, the caking score of HV1 is limited by poor swelling extent. The resultant score assigned to HV1 was 6 (C, Cf) defining HV1 as a caking coal.

MV4 attained the highest caking score out of the four coals and indeed the highest possible score permitted by the index, outlining MV4 as a strong caking coal. As is clear in Figure 19, the residue has undergone significant swelling far greater than the three alternative coal samples. The button was also strong enough to support 500g without pulverising whilst displaying distinct (interior almost hollow) pore space. As a result of these features, the highest possible score was allocated to MV4 – 7 (C, Cg).

The caking scores shown in Table 3 correlate well with the agglomeration that occurs during DTF injection suggesting a link between the two. LV1 has no caking properties at all and sees no agglomeration. Meanwhile, MV3 also cannot be defined as a caking coal and undergoes minimal agglomeration in the

DTF. Conversely, the two coal samples that the index defines as caking coals, MV4 and HV1, both see consistent agglomeration in the DTF, thus suggesting that agglomeration is strongly influenced by the coal's caking properties. More specifically, the coal that has the greatest caking properties, MV4 also has the tendency to produce the largest quantity of agglomerated material during DTF injection indicating that not only the occurrence of agglomeration but the extent of it is also affected by caking parameters.

In order to strengthen the link between caking properties and agglomeration, caking index scores were generated for 36 varied coal samples including whole coals, blends, and pre-heated samples. These caking scores were plotted against the agglomeration percentages (as calculated via the method used in Figure 18) found when these samples were injected into the DTF with the results shown in Figure 20.

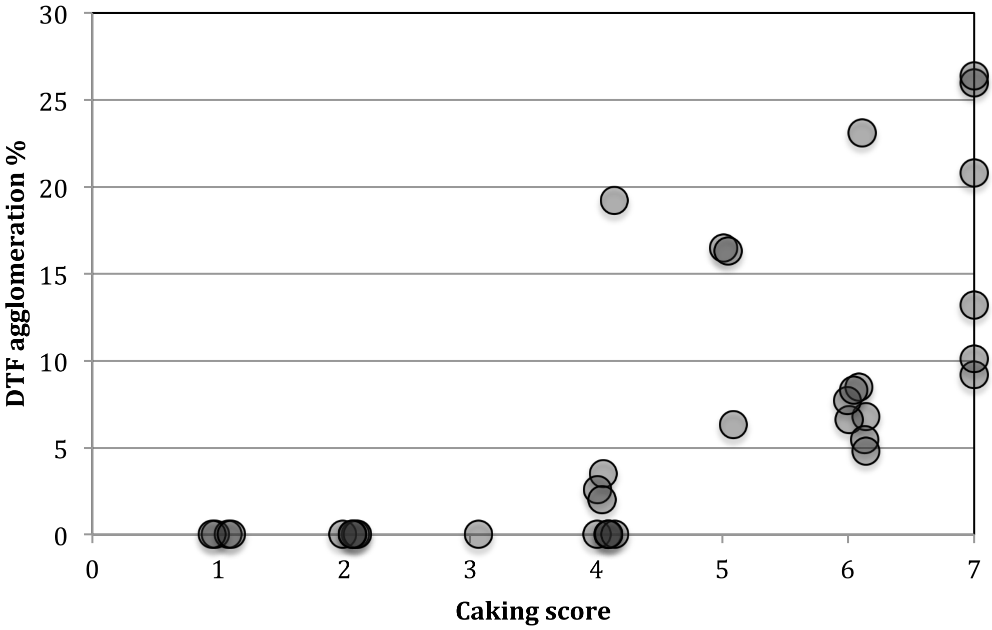


Figure 20: Coal caking scores vs. drop tube furnace char agglomeration percentages for 36 coal samples

This more extensive study of caking properties and the link with DTF agglomeration shows a positive association with a Spearman's rank correlation coefficient of r_s=0.85. The indication is that with an increase in caking score, there is be a higher chance of agglomeration occurring and also occurring in greater quantities. There is a clear split at the caking score of 4 with regards to agglomeration. All 17 coals that score >4 are defined by the index as caking coals (5, 6, & 7) and all undergo agglomeration when injected into the DTF. Conversely, all 10 samples with a caking score of 1, 2, or 3 do not agglomerate at all. The caking score of 4 is the only level at which agglomeration is not consistent with some samples agglomerating and some not; of the coals with a caking score of 4, approximately half experience agglomeration, and half do not. This is likely due to the relatively broad definition for the score of 4, with all coals that form a coherent residue with no swelling being categorised as a 4.

It is evident via these results that the caking performance of a coal is likely linked to agglomeration during injection. Caking coals are more likely to experience agglomeration as a result of a number of developments whilst heating. Due to the likely development of fluidity or viscosity in a caking coal, the particle walls may develop an adhesive texture on the surface resulting in the combination of individual particles that collide during injection. Another property indicative of caking coals: swelling will result in an increase in particle size, the resultant effect of which is to increase the chance of particle collisions. Finally, the strength of the particle walls and binding structure will also be of importance. Formation/combination structures that are too weak will hinder the formation of agglomerated material and be more likely to unsuccessfully combine.

This more detailed study of 36 coal samples further strengthens the results found when initially assessing caking properties; that agglomeration in the DTF is strongly likely to occur when a caking coal is used as the injection sample. As a result of this DTF agglomeration, it is suggested that the use of caking coals in blast furnace injection could produce agglomerated char and the associated negative effects of this in the blast furnace raceway region. This could explain the generally negative performance of the MV4 coal when injected into the Port Talbot blast furnace (M Greenslade, 2015, personal communication, 10 February).

4.4 Potential Factors affecting Caking and Agglomeration

After establishing a link between caking and agglomeration, it is important to consider the chemical and physical factors that bestow caking properties upon a coal. In order to do this the four main coal samples (LV1, MV4, MV3, and HV1) were subjected to a range of relevant tests and analyses that allow insight into the underlying mechanisms behind caking and ultimately agglomeration. Areas of investigation include chemical examination comprising of proximate, ultimate, and petrographic analysis, in addition to examination of the organic constituents. Additionally, a number of performance-based tests have also been carried out in order to assess physical effects and their link with caking (including fluidity measurements, swelling ratios, and pyrolysis performance and products). Due to the heterogeneity of coal, it is possible that the factors behind the caking performance of the four samples vary in each case.

4.4.1 Proximate, Petrographic, and Ultimate analyses

When evaluating the properties of a coal, one of the foremost sets of analysis used is proximate analysis: the determination of the fixed carbon, ash, and volatile matter content of a coal. Proximate analysis is obtained through heating under a set of standard conditions (BS 17246:2010). In an industrial context, this information is typically used as the primary indicator of coal quality and performance. Through liaisons with blast furnace operators, it has been confirmed that the proximate analysis of coal is one of the primary methods used when selecting injection coals, particularly volatile matter content (M Greenslade, 2014, personal communication, 5 November). The proximate analysis for the injection coals studied in this work is shown in Table 4.

Table 4: Proximate analysis for DTF injection coals

Coal (db.)	Proximate analysis		
	Volatile content (wt%)	Fixed carbon (wt%)	Ash content (wt%)
LV1	9.1	79.7	11.2
MV4	17.6	77.2	5.2
MV3	20.2	70.3	9.5
HV1	34.5	58.3	7.2

Based upon the information provided by proximate analysis, there are no indicators that would strongly suggest high levels of caking or agglomeration in MV4 and HV1 relative to MV3. As such, the prevalence of this test in industry when selecting injection coals would not prove useful with regards to coal agglomeration. However, volatile matter content may be a useful tool in ruling out certain coals that will likely not agglomerate. It is likely that coal fluidity is relevant to a coal being defined as a caking coal (for example, LV1). Fluidity is rarely developed by coals with a low volatile matter content (Speight, 2012), likely due to a relative lack of organic tar-precursor compounds that initiate fluidity through a number of mediums (Grimes, 1982; Kandiyoti et al., 2006). This likely explains why LV1, being a high rank, low volatile content coal does not display any caking or agglomerating tendencies. A relatively high ash content of 11.2% is also a possible contributory factor in a lack of caking properties and may also be an explanation for the limited caking of MV3. During caking phases, mineral matter can be generally considered to be inert material due to the low temperatures involved at this stage. As a result, the inert material will generally play little role in the plastic phase (Price et al., 1992). The lack of caking seen by LV1 and MV3 may be influenced by higher mineral contents than the two coals that develop plasticity.

Regarding MV4 having higher caking properties than HV1, there is limited evidence within the proximate analysis that would suggest this. One possibility is that the 20% lower fixed carbon content in HV1 limits the possible caking. As Ryan et al. (1997) contends, a coal must pass through a viscous cement-like phase to solidify particles together in a new physical form. For example, certain coals may display high degrees of fluidity, but limited caking/coking will occur if there is not enough adhesive carbon to bind the grains together effectively.

Following proximate analysis, it is useful to delve deeper by testing the ultimate analysis of the studied coals – the elemental composition. The elements of particular importance to this study are hydrogen and oxygen as a result of the impact they can have on plasticity and caking. It is generally accepted that greater hydrogen content will increase fluidity and greater oxygen content will inhibit plastic behaviour (Speight, 2012).

Hydrogen is known to increase fluidity through a number of media including the presence of hydrogen-rich liquids and oils (Berkowitz, 1960) forming a metaplast (Fitzgerald 1956; Solomon et al., 1992; van Krevelen, 1993). In addition, greater hydrogen-donation and transferability has been found to prolong the plastic phase (Neavel, 1982).

Regarding oxygen, it is well established that the presence of oxygenated groups within coal e.g. ethers is related to the absence of plastic properties (Larsen et al., 1986; Pis et al., 1988; Sanchez and Rincon, 1997). This is attributed to the presence of oxygen functional groups within the coal cross-linking hydroaromatic structures together reducing metaplast generation until higher temperatures, shortening or eliminating the plastic phase. Oxygen groups will also result in the generation of free radicals, linked to shortened plasticity through their combinations with the coal macromolecule (Solomon et al., 1990).

Table 5: Ultimate analysis for DTF injection coals

Coal (db.)	**Ultimate analyses (%)**				
	C	H	N	S	O
LV1	81.35	3.37	1.18	0.89	1.65
MV4	74.93	4.26	0.97	0.64	0.66
MV3	68.90	4.20	1.72	0.14	1.40
HV1	77.39	5.07	1.38	0.84	5.38

It appears via the ultimate analyses shown in Table 5 that there is no strong link between the elemental analysis provided and DTF agglomeration or caking properties. With relatively low/high oxygen/hydrogen contents respectively, it could be expected that MV4 would have greater plasticity/fluidity than HV1, though this is not the case (as highlighted by Gieseler plastometer results shown in Figure 21). In addition, the differences in caking and DTF performance between MV4 and MV3 are unlikely to be predicted by the evidence provided by the ultimate analysis of these samples. The relatively low hydrogen content of LV1 would suggest a lack of plasticity, caking, and agglomeration, which proves to be correct. To summarise, more detailed analysis with a greater range of coals is likely required in order to strongly correlate these factors with caking or agglomeration.

Coal petrography plays an important role in predicting coal behaviour and should be considered an essential part of a coal analysis program (Esterle and Ferm, 1986; Esterle et al., 1994). Regarding the individual maceral groups, the general consensus is that liptinite macerals are plastic in nature (Patrick, 1933; Speight, 2012). However, as a result of their relatively low quantities, their impact on coal properties is somewhat diminished. Vitrinite is also considered to contribute to coal plasticity and, as a result of relative quantities, largely determines plasticity and thus contributes to caking (Kidena et al., 2002). Inertinite has, in general, proven unlikely to plasticise to any great extent relative to the other groups (Maroto-Valer et al., 1998; Kidena et al., 2002) due to its nature as a hard and friable component.

As the petrographic analysis shows in Table 6, despite exhibiting no signs of caking or agglomeration, LV1 contains the greatest percentage of total “reactive” components with a large percentage of vitrinite. However, this can be explained by the variability in vitrinite behaviour (Derbyshire, 1991). In higher rank coals such as LV1, the vitrinite component is often found to be inert. Meanwhile, in lower rank, high volatile coals (19-33%), the vitrinite is found to strongly contain the coking properties of the coal (Derbyshire, 1991). As is the case with the ultimate analysis discussed previously, the petrographic components of MV4 and MV3 do not differentiate or accurately predict the differences in processing performance. Despite MV4 being a far greater caking and agglomerating coal, the amount of total “reactives” between the two coals is very similar. The main indicator of additional plasticity and caking between the non-agglomerating and agglomerating coals is the increased amount of liptinite in the agglomerating coals. However, when drawing conclusions based on this factor it is important to consider that 6% and 10% liptinites are not considered to be particularly high quantities.

Table 6: Petrographic analysis for DTF injection coals

Coal (db.)	**Petrographic analysis**		
	Vitrinite (vol %)	Liptinite (vol %)	Inertinite (vol %)
LV1	83	1	14
MV4	72	6	20
MV3	78	1	20
HV1	71	10	17

Following the proximate, ultimate, and petrographic analysis undertaken, it is clear that there are no strong consistent parameters shown for these four coals that allow for strong links with caking properties or agglomeration with greater certainty required for industrial usage. The strongest indicators suggest a lack of caking for LV1 including higher ash content, low volatile matter, and low hydrogen content. Regarding the remaining samples, MV3 has a number of components similar to the caking coals, though little to suggest it would agglomerate to a lesser extent whilst the remaining two coals agglomerate consistently. As a result, it is evident that more detailed, specific tests are required in order to provide greater clarification on this matter.

4.4.2 Coal plasticity and swelling

As in coke making, in order for coal particles to form agglomerates, there will likely need to be some degree of particle softening and plasticity (van Dyk et al., 2001). This is required to provide a viscous, adhesive surface on the coal particles that upon collision, results in their sintering prior to resolidification. Plasticity is also necessary for coal particles to undergo certain physical changes as is common with caking coals. For example, in order for a coal to swell, it should be slightly fluid in order for the particle walls to expand with the liberation of volatile gas. As a result of these factors, it is likely that fluidity will be a factor in caking properties.

In order to test the plasticity of the four coals, a Gieseler plastometer was used with all coals tested twice (Section 3.4.1.2, ASTM D2639). A number of relevant temperatures were determined and are included in Table 7. In addition, a common test called the Free Swelling Index (FSI, BS 501:2012) was also carried out in order to assess the extent to which the coals swell and how this affects caking. FSI is often used as a method for determining caking properties though is highly dependent on the swelling extent of the coke button. In addition, due to a slower heating rate and lower maximum temperature it is less applicable to DTF injection than the caking index used in Section 4.3. FSI results are also included in Table 7 with possible scores ranking from 0-9+.

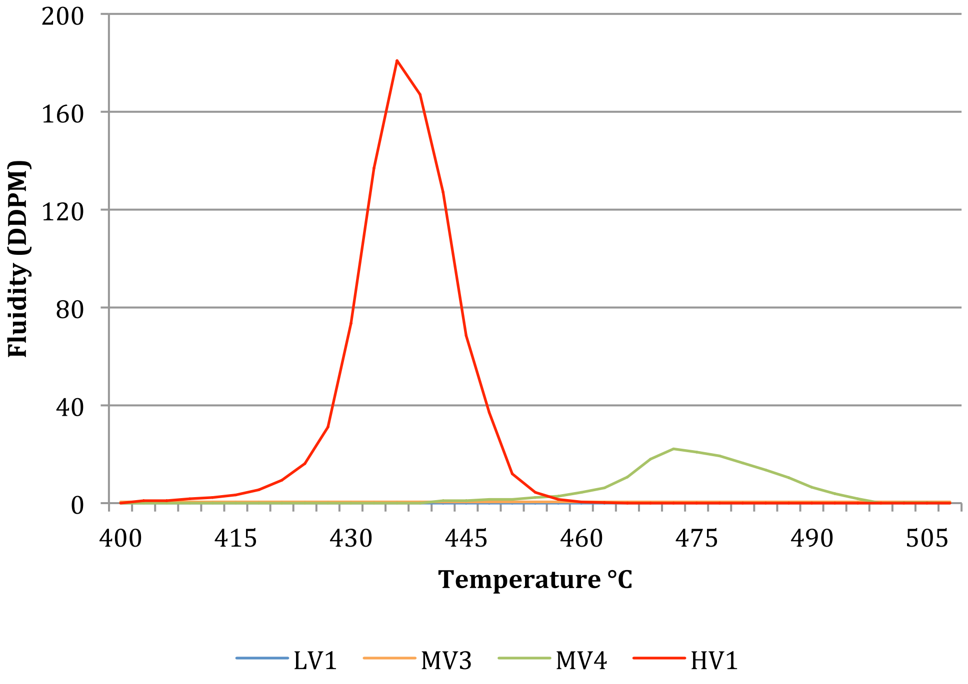


Figure 21: Coal Gieseler plastometer fluidity measurements (DDPM vs. temperature)

Table 7: Free Swelling Index scores and Gieseler plastometer data for the range of injection coals

Coal Sample	**Free Swelling Index Score (0-9)**	**Gieseler Plastometer**			
			Run 1	Run 2	Mean
LV1	0	No softening or fluidity attained via Gieseler plastometer			
MV3	1	No softening or fluidity attained via Gieseler plastometer			
MV4	8.5	Max fluidity (DDPM)	22	21	21.5
		Softening temperature (°C)	442	442	442
		Max fluidity temperature (°C)	472	475	473.5
		Solidification temperature (°C)	502	502	502
		Plastic range (°C)	60	60	60
HV1	0.5	Max fluidity (DDPM)	198	153	175.5
		Softening temperature (°C)	403	418	410.5
		Max fluidity temperature (°C)	435	438	436.5
		Solidification temperature (°C)	463	463	463
		Plastic range (°C)	60	45	52.5

It was not possible to discern any plasticity measurements for LV1 or MV3 due to the fact that neither coal displayed any fluidity throughout the heating program. There are two major differences between the remaining coals, namely the maximum fluidity (measured in dial divisions per minute) and the temperature range at which plasticity is present. HV1 sees greater levels of maximum fluidity than MV4 whilst it also softens and resolidifies at lower temperatures. This can be seen most clearly in Figure 21. The HV1 peak is shown to both rise and fall prior to the most substantial section of the MV4 peak. However, it is important to note that effects of heating rate on coal fluidity is uncertain with varying conclusions found in the literature (Fong et al., 1986; Gerjarusak et al., 1992; Kidena et al., 1998). As the fluidity measurements included for the Gieseler test were obtained at only 3°C per minute, the relevance of these temperatures relative to one another are diminished somewhat due to the rapid heating the coals undergo during DTF and blast furnace injection. However, the time spent under plasticity will be compressed similarly for both coal samples. These results show that the two caking coals that agglomerate in the DTF both see particle fluidity (yet still considered low fluidity relative to typical coking coals which can have scores >1000DDPM) whilst the non-caking, largely non-agglomerating coals do not exhibit plasticity. This lack of fluidity likely explains why LV1 and MV3 have lower caking properties and see little to no agglomeration in the DTF.

On the contrary, MV4 and HV1 have higher caking scores enabled by fluidity and are able to agglomerate as a result. However, these results imply that fluidity is not the dominant factor behind either caking or agglomeration with HV1 experiencing greater fluidity yet lower levels of both caking and agglomeration than MV4. The Gieseler maximum fluidity results for the samples tested show poor correlation with DTF agglomeration and moderate link with caking properties. However, it is believed that surface fluidity of the sample does play a role in providing a viscous “sticky” surface that allow for particles to adhere to one another and thus agglomerate. As such, it is believed that the surface fluidity in MV4 and HV1 promotes particle agglomeration.

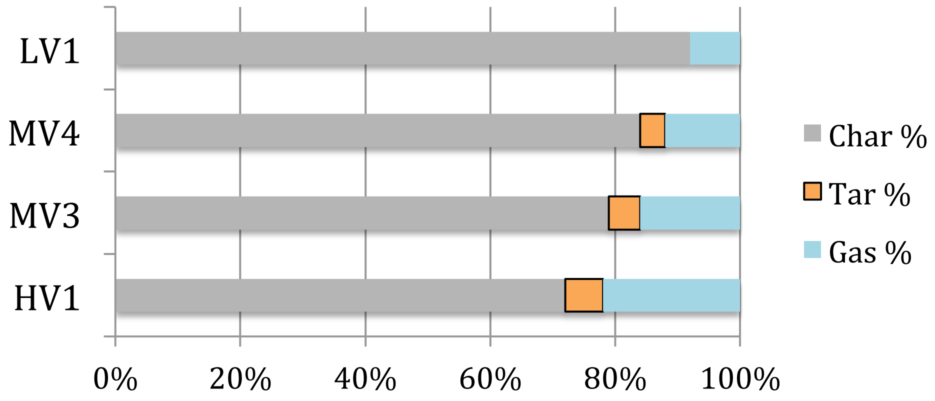
Linking free swelling index with the agglomeration index used prior shows a limited correlation (r_s=0.50) based on the four samples analysed. It is clear that MV4 exhibits exceptionally high swelling properties with a FSI score of 8.5 when compared with the remaining three coal samples (0, 0.5 & 1) as detailed in Table 7. Despite high caking properties as defined by the agglomeration index (score of 6 out of 7), HV1 scores low in the FSI and is not differentiated to any great extent from LV1 and MV3 as a caking, potentially problematic coal. This is a limitation of the FSI in this scenario as the test is too focused on swelling to identify other factors that can identify an agglomerating coal such as the cell development. As a result it may not be as effective at identifying an agglomerating coal on its own (when compared with the caking/test/agglomeration). However, the test can be utilised to provide insight into the coal pyro-plastic properties and show that certain coals likely form differing pore structures during heating which can impact the final particle structure.

4.4.3 Devolatilisation products

Under very high heating rates it is likely that plasticity and caking will occur simultaneously with devolatilisation. This is believed to be the case due to agglomeration taking place during 35ms drop tube furnace injection, whilst the chars are found to have partly undergone devolatilisation during the same time period (e.g. MV4 coal has 17.6% volatile matter content, whilst the post-DTF char has 11.0%).

The prevailing theories of coal plasticity heavily link the fluid metaplast and lubricating components with tar-precursor materials that eventually vaporise as temperatures increase (condensable products defined as tar by Smith et al., 1994; Miura et al., 2004). The effective generation of tar partly governs the degree of fluidity attained by the coal (Kidena et al., 1998). Meanwhile, the gas portion of devolatilisation products can be integral to establishing the physical structure of the resultant particle due to the liberation of gases during heating (Yu et al., 2003b). As a result, it is crucial to establish both gas and tar product yields for the coal samples in order to ascertain how these affect the caking residue.

In order to assess the various product yields, 10g of each coal sample was devolatilised under an inert atmosphere at temperatures rising to 900°C (at a heating rate of ~15°C/min) with the resultant weight yields shown in Figure 22.



	HV1	MV3	MV4	LV1
Char %	72	79	84	92
Tar %	6	5	4	0
Gas %	22	16	12	8

Figure 22: Devolatilisation product yields for DTF injection coals – char, tar, and gas yields

The total volatile matter product yields per coal sample order the same as per their prior volatile matter determination (in terms of ranking amongst the coals).

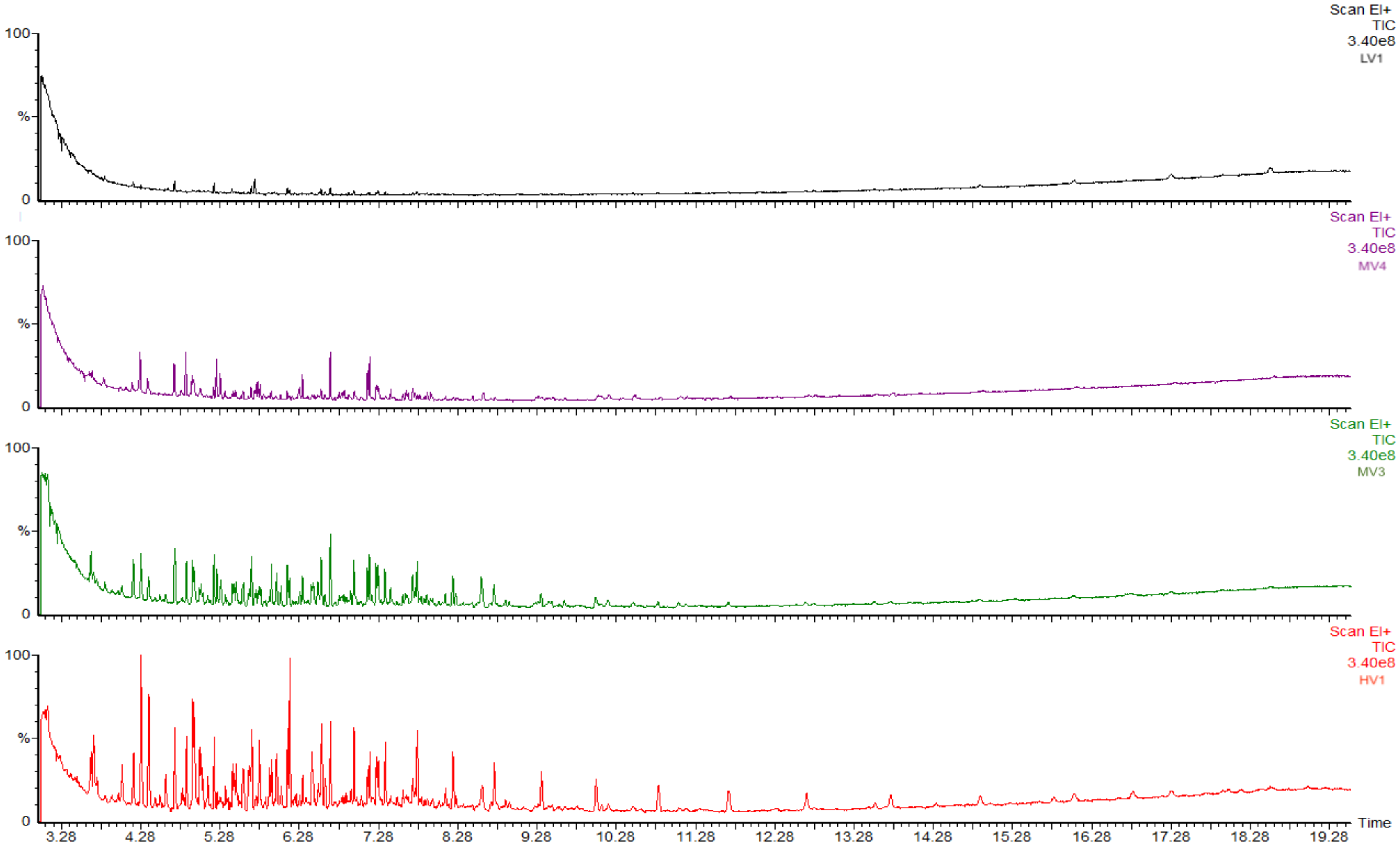
It should be noted that the total yields are mostly lower than in BS 562:2010 standard volatile matter determination due to a lower heating rate used. Gibbins-Matham and Kandiyoti (1988) show that variations in heating rate can alter volatile matter product yields by 8% with higher heating rates resulting in enhanced yields, thus explaining the slightly lower yields shown in Figure 22 relative to the proximate volatile matter contents in Table 4. It is notable that the hydrogen content correlates reasonably well with the amount of tar generated with LV1 containing little tar and HV1 containing the largest percentage of tar.. The tar contents of HV1 and MV4 are not unexpected. Both coals generate a degree of particle fluidity and have strong caking properties; as a result, organic components that generate tar should be present in order to act as lubricants and form metaplast. However, based upon the lack of fluidity shown via Gieseler plastometer, it would not be expected that MV3 had a tar yield greater than that of MV4. It is relevant to note that the fluidity attained by MV4 is minimal – a maximum fluidity of 22 DDPM. Therefore, it is likely that it would only require marginally different components to result in the lack of fluidity shown by MV3. One potential explanation for the lack of fluidity of MV3 is variations in the organic components of tar pre-cursor material (as investigated in Section 4.4.4). Additionally, the marginal properties that result in no fluidity for MV3 could be a combination of minor effects such as the greater mineral content found in MV3 compared to MV4 (9.5 to 5.2 respectively), or the greater oxygen content (1.4 to 0.6% respectively).

As shown, the most tar produced per 10g of coal devolatilised was found in HV1 though only marginally. However, of particular interest here is the high gas yield found. Following the confirmation of large amounts of gaseous volatile matter, it is possible to consider the impacts on swelling and caking properties. Coal swelling occurs as a result of volatile gas liberation during fluidity, resulting in expanding particle walls akin to blowing a balloon. The likely cause for the low swelling property of HV1 (as shown by free swelling index) is as a result of volatile gas liberation resulting in particle wall breakages that can result in wall collapse (Schlosberg, 1985; Khan and Jenkins, 1986; Yu et al., 2003b; Kopak and Toprak, 2007). Due to the higher heating rates involved in the free swelling index and agglomeration index a relatively large quantity of volatile matter gas will be leaving the HV1 particle rapidly meaning the internal gas pressure of the particle will be high. This increases the likelihood of the particle rupturing, resulting in particle collapse and the resultant low swelling properties. Further evidence for this can be seen in SEM imaging in Figure 41 where large pores present can be considered as “blow-holes” (Zeng et al., 2005) where particle rupture and gas liberation has occurred. Conversely, MV4 has a relatively lower gas content that may not cause as substantial internal particle pressures. Additionally, the low plasticity of the MV4 means the particle walls will be less fluid and less prone to rupture, concurring with Yu et al. (2003b) that lower fluidity and high particle wall strength can lead to greater swelling. As such, this may explain the high FSI and caking scores of MV4 relative to HV1.

4.4.4 Hydroaromatic components

When investigating the relatively high caking and swelling properties of MV4 relative to the other samples, it is useful to study the presence of hydrocarbon components in the coal. This was done via solvent extraction of the coals, followed by utilisation of gas chromatography/mass spectrometry. The resultant chromatographs are shown in Figure 23. The primary aim was to provide a qualitative study of any large-ring polyaromatic hydrocarbons in the coals. Additionally, the peak intensities were also used to provide the relative quantities of these compounds in the samples.

Figure 23: GCMS chromatograms for the range of coals tested (Ordered LV1, MV4, MV3, HV1 top-bottom)



It was found that the total yields of organic material aligned with the tar yields established in Figure 22, with organic yields ranked HV1 > MV3 > MV4 > LV1 (greatest to fewest total peak counts). It is generally noted that the hydroaromatic portion of coal is relevant in plasticity due to metaplast formation and presence of donor hydrogen (Neavel, 1982; Clemens and Matheson, 1992; Kidena et al., 1996). Both the total aromatic and total polyaromatic portions of the coals rank in the same order as total organics (HV1 > MV3 > MV4 > LV1) suggesting that the total contents of these materials are not the defining factors in caking properties for these samples (with MV4 not having large quantities, yet having the greatest caking tendencies).

The MV4 scores highly in caking tests due to its significant swelling and also particle strength. Regarding the strength of the residue, additives (e.g. HyperCoal [HPC]) that boost coal caking properties can be used in industry to increase industrial coke strength (Takanohashi et al., 2008; Uchida et al., 2013). These additives are claimed to increase the caking properties of the coal by additional binding of coal particles (Takanohashi et al., 2014). Koyano et al. (2010) found that the addition of 4–carbon ring polyaromatic hydrocarbons (PAHs, e.g. coronene, perylene) to a coal improved coke strength as a result of increased caking, whilst 3-ring components did not have a significant effect. Additionally, Sakimoto et al. (2014) found that coke strength increased with the addition of HyperCoal as a function of the number of aromatic rings in the HPC, increasing with ring number (testing from 1-5 C rings). These large ring components have a relatively high boiling point and as a result are more likely to remain present in the coal during the thermoplastic stage and resolidification. This means they have greater affinity to the post-resolidification coal macromolecule and are able to contribute to particle fusing (Koyano et al., 2010; Sakimoto et al., 2014).

The number of 4≤ ring hydroaromatic carbons in the injection coals were analysed using GC/MS with the total amounts (defined by software as ‘peak counts’) per 5μl coal product shown in Figure 24.

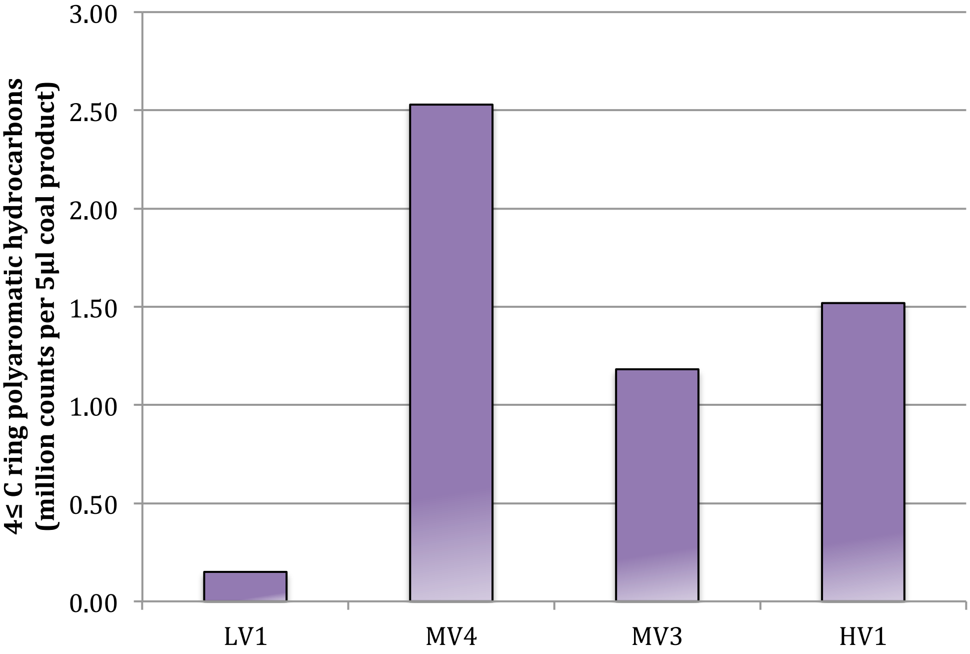


Figure 24: Amount of 4≤-ring polyaromatic hydrocarbons (PAHs) present in the four injection coals

The highly caking MV4 contains the greatest amount of these 4 and higher ring aromatics that are utilised in the literature as “caking additives”. This is despite the lower yields of total aromatic carbons of the MV4 compared with MV3 and HV1. The total peak counts of the 4≤ ring polyaromatics rank strongly with the caking properties of the four coals found in Table 3.

Regarding individual 4 ring polyaromatics, MV4 is found to contain compounds that include triphenylene (boiling point [BP] of 438°C), chrysene (BP of 448°C), benz(a)anthracene (BP of 438°C), 5,6-dihydrochrysene (BP of 448°C), and 7Hbenzo(c)fluorine (398°C). Relative to this, HV1 contains only 8,9-dihydrocyclopenta(def)phenanthrene, whilst MV3 contains relatively low quantities of triphenylene. No 4-ring polyaromatics were identified in LV1. The presence of more of these large ring compounds at higher temperatures may result in their greater influence during MV4's thermoplastic development and contribution to particle fusing, thus resulting in stronger caking/coking as theorised by Koyano et al. (2010) and Sakimoto et al. (2014).

With these materials linked to caking, and the resultant impact of caking on agglomeration, the prevalence of these materials will impact the formation of agglomerated material, with strong binding strength likely required to form agglomerates whilst in an entrained flow.

Although not the main aim for this experimental section, it was noted that the HV1 coal is characterised by aliphatic peaks at the latter retention times (8 minutes and above) relative to the other samples. The most prominent aliphatic compounds found have relatively low boiling points e.g. dodecane (BP of 216°C), undecane (BP of 196°C), and hexadecane (BP of 287°C), though some larger molecular weight compounds such as tetracosane (BP of 391°C) are found. However, the impact of aliphatic materials on coal caking properties is not yet determined with varying conclusions on the importance of short and long chain aliphatic structures (Qin et al., 2010; Li et al., 2016).

When reflecting on the results attained via both GCMS and the various tar yields, it is important to consider the limitations of the small sample size and the heterogeneity of coal, with a greater number of coal samples likely required in order to draw strong conclusions.

4.4.5 Considerations of agglomeration as a mineral effect

Although the literature and previous results strongly suggest that agglomeration in the DTF is a factor of a coal's caking properties, it is still important to test a possible alternative factor – mineral matter fusion. As minerals in the coal are heated at very high temperatures they will deform, soften, and flow, prior to fusing – a potential cause of agglomeration (Basu, 1982; Carty et al., 1988; Khadilkar et al., 2015). These features are generally of more relevance when considering issues of furnace slagging and ash reactor wall build-ups (Speight, 2012). However, due to the possibility of minerals softening and combining potentially causing agglomeration, the role of minerals should be considered and tested. This was done in a number of ways including visual inspection and physical testing of agglomerated material, microscopy methods, and relevant ash tests. For the purposes of this, MV4 was selected as the agglomerated material to analyse due to the amount of agglomerated sample available for testing.

Firstly, examples of large agglomerates were studied. Many of these were at the scale of a number of centimetres meaning the size of the agglomerated minerals would need to be similarly sized, an unlikely prospect considering the amount of mineral matter contained within the coal. Mineral matter within the agglomerated material can be seen as bright white inclusions (Figure 25). Due to the limited prevalence of these minerals it is highly unlikely they are numerous enough to act as a binder and cause agglomeration. In addition, the physical strength of the agglomerated material is poor. Agglomerates can be broken and powdered between fingers with minimal force suggesting that it is the carbon-based material acting as a binder as opposed to the much harder mineral matter. Meanwhile, broken agglomerates show no examples of large mineral/ash inclusions.

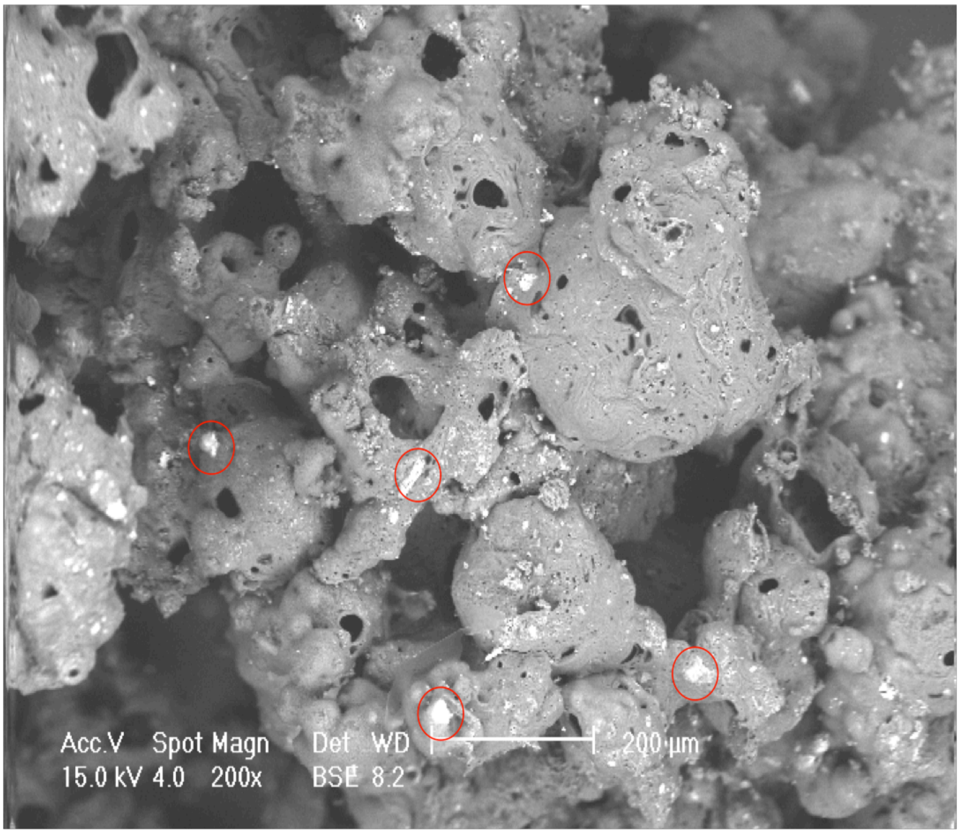


Figure 25: MV4 agglomerated particle showing limited distribution of mineral inclusions (highlighted)

In addition, ash fusibility temperatures were established using a variation of the ash fusion test (BS 540:2008) to show the various temperatures at which mineral matter could soften and potentially cause agglomeration. The resultant temperatures are shown in Table 8.

Table 8: Ash fusion temperatures of MV4 granulated ash

Sample	**Softening temperature (°C)**	**Hemisphere temperature (°C)**	**Flow temperature (°C)**
MV4 ash	1250	1350	1400

When assessing these temperatures it is important to consider the conditions under which agglomeration occurred (1100°C in DTF). The temperatures shown to be relevant by the ash fusion test are noted to be higher than those to which the coal and minerals are subjected to in the DTF. This means that during DTF injection it is unlikely that minerals within the coal particle attained temperatures sufficient to cause fusing and thus cause agglomeration (though not impossible as shown by Stallman and Neavel, 1980). In addition, the amount of time exposed to these temperatures in the DTF is notably lower (35ms) than those in the ash fusion test. These results provide further acknowledgement that mineral matter is most likely not the driving factor behind DTF coal particle agglomeration.

4.5 Repeatability of Drop Tube Furnace Agglomeration

Due to the nature of the agglomeration effect, it is prudent to test the repeatability of the method by running coal samples more than once. As a result of experimental difficulties due to agglomerated material blocking the feeder and collector probes and as such creating furnace pressure changes, a number of runs had to be discounted in order to retain laminar airflow. As such, each DTF run including cleaning and experimental injection could take up to one day dependent on the sample. As a result, duplicate runs per coal sample were chosen due to reasons of pragmatism. The resultant agglomeration for these experimental runs are shown in Table 9.

The chars are found to have good repeatability when considering the nature of the agglomeration effect and the creation/collection of DTF chars. The order of agglomeration from sample to sample would remain the same when considering both the lower and higher agglomerate figures for each char.

Table 9: Agglomerate quantification results – variations between duplicate DTF runs/chars alongside average agglomeration figures and the experimental variance found

Particle Size	**35ms coal char**	**DTF Run 1 Agglomeration %**	**DTF Run 2 Agglomeration %**	**Average Agglomeration %**
Granulated	LV1	0.0	0.0	0.0 ±0.0
	MV4	9.2	13.2	11.2 ±2.0
	MV3	0.0	0.0	0.0 ±0.0
	HV1	6.8	8.5	7.7 ±0.9
Pulverised	LV1	0.0	0.0	0.0 ±0.0
	MV4	26.0	20.8	23.4 ±2.6
	MV3	3.5	0.0	1.3 ±2.3
	HV1	6.6	5.5	6.0 ±0.6

An additional test/accuracy study of the method was carried out when analysing the agglomeration of various coal blends. A theoretical/predicted agglomeration value was assigned to each blend based on the agglomeration percentage of the whole/unblended coal (with the assumption that blends behave as expected based on the blend ratios). Figure 26 plots the theoretical agglomeration values for the blended coals alongside the actual experimental results that were calculated through DTF char creation and agglomerate sieve quantification.

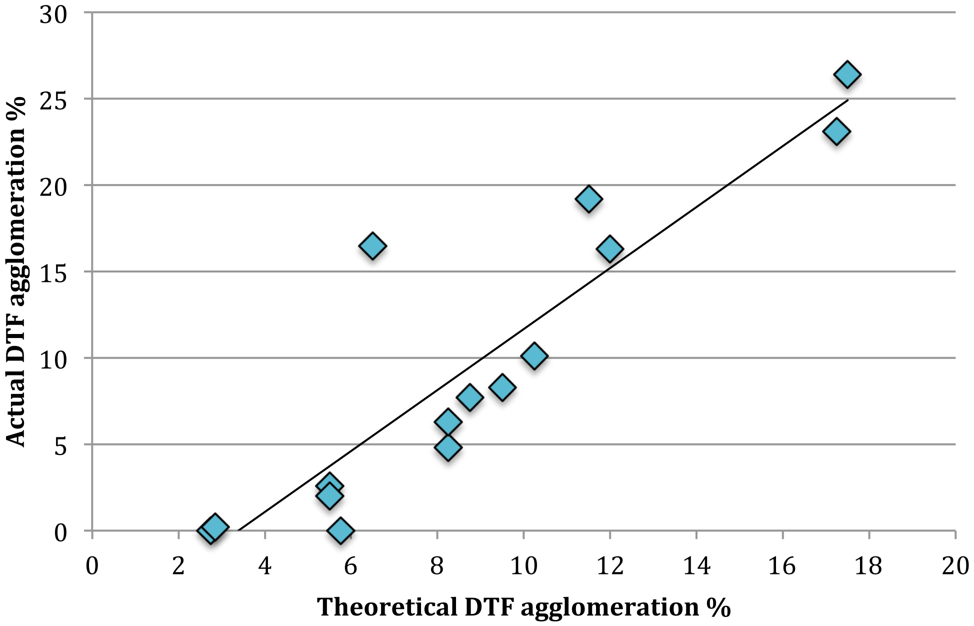


Figure 26: Blend agglomeration: theoretical/predicted values vs. experimental/actual DTF char agglomeration values, calculated via sieve quantification

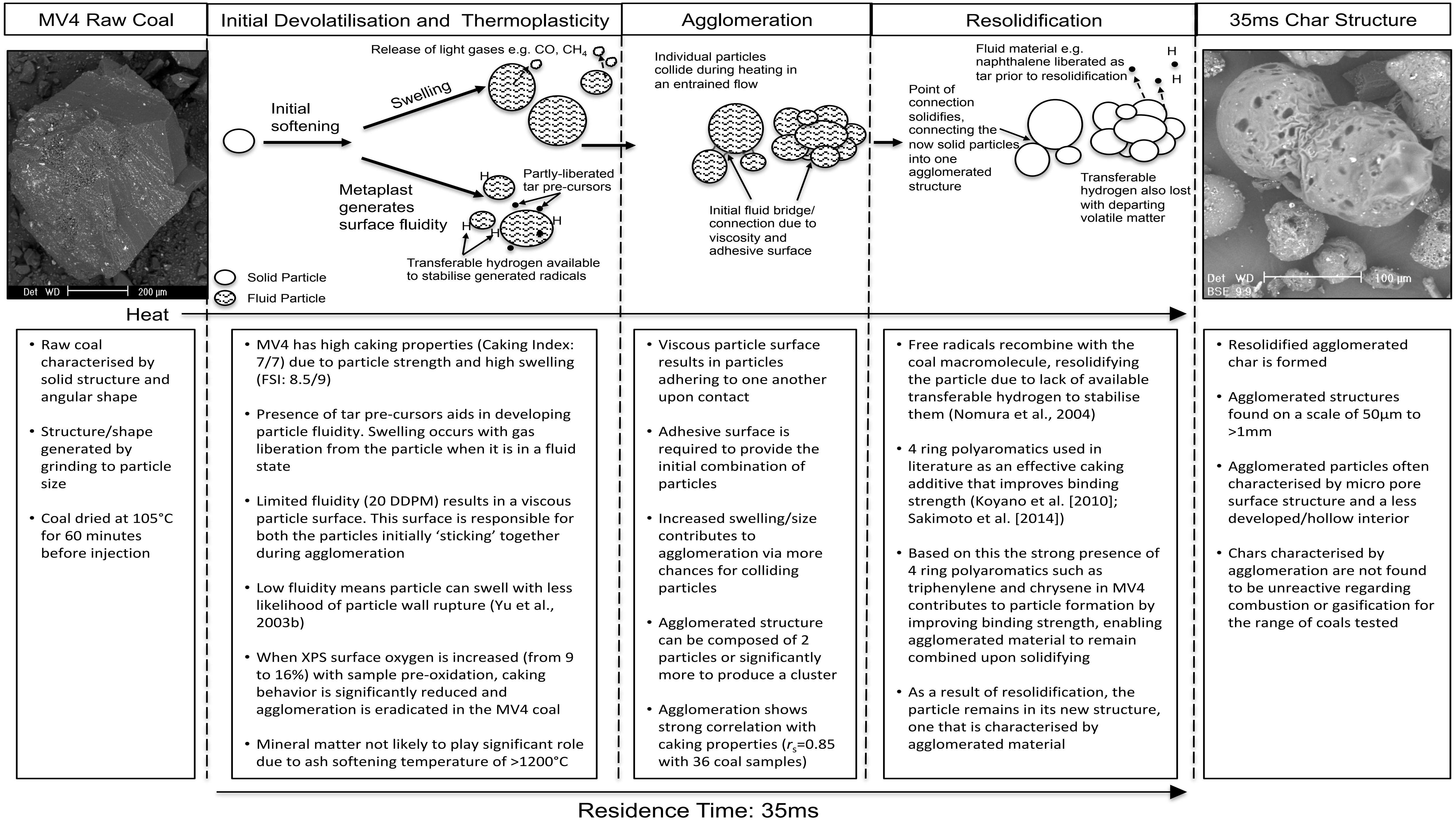
The actual agglomeration values show reasonable correlation with the theoretical values (r = 0.80) with one outlier showing a result that was some distance from the theoretical value. Although there is an area of uncertainty regarding how the blends will perform with regards to agglomeration, the reasonably strong correlation shows that agglomeration in the DTF has some elements of predictability and shows it to be a consistent effect with reliable quantification.

With the drop tube furnace repeatability data in Table 9 and the correlation between predicted and actual DTF agglomeration blend values in Figure 26, there is confidence in the repeatability of DTF char creation and agglomerate formation with a maximum variance from the average of 2.6% in agglomeration. The agglomeration of coals during DTF injection appears to be a consistent effect in certain coals and occurs in blends as would be expected based upon the parent coal blend ratio.

4.6 Schematic Mechanism of MV4 Agglomeration during Drop Tube Furnace Injection

In order to assess the agglomeration mechanism of the heavily agglomerating MV4 coal, it is useful to combine the various influencing factors into a visual model. The following schematic model (Figure 27) displays the effects on the coal particles as they are heated during injection in the DTF. Both the raw coal that enters the DTF and an example of the agglomerated product char collected are shown in SEM images. Meanwhile, the key particle reactions are shown including the devolatilisation and thermofluidity stage, the initial agglomeration, and the resolidification stage that results in the adhering particles solidifying into one agglomerated structure. Below the images are key considerations from the literature and MV4 experimental results that it is believed contribute to the mechanism.

Figure 27: Proposed model for coal particle agglomeration during drop tube furnace injection



MV4 Raw Coal

- Raw coal characterised by solid structure and angular shape
- Structure/shape generated by grinding to particle size
- Coal dried at 105°C for 60 minutes before injection

Initial Devolatilisation and Thermoplasticity

- MV4 has high caking properties (Caking Index: 7/7) due to particle strength and high swelling (FSI: 8.5/9)
- Presence of tar pre-cursors aids in developing particle fluidity. Swelling occurs with gas liberation from the particle when it is in a fluid state
- Limited fluidity (20 DDPM) results in a viscous particle surface. This surface is responsible for both the particles initially 'sticking' together during agglomeration
- Low fluidity means particle can swell with less likelihood of particle wall rupture (Yu et al., 2003b)
- When XPS surface oxygen is increased (from 9 to 16%) with sample pre-oxidation, caking behavior is significantly reduced and agglomeration is eradicated in the MV4 coal
- Mineral matter not likely to play significant role due to ash softening temperature of >1200°C

Agglomeration

- Viscous particle surface results in particles adhering to one another upon contact
- Adhesive surface is required to provide the initial combination of particles
- Increased swelling/size contributes to agglomeration via more chances for colliding particles
- Agglomerated structure can be composed of 2 particles or significantly more to produce a cluster
- Agglomeration shows strong correlation with caking properties (r_s=0.85 with 36 coal samples)

Resolidification

- Free radicals recombine with the coal macromolecule, resolidifying the particle due to lack of available transferable hydrogen to stabilise them (Nomura et al., 2004)
- 4 ring polyaromatics used in literature as an effective caking additive that improves binding strength (Koyano et al. [2010]; Sakimoto et al. [2014])
- Based on this the strong presence of 4 ring polyaromatics such as triphenylene and chrysene in MV4 contributes to particle formation by improving binding strength, enabling agglomerated material to remain combined upon solidifying
- As a result of resolidification, the particle remains in its new structure, one that is characterised by agglomerated material

35ms Char Structure

- Resolidified agglomerated char is formed
- Agglomerated structures found on a scale of 50µm to >1mm
- Agglomerated particles often characterised by micro pore surface structure and a less developed/hollow interior
- Chars characterised by agglomeration are not found to be unreactive regarding combustion or gasification for the range of coals tested

4.7 Chapter Summary

The aim of this work was to test the agglomeration of injection coals in a laboratory environment, and to test whether agglomeration occurs as a function of a coal's caking properties. Additionally, inferences are made towards the possibility of agglomeration occurring during blast furnace coal injection.

In order to test this, a drop tube furnace was used to study the injection of coal under high temperature, high heating rate, short residence time conditions that are comparable to the blast furnace hot blast region.

Initially, four coals (each at two particle sizes) were selected as injection coals and tested in the drop tube furnace with the collected char material analysed for signs of agglomeration. Of the four coals, one did not agglomerate (LV1), one showed limited signs of agglomeration (MV3), with the remaining two samples (MV4 & HV1) agglomerating consistently at both particle sizes. These results in the DTF suggest that agglomeration of some particles can occur under blast furnace initial heating conditions. Agglomeration in the blast furnace may manifest in furnace permeability issues and potentially injection lance blockages. The ratio of large char material in the raceway region would increase resulting in char accumulation, hindering the ascension of gas and obstructing burden descent causing increased pressure build-ups. The overall result would be one of gas flow blockages and furnace instability. It is possible that the agglomeration of MV4 is a factor in the coal's poor real-world blast furnace performance.

In order to establish further confidence in the DTF method and test a possible route of mitigation, a series of fifteen coal blends were injected. The blend performances showed that blending the agglomeration heavy MV4 with non-agglomerating samples would often reduce and sometime eradicate agglomeration. In both whole coals and blended samples, the pulverised sample saw a greater extent of agglomeration than granulated injection. This is likely due to the greater number of individual particles injected at a given time increasing the chances of particle collisions and combination.

After establishing strong tendencies to agglomerate in two of the four coal samples, it was necessary to determine what factors were prominent in causing the effect. An assessment of coal caking properties found that the two strongly agglomerating coals are defined by the method as "caking coals", whilst the remaining two samples are not. Furthermore, the coal that was found to agglomerate to the greatest extent, MV4, scored in the highest caking category possible – C,Cg with a score of 7.

A statistical analysis of caking properties vs. DTF agglomeration was carried out using 36 varied samples. A Spearman's correlation of 0.86 was found indicating strong links between the caking properties of a coal and the likelihood of agglomeration. Results showed there is a point at which the caking properties will likely result in a coal agglomerating. All samples that had a caking score of 5 or above agglomerate without fail in the DTF, whilst the samples scoring 3 or below do not agglomerate at all. The only caking score at which agglomeration is variable as to whether or not it occurs is at a caking score of 4 (with a 4:5 split for these 9 coals). These results suggest that use of a caking coal in DTF and blast furnace injection is more likely to result in agglomerated char material whilst non-caking coal use should not result in agglomeration.

It does not appear that proximate, petrographic, or ultimate analyses are able to accurately predict agglomeration in the drop tube furnace, suggesting that the use volatile matter in selecting injection coals in not suitable in determining how a coal will perform in the blast furnace with regards to agglomeration.

Gieseler fluidity data and free swelling index information provide insight into the caking properties of the samples. Caking is limited in LV1 due to a lack of fluidity, whilst it is believed that the generation of low fluidity in MV4 allows it to develop a viscous nature relative to the more fluid HV1. This allows it to develop significant swelling during volatile gas liberation, thus increasing particle surface areas and increasing the possibility of particle agglomeration. Regarding HV1, a relative lack of swelling is likely as a result of particle wall ruptures and collapse during volatile matter gas liberation (Yu et al., 2003b; Khan & Jenkins, 1986), possibly due to the increase volatile matter gas yield identified in Section 4.4.3.

When analysing the hydroaromatic portions of the coals, it was noted that the MV4 sample contained a greater amount of large-ring (4-ring and above) polyaromatic hydrocarbons relative to the other coals. These materials compose the product HyperCoal which has been found in the literature to improve caking and coking strength by improving the binding strength of a particle (Koyano et al., 2010; Sakimoto et al., 2014; Takanohashi et al., 2014). The greater presence of these materials in the MV4 sample may have the effect of promoting agglomeration.

In order to further establish caking properties as the key coal-based factor in agglomeration, the role of mineral matter was questioned and tested through the study of agglomerated materials ash fusion temperatures. The resultant information confirms that mineral matter is likely not responsible due to lack of mineral quantities and DTF temperatures being too low to engage any significant mineral softening in the coal.

In summary, the various caking properties per coal can be explained by a combination of the physical and chemical parameters of the coal and the ways in which they interact with one another during heating. Based on the correlation between caking properties and agglomeration, it is concluded that the caking properties of a coal go on to directly affect whether agglomeration will occur during injection. As a result, consideration should be taken when considering the use of caking or slightly caking coals in the blast furnace due to potential agglomeration effects.

Chapter 5: Results of Pre-oxidation on Caking Properties, Agglomeration, and Coal Performance

5.1 Introduction

In previous chapters, the link between the caking property of a coal and the effect on agglomeration was discussed, tested, and established. When considering means of mitigating agglomeration, reduction in caking is a clear area for investigation. As discussed previously, a number of factors are integral to a coal having strong caking ability, namely the development of plasticity, strong particle structure, and swelling abilities. Due to the importance of particle fluidity in caking, targeting of plastic properties is considered. It is well established that weathering at low temperatures effectively reduces the thermoplastic properties of coals via oxidation (Maloney et al., 1982; Cox and Nelson, 1984; Wu et al., 1988; Alvarez et al., 1998; Jha et al., 2014; Miroschnichenko et al., 2017).

The periods of time required to sufficiently weather the coal will vary per sample. However, the process can be accelerated through the use of increased temperatures (Guerrero et al., 2013; Fu et al., 2016). The resultant impact is that partial oxidation of coal will result in a reduction or total loss of caking properties (Kavlick and Lee, 1967; Forney et al., 1967). McCarthy (1981) found pre-oxidation to be effective in reducing agglomeration at temperatures of 600°C using a small-scale entrained flow pyrolyser.

The aim of this chapter is to replicate this under DTF conditions more suitable for relating results to blast furnace coal injection. This is in order to test a potential means of quickly mitigating agglomeration of coal via oxidation, thus providing iron makers with a method of utilising caking coals in the blast furnace without risk of the potential negative effects derived from agglomeration. In addition, this chapter will provide additional confidence in the link between caking properties and agglomeration.

Following initial pre-oxidation of the MV4 coal, tests of the samples' caking and agglomeration performance is carried out to establish the effectiveness of oxidation on this particular coal.

After determining the effect on agglomeration in the DTF, the char samples are analysed with regards to combustion and gasification with the aims of inferring what impact agglomeration has on coal performance in the DTF and blast furnace.

5.2 Pre-heating: Inert vs. Oxidative atmosphere

In order to test the process of reducing caking properties through oxidation in the coal, a method was designed with the aims of minimising volatile matter loss and avoiding the engagement of coal plasticity (MV4 initial plasticity occurs at approximately 420°C via Gieseler plastometer). A temperature of 300°C was chosen with a residence time of 60 minutes with the strongly agglomerating MV4 coal sample used for testing. Initial pre-treatment was carried out in both inert (N_2) and oxidative (air) atmospheres in order to highlight changes as oxidative as opposed to thermal effects. The MV4 coal without or prior to pre-oxidation in its standard format will be referred to as either MV4 or MV4 "standard" throughout this chapter.

Initial testing was undertaken using 10 mg of MV4 via TGA analysis with a view towards checking for oxidation and volatile matter loss. Thermogravimetric analysis allows for oxidation to be highlighted by sample mass gain whilst volatile matter loss will be present as mass loss.

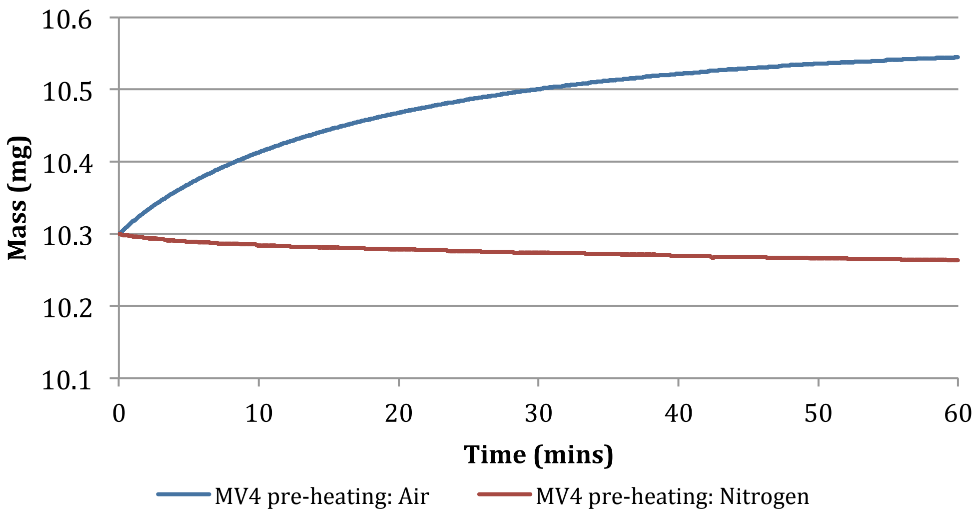


Figure 28: Thermogravimetric analysis of pre-heating MV4 in air and in nitrogen at 300°C for 60 minutes.

As is shown by Figure 28 there is an oxidative effect on the sample when heated in air compared to heating under an inert environment. Heating in air shows a mass increase of approximately 2.5% as a result of oxidation on the available surface of the coal. Contrastingly, the sample heated in nitrogen shows minimal weight change with a minor decrease due to volatile matter losses (volatile matter loss for the oxidised sample hidden by oxygen adsorption). The volatile matter calculations as carried out by BS 562:2010 are displayed in Table 10 showing equal volatile matter losses in the two preheated coal samples.

Following TGA testing, the method was repeated on larger batches of MV4 using a muffle furnace with the intention of testing caking properties and DTF agglomeration.

Table 10: Variants of MV4 proximate analysis and XPS oxygen content following heating at 300°C in air and nitrogen

Coal Sample	**Volatile matter (wt%)**	**Fixed carbon (wt%)**	**Ash content (wt%)**	**XPS oxygen % ($O1_s$)**
MV4 "standard"	17.6	77.2	5.2	8.9
MV4 pre-heated - N_2	16.9	77.9	5.2	n/a
MV4 pre-heated - Air	16.9	77.8	5.3	16.1

5.3 Pre-oxidation effect on Coal Properties

With larger batches of the pre-heated coals now available for analysis, the samples were subjected to the caking test used extensively in Chapter 4, Section 4.3 (test criteria detailed in Table 1). The aim of pre-heating the samples was to clarify firstly, that pre-heating could effectively reduce caking properties in the problematic MV4 coal. Additionally, the effect on agglomeration upon loss of caking is tested. The caking residue buttons are shown in Figure 29 alongside the "standard" MV4 button for reference.

There are significant physical differences between the residues that, as a result, give the samples varying caking scores. As previously established, the standard MV4 coal scores highly in the caking test with a score of 7 due to very strong swelling and cell development. As a result, it is defined as a good caking coal. Regarding the sample pre-heated in a relatively inert nitrogen environment, the caking properties did not change as a result of heating with a caking score of 7. The button is also characterised by strong swelling and is strong enough to support a 500g weight.

'Standard' MV4 caking residue
Caking score – 7, C, Cg

Pre-heated MV4 - Inert (N_2) caking residue
Caking score – 7, C, Cg

Pre-heated MV4 -Oxidative (Air) caking residue
Caking score – 2, NA, NAb

Figure 29: Agglomeration Index residues for MV4 variations showing changes in caking properties with pre-heating

Conversely, the pre-oxidised caking button is vastly altered. Key characteristics noted of the sample are as a weakly held button that cannot support a 500g weight without pulverising. Additionally, the sample was dull in sheen with no cell structure or swelling. The resultant test criteria gave a caking score of 2, NA, NAb as highlighted in Table 11. This signifies that pre-oxidisation has effectively removed almost all of the caking properties of the MV4 sample. This variance in results between inert and oxidative environment concurs with results published by Wu et al. (1988) who found little to no change in rheological properties for their N_2 heated coals relative to those in air.

Table 11: Variants of MV4 caking scores as per BS 562:2010 residues

Coal	Caking score	Coal characteristics
MV4 "standard"	7 - C, Cg	Strong swelling and pronounced cell structure
MV4 (Inert)	7 – C, Cg	Strong swelling and cell structure
MV4 (Oxidative)	2 – NA, NAb	Cannot support weight, weak, dull button shape, no swelling or structure

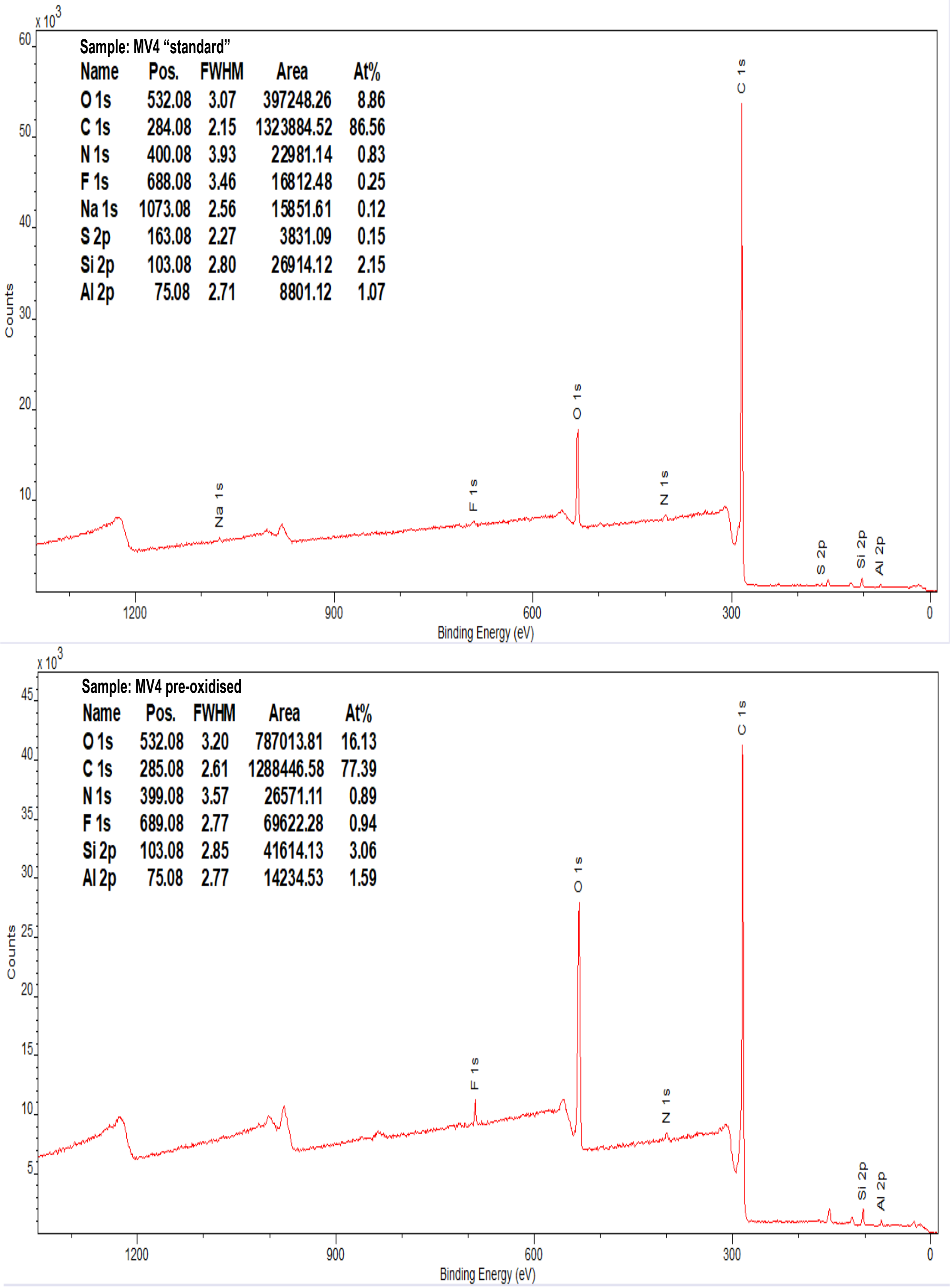
After establishing that oxidation can effectively remove the caking components of the MV4 coal, it is important to analyse the sample further to assess which property changes have resulted in reduced caking.

As discussed in Section 2.4, higher oxygen content can result in lower coal plasticity and caking. In order to assess this, X-ray Photoelectron Spectroscopy (XPS) was used. A survey spectrum analysis of the pre-oxidised coal sample shows a significant increase in the amount of surface oxygen (data shown in Table 10 and spectra in Figure 30).

Whilst the standard MV4 sample gives a $O1_s$ atomic surface oxygen figure of 8.9%, this is increased to 16.1% for the pre-oxidised sample. This increase signifies the likely formation of additional oxygen functional groups and ethers on the surface of the coal (Wachowska et al., 1974; Painter et al., 1981; Gong et al., 1998). As a result of these groups, chemical cross-linking may occur during heating, linking them to the coal macromolecule and aromatic ring structures (Marsh and Walker, 1979; Neavel, 1982). These linked structures mean that bond breakages during heating are limited; reducing metaplast generation before resulting in diminished plasticity and caking. There is no shifting of the $O1_s$ peak with binding energy of 532.08 eV found in both samples.

The carbon $C1_s$ peak sees a shift in binding energy from 284.08 to 285.08eV from the standard MV4 sample to the oxidised coal. It is stated that the $C1_s$ peak will shift to a “slightly higher” binding energy (approximately 0.8eV) with an increase in the amount of sp^3 bonding in the carbon structure of an XPS sample (XPSSimplified.com, 2018). As a result, the shift in $C1_s$ peak binding energy could indicate an increase in sp^3 bonding that may play a role in the limited thermoplastic behaviour of the coal with variations in carbon bonding found to impact coal fluidity (Schulten et al., 1992).

Figure 30: XPS Survey Spectrum for the “standard” MV4 sample and the pre-oxidised MV4 sample



Sample: MV4 “standard”

Name	Pos.	FWHM	Area	At%
O 1s	532.08	3.07	397248.26	8.86
C 1s	284.08	2.15	1323884.52	86.56
N 1s	400.08	3.93	22981.14	0.83
F 1s	688.08	3.46	16812.48	0.25
Na 1s	1073.08	2.56	15851.61	0.12
S 2p	163.08	2.27	3831.09	0.15
Si 2p	103.08	2.80	26914.12	2.15
Al 2p	75.08	2.71	8801.12	1.07

Sample: MV4 pre-oxidised

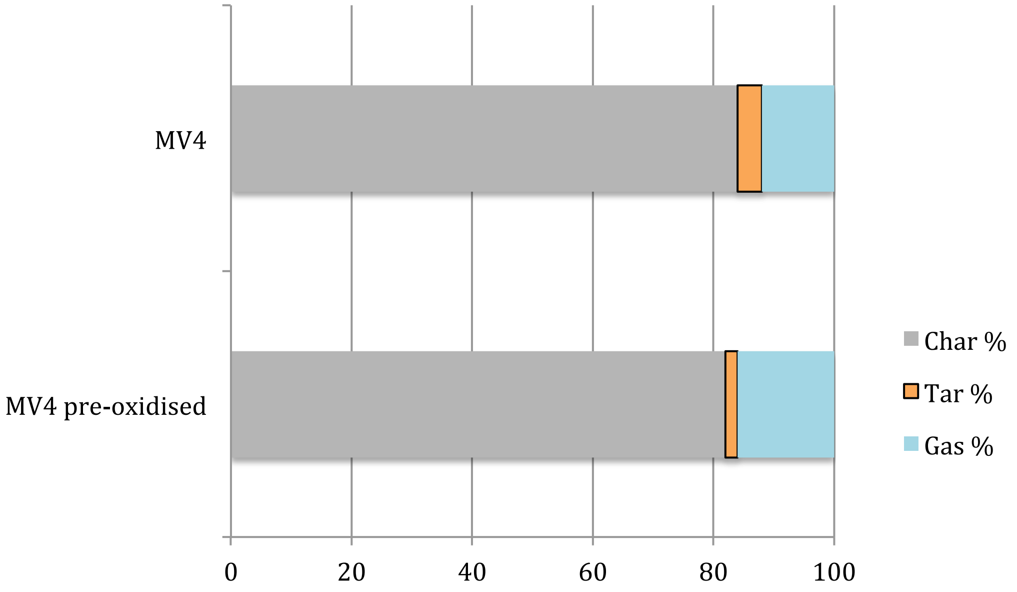
Name	Pos.	FWHM	Area	At%
O 1s	532.08	3.20	787013.81	16.13
C 1s	285.08	2.61	1288446.58	77.39
N 1s	399.08	3.57	26571.11	0.89
F 1s	689.08	2.77	69622.28	0.94
Si 2p	103.08	2.85	41614.13	3.06
Al 2p	75.08	2.77	14234.53	1.59

Also visible are a range of unidentified peaks. It is believed that these are auger electron peaks as opposed to photoelectric peaks, as identified by their broader peak profiles (Gunawardane and Arumainayagam, 2006; Kohli, 2012).

Oxidation is also known to result in a loss of hydrogen (Grossman et al., 1993; Nehemia et al., 1999; Wang et al., 2017), often a key factor in plasticity and caking. The organic components of oxidised samples are often altered with a reduction in tar generation (Schmidt et al., 1940; Wachowska and Pawlak, 1977). Results of ultimate analysis and pyrolysis testing in Chapter 4 suggest that the total hydrogen and tar contents of the samples are not the defining factors in coal caking properties for this range of coals with MV3 containing more tar than MV4 yet lower caking properties. Meanwhile, caking test and XPS results of the oxidised sample suggest it is the presence of surface oxygen functional groups and potentially alterations in carbon bonding that are reducing caking.

Due to the role of tar precursor material in the generation of metaplast, fluidity, and caking (Grimes, 1982; Kandiyoti et al., 2006), the effect of oxidation on these products is considered. A prior pyrolysis method described in Section 3.4.1.3 was used in order to calculate char, gas, and importantly tar yields for the pre-oxidised sample when compared with the standard coal. The resultant data are shown in Figure 31.

It is noted that the pre-oxidised MV4 sample sees a reduction in tar content with tar yield dropping from 4% to 2% of the total pyrolysis products post oxidation. Additionally, volatile gas production increased due to the evolution of oxides of carbon, mostly in the form of CO_2 (Schmidt et al., 1940; Gomez et al., 1956). It is possible that the reduction in tar-bearing components has contributed to reduced caking properties in the oxidised sample by means of less transferable hydrogen present and hydrogen for metaplast generation.



	MV4 pre-oxidised	MV4
Char %	82	84
Tar %	2	4
Gas %	16	12

Figure 31: Devolatilisation product yields. MV4 and pre-oxidised MV4 coal

5.4 Pre-oxidation effect on Coal Performance

5.4.1 Impact of pre-oxidation on agglomeration

Following the testing of pre-oxidation effects on the caking properties of MV4, it is important to investigate whether the effects continue with regards to reducing agglomeration. When considering the caking score of the pre-oxidised MV4 (score of 2), it is useful to study the previous analyses of caking vs. agglomeration discussed in Chapter 4 (Section 4.3); Figure 20 shows that no coals with a caking score of 2 agglomerate in the DTF to any extent, suggesting that the pre-oxidised MV4 sample would not agglomerate. DTF testing was carried out under the conditions used to create chars and agglomeration in Chapter 4 with the char agglomeration percentages shown in Figure 32.

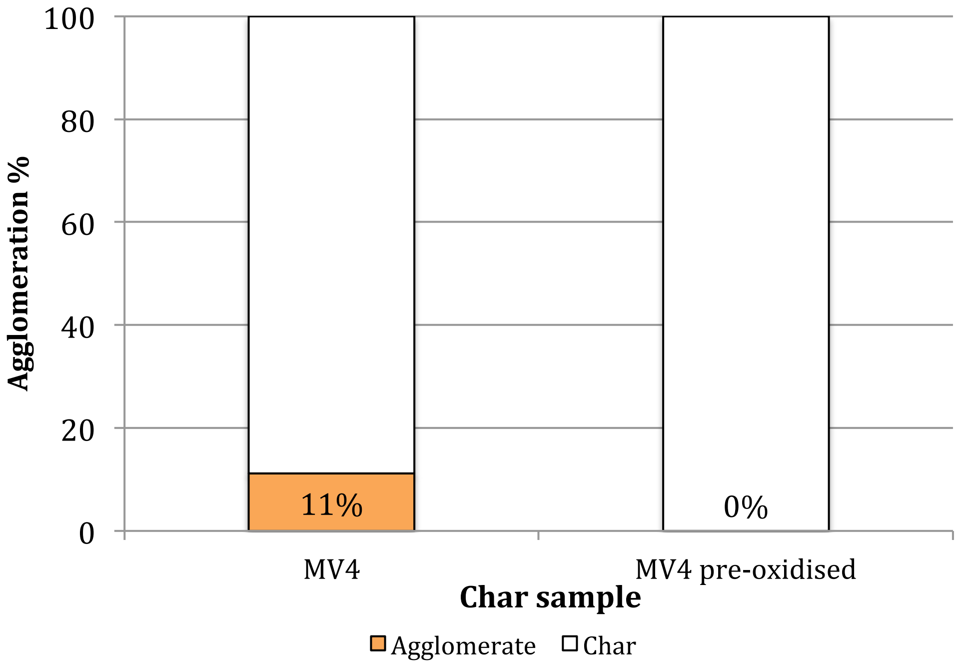


Figure 32: DTF 35ms char agglomeration. MV4 char vs. pre-oxidised MV4 char. Characterised via sieve analysis

As previously established in Section 4.2.1, the standard MV4 granulated coal saw an average of 11% agglomeration in the DTF. This agglomerated material is quantified by sieve classification, and observed in detail via SEM imaging (Section 4.2.1 and 6.3.1 respectively). However, following oxidation prior to injection, agglomerated material is eradicated completely from the char as highlighted by lack of agglomerates detected by sieve analysis in Figure 32. Additionally, no evidence of finer agglomerated particles can be seen within the char when analysed using an SEM as displayed in Figure 33.

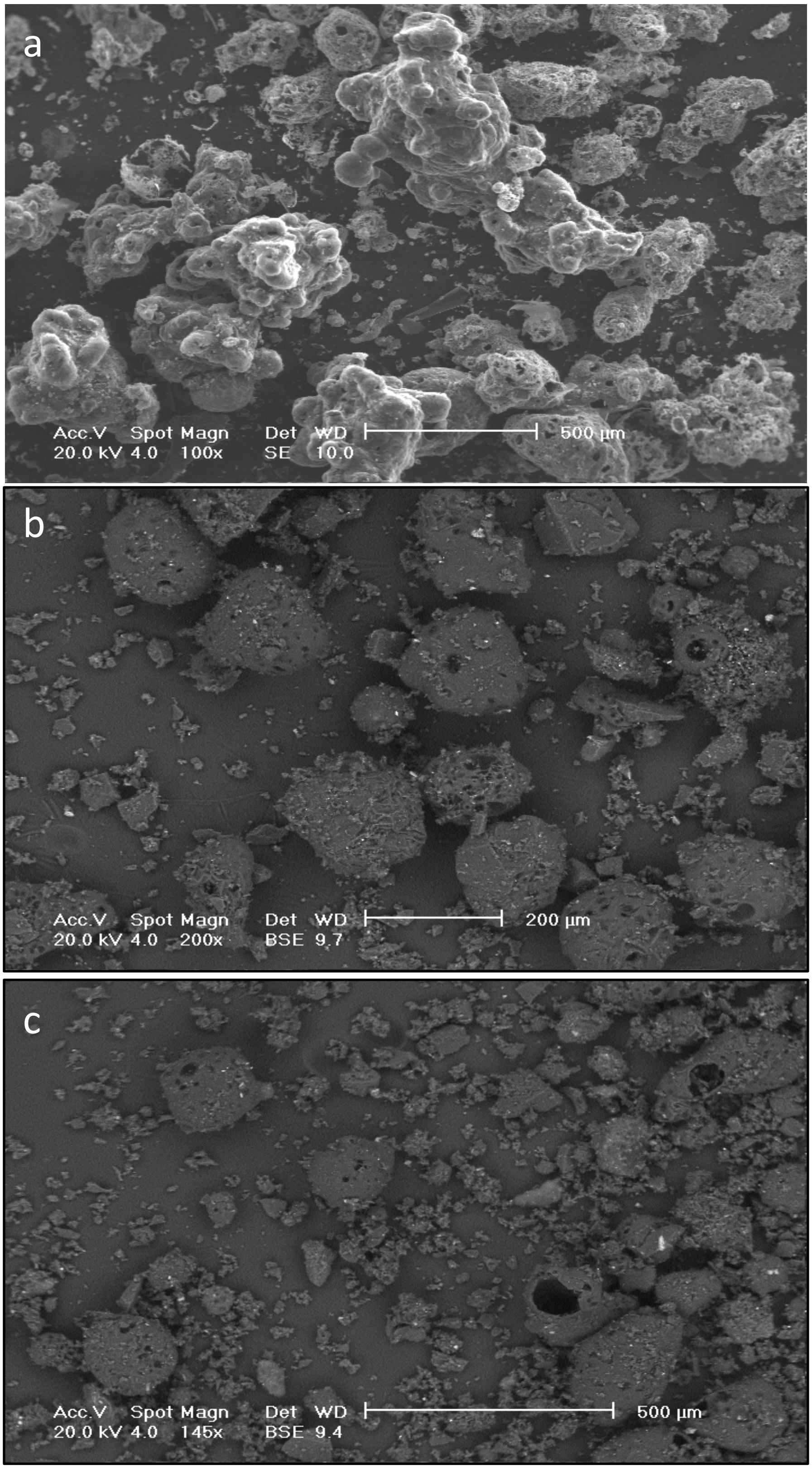


Figure 33: SEM images of “standard” MV4 char (a), and pre-oxidised MV4 DTF char (b & c) after 35ms residence time

When studying Figure 33, it appears that the char is limited to singular particles. There are no signs of the agglomerated particles or clusters that are prevalent in the image of the standard MV4 char shown in Figure 33a and also in Figure 39 (Section 6.3.1). The char particles are generally individual, rounded particles.

These data suggest that that oxidation can be an effective tool in reducing coal agglomeration during DTF high heating rate conditions. The simultaneous eradication in both caking properties and agglomeration further strengthens the link between these two variables. Additionally, the pre-oxidised sample was significantly less problematic in DTF injection than the non-oxidised coal, with no occurrences of probe blockages.

With regards to the industrial impacts, the injection of oxidised coal should reduce risk of potential agglomeration-derived issues in the blast furnace such as blockages and accumulation. As mentioned previously, it is not possible to determine exactly what form agglomeration will take in the blast furnace (i.e. size, shape, strength) though injection lance blockages and char accumulation are potential problems. The reduction of agglomeration should reduce the likelihood of these problems occurring, allowing for more effective coal injection.

5.4.2 Impact of pre-oxidation on combustibility

Although the presence of agglomeration will impact coal performance in the blast furnace, it is also necessary to consider and test other variables; namely raceway combustibility in the form of DTF burnout, and gasification reactivity outside of the raceway via TGA reactivity.

It is generally believed in industry that a more combustible coal will provide optimal injection performance; allowing for increased coal burnout and thus a greater coal injection rate, increasing the coke replacement ratio (M Greenslade, 2014, personal communication, 5 November). Additionally, coals that react more readily in the raceway are less likely to travel deeper into the furnace and accumulate. In order to assess combustibility, DTF chars were analysed using an ash tracer method to infer how much material was lost during DTF injection. Figure 34 shows the burnout percentage of the pre-oxidised MV4 alongside the standard MV4 with both chars collected after 35ms DTF residence time.

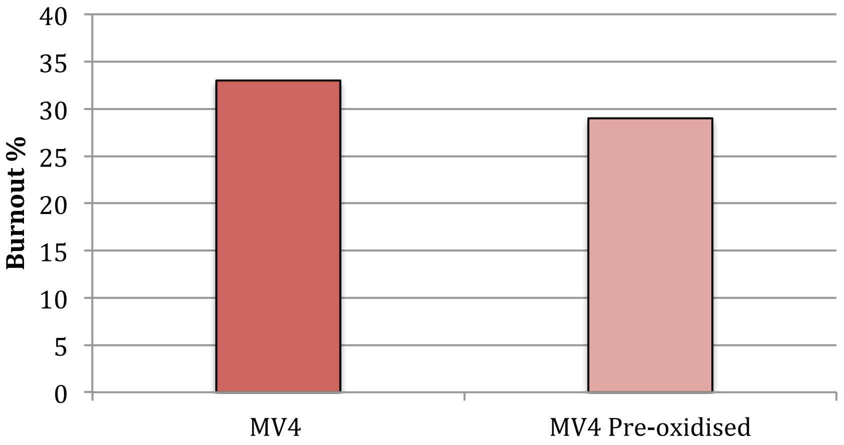


Figure 34: DTF 35ms char burnout. MV4 vs. pre-oxidised MV4. DTF operating temperature of 1100°C with a residence time of 35ms in an air atmosphere

The combustibility of the pre-oxidised MV4 coal has been reduced slightly with a minimal decrease of 4% burnout. For the range of burnouts percentages collected for the total range of char samples (across all coals studied), this is a minor change (burnouts range from 4% to 52%). This suggests that the generation and presence of agglomerates within the standard coal does not hinder the combustion of the coal to a significant extent. As a result, it appears that the presence of agglomerated material during injection in the blast furnace will not result in increased unburnt char leaving the raceway region compared with a non-agglomerating sample. Due to this, it is not believed that the coal injection rate will need to be lower when injecting an agglomerating sample (with regards to combustion performance, also dependent on other factors including char reactivity).

5.4.3 Impact of pre-oxidation on char gasification reactivity

Another key performance factor in coal injection is the reactivity of the char produced. Upon leaving the >2000°C raceway region, furnace temperatures and oxygen availability both decrease (Geerdes et al., 2009; Kamijou and Shimizu, 2000). In this lower temperature (1100-500°C), carbon-rich environment, the driving mechanism controlling char reactivity is internal pore diffusion with gas accessibility to the internal particle being controlled by gas access through the pore structure. It is believed that the physical structure of the char is the rate-limiting factor (Essenhigh, 1981; Prado et al., 1987) with Irfan et al. (2011) stating that the reaction rate is governed by reactant gas accessibility to active sites located on the internal surface of the char.

In order to test char reactivity, a TGA gasification program was utilised with the reactivity derived from $t_{0.5}$ times: the time taken in minutes for the char to reach 50% conversion. The resultant gasification performances for the standard and pre-oxidised MV4 35ms chars are shown in Figure 35.

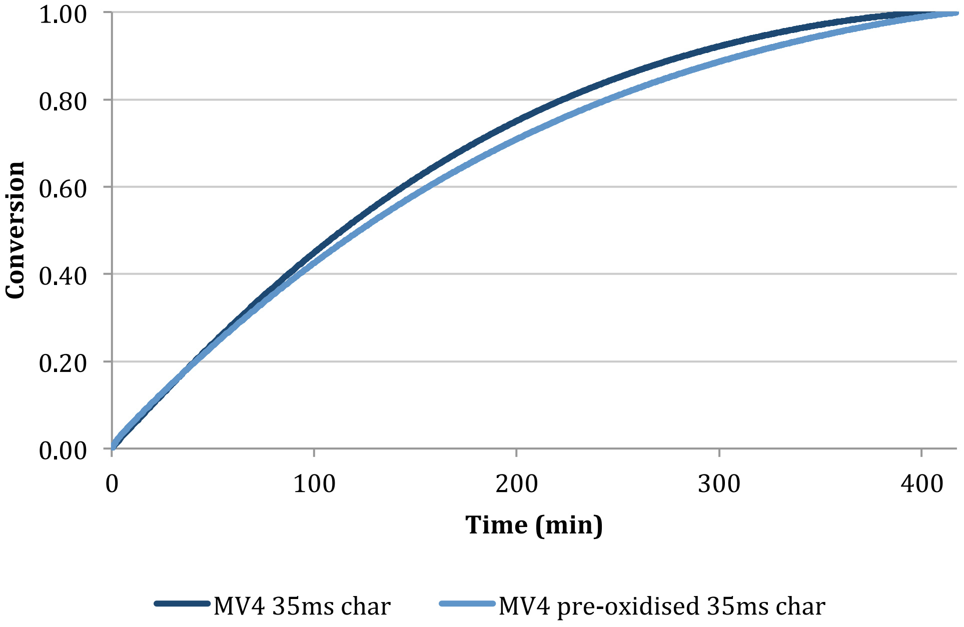


Figure 35: Char gasification TGA curve. MV4 vs. pre-oxidised MV4. Conversion vs. time at 900°C in CO_2. Method standard deviation of 1.3 minutes

As can be seen in the conversion vs. time graph displayed (Figure 35) there is a minor difference in the char reactivity between the standard and pre-oxidised chars with $t_{0.5}$ (50% conversion) figures of 113 and 121 minutes respectively. Note that 0.00 refers to the char at 0% conversion (ungasified), whilst 1.00 refers to complete conversion (only ash remaining). It is noted that for the range of chars gasification times analysed in Chapter 6 (Section 6.3) the time difference between the standard and pre-oxidised chars is minimal and could be attributed to experimental error in the test ($t_{0.5}$ test error ranges from 0 to 19 minutes for all samples tested). Based upon the conventional theories of char gasification, it would have been expected that the pre-oxidised char had improved reactivity due to the differing physical structure as stated by Nelson (1989). Prior SEM analysis shows the standard MV4 char to be heavily characterised by agglomerated clusters and micro pores – features that would not be expected to be conducive to strong reactivity. Conversely, the pre-oxidised char is typically constituted of singular particles with varied pore types. Yet despite the physical variances between the char samples, gasification reactivities are similar. This may be due to their similar specific surface areas (m^2/g) with the “standard” char having SSA of 10 m^2/g and the pre-oxidised char 11 m^2/g. This suggests that, where gasification is concerned, fine char agglomeration is not overly detrimental to char performance, potentially due to the resultant surface area being relatively unaffected.

Regarding char performance in the blast furnace, this result implies that physically small examples of agglomeration will not be significantly problematic regarding char gasification performance, with the char performing in a similar manner irrespective of physical structure (albeit with similar specific surface areas).

5.5 Chapter Summary

The aim of this chapter was to gain additional information and clarification on the process of an agglomerating coal by testing how pre-oxidation of a problematic injection coal affects its caking properties and DTF injection. Additionally, it was possible to analyse combustion and gasification data in order to test how performance varies with and without the presence of agglomeration.

Initially, coals heated at 300°C in both inert and oxidative environments were created and evaluated using thermogravimetry and a caking test. The coal sample heated in an oxidative atmosphere was shown to see weight gain due to surface oxygen adsorption. Crucially, the oxidised sample was found to have significantly reduced caking properties (from a score of 7 to 2) whilst the inert heated coal did not differ from the "standard" coal (caking score remained 7).

Following the reduced caking properties of the oxidised coal, further analysis provided information on factors that are relevant to caking. XPS analysis showed a large increase in surface oxygen of the oxidised coal relative to the standard sample, with theories taken from the literature as to the effects of surface oxygen functional groups on coal plasticity and caking. The coal tar yield was determined, showing reductions from the "standard" sample that would suggest a reduction in metaplast generation during heating – a factor in caking ability.

After determining strong links between caking and agglomeration in Chapter 4, it was necessary to assess whether the successful reduction of caking properties in the oxidised MV4 coal translates to a reduction in agglomeration. DTF injection was carried out with the resultant chars analysed via sieve classification and SEM imaging. Sieve analysis showed that large >1mm agglomerates were eradicated from the oxidised char whilst the standard coal saw 11% agglomeration. Additionally, SEM imaging highlighted the lack of small-scale agglomerated fines in the oxidised sample with the char characterised by singular particles. This signifies that reducing the caking properties of an agglomerating coal can effectively reduce agglomeration under high heating rate conditions.

The combustion performance of the oxidised sample was tested alongside the standard sample with an ash tracer method used to assign a DTF burnout percentage. The non-agglomerating oxidised sample saw minimal change in burnout signifying similar combustibility regardless of agglomeration. This suggests that agglomeration is unlikely to be overly problematic with regards to the combustion of coal in the raceway and the amount of char leaving the raceway unreacted.

With regards to char performance leaving the raceway, reactivity of the non-agglomerated char sample does not differ significantly from the agglomerated char (as is also the case for combustibility). It appears that either the agglomerated material is not particularly problematic physically with regards to surface area and pore structure, or, that the physical structure of the char is less significant than generally considered with an underlying chemical factor being more prominent in deriving char reactivity.

In summary, pre-oxidation has been used as an effective tool in reducing the caking properties of the MV4 coal, due to oxygen adsorption and alterations to the organic components of the coal. As a result, the potentially problematic agglomeration effect is eradicated during DTF injection. Regarding coal performance, the presence of agglomeration does not appear to hamper coal combustion in raceway conditions whilst char gasification reactivity is also relatively unaffected by the presence of fine agglomerated material in the char.

Chapter 6: Performance Testing of Agglomerating Coals in Blast Furnace Conditions

6.1 Introduction

With regards to the performance of agglomerated coals, it is important to consider the performance upon injection into the raceway region, and also how the resultant char will perform in the furnace cohesive zone and stack. This chapter firstly assess the impact of agglomeration during initial injection into the raceway via use of a drop tube furnace to study coal injection in conditions that are comparable to hot blast combustion conditions. Coal burnout is used in order to evaluate combustibility of the agglomerated samples.

Following this, the performance of coal chars upon leaving the raceway and entering into a carbon rich, lower temperature environment is tested using a TGA. A gasification test method is applied to various coal chars with a reactivity indicator assigned based upon the sample conversion over time. This allows for an insight into the char performance deeper in the furnace, where char accumulation is problematic.

Using these methods, the key performance criteria of the coals are assessed, providing details of performance upon initial injection through to the latter stages of the coal particle lifespan.

6.2 Coal Combustion

Following the initial injection of coal into the blast furnace, the particles are briefly subjected to high temperatures in a relatively oxygen rich environment (Kamijou and Shimizu, 2000). Under these conditions, oxidation rates are controlled by the external diffusion of oxygen to the particle surface (Essenhigh, 1981; Prado et al., 1987), highlighting surface area available for reaction as a key parameter. Coal combustion in the raceway is an important consideration as it affects the amount of coal that can be injected; coal with a high burnout allows a higher injection rate thus increasing the coke replacement ratio. Meanwhile, poor burnout can result in operational issues, chiefly through reduced permeability due to unburnt char.

In order to assess combustibility, an ash tracer method (Steer et al., 2015a; Steer et al., 2015b) has been used to ascertain a burnout for each coal sample. The burnout percentages given in Figure 36 show how much the coal has reacted during the 35ms residence time in the 1100°C DTF reacting in air, signifying the combustibility of the coal.

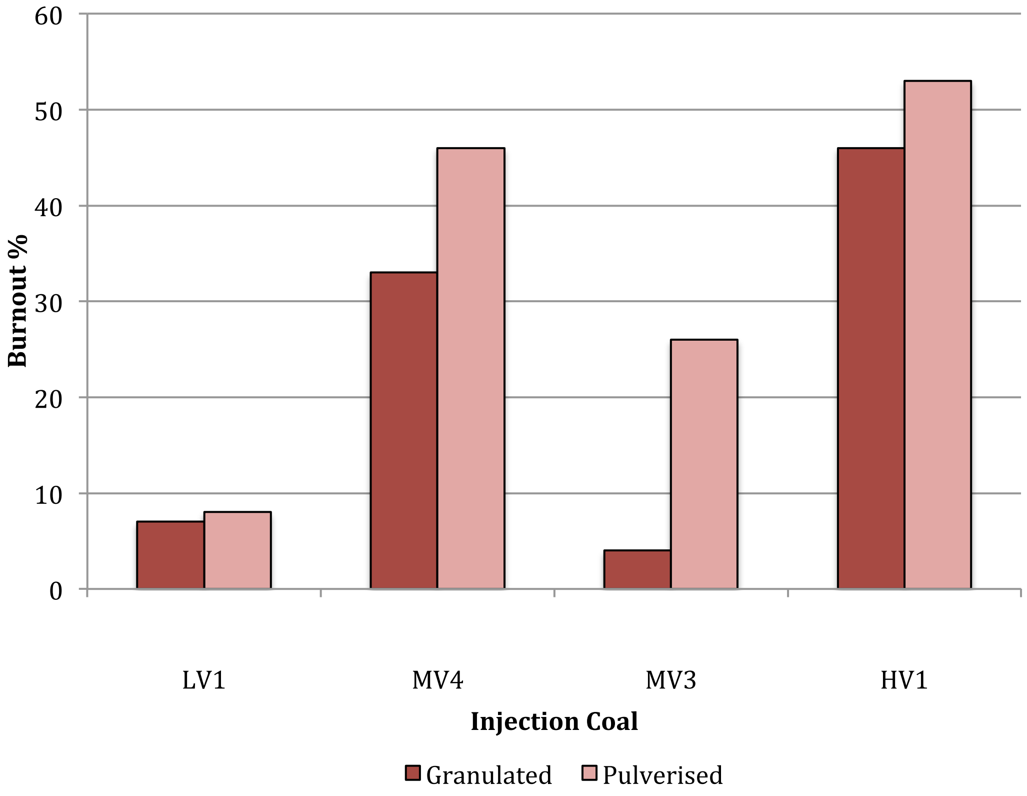


Figure 36: DTF 35ms char burnout for the range of coals at both granulated and pulverised size specification

It is clear that there is an increase in burnout with the injection of pulverised coal particles relative to granulated. All coal samples saw burnout improvements with grinding to pulverised size specification. Due to the mechanisms involved in coal combustion, the increased area available for reaction often results in superior combustion performance for the smaller coal particle sizes as often found in the literature (Barranco et al., 2006; Chen et al., 2007). This suggests that grinding to a smaller size could benefit blast furnace operators with regards to coal performance in the raceway.

However, with the purpose of this work being to investigate agglomeration, it is important to note that the two coals that see consistent levels of agglomeration in the DTF: MV4 and HV1, both have stronger combustion performance upon injection than the non-agglomerating coals: LV1 and MV3. Furthermore, whilst the pulverised sample of MV4 sees significantly more agglomeration than the granulated sample, it also has greater burnout performance. As a result, agglomeration during injection does not appear to negatively affect the combustion performance of the coal relative to the other samples to any large extent (as is also found in Section 5.4.2: pre-oxidised MV4 burnout relative to standard MV4 – burnout is not affected by agglomeration). It is possible that the increased burnout of the MV4 and HV1 coals can be explained by the physical changes provided by the caking properties. Although one of the physical changes is agglomeration, there will also be occurrences of fragmentation and swelling which may impact coal combustion. As a result of the physical changes during initial heating and devolatilisation, with particles potentially becoming more porous and developed, the resultant particle may be better optimised for strong combustion than the non-caking samples that are relatively unchanged physically, often remaining solid.

In order to further test for a link between agglomeration and combustion performance (signified by burnout), Figure 37 displays these variables plotted alongside one another.

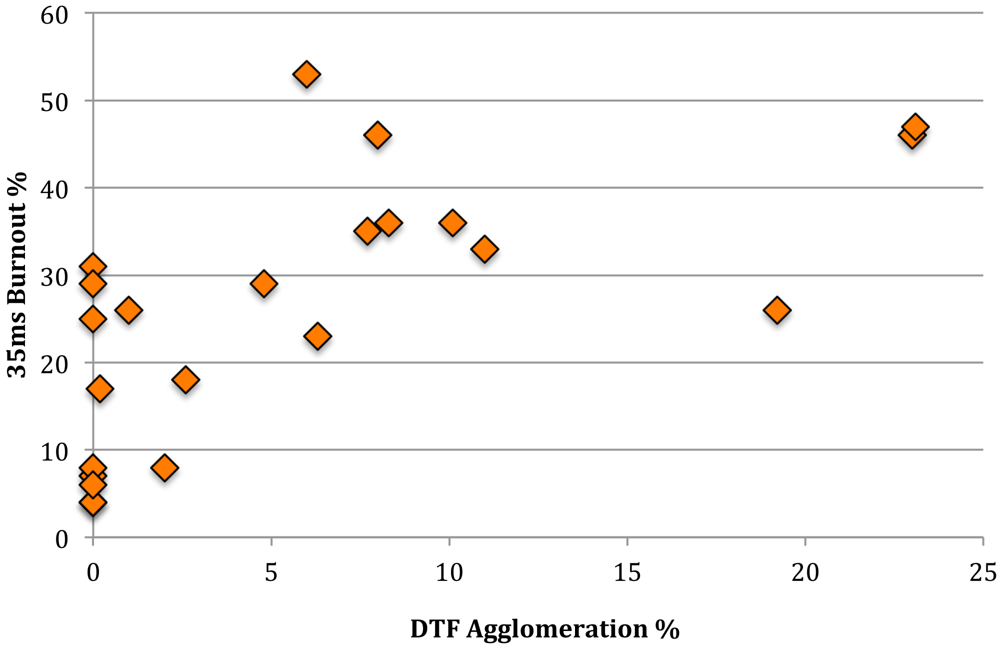


Figure 37: DTF agglomeration vs. burnout percentage for a range of whole, blended, and oxidised coal samples

It is evident that there is no strong correlation between burnout and agglomeration (r = 0.65) with the graph showing no clear linear distribution of the data. A number of highly agglomerating coals are shown to have strong burnout characteristics, suggesting their combustion has not been impacted by agglomeration to any significant negative extent. Additionally, the coal samples that do not agglomerate see a range of burnout scores, from minimal burnout to upwards of 30% (although they are typically weaker with regards to burnout than the agglomerating coals).

Prior to the experimental work being carried out it was hypothesised that the agglomeration effect would result in poor combustion performance. This was based on the fact that agglomeration would result in increased particle size with the transformation of coals from finer individual particles, to more coarse agglomerates. However, as the results show, this does not appear to be the case with strongly agglomerating coals often showing strong burnout performance relative to the range of samples tested. It is believed that the strongly combusting coals will do so irrespective of the impacts of agglomeration (as suggested by minimal burnout change with removal of agglomeration for pre-oxidised MV4 in Section 5.4.2) due to their inherent reactivity, a topic that will be discussed further in the following sections.

6.3 Char Gasification Reactivity

After establishing that agglomeration does not significantly reduce coal burnout in this range of coals, it is necessary to consider the impact of agglomeration on char performance upon leaving the raceway region. As discussed previously, it is common for coal chars to leave the raceway unreacted, with unburnt char consumption being a key consideration in coal injection rates (Carpenter, 2006). Unburnt char can accumulate in the blast furnace where it can result in blockages, whilst reducing furnace permeability and stability (Ichida et al., 1992; Akiyama and Kajiwara, 2000; Dong et al., 2003; Nogami et al., 2005).

The consumption mechanism for unburnt char in the blast furnace stack is gasification via CO_2 in the reverse Boudouard reaction (Steer et al., 2018). Schott (2015) states that a key factor causing permeability issues in the blast furnace is inefficient char gasification.

The gasification reaction in the blast furnace is mostly pore diffusion controlled (Essenhigh, 1981; Prado et al., 1987) whilst Irfan et al. (2011) state that char gasification rates are governed by the accessibility of reactant gas to the active sites on the internal char surface. It is claimed that low reactivity will occur when a particle has a relative lack of large “feeder-pores”, thus resulting in lowered gas diffusivity due to access through smaller micro-pores.

With these factors in mind, it is clear that the presence of agglomerated material within chars has the potential to limit char gasification reactivity by increasing accumulation and affecting blast furnace permeability and stability. As a result, the gasification performance of the chars was tested via TGA analysis.

6.3.1 Char physical structure

In order to establish the impacts of agglomeration on char reactivity, it was prudent to examine the chars for evidence of agglomeration and determine how prominent the effect is in the resultant DTF chars with scanning electron microscopy used to do this. Additionally, the link between char reactivity and char physical structure is also assessed. The following SEM images (Figure 38-Figure 41) show a number of char particles that are representative of the coal chars with the images taken from both 35ms granulated and pulverised chars. Large-scale (>1mm) agglomerates are removed from the chars following DTF collection (due to uncertainty around the form of larger agglomerates in the blast furnace) to allow the study of smaller examples of char agglomeration that it is believed are more likely to be present in the blast furnace in a similar manner. These large agglomerates make up a minority of the total char collected. Particular attention has been given to the MV4 chars due to the prevalence of agglomeration in this coal. To aid in viewing, the SEM images have been annotated, with the following labels used: I = agglomerated particle(s), II = reacted singular particles, III = physically unreacted particles, and IV = mineral matter.

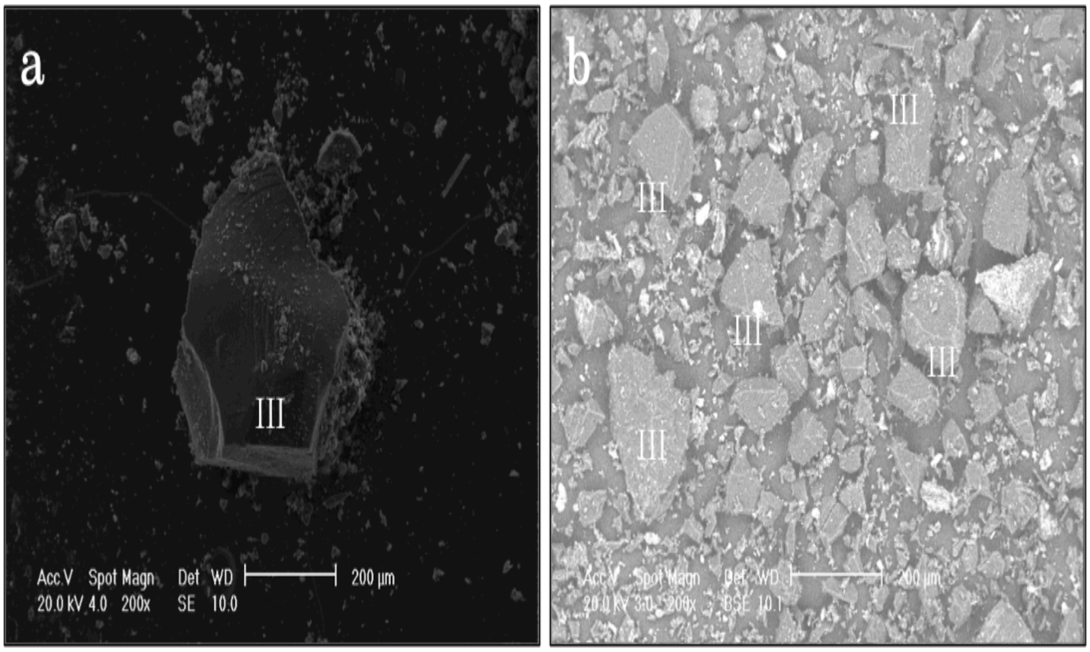


Figure 38: SEM images of post DTF 35ms LV1 chars: a) granulated, b) pulverised. Images contain: III = physically unreacted particles

Figure 38 confirms the lack of agglomeration of the LV1 sample with no examples of combined, agglomerated material. Both the granulated and pulverised chars strongly resemble milled raw coal despite their injection through the DTF. This lack of physical change is likely due to the absence of caking properties of the LV1 sample. The angular shape and solidity of the particles comply with the relatively poor combustion performance of the LV1 coal in the DTF, as confirmed by minimal burnout of these samples in Figure 36).

With regards to the reactivity of the char, based on the prevailing theories on char gasification, it would be expected that these chars are highly unreactive (as confirmed via TGA reactivity in section 6.3.2.) This is most likely due to a lack of pore development, limiting reactant gas accessibility to the internal active sites of the char. Alternatively, an inherent lack of chemical reactivity may result in low gasification reactivity.

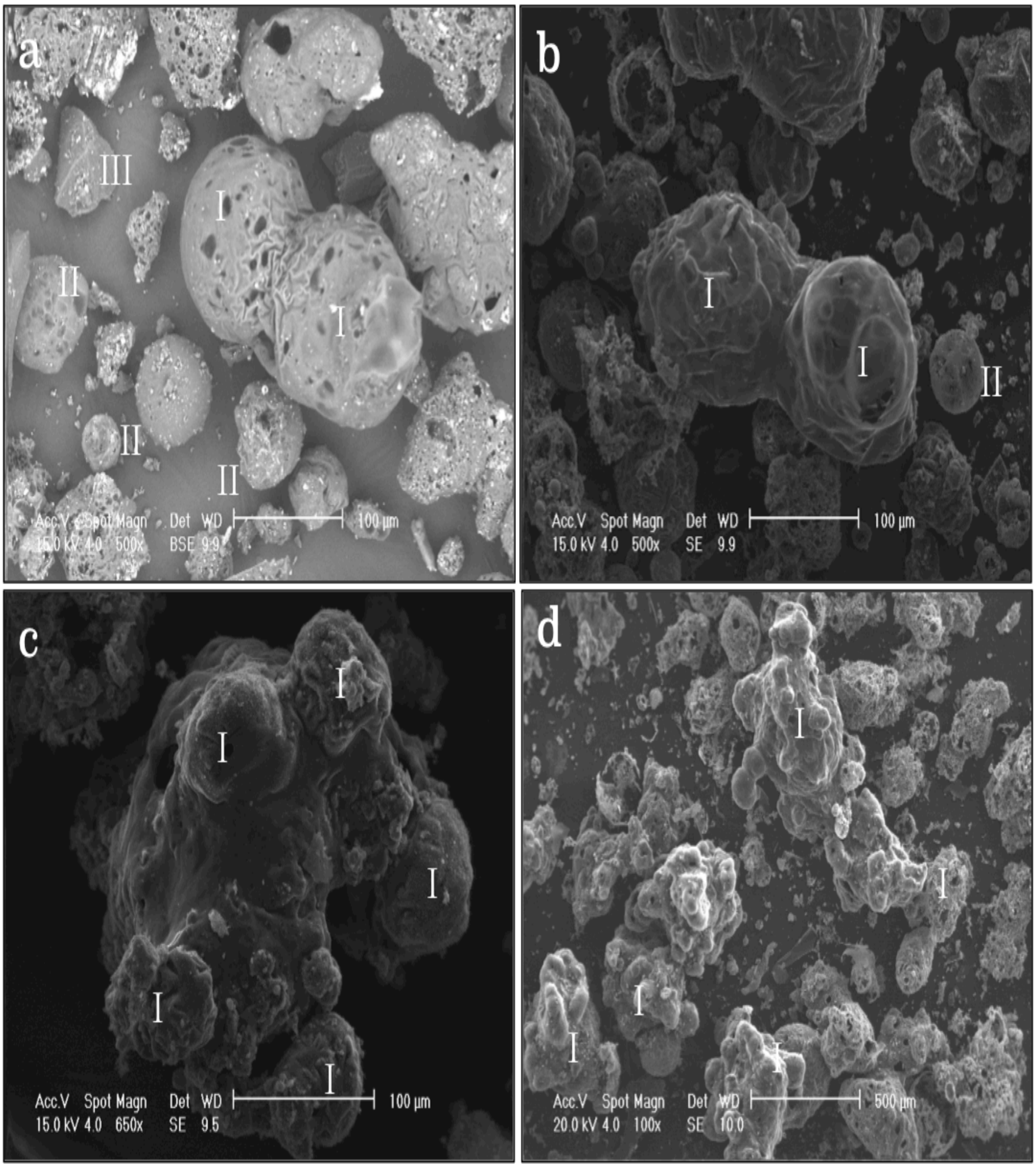


Figure 39: SEM images of post DTF 35ms MV4 chars: a & b) granulated, c & d) pulverised. Images contain: I = agglomerated particle(s), II = reacted singular particle, III = physically unreacted particle

The chars produced by the strongly agglomerating MV4 coal are shown in Figure 39 and provide evidence of finer, <1mm particle agglomeration. As detailed in Chapter 4, the MV4 sample has strong caking properties that result in thermofluidity during heating. As a result of this, the MV4 char particles have undergone significant physical changes when compared with the angular profile of a raw coal particle or a relatively unreacted char as shown with LV1 in Figure 38. The MV4 particles exhibit examples of rounded particles with varying degrees of porosity. However, the volume of the chars are mostly characterised by agglomerated particles. For example, Figure 39a) is a typical example of two rounded particles that have agglomerated together. The point of original contact is evident with a bridged connection between the two. The most common profile of agglomerates in MV4 is that of coarse multi-particle clusters as seen in Figure 39d. These are comprised of a greater number of particles that have fused into one structure. With regards to the features of the agglomerated particles, they appear to be relatively heterogeneous with varying size, shape and thickness. In general, they do not appear to possess large feeder-pores and are not as well developed as swollen chars. The MV4 char particles occur as a result of the strong caking properties of the coal, imparting thermofluidity during heating. This fluidity allows the particle walls to flow and change shape with gas flow, also providing the adhesive surface to combine particles together prior to resolidification. Additionally, the greater physical change found in the MV4 compared with the LV1 is likely impacted by the higher MV4 burnout in the DTF as seen in Figure 36.

Linkages between the physical structure of the MV4 chars and the gasification reactivity will be discussed in more detail in section 6.3.2, however based on the SEM images shown, the agglomerates do not appear to be significantly porous or well developed which would not be expected to be conducive to effective gasification (though likely more so than the LV1 chars).

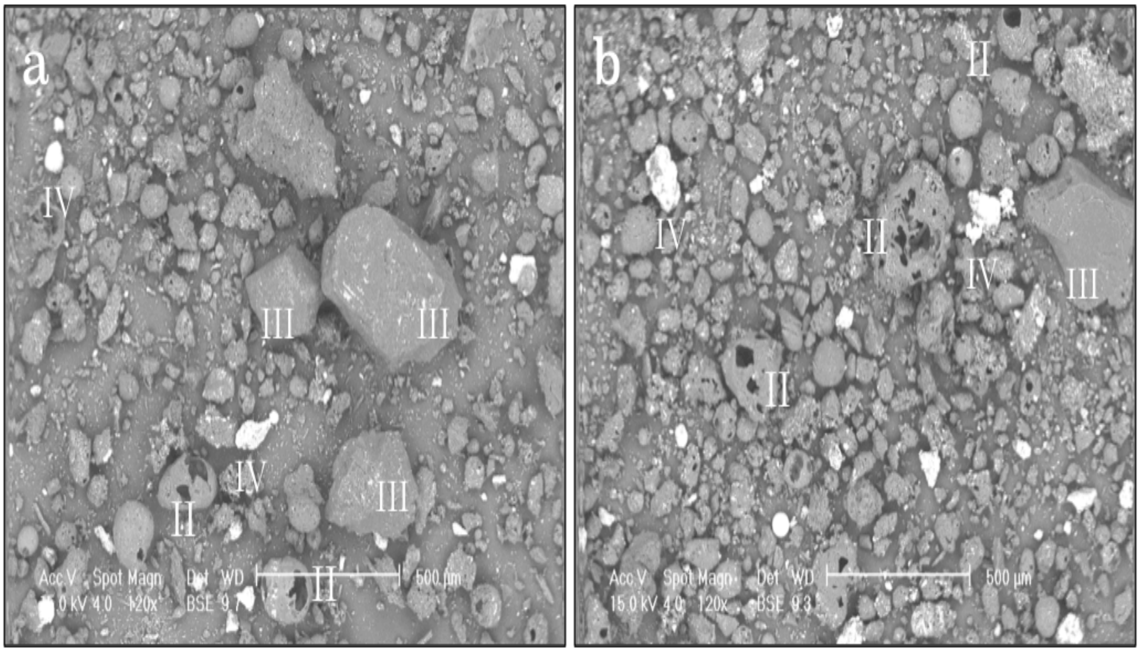


Figure 40: SEM images of post DTF 35ms MV3 chars: a) granulated, b) pulverised. Images contain: II = reacted singular particle, III = physically unreacted particle, IV = mineral matter

The MV3 chars shown in Figure 40 are heterogeneous in their shape and structure. As would be expected based on sieve analysis following DTF injection, neither granulated nor pulverised sample shows strong evidence of agglomerated material. Both samples are composed of large, relatively angular particles that are solid in nature, whilst rounded, porous particles are also present. The presence of coarse, solid particles will likely have a strong impact on the char’s gasification performance with their solidity resulting in poor reactivity.

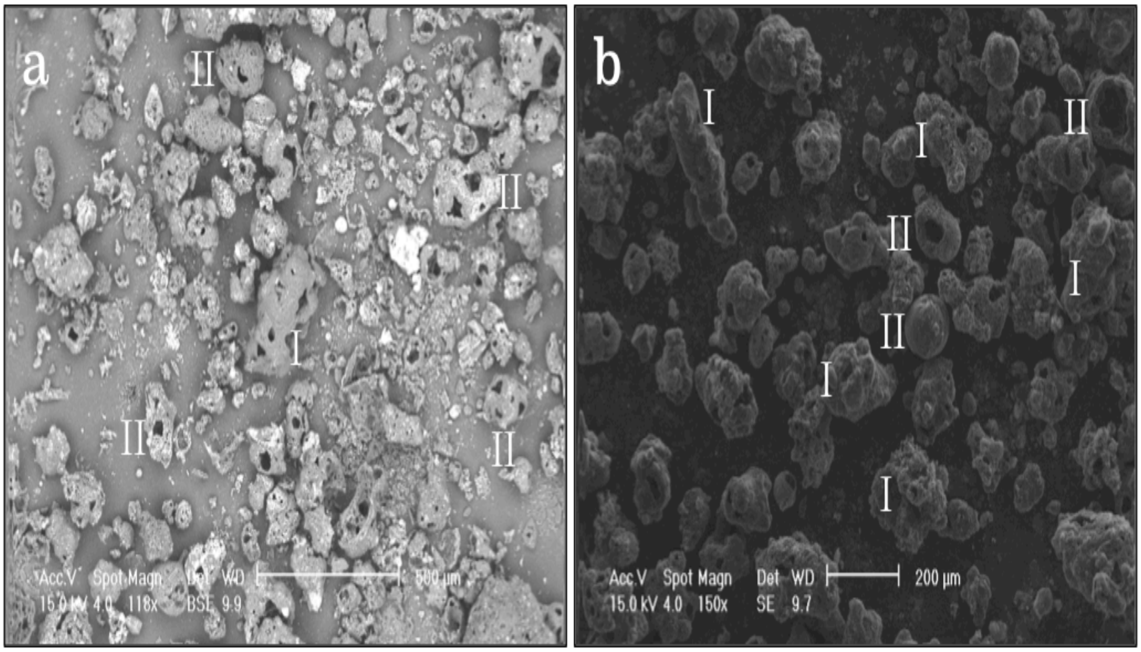


Figure 41: SEM images of post DTF 35ms HV1 chars: a) granulated, b) pulverised. Images contain: I = agglomerated particle(s), II = reacted singular particle

Both the granulated and pulverised HV1 chars shown in Figure 41 show similar char structures. Examples of agglomerated materials are present. However, when compared with those seen in MV4 chars, there are fewer occurrences of agglomeration. It is also notable that the HV1 chars appear to have greater occurrences of feeder-pores than the MV4 chars. These pores are an effective component in reactant gas diffusion into the particle, and product desorption out of the char, resulting in strong gasification reactivity of the HV1 chars (as shown in section 6.3.2). It is possible that the presence of these large pores can explain the lower caking properties found in the HV1 coal than those of the MV4. As discussed in Chapter 4, the caking score of HV1 is limited by minimal swelling relative to MV4. Coal particles are prone to rupturing during volatile matter liberation (Yu et al., 2003b), leaving large pores that can be described as “blowholes” (Zeng et al., 2005). The presence of these blowholes in the HV1 chars can explain the limited swelling of the HV1 caking button due to the sample effectively expelling volatile gas through these pores, an effect that can result in a collapsed particle.

SEM analysis has allowed for further evidence of the presence of agglomeration in certain coals. Additionally, it is possible to make inferences and explanations as to the unground char reactivity seen in the TGA.

6.3.2 TGA gasification reactivity

Thermogravimetric analysis was used to determine the char gasification reactivity for the various 35ms DTF chars. The resultant gasification data are shown in Table 12, with the unground reactivity conversion curves also displayed graphically for granulated and pulverised particle sizes in Figure 42 and Figure 43 respectively.

Table 12: TGA 35ms char gasification $t_{0.5}$ conversion scores and specific surface area data

Particle size	DTF 35ms char	Unground char gasification time: $t_{0.5}$ (m)	Specific Surface Area (m^2/g)
Granulated	HV1	70	17
	MV4	113	10
	MV3	166	30
	LV1	207	5
Pulverised	HV1	62	40
	MV4	72	40
	MV3	107	75
	LV1	214	5

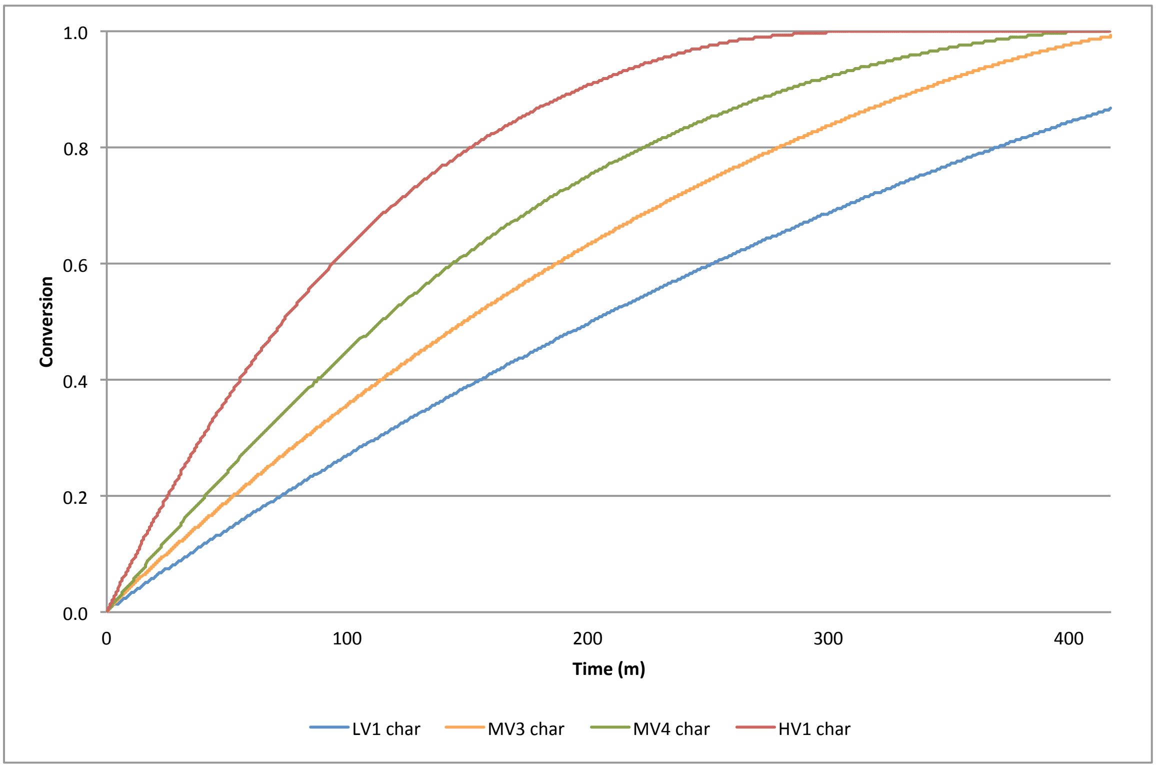


Figure 42: Granulated char gasification curves. Conversion with time at 900°C in CO_2

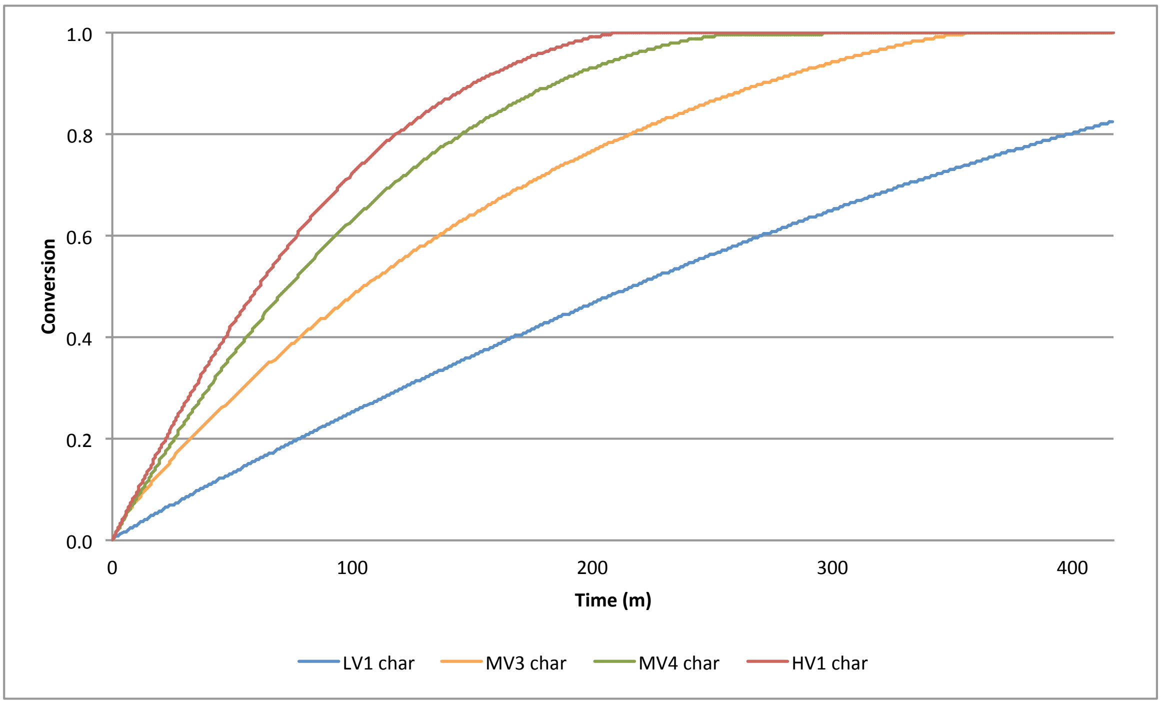


Figure 43: Pulverised char gasification curves. Conversion with time at 900°C in CO_2

As can be seen in the data presented in Table 12, Figure 42, and Figure 43, the unground pulverised chars generally reach $t_{0.5}$ faster than their granulated counterparts, indicating higher reactivity. This is likely a result of the pulverised chars having a greater surface area available for reaction than the equivalent granulated chars. Physical effects during devolatilisation such as the swelling of finer particles compared with the fragmentation of larger ones may also be of relevance in producing a more porous, reactive char (Steer et al., 2015b).

It is notable that the coal combustion performances during initial DTF injection rank strongly with those of gasification reactivity with high burnout coals also being more reactive during gasification. When plotted alongside one another (Figure 44), the char burnouts and gasification times show a strong correlation coefficient of r = 0.94.

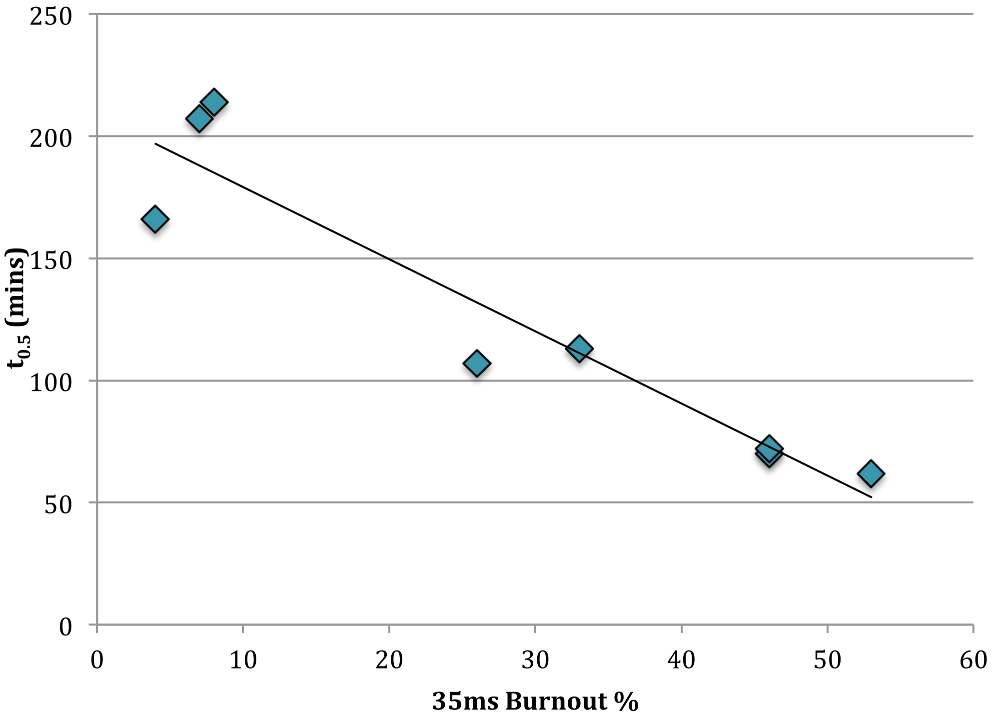


Figure 44: DTF burnout % vs. char gasification $t_{0.5}$ times for the range of 35ms chars

This strong link between combustion and gasification performance highlights the potential role of the initial combustion phase in producing a well-developed, porous char, with samples such as LV1 and MV3 granulated remaining relatively unburnt during the combustion phase and forming an often solid (see Figure 38 and Figure 40a), unreactive char as a result. Alternatively, it may also be that a chemically reactive coal will remain as such throughout the combustion and gasification process with physical structure being less dominant than often considered in gasification reactivity (to be discussed further following analysis of ground chars in Section 6.3.3).

With regards to agglomeration and the effects on char reactivity, it should be noted that the most reactive chars are those in which agglomerated particles are prevalent – MV4 and HV1. One possible reason behind this is that the relatively solid, unreacted chars of the LV1 and MV3 coal prove particularly unreactive due to their lack of physical development. Additionally, whilst the agglomerated particles in the MV4 and HV1 chars appear to have some pore development (albeit limited in the case of MV4) it appears at this stage that this development is sufficient in providing greater reactivity.

Alternatively, the inherent chemical reactivity of the agglomerating coal samples may be dominant to the extent that agglomeration and physical structure are of less importance. Potential chemical influences of reactivity include structural ordering, mineral effects, and varying chemical functional groups (Fung and Kim, 1984; Lu et al., 2002; Zhang et al., 2005; all cited in Steer et al., 2018).

For the range of samples tested, the impacts of fine particle agglomeration on gasification reactivity are not significantly detrimental with char characterised by agglomeration typically showing strong reactivity. This suggests that small examples of agglomerated char will not remain in the blast furnace to any greater extent than a 'standard' char particle would. As a result, the presence of fine agglomerated chars in blast furnace injection is likely to provide similar performance to that of chars derived from non-agglomerating coals (with regards to the coals used in this study).

6.3.3 Ground char gasification reactivity

In order to test further the role of the char physical structure and agglomeration in gasification, the DTF chars were ground in a mortar and pestle (ground product passes through a 50μm sieve). The aim of grinding was to alter the physical structure and agglomerated material that had developed during devolatilisation/combustion in the DTF and bring the range of chars to as close to a uniform physical state as possible prior to TGA analysis. SEM images of the ground char shown in Figure 45 highlight the relative conformity between ground chars with angular particles and no examples of agglomeration or pores found.

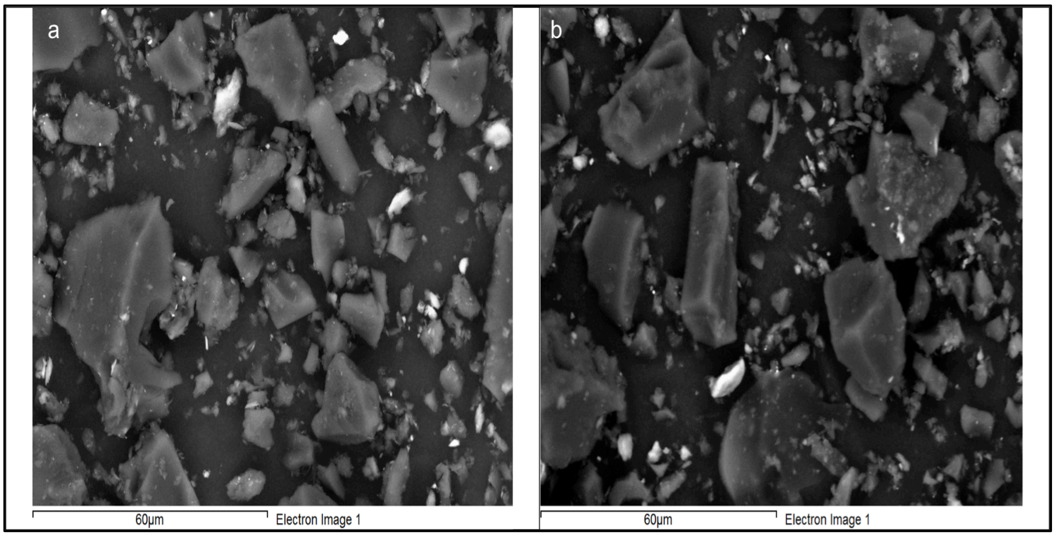


Figure 45: SEM images of 35ms DTF chars post grinding in a mortar and pestle. a = LV1 char, b = MV4 char

An amended gasification data table is shown as Table 13 that displays both the unground and ground char $t_{0.5}$ times. In order to display the relationship between the variables more clearly, the $t_{0.5}$ figures for the unground and ground chars are plotted together and shown in Figure 46.

Table 13: TGA gasification times: unground and ground chars

Particle size	**DTF 35ms char**	**Unground char gasification time: $t_{0.5}$ (m)**	**Ground char gasification time: $t_{0.5}$ (m)**
Granulated	HV1	70	58
	MV4	113	93
	MV3	166	136
	LV1	207	177
Pulverised	HV1	62	61
	MV4	72	61
	MV3	107	76
	LV1	214	168

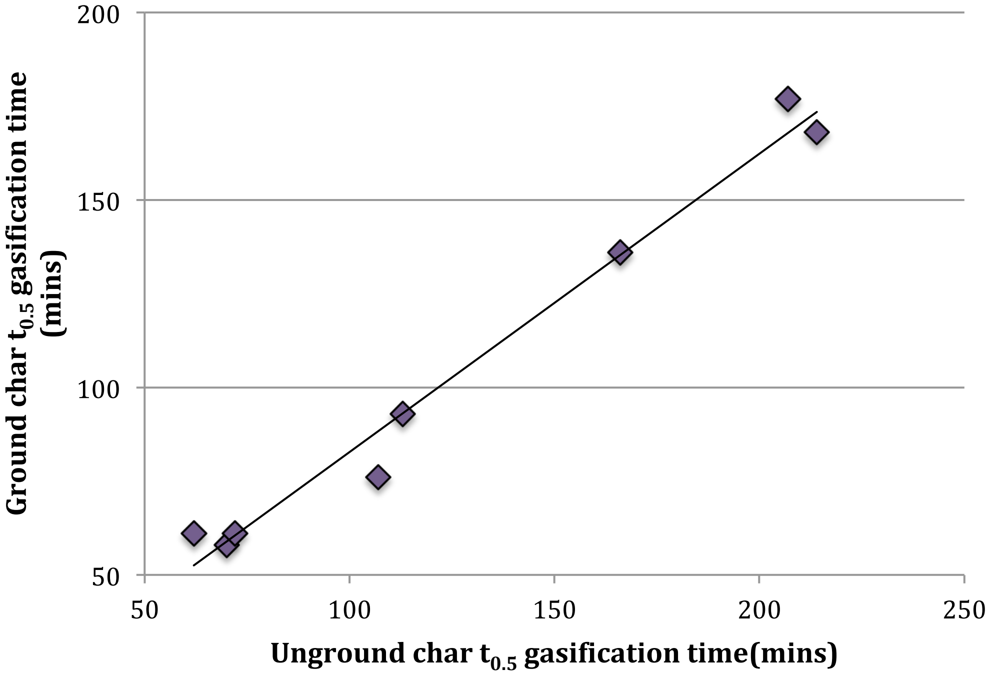


Figure 46: Char gasification in TGA: $t_{0.5}$ data for the range of chars, unground (as received from DTF) vs. ground (in mortar and pestle)

It is evident via the data plotted in Figure 46 that there is a strong relationship between unground and ground char reactivity times with a correlation coefficient of r = 0.99. This signifies that a reactive char will remain as such even after the macro physical properties are altered with new surfaces generated that are less varied between samples. As would be expected, the ground chars are more reactive than their unground counterparts, possibly due to increased surface area. There are no clear improvements in any particular type of char with both agglomerated and non-agglomeration chars seeing varying reactivity improvements with grinding. Notably, the order of reactivity of the samples remains relatively unchanged with grinding. This suggests that the physical structure of the char is not the most prominent factor in generating the reactivity of the char. Instead it appears that the chars have an inherent chemical reactivity that is a dominant factor in determining gasification reactivity. A resulting impact of this is that the importance of agglomeration with regards to gasification reactivity is limited with the presence of small agglomerated material unlikely to cause significant reductions in reactivity and thus a lower likelihood of char-derived operational issues in the blast furnace.

6.4 Repeatability of Char Performance Techniques

6.4.1 Ash tracer method

As discussed in Section 3.2.3.2, the ash tracer method has a number of potential inaccuracies, however, steps were taking to reduce the likelihood of this including extensive cleaning of the drop tube furnace collector probe between each experimental run. The test was carried out twice per coal with the experimental variance shown below in Table 14.

Table 14: Ash tracer method repeatability data for the range of 35ms drop tube furnace chars

Particle Size	35ms coal char	Ash tracer 1 Burnout %	Ash tracer 2 Burnout %	Average burnout %
Granulated	LV1	6.4	8.2	7.3 ±0.9
	MV4	34.1	31.2	32.7 ±1.5
	MV3	4.1	4.6	4.4 ±0.3
	HV1	45.6	45.9	45.8 ±0.2
Pulverised	LV1	8.0	8.8	8.4 ±0.4
	MV4	46.8	45.5	46.2 ±0.7
	MV3	26.7	25.4	26.1 ±0.7
	HV1	52.5	53.1	52.8 ±0.3

As shown, the variability of the test is limited with minor variations in the resultant burnout percentages found.

6.4.2 Char gasification TGA testing

The TGA gasification method was carried out twice per char with the average of the experiments taken as the final indicator of gasification reactivity for that char. The results are shown in Table 15.

Table 15: TGA char gasification results for 35ms char runs one and two also showing average $t_{0.5}$ times.* Please note MV4 pulverised results not included due to their further discussion following

Particle Size	**35ms coal char**	**Run 1 Char: $t_{0.5}$ (mins)**	**Run 2 Char: $t_{0.5}$ (mins)**	**Average $t_{0.5}$ (mins)**
Granulated	LV1	199	215	207 ±8
	MV4	113	113	113 ±0
	MV3	147	184	166 ±19
	HV1	67	73	70 ±3
Pulverised	LV1	208	220	214 ±6
	MV4*	*	*	72 ±2
	MV3	109	104	107 ±3
	HV1	63	60	62 ±2

In order to further test the repeatability of the method, one of the chars (MV4 pulverised) was subjected to repeated testing six times using the aforementioned TGA gasification method. This char was chosen due to initial suspicions that the results would be the most variable of the char range due to the large amount of agglomerated material within the char, though that did not prove to be the case.

As shown in Table 16, the $t_{0.5}$ times are consistent for the range of chars with a minimal deviation in the sample tested 6 times. Detailed testing on the MV4 pulverised char showed excellent repeatability with a range of less than five minutes shown for the six runs. Though the repeatability does vary in some of the other chars, the results are generally acceptable in determining the relative reactivities of the char. As a result, there is high confidence in the TGA gasification method repeatability and reactivity determinations.

Table 16: TGA gasification test repeatability results for pulverised MV4 35ms char with standard deviation

	Char gasification: $t_{0.5}$ (mins)							
35ms coal char	**Run 1**	**Run 2**	**Run 3**	**Run 4**	**Run 5**	**Run 6**	**Average $t_{0.5}$**	**Standard Deviation (mins)**
MV4 (pulverised)	73	73	74	71	71	71	72	1.3

When considering char gasification, the reaction rate is thought to be determined by the reactant gas accessibility to active sites on the surface and interior of the char. During surface area determinations it is necessary to degas the char due to the possibility of pores in the char being blocked by adsorbed water on the surface and gases located within the char. Relating this to gasification there is the potential for this to impact reactant gas accessibility and thus affect reactivity. In order to test this potential inaccuracy in the method, a degassed MV4 pulverised char was subjected to TGA gasification. The resultant $t_{0.5}$ gasification score for the degassed char was 78 minutes compared with 72 minutes for the un-degassed char, highlighting that reactivity is not reduced by any gases within the sample. It is likely the case that any water/gas blockages are removed during the heating process up to 900°C in the TGA.

6.5 Chapter Summary

The experimental work in this chapter was designed to assess the performance of agglomerating coals in blast furnace environments, as per one of the original objectives of this investigation. The impacts of agglomeration were tested and evaluated with regards to coal combustion to assess coal performance in the blast furnace hot blast and raceway region. Additionally, the gasification reactivity of the resultant chars was assessed in order to test performance in a carbon rich, lower temperature environment, found outside of the raceway.

A drop tube furnace was used in order to study coal injection with conditions that are comparable to the initial injection of coals in the blast furnace hot blast region. Regarding combustion performance it was found that the finer, pulverised coals consistently saw higher levels of burnout than their granulated counterparts. Notably, the coals that were prone to agglomeration, MV4 and HV1, both saw greater burnout than the non-agglomerating samples MV3 and LV1. This, alongside burnout analysis in Chapter 5, Section 5.4.2 suggests that the combustion performance of the selected coal range is not greatly limited by occurrences of agglomeration. Industrially, these results indicate that the use of agglomerating coals in the blast furnace would not result in an increase in char fines leaving the raceway region relative to other injection coals (based only on combustion performance).

Following the analysis of coal combustion, it was necessary to consider the gasification reactivity and the effects of agglomeration. Due to the nature of the blast furnace environment during gasification, it is generally accepted that the physical structure of the char is of importance. As a result, the chars were visually analysed using SEM imaging. Whilst the char shape and pore development was discussed, additional evidence of smaller-scale agglomeration was of particular interest and relevance to this investigation. It was found that the MV4 and HV1 chars were characterised by varying degrees of agglomeration whilst the MV3 contained both porous and solid char material.

Regarding gasification reactivity, it was found that the chars produced by pulverised coal were consistently more reactive than their granulated counterparts, most likely due to their greater specific surface area. A strong correlation between the combustion and gasification performance of the coal/chars was found suggesting that some of the samples are inherently reactive/unreactive, a possibility supported by ground char reactivities. In order to largely remove the effect of differing physical structure on reactivity, the char samples were ground in a mortar and pestle prior to TGA gasification. The resultant $t_{0.5}$ reactivity results showed very strong correlation with the unground chars. This suggested that the performance of the chars relative to one another is not significantly dependent on physical structure, with the inherent chemical reactivity dominant.

With regards to agglomeration and char reactivity, the agglomerated char samples (MV4 & HV1) were generally more reactive than the non-agglomerated chars (LV1 & MV3). This is likely due to a combination of limited pores development of the non-agglomerated chars, and the inherent reactivity of the samples. As a result of evidence via ground vs. unground chars concluding that physical structure is not likely to be the most dominant factor in gasification reactivity between chars of similar sizes, it is probable that the impact of fine agglomerated material on char gasification is minimal and not likely to be significant. With regards to industrial performance, these results suggest that chars characterised by fine agglomeration are unlikely to be any more problematic than a “standard” char where reactivity in the blast furnace is concerned.

To summarise, the presence of agglomerated material does not appear to influence coal performance to any significant extent during either the combustion or gasification stages of blast furnace coal injection. It is not expected that the injection of an agglomerating coal in the blast furnace would reduce combustion performance, nor affect the likelihood of char accumulation to any extent over a “standard” injection coal. However, it should be noted that the propensity for blockages due to large agglomerates could not be assessed in this work (due to uncertainties regarding the form of agglomerates in the blast furnace) and is a possibility for greater disruptions to blast furnace permeability.

Chapter 7: Implications for Industry

Modern steelmakers face a range of challenges at the time of writing. Chinese surplus steel has driven down global steel prices, whilst emissions regulations, trade tariffs, carbon taxes, and increased energy prices have resulted in rising operational costs (Pooler, 2017; Greenwood, 2017; de Lusignan, 2017; Pooler, 2018; Mayeda et al., 2018). As a result, many steelmakers are looking to improve process efficiency, reduce costs and carbon waste, and invest in sustainability wherever possible. By optimising blast furnace coal injection it is possible to reduce raw material costs (via lower coke requirements) and reduce carbon waste emissions through more efficient coal reactions in the furnace.

This body of work investigated the potential issue of coal particle agglomeration during blast furnace injection. The possibility of agglomeration was initially tested, followed by an assessment of the coal properties responsible. Following this, the performance implications of coal agglomeration with respect to combustion, and gasification were considered from an industrial perspective. This chapter summarises the results in an industrially relevant manner and presents some suggestions for industrial practice as a result of the thesis findings.

7.1 Occurrence of Agglomeration

Experimental injection testing in a DTF showed that coal agglomeration occurs reliably in high heating rate (10^4°C/s), high temperature (1100°C) conditions resulting in chars that are largely characterised by agglomerated particles (notably MV4 coal). Due to similarities in a range of key parameters, it is possible to relate results from the DTF to the blast furnace hot blast region. Agglomeration consistently occurs in the DTF despite injection of a dilute stream relative to the blast furnace, whilst heating rate and blast temperatures are both replicated in the DTF. As a result, it is believed that agglomeration of some form is a potential occurrence during blast furnace coal injection. However, due to the differences in DTF and BF environments, it cannot be accurately determined what form (shape, size) agglomerates would take in the blast furnace. The blast furnace injection and raceway region are dynamic environments with a range of fluctuating conditions that cannot always be satisfied in the DTF. For example, the blast furnace contains pressurised coal transport systems that vary per furnace with a typical range of 1-5m/s and 15-20m/s for dense and dilute phases respectively [Carpenter, 2006]) and variable injected oxygen concentrations (oxygen enriched air may be injected at 22-24% $O_{2)}$). Additionally, blast furnace raceway temperatures (>2000°C) are not replicated in the DTF. Crucially, the temperature under which the coal particles are initially heated and agglomeration should occur (hot blast temperature of 800-1300°C) is replicated by the 1100°C DTF. Due to the higher raceway temperatures following the hot blast, the presence of agglomeration after the raceway is unknown. However, it is widely accepted that char leaves the raceway (following exposure to this temperature) and accumulates (Ichida et al., 1992; Dong et al., 2003; Nogami, et al., 2005), thus suggesting that agglomerated char material is also likely to leave the raceway. As a result of these differences, agglomeration in the DTF cannot be related to the blast furnace with certainty, though it is believed that occurrences of agglomeration are likely.

The presence of agglomeration in caking coals aligns with considerations in Carpenter (2006) wherein links between caking/coking coals and blocked injection lances are discussed (Nightingale et al., 2003; Atkinson, 2006). The formation of agglomerated materials in the DTF is an indicator that samples that could result in injection lance blockages in the blast furnace due to agglomeration in the lance.

During DTF testing, agglomeration was found to generally occur to a greater extent in the pulverised coal size specification. This is potentially as a result of increased number of individual particles, in addition to particle effects during heating that affect the formation of agglomerates (e.g. swelling of pulverised particles and fragmentation of granulated particles). For this reason, it is believed that any negative impacts of agglomeration in the blast furnace will be exacerbated through the use of pulverised injection coals.

After testing the coal caking properties of 36 samples (whole and blended coals), it was found that samples defined by the caking test as “caking coals” consistently agglomerate during DTF testing (MV4 and HV1 alongside various blend ratios, detailed in Section 4.2.2.). Meanwhile, non-caking coals (LV1 and MV3) generally do not agglomerate in the DTF (though coals on the non-caking/caking boundary do on occasion). This suggests that caking coal use in the blast furnace is increasingly likely to result in some form of particle agglomeration relative to non-caking samples. It is noted that anecdotal evidence provided by blast furnace operators has highlighted the heavily caking and agglomerating MV4 coal as a particularly poor injection coal regarding blast furnace injection and stability (M Greenslade, 2015, personal communication, 10 February).

Although ash-based agglomerates were not the focus of this investigation and no evidence was found in any of the coal samples injected into the DTF, ash fusion temperatures suggest they could form under the 2000°C blast furnace raceway temperatures. However, it is noted that the relative lack of mineral matter in injection coals is not likely to result in large quantities of problematic ash-based agglomerates.

7.2 Mitigation of Agglomeration

Coal blending in the blast furnace is a common practice, with blends used to combine the volatile matter properties of two coals (Steer et al., 2015a). Blending of two coals has proven effective in reducing agglomeration to some extent during DTF injection in this study. Although agglomeration remains in the majority of MV4 blends, certain MV4:LV1 blend ratios do eliminate agglomeration (MV4:LV1 25:75%). Agglomeration in the blends appears to occur as a factor of the parent coal's propensity to agglomerate with actual blend agglomeration showing some correlation with theoretical/predicted agglomeration percentages (based on the parent coal's propensity to agglomerate). As a result, the blending of caking and non-caking coals in the blast furnace is a possible route for reducing agglomeration, with furnace operators able to tailor their blends to the parent coal caking properties. This would theoretically allow for the use of caking coals that may be desirable to operators for alternative reasons, e.g. low purchase cost or surplus stock.

Additionally, the oxidation of the MV4 coal at 300°C prior to DTF injection eliminates all evidence of agglomeration in DTF chars. This is believed to be due to reduced caking properties as a result of increased surface oxygen contents retarding particle fluidity (Jha et al., 2014; Miroschnichenko et al., 2017). It is recommended that a low-temperature study of coal oxidation/weathering be carried out to examine whether the same results are found. If successful, this would prove a pragmatic/cost-effective approach to mitigating coal agglomeration due to the ease of weathering coals in stockyards, though the oxidation process would be notably more time-consuming at lower temperatures. Alternatively, it may be possible for certain plants to make use of higher coal drying temperatures in order to oxidise caking coals for injection.

7.3 Performance Implications of Injecting Agglomerating Coals

For the range of coals studied, combustion performance did not appear to be significantly impacted by coal agglomeration with the agglomerating samples consistently showing higher burnouts than the non-agglomerating coals (burnouts ranging from 4-26% for non-agglomerating coals, and from 33-53% for the agglomerating coals). This is potentially due to changes in physical particle structure occurring during devolatilisation, and the inherent reactivity of the coals. As the agglomerating coals show higher burnouts, the samples are believed to be more combustible than the non-agglomerating coals. As a result, it is not believed that coal combustion in the blast furnace raceway will be reduced to any significant extent via the use of these agglomerating samples. Based on the combustion behaviour of the coals tested, using agglomerating coals in the blast furnace should not result in a net increase of unburnt char leaving the raceway when compared with the non-agglomerating coals tested. Having a coal with strong combustion performance can allow for an increased coal injection rate, thus increasing coke replacement and saving costs (Nomura and Callcot, 2011). Effective combustion performance will result in less char leaving the raceway region and less gasification competition between char and coke (wherein char is preferentially gasified to coke [Akiyama and Kajiwara, 2000]), thus increasing coke degradation. Additionally, less char leaving the raceway should result in fewer instances of char accumulation and blockages – a crucial factor in furnace instability. Furnace instability may result in reduced hot metal generation and result in less efficient performance, thus damaging productivity.

Regarding the gasification performance of the chars upon leaving the raceway and entering the carbon rich cohesive zone and stack, TGA testing shows that the chars characterised by fine agglomeration are faster reacting than the non-agglomerated chars. This is based on the times taken for each 35ms DTF char to reach 50% conversion under TGA gasification at 900°C in CO_2. This relatively high reactivity of the agglomerated chars (MV4 and HV1) suggests that the non-agglomerated chars would remain unreacted in the blast furnace (and potentially problematic) for a greater time than the agglomerated chars. Due to this, the likelihood of permeability issues is theoretically greater when the non-agglomerated chars are present (for the range of samples tested). It is noted that the faster reactivity of the agglomerated chars is most likely not as a result of their agglomeration, but the inherent reactivity of these particular coal samples, or/in addition to the solid, undeveloped nature of the non-agglomerated chars (as highlighted by SEM imaging).

Via grinding DTF chars prior to TGA gasification testing (discussed in Section 6.3.3), the influence of physical structure on char reactivity was assessed. It was found that the most reactive chars (MV4 and HV1) as received from the DTF (unground), generally remained as the most reactive chars following grinding to a uniform state (ground chars). This implies that the inherent reactivity of the char will be significant in determining char gasification reactivity (inherent reactivity may be influenced by carbon ordering, mineral catalysis, and varying chemical functional groups [Steer et al., 2018]). As a result, an agglomerating coal that performs well with regards to combustion and gasification performance may prove less problematic in the blast furnace than a non-agglomerating yet unreactive coal in spite of the presence of agglomerated material (as is the case for the range of coals tested). It should be noted however that potential differences in the form of agglomerates between the DTF and blast furnace is an area of uncertainty regarding this research.

7.4 Suggestions for Industrial Practice

Regarding coal selection, blast furnace operators currently rely heavily on the proximate analysis of a coal when assessing the likely injection performance with volatile matter content particularly considered. However, the results from this investigation show that proximate analysis alone is not adequate with agglomeration, combustion, and gasification performances not proving dependent on volatile matter content. Alternative suggestions when analysing performance include TGA combustion and gasification testing to determine the general reactivity of coals.

There are no clear indicators in proximate, petrographic, or ultimate analyses that predict agglomeration in the range of coals studied. Instead, a more specific caking test should be implemented. It is recommended that the test referred to as the agglomeration index in Section 3.2.1.2 be utilised. The test provides a general assessment of coal caking properties and has proven more accurate than the alternative FSI due to less dependency on coal swelling/cross-sectional profile. The agglomeration index defines samples as “non-caking” and “caking” coals and assigns scores that have shown strong correlation with coal agglomeration in the DTF and thus are likely to be a good option when predicting blast furnace agglomeration. Additionally, the test can be applied at low cost to blast furnace operators due to its use of a standard volatile matter button making it an attractive option from a pragmatic standpoint.

Due to the uncertainty regarding the precise form of agglomerates in the blast furnace, it is recommended that the use of caking coals is initially monitored carefully in order to limit risk. This is based on results suggesting that high temperature, high heating rate agglomeration is a possible occurrence in the blast furnace. Factors that may be symptomatic of coal agglomeration and as thus should be monitored are as follows (many of the potential impacts of agglomeration are shared with those of char accumulation on which there is more research):

- Blocked injection lances (Nightingale et al., 2003; Atkinson, 2006, as cited in Carpenter, 2006)
- Reduced furnace permeability (Ichida et al., 1992; Dong et al., 2003)
- Altered coke degradation rates (Akiyama and Kajiwara, 2000)
- Pressure build up and hindered gas flows due to blockages and areas of particle accumulation (Lu et al., 2010)
- Char/liquid metal interaction (Lüngen and Poos, 1996)

As opposed to the use of 100% caking coals for injection, it is recommended they be diluted by blending with coals that do not have strong caking tendencies. This can effectively reduce the extent of agglomeration during heating whilst additionally providing an opportunity to operators to tailor the blend to their needs regarding combustion and gasification performance. For example, using the agglomerating MV4 coal at a 25% blend with LV1 (remaining 75%) can eradicate particle agglomeration in the DTF. However, the blending of the coals must be as thorough as possible in order to systematically distribute and mix the particles of the non-caking and the caking coal. It is this thorough blending that allows for the effective reduction of agglomeration with alternating injection coals unlikely to provide adequate particle mixing.

When injecting caking coals into the blast furnace, consideration should be given regarding the potential for injection lance blockages (Nightingale et al., 2003; Mathieson et al., 2004; Atkinson, 2006). If lance temperatures are in the temperature range at which particle caking/plasticity is induced (350-450°C for the range of coals tested), there is the possibility of particles caking and agglomerating together which could block the lance. It would be prudent for blast furnace operators to closely monitor injection of caking coals in this area to assess whether blockages are a more common occurrence in these coals. Alternatively, ensuring lance temperatures remain below approximately 350-450°C (commencement of caking/plasticity) would reduce risk of lance plugging. If it is believed by blast furnace operators that problems arise from the use of caking coals, it is suggested that operators test injection of weathered/oxidised versions of the coal and study the resultant operational effects and differences. Based on pre-oxidation of caking coals in this study, oxidised samples are unlikely to agglomerate and the differences between the injection coal performance in the blast furnace can be assessed as a result (results in Section 5.4 indicate that combustion and gasification performance are not negatively impacted by oxidation to any significant extent). This would provide insight into whether operational issues were as a result of the caking/agglomerative properties of the coal.

Chapter 8: Conclusions and Further Work

8.1 Conclusions

Following experimental testing, it was found that the agglomeration of coal particles in a DTF is a consistent and reliable effect, resulting in chars characterised by agglomeration. As per the initial thesis aim, coal particle agglomeration is found to occur under conditions that can be related to blast furnace injection conditions. As a result, it is believed that particle agglomeration can occur under blast furnace heating conditions. Certain coals are prone to agglomerate consistently and reliably whilst others show minimal/no agglomeration. This could explain the variable performances of the injection coals tested in this study in the industrial environment.

Agglomeration shows a strong correlation with the raw coal caking properties. All coals defined by a caking test as “caking coals”, agglomerate without fail in the DTF. Conversely, the majority of the non-caking samples see no agglomeration. Overall, the caking properties defined by the index are highly linked with agglomeration and are the likely responsible coal properties producing the effect. As a result, hypothesis one can be accepted, with this investigation finding that some coals do agglomerate under blast furnace injection conditions, dependent on their caking properties (hypothesis one: ‘Coals have the potential to agglomerate during blast furnace coal injection conditions dependent on their inherent caking properties’).

Caking coals are likely responsible for agglomeration as a result of a number of occurrences upon heating:

- The particle will develop some degree of fluidity resulting in particle walls acquiring an adhesive texture on the surface, ultimately providing a mechanism for colliding individual particles to combine upon contact with another particle.

    - Particle swelling will result in an increase in particle size, increasing the chance of collisions.
    - Binding/agglomerative strength: particle wall binding strength will be relevant. A poor caking coal with weak binding structures will hinder the formation of agglomerates, increasing likelihood of their breaking apart.

Other potential influencing factors were assessed including proximate, petrographic, and ultimate analysis with no strong indicators of agglomeration performance found. Additionally, tar yields and total aromatic products were established without strong links that allow for prediction of caking or agglomeration. However, links between the prevalence of 4≤-ring polyaromatic hydrocarbons and the caking properties of the coals tested were found.

Regarding the impact of coal mineral matter, the contribution of ash fusion in forming agglomerates of MV4 was found to be unlikely with softening and fusion temperatures greater than those found in the DTF reactor. Additionally, SEM imaging did not highlight any mineral matter present in agglomerated particles.

In terms of predicting agglomeration in the DTF, the general caking test called the agglomeration index was found to be more successful than the more prominent FSI despite a number of shared criteria. This was due to an over-reliance of the FSI on the swelling profile of the residue. Due to this, the FSI fails to distinguish the difference between MV3 and HV1 coals whilst the agglomeration index differentiates the two based upon internal cell development and lustre.

Although fluidity (determined via Gieseler plastometer) is a prominent factor in caking properties and thus agglomeration; it is not the case that greater fluidity results in more caking or agglomeration. This may be due to an lower level of fluidity being optimal for making the coal surface viscous, thus promoting likelihood of coal particles joining together.

The coals that are most susceptible to agglomeration (MV4 and HV1) have stronger DTF combustion performance than the non-agglomerating coals (LV1 and MV3). This suggests that agglomeration in these samples would not be greatly problematic in the raceway region based upon initial combustibility.

Regarding the char particle structure, SEM images suggest that the agglomerated MV4 and HV1 chars are more developed than the LV1 and MV3 chars, despite agglomeration occurring. This is due to the greater caking properties impacting the physical structure via effects such as swelling during heating and more extensive combustion in the DTF.

The char performance in the blast furnace will be partly dependent on the particle gasification reactivity in the blast furnace cohesive zone and stack. Char gasification $t_{0.5}$ times show that the chars characterised by fine agglomerated material (MV4 and HV1) are relatively fast reacting compared with the non-agglomerated chars (LV1 and MV3). It is believed that this is either due to the solid nature of the non-agglomerated chars, or the inherent reactivity of the samples as opposed to a resultant effect of agglomeration. This char gasification reactivity suggests that chars characterised by agglomeration in this form will not be additionally problematic in terms of gasification times and unburnt char accumulation in the blast furnace.

As a result of combustion and gasification testing, hypothesis two can be rejected with the agglomerated chars found to have greater combustion and gasification performance than the non-agglomerated chars, thus suggesting their behaviour in the blast furnace would not be negatively affected relative to non-agglomerating coals (hypothesis two: ‘Agglomerated chars will likely be problematic in the blast furnace as a result of poor combustion and gasification performance').

For the char particle size, pulverised particles are generally more reactive than granulated ones due to their greater specific surface area. Upon grinding in a mortar and pestle to reduce the chars to as close to a uniform size/structure as possible, the char order of reactivity remains largely unchanged. Although physical structure undoubtedly plays a role in reactivity, this lack of change implies that the physical differences between the chars are not the key significant factors responsible for gasification performance. Instead the chars are strongly influenced by their inherent reactivity.

Reliable correlation between the combustion of the coal in the DTF and the gasification performance of the resultant char is established. This indicates that the inherent reactivity of the coal may be dominant throughout the blast furnace process, rendering physical particle effects such as agglomeration of less importance than initially hypothesised.

Regarding the mitigation of agglomeration during injection, it was found that agglomeration under high heating rate (10^4 °C/s), high temperature (1100°C) conditions can be eradicated with sample pre-oxidation prior to injection. Pre-oxidation proved effective in reducing caking properties, the resultant impact of which was to eliminate agglomeration. This is likely as a result of increased oxygen functional groups on the surface of the coal cross-linking the macromolecule and reducing metaplast generation. Another effective tool in mitigating agglomeration is via coal blending. Blending of the highly caking/agglomerating MV4 coal with the low caking LV1 eradicated DTF agglomeration at some blend ratios.

8.2 Suggestions for Further Work

After drawing conclusions regarding the possibility of agglomeration under blast furnace heating conditions, it would be prudent to further develop the experimental method to more accurately replicate the physical coal injection stream. Certain limitations of the DTF method include the low injection coal stream density, differing injection systems, and lack of variable temperatures. This could be resolved via the testing of caking coal injection into a specifically designed pulverised coal injection rig (e.g. Li et al., 2014) that replicates blast furnace injection regions via coal injection lances and blow pipe replicas. This should allow for greater confidence in relating agglomeration to the blast furnace.

More ranging drop tube furnace testing could be carried out, including varying gas atmospheres such as injection in nitrogen or increased oxygen content as these vary across the iron making industry. This would allow testing to study whether there are optimal conditions for reducing coal particle agglomeration. The residence time used in the DTF could also be extended to include 100ms which would replicate the time spent in a longer blast furnace raceway (raceway regions often fluctuate).

In future work, a greater breadth of coal samples should be tested. The limited sample size does not allow the work to establish strong links between combustion/gasification performance and agglomeration. This would also be particularly useful when studying the link between tar yields, hydroaromatic components, and caking. Additionally, the broad particle size distributions of the raw coals (agreed with industrial sponsors and designed to simulate industrial samples) means that identifying agglomeration is not always possible. As a result, future testing should initially use more specific size fractions. This would allow for effective use of particle size distributions that highlight particle effects such as agglomeration rather than them being mistaken for larger particles by a broad particle size distribution. Also, the blend work could be made more applicable to industry by altering the method by blending prior to grinding to particle size, with different coals having different grindability.

Regarding the formation of agglomerates, more research should be undertaken on the controlling factors behind the effect, using a greater number of coal samples. This would allow for development of a more detailed model that may be able to draw stronger conclusions on the coal components that influence agglomeration. Also, the potential impact of mineral matter could be researched further. Ash fusion testing has shown that the minerals present in the MV4 sample would soften if subjected to raceway temperatures. There is potential for ash agglomerates to form at this temperature. Although the prevalence of ash in most injection coals is limited thus making this unlikely, this could be investigated further.

Many of the conclusions of this study mention the inherent reactivity of a coal sample, both regarding combustion and gasification performance. This is an area that should be studied to clarify the factors behind this inherent reactivity (e.g. carbon structure, mineral catalysis, surface oxygen etc.).

For more industrially practical mitigation, the effects of oxidation at lower temperatures/weathering should be investigated, as this is a more pragmatic option for iron makers than higher temperature 300°C oxidation. This is due to the ease of leaving samples in stockyards for a longer time period that will allow for oxidation over time whilst requiring no direct heating of the sample at no extra cost. The effects on caking, agglomeration, and combustion/gasification performance should be established.

Additionally, the study of blast furnace operations data during periods of suspected agglomerating coal use should be carried out alongside analysis of data of non-agglomerating coals.

Publications and Presentations

Journal papers:

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Appendices

Appendix A – Additional images relating to this thesis

Figure A 1: Post DTF non-agglomerated char sample (MV3) remaining as powder

Figure A 2: Post DTF agglomerated char material (MV4). Note that agglomerates of this size result in DTF blockages in the feeder and collector probes, inhibiting gas flow. Largest agglomerated material pictured approximately 2-3cm in length

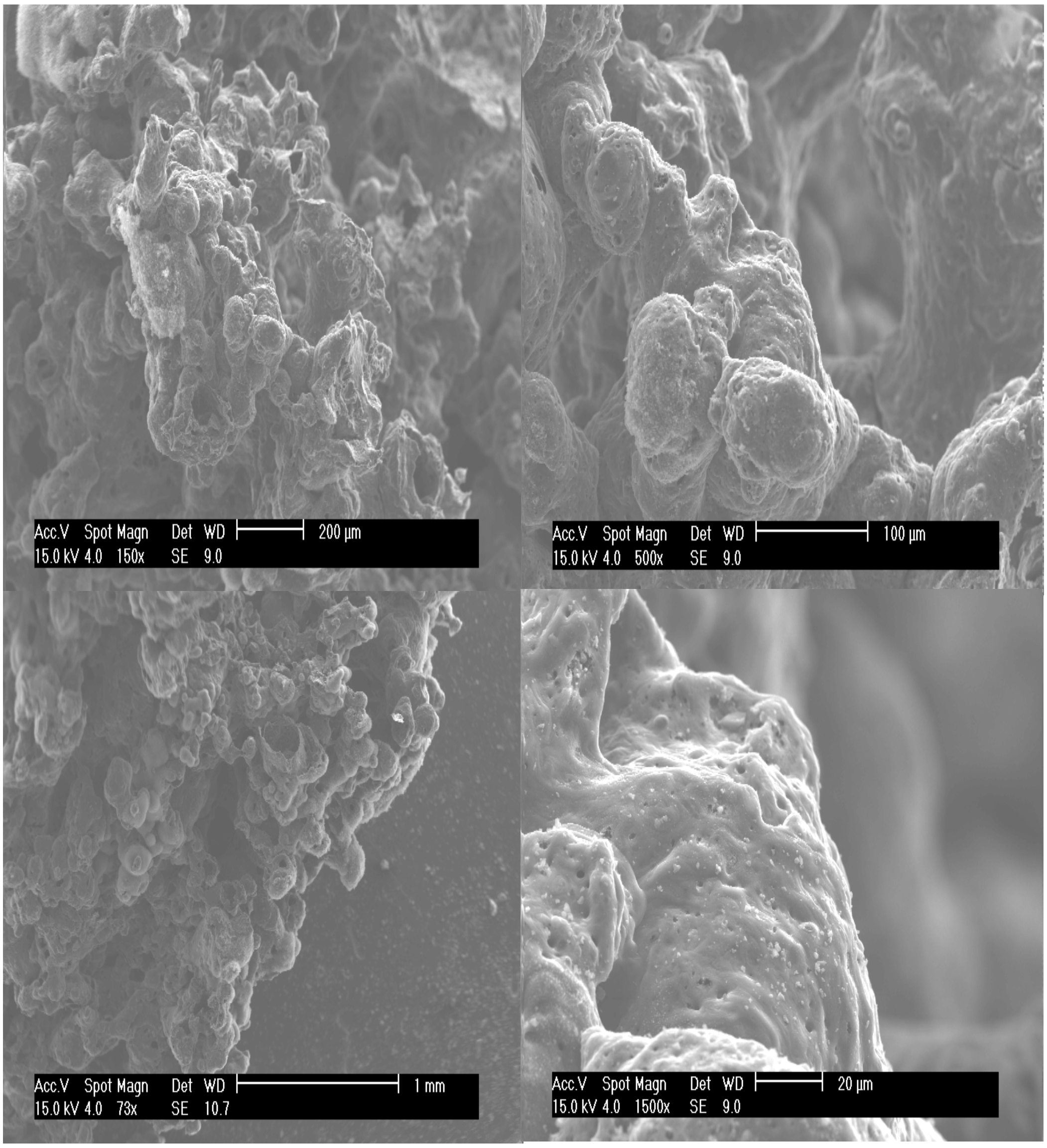

Figure A 3: SEM images of agglomerated char material shown in Figure A 2

Appendix B - Comparison of MV4 <1mm char material and >1mm "agglomerated" material

In order to quantify agglomeration in DTF chars, a sieve classification technique was used. A sieve size of >1mm defined agglomerated material (though there were numerous agglomerates below this particle size that could not be separated via sieve classification). When assessing char performance, the >1mm material remained separate from the <1mm char (containing <1mm agglomerates). In order to be assured that the chemical char properties between the two sieved fractions do not greatly differ, a study of the sample properties was undertaken.

Table A 1: Comparison table of key char properties/performance of the MV4 granulated >1mm and <1mm char sieve fractions

	Volatile matter (wt%)	**Ash content (wt%)**	**35ms DTF Burnout %**	**Ground char gasification time: $t_{0.5}$ (m)***
MV4 <1mm char material	11.0	7.5	33	85
MV4 >1mm char material	11.8	7.2	30	92

It is clear from the results shown in Table A1 that the size fractions of the MV4 char are similar. Unsurprisingly, the larger fraction has undergone slightly less burnout and devolatilisation, though this is to be expected as a result of the larger particle size. The ground char also reacts slightly slower during gasification. However, the burnout and gasification differences displayed above are minor relative to the range of coals studied and as a result it is not believed the materials would behave differently in the blast furnace (based on combustibility and gasification reactivity).

*Note: char gasification time of MV4 char varies from those in main body for same sample due to the TGA equipment being serviced and recalibrated post results shown in Table A1.