Investigating the Effect of Substituting Fractions of Imported Coals with Coke Oven Tar on Coke Quality: Pilot Plant Study

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A research report submitted to the Faculty of Engineering and the Built Environment, University of the Witwatersrand, Johannesburg, in partial fulfilment of the requirements for the degree of Master of Science in Engineering.

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Declaration by candidate

I declare that this research report is my own unaided work. It is being submitted to the Degree of Master of Science in Engineering to the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination to any other University.

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Makgato Seshibe Stanford

02 December 2013

Dedication

This research report is dedicated to my late brother, Makgato Mothabela Jackson who passed on in February 2011 the very same week he completed his M. Cur degree. Brother, I was still on cloud nine that one of us is making it in this academic space then you vanished. You left me speechless. However, nothing compares to the times we shared together. You have always had confidence in me, offered me an encouragement and support in all my endeavours. You were a constant source of inspiration to my life throughout. You are dearly missed, *Robala ka khutso Tau*.

"When the solution is simple, God is answering" Albert Einstein, 1879-1955

Acknowledgement

Isaac Newton said *"If I have seen further it is by standing on the shoulders of Giants."* This is another research step discovered in my life through standing on the shoulders of other Giants.

Without the strength, wisdom, and grace bestowed upon me by my God, this research would not have been possible. Through his grace, the future holds nothing but promise.

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List of Abbreviations

ASTM	American Society for Testing and Materials
BI	Basicity Index
BTX	Benzene, Toluene and Xylene
CI	Catalytic Index
COT	Coke Oven Tar
CSR	Coke Strength after Reaction
CRI	Coke Reactivity Index
FSI	Free Swelling Index
GC	Gas Chromatography
GC-MS	Gas Chromatography Mass Spectrometry
HCl	Hydrochloric Acid
HPLC	High Performance Liquid Chromatography
IAS	Instituto Argentino de Siderurgia
ISO	International Organization for Standardization
I10	Irsid drum index 10
I40	Irsid drum index 40
LDO	Light diesel oil
MF	Maximum Fluidity
MIT	Matter Insoluble in Tar
Max.D	Maximum Dilatation
Max.C	Maximum Contraction
M10	Micum drum Index 10
M40	Micum drum Index 40
PAH	Polycyclic Aromatic Hydrocarbon
QI	Quinoline Insoluble
R^2	correlation factor
RPM	Revolution per minute
SG	Specific Gravity
TI	Toluene Insoluble
XRF	X-ray Fluorescence

Abstract

In this study, coke oven tar addition over a range of 0 – 8 wt.% was evaluated as a possible substitute for imported coals fractions. Coke oven tar used was collected from coke oven tar decanters of the by-products section of the coke making plant. Moisture content in coke oven tar varied depending on the residence time and water carryover from coke oven tar separators to storage tanks. Therefore, various moisture ranges were considered in order to observe its effect on coal blend, carbonization and coke properties. The optimum moisture content in coke oven tar was found to be 3% with a coke oven tar addition of 6 wt.% in the coal blend. At the same coke oven tar addition of 6 wt.% in the coal blend but with 6% moisture content in coke oven tar, coke properties improved, coke yield showed up to 4% decrease. On the other hand, with 1% moisture content in coke oven tar of 6 wt.% in the coal blend, coke yield increased by 1% and low coke properties such as I40 of 42.9 and Stability of 50.3 were achieved. The latter process was characterized by excessive increased in wall pressure and pushing energy. Both wall pressure and pushing energy increase are less desirable due to their detrimental effect on the physical condition of the oven walls. Furthermore, addition of coke oven tar with 1% moisture content to coal blend can be prohibited by its high viscosity. At 3% moisture content in coke oven tar addition of 6 wt.% in the coal blend, coke properties improved. When the amount of coke oven tar was increased to 8 wt.% at the optimum coke oven addition, coke yield was not affected but low CSR of 57.8 against a target of ≥60 was achieved as opposed to CSR of 65.4 at 6 wt.%. Also, coke stability of 52.2 at 8 wt.% as opposed to 56.1 at 6 wt.% was achieved. Moreover, the highest I40 of 50.9 was achieved at 6 wt.% whereas with 8 wt.% coke oven tar, I40 of 47.9 was achieved. However, up to 2% decrease in coke yield was observed. Despite this 2% decrease in coke yield, coke oven tar addition is a positive and viable option based upon economic factors (i.e. this reduces the quantity and cost of imported coals and still achieves improved coke quality which result in improved blast furnace operation and better hot metal quality).

Keywords: coal substitution, coke oven tar, coal moisture, coal blend, coke quality

CHAPTER 1: INTRODUCTION

1.1 Background and Motivation

The development of the iron and steel industry has changed the situation of the international coking coal market throughout the world considerably over the years. The ever increasing change has resulted in giving rise to a prominent increase in coal prices and making it more difficult to obtain coals that were readily available on the market before (Ruiz *et al.*, 1990; Fernández *et al.*, 2012). As a result of economic consideration, coke producers have opted to reduce percentage of these expensive coking coals in the blend. The later statement is supported by Fernández *et al*. (2012) who mentioned that considering economic factor and good quality coking coals availability, it is now necessary to include larger amounts of weakly coking coals in industrial coal blends. In another case, Jackman and Helfinstine (1970) added that the scarcity and high delivered cost of low and medium volatile coals have made it desirable for coke producers to reduce the percentage of these coals in blends for making metallurgical coke. Due to the characteristics of coking coals in South Africa, metallurgical industries have to use coal that would probably be regarded as being of low quality or unacceptable for the same purposes in the USA or Europe. Generally, the deficiencies in South African coal qualities are mainly due to high ash content, high inertinite content and lower rank. Therefore the desire to conserve coking coals worldwide have resulted in the treatment whereby most of the metallurgical coke produced in South Africa is produced from a blends having weakly coking coal such as Waterberg Grootegeluk coal included in the industrial coal blend.

In order to face the escalating worldwide requirements for metallurgical coke with a concern for preserving the base of raw materials, the limited reserves of prime coking coals, semi-soft coking coal and non-coking coal in an environment friendly manner, more and more efforts have been made over the years to find new ways of improving coke quality while conserving the range of cokeable coals. A variety of technologies such as coal pre-treatment, stamped charging, briquetting charging and formed coke, addition of petroleum coke to coal blend

and chemical additives such as oil, diesel and tar to coal blend or to substitute coking coals by non-coking coals have been reported by various researchers (Jackman and Helfinstine, 1970; Kestner *et al.*, 1981; Chatterjee and Prasad, 1982; Leibrock and Petak, 1983; Gonzalez – Cimas *et al.*, 1987; Lin and Hong, 1986; Taylor and Coban, 1987; Alvarez *et al*., 1989; Das *et al.*, 2002; Plancher *et al.*, 2002; Shevkoplyas, 2002; Benk, 2010; Saxena *et al.*, 2010; Benk and Coban, 2011; Melendi *et al.*, 2011; Díez *et al.*, 2012).

A few studies has been done on the use of tar or pitch addition (Grint and Marsh, 1981; Chatterjee and Prasad, 1982; Gonzalez – Cimas *et al.*, 1987; Taylor and Coban, 1987; Collin and Bujnowaska, 1994; Benk and Coban, 2011). Most of the investigations on the use of tar or pitch addition were on modifying abilities of supplied pitch material in coal co-carbonisation using a high volatile caking coal and a broad range of weak coking coals (Grint and Marsh, 1981; Gonzalez – Cimas *et al.*, 1987; Taylor and Coban, 1987; Benk and Coban, 2011). In another case, up to 2.4 wt.% tar addition was added to the prime and medium coal constituents (Chatterjee and Prasad, 1982). The third category of the published paper studied on coal tar – water emulsion added to the single Polish bituminous coal and their blend of different rank (Tramer *et al.*, 2007). Although several authors have proposed versions of tar or pitch addition, the effect of direct additives to a coal mix to alter its basic coking properties has not received equal attention within the South African context where amounts of up to 35 wt.% of inferior coals such as semi-soft coking coal are included in industrial coal blend.

In the current study, coke oven tar addition was chosen as it is a readily available material, relatively inexpensive, and was previously reported to give a good performance as a modifier (Chatterjee and Prasad, 1982; Collin and Bujonwska, 1994). However, some challenges with tar addition do exist, such as facilities for adequate proportioning of the tar mix with coal, proper mixing of coal and tars and deposition of tar on belt conveyors and return idlers (Chatterjee and Prasad, 1982). Despite these reported issues, the use of coke oven tar is still the objective of this study. Namely, the intention is to investigate the effect of substituting

various fractions of imported coking coals with coke oven tar and to confirm whether those challenges encountered by other authors (Chatterjee and Prasad, 1982) could be resolved and whether coke quality could be maintained or possibly optimised.

1.2. Problem Statement

South Africa has limited supplies of prime coking coals, these are mainly from Tshikondeni Mine in Limpopo with very small quantities from KwaZulu-Natal (Jeffrey, 2005). Blend coking coals (or semi-soft coking coals) with less than 10 wt.% ash content are mined at Grootegeluk in the Waterberg. In order to produce coke of sufficient strength and quality, South African iron and steel industries import coking coals from international countries such as USA, New Zealand and Australia, to mention just a few. The imported coals constitute up to 65 wt.% of metallurgical coal blend. Factors such as increased coal consumption, imported coals high prices, reduction in existing coking coal reserves globally, reduction in both qualities and quantities of available blend coking coals, fragile environments and poor roof conditions due to the depth and complex geology as well as insufficiently developed infrastructure to transport coking coals are concerns that the Iron and Steel industry must overcome if they are to remain competitive well into the 21st century. The latter factor is supported by Eberhard (2011) who highlighted that a major current constraint in moving coal to the end user is South Africa's aging and inefficient rail infrastructure. The use of coke oven tar to improve or maintain required coke quality for blast furnace operation while conserving imported coking coals would therefore be of benefits to the country.

1.3 Hypothesis

Coke oven tar will improve coke throughput. Coke throughput is directly dependent on coal blend bulk density. Therefore if practically possible, the highest bulk density should always be the goal.

1.4 Study Objectives

The main objective of this research is:

- To determine the optimum condition for moisture content in coke oven tar.
- To determine the effect of substituting various fractions of imported coking coals with coke oven tar over a range of 0 – 8 wt.% on the carbonization behaviour of the charge; and
- To determine the quality of the metallurgical coke produced.

1.5 Outline of Research Report

The outline of the research report is subdivided into six main parts:

- *Introduction*: where the problem statement for the overall study is outlined and the motivation is given with emphasis on benefits of positive results to be obtained.
- *Literature Review*: containing background information on coking coal characteristics, petrographic analysis, blending of coals, technologies for improving coke quality, carbonization process, important properties of metallurgical coke, and product of coal carbonisation.
- *Materials and Methods*: describing all test equipments and standard procedures used.
- *Characterization – Analytical Results*: containing detail information on individual coals proximate analysis, ultimate analysis, Rheological properties, petrographic analysis and maceral analysis. The preliminary characteristic of coke oven tar in terms of constituent is also outlined.
- *Performance evaluation*: describing analysis of experimental results in terms of the effect of coke oven tar addition on coal blend, carbonization behaviour and coke quality produced.
- *Conclusions*: clarifying the extent to which the expectations of this study were met, the greatest achievement of the study and the limitations resulting in the main observation.

1.6. Summary

In this chapter, the various methods of improving coke quality while sparing good quality coking coals were mentioned. On the basis of availability and costs, the effect of substituting fractions of imported coals with coke oven tar was selected as an option for the current study. The following sections gives detailed information on the literature study, materials and methods used, individual coals and coke oven tar characterizations, performance evaluation of coke oven tar addition, conclusions with recommendation followed by a list of references.

CHAPTER 2: LITERATURE SURVEY

2.1 Introduction

Coal is the main raw material used in making coke. In domestic market, coal is used in electricity generation (110 Mt), petrochemical coal-to-liquid industry (41 Mt), metallurgical industry (7 Mt), general use (8 Mt) and domestic use (7 Mt) (Falcon and van der Riet, 2007). The largest deposits of coking coals are mined and imported from international countries. Jasiehko (1978) reported that coking coals (gas-coking, ortho-coking, metacoking and semicoking) are mined in the USA, USSR, China, UK, German Federal Republic, Poland, Australia and Canada. The latter statement is supported by a another case reported by Díaz-Faes *et al.* (2007) who mentioned that coking coals of excellent quality are mined in China, Australia, the USA or Canada. Table 2.1 shows top coal countries exporter in 2011 **(**Eberhard, 2011). Table 2.1 shows that in 2011 Australia exported 140 million tonnes of high quality (or hard) coking coal representing 64% of total coking coal exports worldwide followed by USA at 29%. Australia's coking coal export value in 2011 was 2.5 times higher than what Hogan *et al*. (1999) reported for 1997 – 98 period indicating the extent of increase in demand. Comparatively, the volume of coking coal exported by Australia in 2011 is of the same magnitude as coal used in electricity generation reported in South African domestic market by Falcon and van der Riet (2007). According to Hogan *et al.* (1999), Asia is Australia's largest export market for high quality coking coal with exports of 35 million tonnes, followed by Europe with exports of 15 million tonnes.

Table 2.1: Top coal exporter in 2011 (Eberhard, 2011)

Country	**Steam**	**Coking**	**Total**
Indonesia	309 Mt	0 Mt	390 Mt
Australia	144 Mt	140 Mt	284 Mt
Russia	110 Mt	14 Mt	124 Mt
USA	34 Mt	63 Mt	97 Mt
Colombia	75 Mt	0 Mt	75 Mt
South Africa	72 Mt	0 Mt	72 Mt
Kazakhstan	33 Mt	1 Mt	34 Mt

According to Ministry of Economic Development's (MED) Crown Minerals site exports of bituminous coal, produced entirely from the West Coast field of New Zealand were reported to be approximately 2.4 Mt for the year ended December 2010. New Zealand coking coal with smaller amounts of thermal and specialist coals is exported mainly to India and Japan, with smaller quantities going to Chile, South Africa, Brazil, China, USA, and Australia.

The primary objective of this chapter is to evaluate information available about the feasibility of improving coke quality through coke oven tar addition to coal blend for steel and metallurgical industry operations. The feasibility evaluation include a review of coke making coals characteristics, various established and emerging coke making, the role of coke oven tar addition in coke quality improvement and mechanisms of coke quality improvement due to coke oven tar. Based on the findings of the review, the chapter will conclude with overall recommendations for implementation of the chosen technology for coke quality improvement.

2.2 Coking Coal

Coking coal is mainly used in a larger proportion to produce the metallurgical coke required in iron and steel making process. Not all coals are coking coals. A coking coal is simply a coal that when heated in the absence of air will melt, swell, vesiculate (become porous) and harden into a sponge like mass of almost pure carbon (Collin and Bujnowaska, 1994; Crelling, 2008). For example, lignites, subbituminous, semi-anthracites, anthracites and meta- anthracites do not coke. According to Snyman (1989), bituminous are the only coals in the lignite –to-anthracite rank series that possess these coking and caking properties.

2.2.1 Coking coal characteristics

For production of metallurgical coke vitrinite – rich coals with pronounced softening, dilation and coking properties are required. In addition, coking coal blend is characterized by similar amount of vitrinite and semifusinite plus

micrinite. For instance, vitrinite contents as low as 40% and semifusinite and micrinite contents as high as 45% suffices in certain cases. Both semifusinite and micrinite have significant role during coke making and for technological purposes these components need to be classified according to reflectance and structure into reactive and inert types (Díez *et al.,* 2002). Table 2.2 shows coking coals specifications. Individual coals used in the current study and prepared coal blend will be characterized using Table 2.2.

Table 2.2: Commercial terminology for metallurgical coals (Erasmus, 2011 after Pinheiro 2009)

Product Type	**VM**	**Indicative VM content (ad), %**	**Max Vitrinite Reflectance (Ro)**	**CSN (FSI)**
HCC	LV	< 22	1.3 – 1.7	7 – 9
	MV	22 – 28	1.1 – 1.5	
	HV	> 28	0.95 – 1.1	
SHCC	As above, but typically higher ash hard coking coals			6 – 8
S/WCC		Predominantly HV	< 1.0	4 – 8
SSCC		Predominantly HV	< 1.0	1 – 4
LV, SA, and A		< 17	> 1.5	0

HCC = Hard Coking Coal; LV = Low Volatile; MV = Medium Volatile; HV = High Volatile; FSI = Free Swelling Index; SHCC = Semi – Hard Coking Coal; S/WCC = Soft or Weak Coking Coal; SSCC = Semi – Soft Coking Coal; SA = Semi Anthracites, A = Anthracites

McCartney and Teichmüller (1972) suggested that bituminous and semi-anthracitic coals be divided into the following rank categories based on reflectance and equivalent American Society for Testing and Materials (ASTM) groups.

Table 2.3: Rank based on Reflectance (McCartney and Teichmüller, 1972)

Rank	Reflectance
High-volatile bituminous	0.50 – 1.12%
Medium-volatile bituminous	1.12 – 1.51%
Low-volatile bituminous	1.51 – 1.92%
Semi-anthracite	1.92 – 2.50%
Anthracite	>2.50%

2.2.2 Origin and formation of macerals

The concept behind the word ‘‘macerals’’ is that the complex of biological units represented by a forest tree which crashed into a watery swamp and there partly decomposed and was macerated in the process of coal formation. During coal formation process, the macerals did not become uniform throughout but still retains delimited regions optically differing under the microscope. These organic units composing the coal mass are called coal macerals and they are descriptive equivalent of the inorganic units composing rock masses and universally called minerals. According to Scott (2002), in 1958 Spackman proposed a definition of the term maceral as organic substance or optically homogenous aggregates of organic substances possessing distinctive physical and chemical properties and occurring naturally in the sedimentary, metamorphic, and igneous materials of the earth.

Therefore, each maceral group includes macerals that have affinities in origin or similarities in properties. Similarities in origin include both botanical affinities and the mode of preservation within the sediment. The relative proportions of the maceral groups determine coal type. Although reflectance is a major distinguishing feature between the maceral groups, morphological differences are of critical factor in defining macerals.

2.2.2.1 Petrographic analysis

Petrographic analysis is the determination of the microscopic organic building blocks of coal, which was formed from the original plant tissues that accumulated

as peat, were decomposed, and finally coalified. The coking properties of bituminous coals depend mainly on the coal rank and petrographic properties (Varma, 2002). The building blocks of coal are called macerals. According to Sun *et al.* (2003), macerals are the microscopically identified organic components of coal and have a distinct physical and chemical property, which reflect differences in original plant during deposition and the degree of coalification or rank and affects the overall behavior of the coal. Macerals are divided into three broad groups; Vitrinite, Exinite (Liptinite) and Inertinite. Short description of each broad group is given below.

(a) Vitrinite.

Vitrinite is the most abundant maceral in most, but not all, coals. In some coals of Palaeozoic or Mesozoic age, inertinite and more rarely liptinite is the most abundant maceral group. Most coals of tertiary age have a very high content of vitrinite, the only exceptions being some relatively rare coals in which resinite or bituminite is unusually abundant. Thus, in volumetric terms, vitrinite is the most important maceral. Not only does this group contain true plant cell walls, but also detrital material and chemical precipitates. For most coal petrologists, a morphological distinction is made between cell walls (telinites), detrital material (detrinites), and gels (gelinites/collinites) (Teichmüller, 1989). In many summaries of coal petrography, vitrinite is equated to woody cell walls, leading to the view that this implies forested peats (Scott, 2002). The vitrinite reflectance of a coal can be taken as a measure of its rank. Vitrinite is distinguished from the other maceral groups primarily on the basis of its morphology, but the morphology of vitrinite in coals varies widely. Other properties of vitrinite are normally taken into account when making identifications of specific phytoclasts.
Vitrinite has optical properties lying between those of the macerals of the liptinite and inertinite groups at low and medium of rank or maturation

(b) Inertinite

The inertinite group of macerals are important components of many pre-tertiary coals but are present only as a minor component in most tertiary coals. Inertinite has a mixed range of origins but all the macerals have reflectances higher than that

of vitrinite in low and medium rank coals. Most inertinite is derived from tissues similar to those that give rise to vitrinite but represent preservation under different conditions. Inertinites is a diverse maceral group, yet they are classified together. Any interpretation on the origin and significance of the macerals must take account of this. The characteristic properties of inertinites include high reflectance, little or no fluorescence, high carbon and low hydrogen contents, and strong aromatization, Scott (2002). The term inertinite was originally claimed to refer to its behavior in coals of coking rank in which the maceral was not thought to soften during carbonization (Scott, 2002). Inertinite has a higher reflectance than vitrinite over most of the range of rank or maturation. This is partly a function of a higher refractive index but is due in large part to a much higher absorptive index

(c) Exinite (Liptinite)

In coals of low and medium rank, liptinite macerals have a reflectance much lower than that of vitrinite and typically show autofluorescence when illuminated with ultra-violet, violet or blue light. With increasing rank, liptinite reflectance increases. Most of the liptinite macerals show botanical structures that clearly indicate the origin of these macerals. Most of the macerals within the liptinite groups are derived from specific tissue types, the exception being liptodetrinite, where the origin is uncertain because of small size of the phyterals. Liptinite is distinguished initially from other macerals on the basis of its lower reflectance. Liptinite from coals of lower or medium rank with low reflectance play, due to their plastic properties, the role of plasticizers and agglomerizers, while liptinite from high rank coking coals with higher reflectance behave in the coking process like vitrinites. Liptinite because of their chemical composition - high carbon and hydrogen content and high content of volatile matter – are responsible to a high degree for the yield and composition of the tar (Jasienko and Kidawa, 1987). Therefore according to Jasienko and Kidawa (1987), liptinite behaved as fluido-plastic substances.

The ratios of these maceral groups with respect to one another and the reflective intensity of the vitrinite group in particular, supply a definite fingerprint to each and every coal that will be unique in its own way. For an example, from the ratio of vitrinite to inertinite, predictions can be made as to how a coal will combust, i.e. high vitrinite low inertinite will produce a better quality flame and burn out will occur much faster whereas high inertinite and low vitrinite coals will take longer to burn out and would require a higher temperature for ignition. But because prime coking coals, with all desired quality requirements for producing coke, are rare, blending coals with different but compatible or complementary coking properties is common practice (Díez *et al.,* 2002). On the other hand, maceral reflectance which is indicative of the rank or maturity of a coal is not only the most informative parameter in the coal, but it can be used to correlate or predict certain key physical and chemical properties of coal. By using petrography the differences between carboniferous coals from the northern hemisphere and the Gondwana coals from the southern hemisphere are easily identified. As an example, Northern coals are higher in vitrinite and lower in inertinite than their southern counterpart.

Many studies have been made of the effects of coal petrographic parameters on the coke properties but it has been established that these predictive methods cannot be used generally although they may be utilized in specific areas (Košina and Heppner, 1985). According to Díaz-Faes *et al.* (2007), the petrographic composition of coal varies depending on the origin. For example, coals of the Southern Hemisphere are characterised by higher amount of inertinite type maceral. Furthermore, the Americans coals exhibit a higher amount of vitrinite type maceral (mean value, 74.8 vol.% mmf), while the Australian and Chinese coals present a higher percentage of semifusinite and fusinite maceral (mean value, 24.5 and 48.5 vol.% mmf) for Australian and Chinese coals respectively (Díaz-Faes *et al.*, 2007).

2.2.3 Blending of coals

Coke making can be categorized into coal blending (B), pre-treatment (P), and carbonization (C). Therefore, the coke quality can be uttered mathematically as follows:

$$\text{Coke quality} = f(\text{B, P, C}) \tag{2.1}$$

In the Eq. (2.1) above, B is called internal factor and both P and C are external factors. According to Tiwari *et al.* (2013), the coke quality depends on approximately 70% of the properties of the coal used and about 30% of the coke making conditions. Therefore according to Tiwari *et al.* (2013), coal blending constitute up to 70% of the coke quality while 30% is made up of both pre-treatment and carbonization. This section covers coal blending of the coke making process. Pre-treatment and carbonization will be discussed briefly in section 2.4.

Coal qualities vary a lot from seam to seam, mine to mine and even region to region. Therefore every coal is only one of its kinds in their property hence coal selection and carbonization preparation conditions is very important. Efficient blast furnace operation requires a blended coal source which is very consistent in quality and exhibits properties which may not be available in a single coal. In addition, normal practice in coke making demands a coal blend that is low in cost, produces a high quality coke, and provides a safe oven pushing performance (Ruiz *et al.,* 1990; Díez *et al*., 2002). The economics of metallurgical coke manufacturing have caused a move towards the use of low rank coals in suitable blends considering the cost of coals from importing countries (Alvarez *et al.*, 1989). South African iron and steel industries import coking coals from international countries. As a result, coal blend varies in number of coals used, the proportion, rank, coking properties, and geographical origin of coal components. Information on interactions between coking coals in blends is well established in literature (Sakurovs, 2003; Díez *et al.*, 2002) and will not be discussed in this study.

2.3 Technologies for Improving Coke Quality

A number of technologies have been used for upgrading coking coals, or to substitute coking coals by non-coking coals in order to improve coke quality. The following subsection detail on those various technologies employed their corresponding effects and viability.

2.3.1 Chemical additives

The possibility of expanding the base of raw materials using chemical additives has been examined by Shevkoplyas (2002). Shevkoplyas (2002) studied the effect of hydrochloric acid (HCl) on the thermoplastic properties of coals to improve their coking ability and to establish the effect of HCl additive on the structure of the parent coal and its change during the carbonization process. Shevkoplyas (2002) results pointed out that HCl additive enhances the decomposition reaction (improving the caking ability of coals) on the other hand, increases condensation reaction (improving the coking ability of coals) and increases the coke strength of the high volatile coal. According to Shevkoplyas (2002), both these components of coal carbonisation take place at the same time. It was summarised from Shevkoplyas (2002)'s findings that HCl has the following effects: catalytic, change quantity and the quality of the products obtained, improvement of the thermoplastic properties of the coal, and increase caking and coking ability of the coal. On the basis of availability and costs, addition of HCl is not a viable option in improving coke quality. There is a limited supply of HCl in South Africa. The main contributing factors to HCl shortage is due to its usage in the production of fertilizer, chlorides, dyes, in electroplating, in the photographic, textile, and rubber industries.

2.3.2 Coke breeze addition

Blending coking coal with small amounts of 'carbonaceous inerts' such as coke breeze has been practised for over a century and the technique is now widely used (Patrick and Stacey, 1975). According to Patrick and Stacey (1975), the addition of an inert material to a coking coal decreases its plastic properties but the effect does not follow a simple addition law. Although the coke tensile strength changed

with the breeze content of the coke oven charge, the changes did not appear to be systematic although from the strength viewpoint an optimum breeze content of about 10% in this instance was indicated. The presence of the breeze in the charge influenced the physical structure of the coke produced as demonstrated by a generally progressive increase in apparent density and decrease in porosity, but these changes were not accompanied by systematic changes in mean pore size or pore-wall thickness (Patrick and Stacey, 1975). Separately, Alvarez *et al.* (1989) concluded that additions of coke breeze or silica sand in small amounts also improved the tensile strength of coke. Although coke breeze addition has been reported to be an established concept, the literature results are very preliminary. Further test will have to be completed in concept consolidation before implementation is proposed. Other concerns for implementation include insufficient coke breeze stock.

2.3.3 Petroleum cokes

The use of petroleum coke has been extensively studied as an additive in coking blends through many years (Jackman *et al.*, 1960; Alvarez *et al.*, 1989; Ruiz *et al.*, 1990; Ruiz, 2001). According to Jackman *et al.*, (1960), petroleum coke was tested in Illinois coal blends as possible replacement for low volatile coal in the production of metallurgical coke suitable for the blast furnace use. Blends containing 10 – 20 wt.% petroleum coke were carbonized in a pilot oven. Higher percentages were not tried as previous tests have shown that over 20 wt. % of petroleum coke caused a great reduction in the hardness index of the resulting product. Of the blends tested, those containing from 15 – 20 wt. % petroleum coke, produced cokes with physical properties most nearly suitable for blast furnace coke (Jackman *et al.*, 1960).

Furthermore, Alvarez *et al.* (1989) used petroleum coke in different proportions, ranging from 5 to 40 wt.%, in the production of metallurgical cokes. Alvarez *et al.* (1989) study showed that the addition at 3 wt.% and different particle size of green petroleum coke produced an improvement of coke mechanical strength and reactivity towards CO. However, when the amount of petroleum coke was

increased to 6 wt.%, only the addition of the finest size fractions had a positive effect on the resultant coke properties. When the finest petroleum coke was added, the coke mechanical strength improved. This improvement may be explained by the decrease in total porosity and the greater mutual interaction between metallurgical coke and petroleum coke transitional and fused interfaces (Alvarez *et al.*, 1989). Thus, the decrease in micropore volume contributes to a decrease in reactivity towards CO. However, the larger particle size tested has the opposite effect and produced a greater amount of poorly bonded interface with the coke matrix. As a result the metallurgical coke has a lower mechanical strength.

In another case, Ruiz *et al.* (1990) carried out the study on possible utilization of petroleum cokes of different qualities in the production of metallurgical cokes. The use of blends of high volatile coking coal with petroleum cokes (high, medium and low volatile content) was studied. It was found that when high volatile content petroleum coke was used, a better quality of metallurgical coke (lower reactivity to CO_2 and lower fines production in microstrength test) was obtained. Using other petroleum cokes (low and medium volatile content), it was still possible to lower the fines production but the reactivity to CO_2 was higher than that of the coke obtained from single coal. According to Ruiz (2001), the benefits of using petroleum coke are related to the reduction of ashes in carbon content of the metallurgical coke, increasing coke oven productivity assuring coke oven life and reducing coke rate in the blast furnace. In addition, the more petroleum cokes in the blend, the lower the amount of ashes (Ruiz, 2001). Ruiz (2001) added that depending on the kind of petroleum coke and the amount added to coal blend, coke stability, Micum 10 (M10), Micum 40 (M40), CSR may improve and reduce the risk of oven wall pressures, extending the life of the battery. The use of petroleum coke in coking blends could be feasible depending on factors such as cost of petroleum cokes, geographical situation and the quality of petroleum coke, commercial strategies and technical problems. On the basis of these factors, petroleum coke addition is not an alternative option to consider at this stage.

2.3.4 Municipal plastic wastes

Melendi *et al.* (2011) incorporated plastic wastes into coal blends as additives for metallurgical coke production. Melendi *et al.* (2011) results indicated that plastic waste practically does not affect the coke reactivity towards CO_2 (difference of one point) and in the case of CSR, it is considerably improved by four points. Therefore, the coke from plastic waste does not follow the general trend observed for the CRI and CSR of the blast-furnace cokes: i.e. the lower the CRI, the higher the CSR index. According to Melendi *et al.* (2011), incorporated plastic wastes into coal blends has been demonstrated to be viable at industrial scale and provides a way to increase energy recovery and feedstock recycling while at the same time, offering economic, social and environmental benefits.

The effect of plastic addition on coal caking property was also investigated by Nomura *et al.* (2003) in a separate case. Nomura *et al.* (2003) revealed that thermal decomposition products of plastics interacted with bituminious coal during carbonization in a coke oven. Also the effect of plastic addition on coal caking property varied with the types of plastics. The addition of aliphatic polymers such as polyethylene (PE), polypropylene (PP) and poly vinyl chloride (PVC) had only a small effect on coal caking property and coke strength. On the other hand, the addition of polystyrene (PS), poly ethylene terephthalate (PET) and terephtalic acid (TFA) inhibited coal expansion and fusion, decreased maximum fluidity and total dilatation and deteriorated the coke strength. These differences were discussed from the viewpoint of the interaction between thermal decomposition products of plastics and hydrogen in coal. The use of plastic waste as a substitute for coal in the steelmaking industry may be regarded as an eco-efficient alternative for solving the problem of plastic disposal and for dealing with plastic wastes which are not easy to recycle by mechanism means. However, the results are very much preliminary and further tests are required to consolidate the proof of concept. Consistent plastic waste and availability should be guaranteed from municipalities which was not the case.

2.3.5 Biomass material

Biomass material has been included in the blend lately in order to study its effect of coke quality. The effect of blending different biomass material with Indian non-coking coal was investigated by Das e*t al.* (2002). Non – coking coal from Western Coalfields Limited in India with high volatile matter was used in the study. Biomass material with low ash and hydrogen contents between 5 – 7 wt.% was used for blending of coal with high ash content (32 wt.%) and low hydrogen content (3 wt.%). The strength of coke as found by Micum and shatter index tests was suitable for utilisation in the foundry. Although the findings are preliminary, biomass addition in coal blend is still at its development stage and more tests will have to be completed to validate the concept.

2.3.6 Pre – heating method

Pre-heating methods have been developed further during the last years in France, England and Germany (Leibrock and Petak, 1983). According Leibrock and Petak (1983), pre-heating methods differs from other methods simply in the way of charging of ovens. Pre-heating methods entails top charging. According to Leibrock and Petak (1983), apart from the increase in high volatile obtained from the pre-heating method, the heat transport which is considerably changed due to the lack of water, contributes in a decisive way to improvement in the coke's mechanical quality properties. Pre-heating methods aid with producing blast furnace coke with good mechanical properties even from coal blends with a swelling index on only 4 – 6 and a dilatation of the pre-heating leads to a higher productivity of 30 – 60% (Leibrock and Petak, 1983). Experimental coking studies show also that coke stability may be increased by preheating certain of these coal blends in which the amount of high volatile constituent has been reduced materially (Jackman and Helfinstine, 1970).

In a separate case, Menendez and Alvarez (1989) mentioned that preheating is a technique which substantially improves coke quality from low rank coals. It also produces an increase in oven and battery throughput (as much as 50% for the lower rank coals). According to Alvarez *et al.* (1989), the use of preheating

increases coke tensile strength and abrasion resistance. Other advantages derived from the elimination of the water from the charge include more uniform heating and a reduction in the thermal shock. Applications of preheating also provide more effective smokeless charging, elimination of routine mechanical levelling and a decrease of pollution during the pushing operation (Menendez and Alvarez, 1989). The disadvantages of the preheating process are related to the difficulties of handling fine hot coal and the increased carryover of fines. Coking pressure during carbonization must also be strictly controlled and for that reason coking batteries charged with preheated coals have more technical problems. In addition, preheating process does not necessarily reduce the volume of coals required for preparing a blend.

2.3.7 Addition of coal with different volatile matter

In another case, Hartwell *et al.* (1982) established that the addition of coals of volatile matter content less than 16% to a number of medium or high volatile coals of 25 – 26 wt% volatile matter result in changes in coke tensile strength. The strongest cokes were generally 20% higher in tensile strength and 4 – 5% lower in porosity than those made from the base coals. Further addition of the low volatile coals above the amount required to produce the strongest cokes led to a reduction in coke strength due to the inability of the excess low volatile additive to be incorporated within the coke matrix.

2.3.8 Briquetting method

Coal briquetting consists of applying pressure to small coal particles with or without the addition of a binder to form compact or agglomerate – shape fuels for domestic or industrial applications (Diez *et al.*, 2012). Since about 1950 efforts were made at the coking plant of the steel company, Röchling – Burbach to attain a density increase in the top-charging method. Briquette blend coking process was most commonly used in Japan as a technique to use low grade coals (Menendez and Alvarez, 1989). According to Menendez and Alvarez (1989), Japan investigated the possibility of increasing the bulk density by a part-briquetting since early 1970s.

The literature reported that two methods were used in achieving partial briquetting in the literature. In the first method, about 30% of the charge was taken, ground and briquetted after the addition of the binder. The briquettes are mixed with the other parts of the coal. The content of poor caking coals can only be increased slightly by this method (Leibrock and Petak, 1983). In the second method a separate blend was produced for the briquetting with an increased utilization of poor caking material in the blend. In the later case, the briquetted portion of the blend had positive effect of the density of poor caking coals, e.g. carbon carries.

Menendez and Alvarez (1989) investigated the possibilities of substituting coking coal with non-coking coal and poorly caking coals by applying briquetting method in order achieve coke with a suitable strength. It was found that an increased bulk density in the coke oven could be attained by briquetting wet charge coal without binder. The major advantages of briquetting method is weakly- coking coal or non-coking coal can be used in limited amount in the metallurgical coke production, coking process is thermally more efficient, increased in bulk density in coke ovens translated to productivity of coking plant increase and coals of different properties are distributed more homogeneously in the coke – chamber, hence the mechanical strength of the coke is increased. A further advantage of the method lies in the considerable limitation of the "carry-over" which is undesirable in the charging of pre-heated coals.

In another case, Díez *et al.*, (2012) studied the manufacture of briquettes by using carbon containing waste from steelmaking as fillers and binders for use in coke ovens to produce metallurgical coke. In general, the coke quality parameters did not show any significant deterioration as a result of the addition of carbon briquettes when the amount and the nature of the binder and the particle size of the filler were optimized. (Díez *et al.* 2012). Although briquetting can increase the handleability of coal, operational costs cannot be underestimated.

2.3.9 Stamp charging method

The stamping charging method has been known since the end of the 19th century. Differently from briquetting, with stamp-charging method a large volume of coal charge is compacted to one single coal cake before entering the coke oven chamber. According to Leibrock and Petak (1983), advantages of this kind of densification are high density, good homogeneity over all the cake and the possibility of building the gas collecting room relatively small and compact. Stamp-charging method is used in places where high volatile or poor coking coals are mined such as Poland, Czechoslovakia, Romania, China, Lorraine/France and in the Saar region.

The technological result of the application of the stamping method is the possibility of producing high quality coke from high volatile and low baking coal in a blend with low volatile charging material. According to Menendez and Alvarez (1989), stamping increases bulk density of the charge and improves coke strength, especially resistance to abrasion. Menendez and Alvarez (1989) added that stamp charging increase oven throughput, coking coal conservation due to use of higher proportion of high volatile and poor coking coal in the blend, improvement of coke quality (M10 improves by 3 – 5 points with respect to a base value), lower coke reactivity, increase in blast furnace coke yield (3 – 4%). Although stamp charging increase oven throughput and improve coke quality, a higher bulk density increase results in high coking pressure and hard pushes.

2.3.10 Tar and pitch additions

Due to the progressive decrease in unavailability and high cost of prime coking and strongly caking (high rank) coals suitable for production of metallurgical coke, there have been an interest in the use of pitch additives and tar in coal blends for making of metallurgical coke. The previous work conducted on direct tar or pitch addition to a coal blend has been cited by Grint and Marsh (1981); Chatterjee and Prasad (1982); Gonzalez – Cimas *et al.* (1987); Taylor and Coban (1987); Collin and Bujnowaska (1994); Benk and Coban (2011).

The interaction of high volatile caking coal blend and pitches has been investigated since the early eighties by Grint and Marsh (1981). Grint and Marsh (1981) found that industrially supplied pitch materials have quite different modifying abilities in coal co-carbonization. As the chemical composition of coals and pitches is extremely complex, no exact explanation exists of differences in size and shape of optical texture of resultant cokes in terms of the pyrolysis chemistry of the carbonization process (Grint and Marsh, 1981). Grint and Marsh (1981) suggested that the presence of naphthenic groups and aromatic ring systems in molecular constituents promote the growth of larger anisotropic areas (optical texture) whereas the presence of heteroatoms and functional groups promote the growth of smaller optical texture. According to Grint and Marsh (1981), it appeared that addition of selected pitch materials to a coal blend co-carbonization system can result in both an increase in coke strength and a decrease in coke reactivity.

In Chatterjee and Prasad (1982)'s study, tar was added to the prime and medium coal constituents. By adding tar alone it was found that 1.8% tar (without any addition of LDO) gave the same properties as did the briquette blended charge and when the tar amount was increased to 2.4 wt.%, the properties improved even further. According to Chatterjee and Prasad (1982), the addition of 1.5 wt.% tar and anthracene oil mix improved the quality of the resultant coke by a minimum of 2 points in terms of the Ml0 index, irrespective of the proportion of blendable coal in the final mix, while the M40 index improved by 1 point minimum. Such improvements are well within reproducibility and are therefore not considered significant. A cursory study of the Irsid as well the Japanese drum indices also confirmed significant improvements in coke strengths on account of tar addition. Chatterjee and Prasad (1982) established that factors associated with improvement of coke quality following tar addition were due to increase in bulk density, increase in maximum fluidity and plastic temperature range, and increase in maximum thickness of the plastic layer. It can be concluded that increasing the fluidity of coal blends in the coking process by tar addition favours wetting of non-softening coal grains, effects the homogenization of coal mass and facilitates

moving and binding of the structural elements. Chatterjee and Prasad (1982) recommended that if tar addition can permits the use of inferior coals in the coking blend while maintaining the same coke quality, major savings would arise.

The challenges with tar addition such as facilities for adequate proportioning of the tar mix with coal, proper mixing of coal and tars, deposition of tar on belt conveyor and return idlers and the damage thereof were mentioned by some earlier researchers (Chatterjee and Prasad, 1982). However, coke oven tar addition could be a simple and practical approach for bringing about satisfactory improvement in coke quality in certain in many cases.

In another case Gonzalez – Cimas *et al.* (1987) investigated the influence of pitch addition on charges of single low rank caking coals and to a blend of low and high rank coals using a small oven capable of producing dense, high strength coke in amounts sufficient to permit measurement of strength and structural parameters. Addition of any of these pitches studied resulted in reduced coke tensile strength, the reduction being greatest for those pitches which most markedly enhanced the coke textural index. Gonzalez – Cimas *et al.* (1987) results indicated that pitch addition resulted in increased textural index and microstrength and reduced porosity but only small changes in tensile strength.

In a separate case, Taylor and Coban (1987) investigated the possibility of producing metallurgical quality formed coke from the char and coal tar pitch binder. In Taylor and Coban (1987) investigation, the char was produced by carbonizing the Turkish lignite in a series of fluidized beds operating at different temperature of increasing order. The main conclusions of their study could be summarised as follows: it was possible to produce formed coke of much higher tensile strength than that of the metallurgical coke. The tensile strength of the briquettes varied markedly with the type of binder preparation procedures.

Collin and Bujnowaska (1994) established that co-carbonization of coals with pitches seems to be possible to use a broad range of weak – coking coals for the

production of high strength metallurgical cokes for the blast furnace process. In addition, Benk and Coban (2011) investigated the possibility of producing metallurgical coke from coke breeze and anthracite fines. Benk and Coban (2011)'s findings highlighted the fact that 50% (w/w) air blown coal tar pitch and 50% (w/w) phenolic resins blend was the overall optimum. The results made more economical sense due to coke breeze briquettes of the highest tensile strength.

2.3.11 Coal tar–water emulsion

Coal tar–water emulsion added to the single coals and their blends in the amount of 2, 3 and 4% of the charge was studied by Tramer *et al.* (2007). The emulsion was prepared from coal pyrolysis products: coal tar and raw ammonia liquor in the ratio 1:1. The tar used to prepare the emulsion contained 5.1% of components insoluble in toluene, 2.2% insoluble in quinoline, and 54% of distillation bottoms (pitch). Polish bituminous coals of different rank such as the lower rank coals, the medium rank coal B and higher rank coals were used. It was found that the addition of coal tar –water emulsion to coal during pyrolysis affects the structure of the plastic layer, changes the thickness of its zones as well as the parameters characterising the dynamics of the plastic mass movement during carbonisation.

2.4 Carbonization Process

Coke making process involves carbonization of coal at high temperatures in an oxygen deficient atmosphere in order to concentrate the carbon. Coke is the hard, porous carbon residue from the carbonization of coals or coal blends. According to Varma (2002), when coal is heated it undergoes physical and chemical changes giving rise to moisture content, volatile matter, and solid residue composed mainly of carbon. When coking coal is heated in the absence of oxygen, it soften (around 375 – 400 °C) and then as heating progresses it resolidify (around 500 °C) into hard and porous pieces of coke (Díaz-Faes *et al.*, 2007). In summary, the coal-to-coke transformation takes place as follows: The heat is transferred from the heated brick walls into the coal charge. From 300 – 400 °C, the coal decomposes to form plastic layers near each wall. At about 425 – 600 °C, there is

a marked evolution of tar, and hydrocarbon compounds, followed by resolidification of the plastic mass into semi – coke. At 600 – 1000 °C, the coke stabilization phase begins. This is characterized by contraction of coke mass, structural development of coke and final hydrogen evolution. Despite the plastic stage, the plastic layers move from each wall towards the centre of the oven trapping the liberated gas and creating in gas pressure build-up which is transferred to the heating wall. Once the plastic layers have met at the centre of the oven, the entire mass has been carbonised. The incandescent coke mass is pushed from the oven and wet quenched.

Varma (2002) provided an atlas on carbonisation process. Two physiochemical changes are observed during heating of coal, thermoplastic stage and solid material contracts at higher temperature range. The thermoplastic stage act as initial phase usually with slow decomposition rate yielding water, oxides of carbon and hydrogen, sulphides from thermally labile constituents or from facile condensation reactions. Above 200 °C, carbon isomerisation seems to start. In the thermoplastic stage breaking of cross – linkages comprising either oxygen or nonaromatic carbon bridges between adjoining aromatic groups take place which results in mobility of some decomposition products. Components having lower molecular weight can undergo further change to give rise to gaseous and highly complex mixtures in coal tar. The degree of molecular mobility controls the plasticity of the coal during the fluid stage and subsequently caking power at resolidification. Pores are primarily bubbles like structure formed as gas evolved in molten coal during carbonisation. Table 2.4 shows summary of temperature ranged when coal is carbonised to coke.

Table 2.4: Temperatures from coal to coke (Erasmus, 2011)

Temperature	Condition of the coal and/or coke.
Room Temperature	No plastic properties evident.
About 100 °C up	Water (surface and hydration) driven off.
300 – 440 °C	Most coking coals begin to soften.
About 425 °C	Rapid decomposition begins with evolution of tars, oils and gases.
425 – 440 °C	Degree of fluidity and rate of decomposition increase rapidly.
440 – 480 °C	Fluidity decreases, usually rapidly.
450 – 510 °C	Material solidifies to semi – coke.
About 495 °C	Evolution of condensable products ceases but production of fixed gases continues.
495 – 870 °C	Further decomposition and shrinkage of the semi-coke to form high temperature coke with evolution of carbon monoxide, hydrogen, and some hydrocarbons, such as methane and ethylene.
870 – 980 °C	Continuing of shrinkage of the coke. Gases evolved are principally hydrogen and small amount of carbon monoxide and methane.
925 – 1040 °C	Coke is ready to be pushed.

2.5 Product of Coal Carbonization

Coke oven tar is one of the by-products generated during condensation and cooling of coke oven gas. High temperature coal tar from coke ovens is a very complex material, consisting of a variety of compounds of different functionality and a wide range of molecular weight (Díez *et al.*, 1994). According to Li and Suzuki (2009), tar is a complex mixture of condensable hydrocarbons which includes single ring to 5-ring aromatic compounds along with other oxygen-containing hydrocarbons and complex polycyclic aromatic hydrocarbon (PAH).

Typical coal oven tar composition includes pitch (62%), light oils (up to 200 °C 5%), middle oil (200 – 250 °C 17%), heavy oil (250 – 300 °C 7%), anthracene oil (250 – 350 °C 9%). Coal oven tar accounts for about 10 – 15% of the benzene,

toluene and xylene (BTX) production and about 95% of the larger aromatics (Crelling 2008). According to Crelling (2008), it is usually refined into coal tar pitch which is used to make chemicals, roofing and road tar, pipe enamels, and binder pitch in the manufacturer of bakes anodes and graphite electrodes. An additive like tar is a viscous liquid at ambient temperature but softens at temperature below or within the plastic temperature range of a coking coal blend (Chatterjee and Prasad, 1982).

Among binder feedstocks, coal-tar pitch has been one of the earliest and most extensively used bituminous binders until now (Díez *et al.*, 2012). According to Saxena *et al.* (2010), coal tar pitch is a resinous material containing α and β type of resins, indicated by the difference between Quinoline Insoluble (QI) and Benzene/Toluene Insoluble (BI/TI), which contributes significantly to the binding of coal particles. In addition, additives such as coal tar and pitch commonly referred to as fluidity enhancer can play a more direct role in improving the strength characteristics of the resultant coke (Saxena *et al*., 2010). Gonzalez – Cimas *et al.* (1986) emphasized that a wide range of carbonaceous materials – tars, coal-tar and petroleum pitches, solvent refined coals, coal extract and individual organic compounds have all been shown to modify the texture of cokes. Based on the molecular weight of tar compounds, some researchers (Li and Suzuki, 2009) divided tar components into five groups as shown in Table 2.5 below.

Table 2.5: List of tar compounds for different tar classes (Li and Suzuki, 2009)

Class	Class Name	Property	Representative compounds
1	GC-undetectable	Very heavy tars, cannot be detected by GC.	Determined by subtracting the GC-detectable tar fraction from the total gravimetric tar
2	Heterocyclic aromatics	Tars containing hetero atoms; highly water soluble compounds	Pyridine, phenol, cresols, quinoline, isoquinoline, dibenzophenol
3	Light aromatic (1 ring)	Usually light hydrocarbons with single ring; do not pose a problem regarding condensability and solubility.	Toluene, ethylbenzene, xylenes, styrene
4	Light PAH compounds (2–3 rings)	2 and 3 rings compounds; condense at low temperature even at very low concentration.	Indene, naphthalene, florene, methylnaphthalene, biphenyl, acenaphthalene, phenanthrene, anthracene
5	Heavy PAH compounds (4–7 rings)	Larger than 3-ring, these components condense at high-temperatures at low concentrations.	Fluoranthene, pyrene, chrysene, perylene, coronene

PAH - polycyclic aromatic hydrocarbon

The interaction between coal and coke oven tar during carbonization has been well studied in the literature. Some authors found that interaction occurred due to the presence of naphthenic groups and aromatic ring systems in molecular constituents to promote the growth of larger anisotropic areas (optical texture)

whereas the presence of heteroatoms and functional groups promote the growth of smaller optical texture. Coke oven tar excellent properties enable it to agglomerate fine coal particles into a coherent briquette by applying a soft thermal treatment with steam to allow the pitch to be fluid (Díez *et al*., 2012).

2.6 Important Properties of Metallurgical Coke

Coke is a major source of carbon in the blast furnaces operations. A high quality coke should be able to support smooth descent of the burden with as little degradation as possible, while providing the lowest amount of impurities, high thermal energy, high metal reduction and optimum permeability for flowage of gaseous and molten products. In the furnace the coke has four function: it is a fuel to provide heat and drive the chemical reactions, it reacts with blast air to form carbon monoxide which reduces the iron oxide to metallic iron, it maintains permeability in the furnace, and as the only solid material in the reaction zone, it supports the burden in the furnace (Díaz-Faes *et al*., 2007; Crelling, 2008; Nomura and Arima, 2013). To successfully fulfil its support function, coke must have sufficient strength to avoid being crushed. Thus the strength of metallurgical coke is its most important property. The later statement is supported by another case reported by Díez *et al.* (2002) who mentioned that the importance of coke physical properties is linked to the need to support the ferrous burden and to give a permeable matrix through which reducing gases can flow and molten material can percolate in the lower blast furnace region.

Coke properties that generally affect blast furnace performance are chemical composition, size, strength and reactivity. Composition of coke is usually measured in terms of volatile matter, ash, sulphur, alkali and phosphorus contents. Coke physical properties such as its size (mean and distribution), its resistance to breakage and abrasion, depend largely upon the coal and the nature of organic additives (if any) used in its production and the temperature at which it was carbonised (Košina and Heppner, 1985; Gray and Champagne, 1988).

Coke properties are characterised by a number of indices. According to van der Velden *et al.* (2011), strength and the reactivity towards CO_2 are the common parameters. It is well known that two factors which control coke strength are mean rank of coalification of blended coal, and plastic properties of the blend (Lin and Hong, 1986). Coke reactivity tests indicate the rate at which carbon is converted to carbon monoxide by reaction with CO_2 under specified conditions of temperature and gas flow. Coke reactivity to CO_2 has been regarded as an indicator for its quality since 1970s, when the Nippon Steel Corporation introduced a test that has been generally accepted as an effective method of assessing coke quality for the steel industry (Fernández *et al.*, 2012). Nevertheless, Fernández *et al.* (2012) claimed that it does not truly represent the behaviour of coke in the blast furnace because of the changing composition of the reacting gas and the change in temperature in the blast furnace as the coke descends.

Other parameters such as M10/I10 and M40/I40 are used to characterise the resistance against abrasion of coke and the resistance against breakage respectively. Usually, the coke size decreases due to breakage during transport from the coke making plant to the blast furnace. Strength is the most important physical property of coke with considerable effort attempting correlations with coal rank and type in terms of total inert content, rheology as indicated by maximum fluidity, total dilatation, and parameters deduced from petrographic compositions of coal (Díez *et al*., 2002).

The rheological properties of coals such as caking properties (expressed by Gieseler fluidity, caking index G, total dilatation and maximum thickness of plastic layer Y) play an important role in coke thermal properties (Zhang *et al*., 2004). According to Zhang *et al*., (2004), these properties are not always proportional to the coking power of coal but they are essential factors determining the quality of coke made of the coal. The degree of aging of coal, described by the rank of the coal is very important indicator of the properties of the coke made from the coal.

Dilatometer measures the expansion and contraction behaviour of coal. According to Royce *et al.*, (1990), the Ruhr Dilatometer indicates the shrinkage and swelling a sample of coal in the form of a pencil undergoes during uniform heating. The dilatation of a coal at a given heating rate is dependent on many factors including coal rank, the relative proportions of vitrinite, exinite and inertinite in the coal, the amount and size distribution of any mineral matter present and the state of oxidation of the coal (Marshall, 1976). To measure the coking capacity of a coal, most classification systems use some measure of a coal's swelling ability on heating, e.g. Gray – King assay, Roga Index, dilatometer test (Marshall, 1976). From dilatometer test values, the Caking Capacity G as a measure for the coke –forming ability of the tested coal or coal blend can be calculated by the formula, Collin and Bujnowska (1994):

$$G = \left(\frac{T_1 + T_3}{2} \right) \times \left(\frac{C + D}{C \times T_3 + D \times T_1} \right) \tag{2.2}$$

where:

T_1 = Softening Temperature (°C), T_3 = Maximum Dilatation Temperature (°C),
C = Maximum Contraction (%), D = Maximum Dilatation (%)

The impurities present in the coke include moisture, volatile matter, ash, sulphur, phosphorus and alkali contents. According to Díez *et al.*, (2002), these impurities affect coke performance in the blast furnace by decreasing its role as a fuel in terms of amounts of carbon available for direct and indirect reduction roles and also its role as permeable support. Therefore their levels have to be kept as low as possible. According to Ndaji and Imobighe (1989), coke ash and sulphur contents are dependent upon the ash and sulphur contents of the precursor coal as revealed in equations (2.3) and (2.4) which shows the empirical relationships between ash and sulphur contents of cokes and those of precursor coals:

Coke Sulphur = 0.66 (Coal Sulphur) + 0.184 (2.3)

Coke Ash = 1.32 (Coal Ash) + 0.53 (2.4)

Excessive ash in metallurgical coke gives rise to high slag volume and low efficiency of the blast furnace (Ndaji and Imobighe, 1989). Also, excessive ash in metallurgical cokes result in high coke rate that arises from the accelerated oxidation of coke by carbon dioxide and oxygen which is caused by the catalytic activities of the numerous metallic oxides that are contained in the coke ash (Ndaji and Imobighe, 1989). On the other hand, excessive high amounts of sulphur in the metallurgical cokes give rise to brittleness in the iron and also render the final product highly vulnerable to corrosion (Ndaji and Imobighe, 1989).

For prediction of coke quality, several mathematical models are available. According to Díez *et al.* (2002) and Tiwari *et al.* (2013) the models are broadly divided into two groups. The first type of models focuses on the prediction of cold strength of coke and the second-type of models are on prediction of hot strength (Díez *et al.,* 2002; Tiwari *et al.,* 2013). Some literature reported on prediction of coke quality based on its petrographic analysis while another study reported that the rank of the coal blend (mean R_0%) should be high for producing coke with high CSR (Tiwari *et al.,* 2013). Petrographic evaluation of coking coal is relied upon to predict the quality of the coke that can be expected, particularly the stability index of the coke (Díez *et al.*, 2002). The basis for this reliance is evident from the findings of prior investigators (Díez *et al*., 2002; Tiwari *et al.*, 2013). Table 2.5 below shows typical coke size and strength values for European blast furnaces together with those reported for current operation in Australia BHP Port Kembla, American and Japanese blast furnaces (Díez *et al*., 2002). These properties as mentioned in Table 2.6 below will be measured for various range of coke oven tar addition in the metallurgical blend used in this study.

Table 2.6: Physical properties of the blast furnace coke (Díez *et al.*, 2002).

Coke properties	**European Range**	**Australian Range**	**American Range**	**Japan Range**
Mean size (mm)	47 – 70	50	50	45 – 60
M40 (+60 mm)	> 78 – >88	85	n.a	n.a
M10 (+60 mm)	<5 – < 8	6.5	n.a	n.a
I40	53 –55	n.a	n.a	n.a
I20	> 77.5	n.a	n.a	n.a
D1150/15	n.a	84.4	n.a	83 – 85
ASTM Stability	n.a	63.6	60	n.a
CSR	> 60	74.1	61	50 – 65
CRI	20 - 30	17.7	23	n.a

n.a. – not available

2. 7 Summary

Important criteria for evaluating coals for coking process include petrographic composition, volatile matter, reflectance and coking properties. From the literature survey, it can be summarised that various methods of improving coke quality has been investigated since the early sixties. The intensity of research in both extent and depth shows deepening continuous concern over the scarcity of coking coal and reserves as well as the desire to maintain high quality coke for blast furnaces around the world. In spite of the wide research conducted, challenges with achieving low cost coal blend giving high quality coke still remain. On the basis of availability, cost and equipments requirement, coke oven tar addition is a viable option in many cases. Although some authors highlighted the fact that mixing of coke oven tar with coal blend posed certain operational problems such as conveyor damages, uniformly mixing coal with tar, these operational challenges will be addressed in the current study.

CHAPTER 3: MATERIALS AND METHODS

3.0 Summary of Experimental Procedure

The four coals used to make the blend in this study were supplied by members in the South African steel industry as these coals are frequently included in the industrial blends to produce metallurgical coke. The coals being tested cover a wide range in volatile matter content, thermoplastic properties and geographical origin. The blending was conducted by mixing the four bituminous coals in specific proportions similar to those used in commercial blending procedures. This blend was then divided into representative parcels for testing with coke oven tar.

The coke oven tar produced from an industrial coal blend similar to the base coal blend used in the current study at 55 ± 2 °C was collected from tar decanters in the by-products coking plant, mixed with coal blend as shown in Table 3.1. In order to get coke oven tar uniformly mixed with coal blend, a RV11 mixer was optimized to run for 30 seconds. Up to 2 – 8 wt.% of coke oven tar with varied in moisture content of 1%, 3% and 6% was used. Moisture in coke oven tar was measured using Karl Fischer titration method. The study did not include coke oven tar of 10 wt.% or higher due to operational problems when working with such large volumes.

Table 3.1: Blend composition

Blend	**0 wt.% Tar**	**2 wt.% Tar**	**4 wt.% Tar**	**6 wt.% Tar**	**8 wt.% Tar**
Coal A	35	35	35	35	35
Coal B	8	7.8	7.5	7.3	7
Coal C	38	36.8	35.7	34.5	33.3
Coal D	19	18.4	17.8	17.2	16.7
Tar	0	2	4	6	8
Total	100	100	100	100	100

3.1 Test Equipments and Procedures

The following test equipments and standard procedures under ASTM or ISO are given. Referring to the appropriate standard is considered adequate unless the procedure used deviates from the ASTM or ISO standard procedure.

3.1.1 Bulk Density Measurement ISO 23499: 2008

The bulk density of the prepared blend was determined as per ISO 23499 standard procedure.

3.1.2 Pilot Plant Oven

Carbonization tests were carried out in a pilot plant oven of approximately 350 kg capacity as shown in Fig.3.1. The dimensions of the oven are 915 mm L x 455 mm W x 1015 mm H with a usable volume of 0.35 m^3. The distance between thermocouples was: ±60 mm between middle and top, ±60 mm between top and wall and ±140 mm between middle and wall. A programmable controller was used to control the oven temperature. The temperature at the centre of the coal charge was monitored by means of a thermocouple connected to a computer. The coal was gravity charged into the oven when the oven reached 1200 °C. The temperature of the wall was kept constant throughout the test. The coking time was fixed at approximately 19 h throughout all the tests.

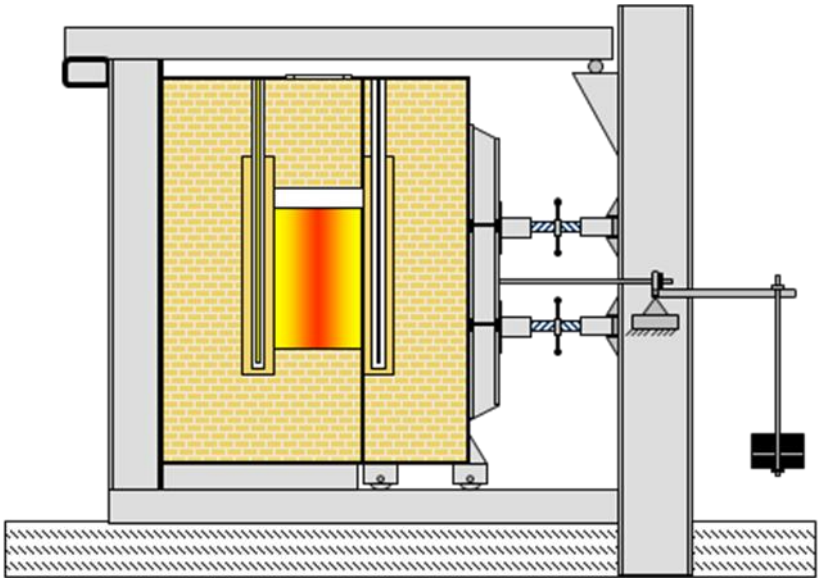

Figure 3 1: Schematic representation of Pilot Plant Oven

3.1.3 Roga index ISO 335:1974

Roga index tests the caking power of the coal, but as in the case of the swelling index, Roga is also just indicative. Roga values only indicate the possible caking power of coal and as such they do not quantify the coking ability. Roga index was tested following the ISO 335 standard procedure.

3.1.4 Gieseler Plastometer ISO 10329:2009

The thermoplastic properties of coals and the prepared blends were tested by the Gieseler Plastometer method following the ISO 10329 standard procedure. Fig.3.2 shows typical Hans Prüfer Gieseler Plastometer instrument used.

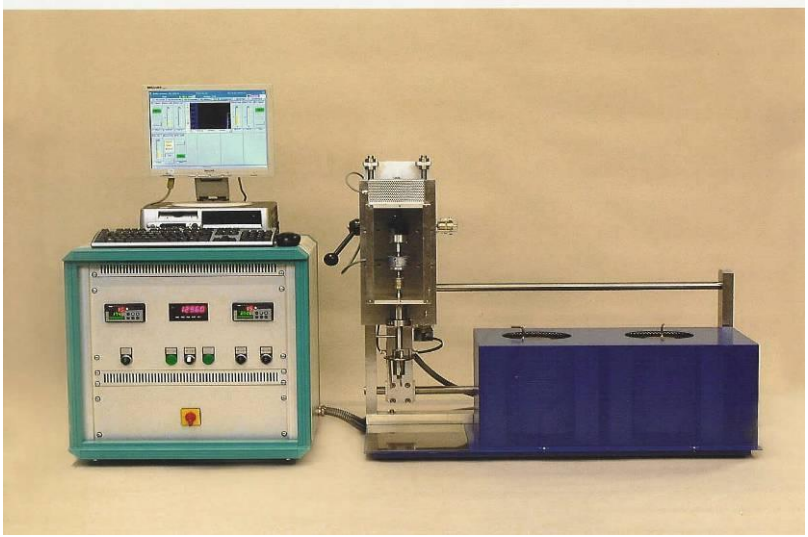

Figure 3.2: Gieseler Plastometer

3.1.5 Ruhr Dilatometer - ISO 349:1975

Total dilatation was measured for coal/plastic mixtures using a Ruhr dilatometer shown in Fig. 3.3 as per ISO 349 standard procedure.

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Figure 3.3: Ruhr Dilatometer

3.1.6 Coal and Coke Chemical Analysis using XRF techniques

Inorganic ash components in both coal and coke chemical analysis were determined using X-Ray Fluorescence and neutron activation analysis as shown in Fig. 3.4.

Figure 3.4: Phillips Axios Spectrometer

3.1.7 Coal Screen Analysis

Sizing was done with Automatic Dabmar Screen. Screen sizes used are: 100, 80, 60, 40, 30, 20, and 10 mm.

3.1.8 Petrographic Analysis

Petrographic analysis included sample preparation and maceral group analysis.

3.1.8.1 Sample Preparation ISO 7404/2: 1985

Sample preparation was performed as per ISO 7404/2 standard procedure.

3.1.8.2. Maceral Group analysis ISO 7404/3: 1985

Maceral group analysis was performed as per ISO 7404/3 standard procedure.

3.1.9 Reflectance measurements ISO 7404/5:1985

Vitrinite reflectance is measured as the amount of reflected light from coal particles viewed under microscope on prepared tablets. Reflectance measurements were performed as per ISO 7404/5.

3.1.10 Coke Moisture Measurements

Moisture content was determined by establishing the mass loss of a sample after drying it in an oven with set temperature of 150 ± 5 ℃ and forced air circulation.

3.1.11 Coke Micum Indices measurements

Coke Micum indices measurement was evaluated as per ISO 1881 standard procedure.

3.1.12 Coke Irsid Indices Measurements

Coke cold strength was evaluated by the Irsid test according to the ISO 556 standard procedure.

3.1.13 Proximate Analysis

Proximate analyses include moisture in the analysis sample, ash, volatile matter and fixed carbon by difference.

3.1.13.1 Moisture in the analysis sample Moisture: SANS 11722 : 2005

Moisture in the analysis sample was performed following the SANS 11722 standard procedure.

3.1.13.2 Volatile Matter: ISO 562: 2010

Volatile matter was performed following the ISO 562 standard procedure.

3.1.13.3 Ash: ISO 1171: 2010

Ash was performed following the ISO 1171 standard procedure.

3.1.13.4 Fixed Carbon

The solid remains after the determination of the volatile matter is the whole of the mineral matter and the non-volatile matter in the coal. The non-volatile organic matter is termed "fixed carbon". In the proximate analysis, this value is determined by subtracting the total of the percentage moisture, volatile matter and ash from a hundred.

3.1.14 Determination of CRI and CSR

Coke sample produced was prepared and tested for CSR and CRI measurement as per specification in the ASTM D5341 – 99 standard procedure.

3.1.15 Free Swelling Index ISO 501:2013

Free Swelling Index was determined following the ISO 501 standard procedure.

3.1.16 Stability and Hardness Factors Determination

For stability and hardness, each sample of dry coke of designated size (- 75 +50 mm) was weighed to the nearest 0.025 kg. A 10 ± 0.25 kg was tumbled in a rotating drum for a total of 1400 revolutions. Two indexes of strength, the stability

factor and the hardness factor, were determined by sieve analysis of the coke after treatment. All of the coke were removed from the drum and sieved using a 25 mm square mesh sieve and a 6.3 mm square-mesh sieve. The coke remaining on each of the sieves and the coke that passes through the 6.3 mm sieve were weighed.

3.1.17 HPLC Analysis of coke oven tar

The High – Performance Liquid Chromatography (HPLC) analysis of the aromatic compounds present in the primary coke oven tar was carried out using a Hewlett – Packard HP1100 system incorporating two PLGel columns (300 mm length x 7.5 mm i.d.) packed with poly (styrene/divinylbenzene) of different nominal pore sizes (500 and 100 Å, respectively) and connected in series. A UV detector operating at 254 nm was used. Two main regions corresponding to PAHs with *cata* (elution volume from 12 to 19.8 ml) and *peri*-condensation (elution volume greater than 19.8 ml) were assigned. The procedure employed to separate the *cata* – *peri* –condensed PACs was based on a previous method reported by Lafleur and Wornat (1988).

3.1.18 GC/MS analysis of coke oven tar

Coke oven tar was dissolved in dichloromethane and the water in tar was absorbed by Na_2SO_4. The solution was filtrated to remove Na_2SO_4 and then distilled at 300 °C to meet the GC demand. Distillate including CH_2Cl_2 was kept in chromatogram bottle for analysis. GC analysis of coke oven tar was carried out using an Agilent 6890N gas chromatograph equipped with a HP-5 capillary column and a flame ionization detector (FID), and helium as carrier gas with a flow rate of 1.2 ml/min. The detector and injector temperatures were 280 °C and the column temperature was started at 60 °C for 5 min, and then heated to 280 °C at a heating rate of 4 °C/min and holding 10 min at 280 °C. The compounds were identified by GC/MS using an Agilent 6890N gas chromatograph coupled with Agilent 5975 mass detector.

CHAPTER 4: CHARACTERIZATIONS –ANALYTICAL RESULTS

4.1 Introduction

The coals used in the study were characterized through physical, chemical, rheological and petrographic analysis. Coals of different geographical origin present coking properties that are different to those of other coals of the same volatile matter content. The following sections detail characteristics of individual coals and coke oven tar used in the current study.

4.2 Coal Characterisation

Table 4.1 up to 4.6 shows the properties of individual coals used in this study. Duplicate results are presented for each product in order to indicate repeatability.

Table 4.1: Coking coals origin and properties

Coal	Origin	FC (wt.% db)	VM (wt.% db)	Ash (wt.% db)	Moisture (wt.% db)	RoVr%	FSI (ISO)
Coal A	RSA	47.0	37.2	10.0	5.8	0.71	6.0
		47.8	37.0	9.8	5.4	0.71	6.1
Coal B	NZL	57.3	32.0	3.8	6.9	1.12	9.6
		57.8	32.2	3.4	6.6	1.10	9.3
Coal C	AUSTRALIA	58.9	24.5	9.8	6.8	0.90	8.3
		58.6	25.0	9.9	6.5	0.92	8.1
Coal D	USA	60.0	26.7	6.9	6.4	1.32	8.5
		60.2	26.3	6.9	6.6	1.33	8.4

FC: fixed carbon; db: dry base; FSI: Free Swelling Index; VM: volatile matter; db: dry basis

Table 4.1 shows coking coals origin and properties. Volatile matter content of coal C is less than that of coal A, coal B and coal D and ash content of coal B is less than that of coal A, coal B and coal D. The results in Table 4.1 are in good agreement with Van Niekerk and Mathews (2010) who reported volatile matter and ash contents of 38.0 and 10.0 respectively for South African coal A. In another case, Van Niekerk *et al.* (2008) reported volatile matter and ash contents

of 35.94 and 8.42 respectively for the same coal A. The difference in Van Niekerk *et al.* (2008) values between 2008 and 2010 can be attributed to decrease in coal quality over time period. In addition, Wagner and Tlotleng (2012) reported that volatile matter, Ash and R_oV_m as 34.6, 8.9 and 0.66 respectively for South African coal A.

Furthermore, the results are supported by another case reported by Tiwari *et al.* (2013) whose results are as follow: coal B – ash (2.97%), volatile matter (35.95%), S (0.59%), Ro (0.90), MF (159); coal D – ash (7.39%), volatile matter ((31.78%), coal C – ash (9.50%), volatile matter (25%), S (0.63), R_0 (1.18) Casal *et al.*, (2008), coal C – ash (9.7%), volatile matter (22.9%) and R_0 (1.14); coal D – ash (7.0%), volatile matter (32.1%), R_0 (0.95). Previously Casal *et al.*, (2003) reported volatile matter (23.2%), ash (9.9%), Total S (0.60%) and Ro (1.14) for coal C. Díaz-Faes *et al.*, (2007) reported volatile matter (25.8%) and ash (9.2%) for coal C and volatile matter (26.1%) and ash (8.8%) for coal D. According to DuBroff *et al.*, (1985), for USA coal D, the ash content generally should be in the range of from about 4 – 7%. Qualities change or vary over time, therefore any differences in qualities of similar coals over years should be attributed to variation of quality over time. However, the results from the study shows that the qualities are rather comparable to past reported for coals from same mines/region.

Table 4.2: Coking coals ultimate analysis and sulphur

Coal	C (db)	H (db)	N(db)	S (pyritic)	S (SO_4)	Total S
Coal A	75.0	4.81	1.40	0.12	0.01	1.06
	75.2	4.80	1.38	0.10	0.01	1.08
Coal B	85.0	5.4	1.3	0.12	0.01	1.0
	84.8	5.2	1.4	0.10	0.01	1.09
Coal C	81.4	4.53	1.90	0.10	0.03	0.65
	81.6	4.55	1.91	0.10	0.02	0.65
Coal D	70.2	5.3	1.2	0.13	0.01	1.08
	70.0	5.2	1.2	0.12	0.01	1.09

db: dry basis

Table 4.2 shows coking coals ultimate analysis and sulphur. Oxygen can be found by difference. The results are in good agreement with Niekerk *et al.* (2008)'s results who reported Sulphur of 1.1 for South African coal A. Van Niekerk *et al.* (2008) reported Sulphur of 1.13 for coal A. The results are supported by another case reported by Wagner and Tlotleng (2012) who reported S as 1.19 for South African coal A. Casal *et al.*, (2003) reported Total S (0.60%) for Australian coal C as well as Total S (0.81%) for coal D.

Table 4.3 shows ash composition found in individual coals. The results are supported by Wagner and Tlotleng (2012) who reported Na_2O, MgO, Al_2O_3 ,SiO_2, P, Fe, K_2O, CaO, TiO_2 ,and Mn of 0.14, 0.50, 19.8, 0.09, 1.19, 0.66, 1.37 and 0.069 respectively for South African coal A.

Table 4.3: Ash composition found in individual coals (wt.%)

Coals	**Na_2O**	**MgO**	**Al_2O_3**	**SiO_2**	**P**	**Fe**	**K_2O**	**CaO**	**TiO_2**	**Mn**
Coal A	0.01	0.04	2.1	6.6	0.005	0.53	0.12	0.11	0.27	0.013
	0.01	0.05	2.0	6.5	0.004	0.55	0.11	0.11	0.26	0.011
Coal B	0.07	0.06	2.5	5.0	0.070	0.59	0.12	0.22	0.21	0.008
	0.05	0.06	2.4	5.2	0.067	0.63	0.12	0.23	0.22	0.007
Coal C	0.01	0.06	0.9	1.3	0.009	0.30	0.13	0.05	0.07	0.002
	0.02	0.06	1.0	1.3	0.008	0.29	0.14	0.04	0.06	0.001
Coal D	0.03	0.06	2.0	3.9	0.012	0.70	0.18	0.18	0.15	0.006
	0.03	0.05	2.1	4.0	0.013	0.67	0.19	0.15	0.14	0.005

Table 4.4 shows Gieseler Fluidity values and Rheological properties for individual coals used. The result in Table 4.4 shows that poor coking high and low volatile coals have low fluidity and a narrow plastic range. The thermoplastic properties of coals depend on their rank, but the degree of coalification (rank) is not the only factor that influences the thermoplasticity of a given coal (Díaz-Faes *et al.*, 2007). Other factors including the proportion of macerals (vitrinite in particular) and their associated microlithotypes also play a major role. Vitrinite is the predominant maceral in coking coal and the main contributor to coke quality. The reflectance of vitrinite indicates the rank or the degree of coalification of coal which, in turn,

controls the coking capacity in the vitrinite macerals in the coal (*i.e.* the properties of swell, plasticity and fusion). Generally, coal rank is directly proportional to volatile matter and carbon content in European and US coals but due to the heterogeneous nature of RSA coals, rank in RSA is more reliably determined by vitrinite reflectance (see Table 4.5 for vitrinite reflectance distribution and mean values).

Table 4.4: Gieseler Fluidity values and Rheological properties for individual coals

Plasticity	**Coal A**	**Coal B**	**Coal C**	**Coal D**
Initial Softening Temp. ºC	378	381	385	393
	380	380	384	396
Max Fluidity (ddpm)	18	250	2233	3728
	20	255	2230	3730
Max Fluidity Temp. ºC	436	441	470	495
	438	445	468	453
Resolidification Temp. ºC	450	468	500	493
	453	471	503	490
Maximum C%	29.4	29.1	28.5	29.0
	28.9	29.3	28.7	28.9
Maximum D%	14.6	65.4	188.1	191.5
	14.5	94.8	189.0	190.9
Plastic Range ºC	47	85	99	98
	46	85	99	97

Table 4.5: Maceral Analysis of individual coking coals

Maceral	**Coal A**	**Coal B**	**Coal C**	**Coal D**
Vitrinite [vol.%]	78.4	70.2	88.0	84.0
	76.2	71.0	89.0	84.0
Liptinite (Exinite) [vol.%]	4.6	1.2	2.4	0.0
	5.0	1.0	1.9	0.0
Semifusinite [vol.%]	3.5	5.1	5.0	15.1
	3.9	4.8	4.7	15.3
Pseudovitrinite [vol.%]	8.0	0.8	1.4	0.0
	8.7	0.7	1.0	0.0
Inertinite [vol.%]	5.5	13.0	3.0	0.0
	6.2	13.0	3.1	0.0

Table 4.6: Vitrinite reflectance distribution of individual coals used

Vitrinite Distribution	**Coal A**	**Coal B**	**Coal C**	**Coal D**
V5 (0.50 – 0.59) [%]	4	0	0	0
V6 (0.60 – 0.69) [%]	38	0	0	0
V7 (0.70 – 0.79) [%]	55	0	0	0
V8 (0.80 – 0.89) [%]	1	0	0	0
V9 (0.90 – 0.99) [%]	0	7	46	0
V10 (1.00 – 1.09) [%]	2	31	20	0
V11 (1.10 – 1.19) [%]	0	51	11	13
V12 (1.20 – 1.29) [%]	0	9	9	41
V13 (1.30 – 1.39) [%]	0	1	14	39
V14 (1.40 – 1.49) [%]	0	0	0	7
V15 (1.50 – 1.59) [%]	0	1	0	0
RoVr%	0.712	1.121	0.90	1.32

Vitrinite is the predominant maceral in coking coal and the main contributor to coke quality. The reflectance of vitrinite indicates the rank or the degree of coalification of coal which, in turn, controls the coking capacity in the vitrinite macerals in the coal (i.e. the properties of swell, plasticity and fusion). Generally,

coal rank is directly proportional to volatile matter and carbon content in European and US coals but due to the heterogeneous nature of RSA coals, rank in RSA is more reliably determined by vitrinite reflectance (see Table 4.6 for vitrinite reflectance distribution and mean values). From Table 4.6, it will be noted that coal A is a weakly caking *Bituminous C* coal (RoVr% = 0.712). Coals B and D fall in the mid Bituminous prime coking range of rank, *i.e. Bituminous B* (RoVr% = 1.1 – 1.3), and coal C falls border line *between Bituminous B and C* (RoVr% = 0.9), *i.e.* just below and marginal to the prime coking category.

4.3 Coke Oven Tar characterization

The first part of coke oven tar characterization involved using analytical methods to determine moisture, matter insoluble in tar, quinoline insoluble, and specific gravity. Table 4.7 shows properties of coke oven tar over a range of moisture content. In the second part, the coke oven tars was attempted to be initially analyzed by HPLC and later confirmed with GC-MS.

Table 4.7: Properties of coke oven tar with various moisture content

	H_2O (%)	**MIT (wt.%)**	**Ash (wt.%db)**	**QI (wt.%)**	**SG (gcm^{-3})**	**Flue Temperature (°C)**
Target	5.0	6.0	0.16	6.0	1.20	1233
Tar 1	6.0	5.3	0.04	3.8	1.12	1230
	5.98	5.6	0.04	3.6	1.14	1232
Tar 2	3.1	5.3	0.04	3.4	1.15	1233
	2.8	5.5	0.02	3.8	1.17	1232
Tar 3	1.1	5.4	0.02	4.2	1.17	1231
	1.0	5.5	0.03	4.0	1.16	1233

MIT – Matter Insoluble in Tar; db – dry basis; QI - Quinoline-Insoluble ; SG –Specific Gravity

The properties of coke oven tar as given in Table 4.7 above are in good agreement with Díez *et al.* (1994) who characterise coal tar as follows: Ash (0.04%), SG (1.17), mean flue temperature (1230) and QI (2.9). It is known that the presence of inert quinoline insoluble (QI) particles has an effect on the anisotropy present in

the carbonized pitch, and now the present work demonstrates that the rank of coal from which the pitch was obtained also has a marked influence (Patrick *et al.*, 1983). The densities of the coke oven tars produced showed a decrease with increasing moisture content in coke oven tar. The decrease in bulk density was independend of carbonization temperature assessed as the mean flue temperature.

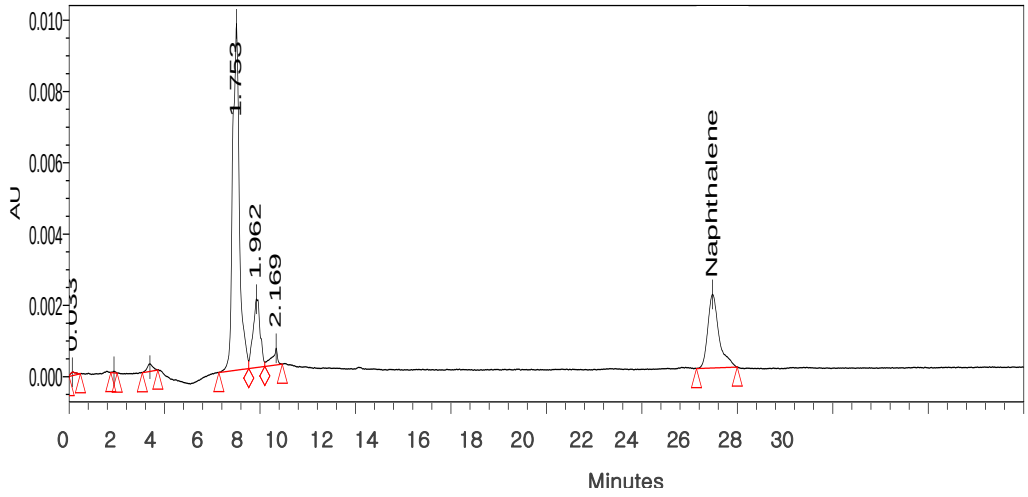

Figure 4.1: Typical hydrocarbons found in Coke oven tar

HPLC has indicated few hydrocarbons found in coke oven tar indicating that compositions identifiable by this instrument were limited. Figure 4.1 above shows a typical example of the analysis obtained. Coke oven tar characterization requires the use of analytical tools that are able to work over a range of molecular masses such as GC-MS. Therefore, GC-MS was employed to provide detailed analysis of coke oven tar hydrocarbons. Typical compound chromatogram of coke oven tar composition from GC –MS is depicted in Figure 4.2 shown in the next page. Qualitative data from GC analysis of coke oven tar samples is reported on Table 4.8. Although GC-MS identified quite a few compositions as opposed to HPLC, identifiable by these instruments were limited.

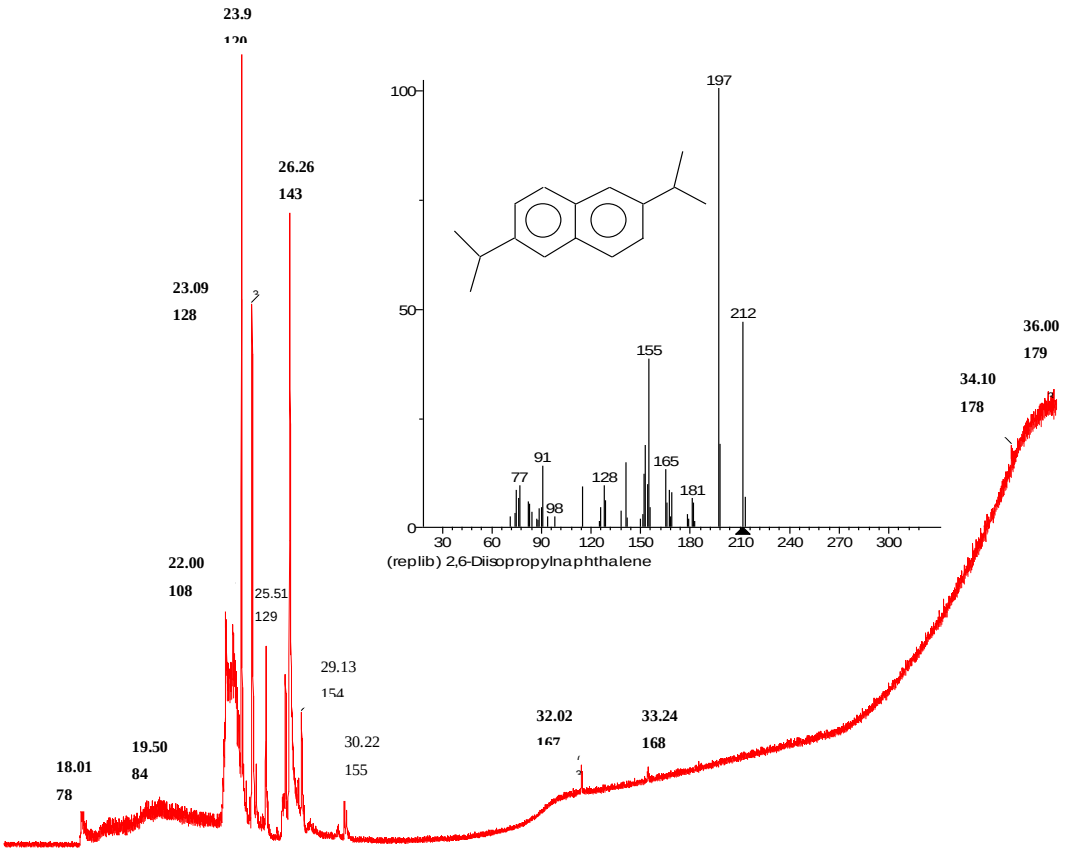

Figure 4.2: Typical compound chromatogram of coke oven tar composition

Characterization of coke oven tar is an established topic in the literature. Various researchers (Blekkan *et al.*, 1992; Pindoria *et al.*, 1997; Diez *et al.*, 1994; Li and Suzuki, 2010; Lazaro *et al.*, 2001) have studied the characteristics of coke oven tars. For the purpose of the current study, only preliminary characterization will be completed since the purpose of the study in not mainly based on characterization of coke oven tars. The results as shown in Table 4.8 are also in good agreement with Díez et al., (1994) Lazaro *et al.*, (2001), Benk and Coban (2011), Li and Suzuki (2009), Pindoria *et al.*(1997) who provided analysis of crude coal tar. According to Pindoria *et al.*(1997), both coal-derived tars showed aromatics up to perylene, with alkanes showing up in the Coke Oven Tar (COT) after elution times corresponding to perylene. As already mentioned, characterisation of coke oven tar is not the main purpose of this study, the analyses were not detailed but preliminary. The amount of light hydrocarbons depends closely on the mean flue temperature.

Table 4.8: Qualitative data from GC analysis of coke oven tar samples

No	RT(min)	Compound	Formula	MW (g/mol)
1	18.01	Benzene	C_6H_6	78
2	19.50	Thiophene	C_4H_4S	84
3	21.45	Phenol	C_6H_6O	94
4	22.00	o-cresol	C_2H_8O	108
5	23.09	Xylenol	$C_8H_{10}O$	120
6	24.38	Naphthalene	$C_{10}H_8$	128
7	25.51	Quinoline	C_9H_7N	129
8	26.26	Methylquinoline	$C_{10}H_9N$	143
9	29.13	biphenyl	$C_{12}H_{10}$	154
10	30.22	Phenylpyridine	$C_{11}H_9N$	155
11	32.02	Carbazole	$C_{12}H_9N$	167
12	33.24	Dibenzofuran	$C_{12}H_8O$	168
13	34.10	Anthracene	$C_{14}H_{10}$	178
14	36.00	Benzoquinoline	$C_{13}H_9N$	179
15	36.44	Fluorenol	$C_{13}H_{10}O$	181
16	38.07	Pyrene	$C_{16}H_{10}$	202

RT = Retention Time

Ashes in coke oven tar were sampled and analysed. Table 4.9 in the next page shows typical element concentrations determined on the coke oven tar ashes. The results are presented in duplicate in order to indicate repeatability.

Table 4.9: Typical element concentrations determined on the coke oven tar ashes

Elements	**Sample 1**	**Sample 2**
SiO_2 [%]	23.12	24.01
TiO_2 [%]	1.10	1.15
Al_2O_3[%]	18.48	18.15
Fe_2O_3[%]	11.34	11.21
MnO [%]	0.53	0.49
MgO [%]	0.80	0.85
CaO [%]	6.74	6.65
Na_2O [%]	13.01	12.98
K_2O [%]	2.8	2.7
P_2O_5[%]	0.61	0.59
SO_3 [%]	9.27	9.30

4.4. Summary

Coking coals used in this study showed that their properties differed in many ways from each other. These differences may be ascribed to the different in geological conditions of formation. The reflectance of vitrinites and means maximum reflectance values was determined. Coke oven tar characterization provided valuable information about the carbonization behaviour of coal – coke oven tar fractions and the thermo-chemical process evolution during carbonization. Obviously their influence on the mesophase formation with developing isotropic and anisotropic coke textures cannot be underestimated. This information has a significant importance from the viewpoint of coal – coke oven tar performances as binder component of coal blends. PAH in particular confer binder properties to coke oven tar.

CHAPTER 5: DISCUSSION – PERFOMANCE EVALUATION

5.1 Introduction

The possibility of substituting a fraction of imported coals with coke oven tar was evaluated over a range of 0 – 8 wt.% coke oven tar addition. In order to meet the objective of the current study, it was considered necessary to thoroughly evaluate performance of coke oven tar addition process by measuring its effect on ash composition in both coal blend and coke, proximate, coal blend Roga, maximum contraction and maximum dilatation, Free Swelling Index, coal particle sizes, coal blend moisture, bulk density, on plasticity and fluidity, carbonisation properties, coking pressure, pushing energy, coke yield, coke properties and conclude with economic evaluation of coke oven tar addition.

In cases where there was insignificant change in values evaluated due to moisture content in coke oven tar addition, only optimum condition values over a range of 0 – 8 wt.% will be presented in duplicate in order to indicate repeatability. Such cases include the effect of coke oven tar addition on ash composition and phosphorus in coal blend and coke, coal blend Roga, maximum contraction and maximum dilatation, Free Swelling Index, coal particle sizes, plasticity and fluidity, carbonisation properties, and Catalytic Index.

5.2 Effect of coke oven tar addition on ash composition and phosphorus in coal blend

Table 5.1 illustrate the rest of ash composition except for phosphorus showed no significant change with coke oven tar addition. However in case of phosphorus, as coke oven tar addition increases, phosphorus decreases. Good phosphorus values are obtained at coke oven tar addition of 2 – 8 wt.% against a target of $P \leq 0.036$ wt.% in coal. Therefore coke oven tar addition helps reducing phosphorus content in coal.

Table 5.1: Ash composition in various coal blends

Coals	Na_2O	MgO	Al_2O_3	SiO_2	P	Fe	K_2O	CaO	TiO_2	Mn
0 wt.% Tar	0.05	0.04	2.5	5.0	0.038	0.50	0.12	0.16	0.21	0.006
	0.05	0.03	2.5	5.1	0.039	0.50	0.14	0.17	0.20	0.007
2 wt.% Tar	0.05	0.06	2.6	4.6	0.035	0.60	0.13	0.18	0.22	0.008
	0.04	0.05	2.5	4.9	0.037	0.62	0.12	0.16	0.21	0.007
4 wt.% Tar	0.04	0.04	2.6	5.8	0.028	0.70	0.14	0.15	0.21	0.010
	0.03	0.03	2.5	5.7	0.027	0.72	0.13	0.15	0.21	0.009
6 wt.% Tar	0.03	0.04	2.2	5.0	0.024	0.60	0.13	0.17	0.20	0.009
	0.02	0.04	2.2	4.9	0.023	0.65	0.12	0.16	0.21	0.008
8 wt.% Tar	0.04	0.05	2.1	5.2	0.023	0.60	0.14	0.13	0.21	0.009
	0.04	0.04	2.1	5.0	0.024	0.60	0.13	0.13	0.22	0.007

5.3 Effect of coke oven tar addition on proximate

Other impurities such as ash, sulphur and volatile content of coals are shown in Table 5.2 below. At 2 wt.% coke oven tar addition, ash content reduced from 9.2 to 8.5 wt.% against a target of < 10 in coal blend. However with further addition of coke oven tar from 4 – 8 wt.%, ash content stayed constant at 8.6 wt.%. Therefore, coke oven tar decreases ash content in all blends by an average of 0.7 wt.%. The finding is excellent because according to Tiwari et al. (2013), the ash content of the coal charge is one of the most important parameters which influences the coke sizes with other operating conditions remaining the same. However, in case of sulphur, there was an increase from 0.87 to 0.99 at 2 wt.% coke oven tar addition against a target of <1% sulphur in coke and this remained constant at an average of 0.98 as coke oven tar increases. Sulphur is the single most influential chemical component in coal that affect CSR, and it is less desirable than coke oven tar given that it raises the sulphur content very close to the target value. Volatile matter of coal blend affects both coke quantity and coke quality. Volatile matter content reduced from 31.1 to 30.0 against a target of <30 and then remained constant. Therefore, coke oven tar helped improving volatile matter content in all coal blends to an accepted level.

Table 5.2: Proximate Analysis

1 and 3% moisture content in coke oven tar				**6% moisture content in coke oven tar**		
% Tar	Ash (wt.% db)	S (wt.% db)	VM (wt.% db)	Ash (wt.% db)	S (wt.% db)	VM (wt.% db)
0	9.1	0.86	30.8	9.2	0.87	31.1
	9.0	0.89	31.0	9.0	0.88	30.9
2	8.6	0.98	29.3	8.5	0.99	30.0
	8.4	0.96	29.7	8.6	0.97	30.1
4	8.4	0.98	29.0	8.6	0.98	30.1
	8.5	0.98	29.1	8.6	0.99	30.1
6	8.5	0.96	28.8	8.6	0.97	30.2
	8.6	0.96	39.0	8.4	0.97	30.0
8	8.7	0.97	28.9	8.6	0.99	30.4
	8.4	0.96	28.5	8.6	0.98	30.2

S: Sulphur; VM: volatile matter; db: dry basis

5.4 Effect of coke oven tar addition on coal Roga

Roga index is determined as measure for caking propensity of coals and their blends (Collin and Bujnowaska, 1994). Figure 5.1 depict the relationship between Roga and coke oven tar addition. As coke oven tar addition increases, Roga increases exponentially. Generally, the higher coke oven tar addition, the higher the Roga index and therefore the better the caking properties of coals. In terms of the correlation factor, 81.3% is considered a good correlation.

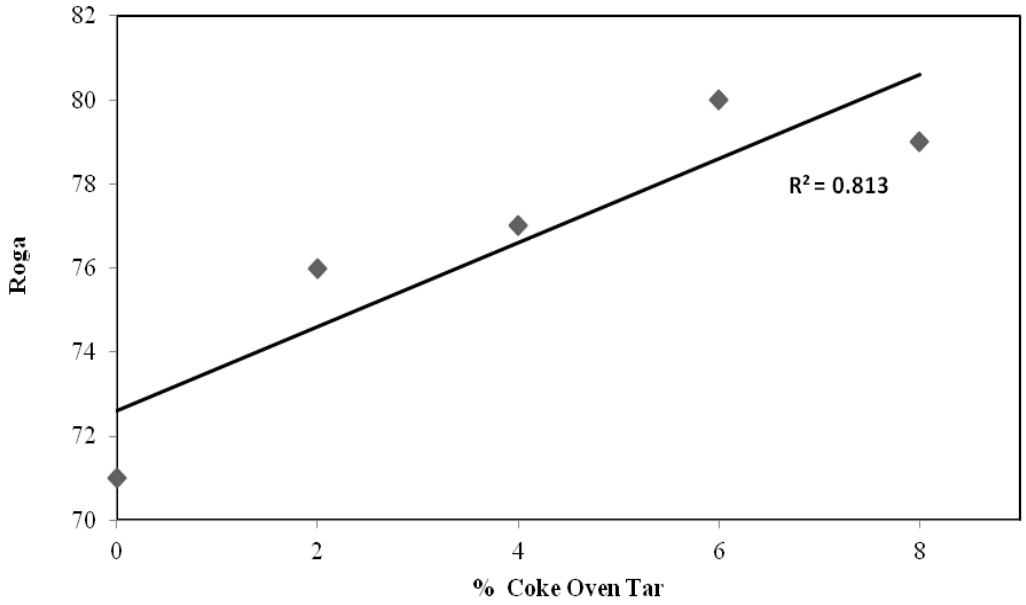

Figure 5.1: Relationship between Roga and coke oven tar addition

5.5 Effect of coke oven tar addition on maximum contraction and dilatation

Maximum contraction and maximum dilatation were measured in accordance with the ASTM standard. In measuring the standard, the weight of the coal pencil piece was measured. Table 5.3 shows the effect of coke oven tar on maximum contraction and maximum dilatation. As coke oven tar increases from 2 – 4 wt.%, maximum dilatation decreases. Further addition of coke oven tar from 6 – 8 wt.% increases maximum dilatation. As already mentioned, the dilatation percent of the coal indicates its coking properties. Therefore, coke oven tar improves maximum dilatation between 6 and 8 wt.% ranges. Correlation coefficient of 87.2% clearly reflects this. In case of maximum contraction, at 2 – 6 wt.%, maximum contraction increased to 29.7 and stayed constant. However, as coke oven tar addition was further increased to 8 wt.%, maximum contraction remained uniformly constant. No change in maximum contraction at 8 wt.% coke oven tar addition could be attributed to agglomeration formed at higher moisture content. The degree of maximum contraction of the coal charge appears to be one of the

most important factors for coking pressure since this determines the final volume of the carbonised mass relative to the initial coal charge.

Table 5.3: Coal blend Rheological Properties

Coals	T_1 (°C)	T_2 (°C)	T_3 (°C)	Max C%	Max D%
0 wt.% Tar	381	411	426	27.5	36.0
	381	412	425	27.7	36.1
2 wt.% Tar	381	414	465	29.8	35.3
	380	414	466	28.7	35.4
4 wt.% Tar	375	411	462	29.5	38.9
	376	410	462	29.2	38.5
6 wt.% Tar	360	402	483	29.6	47.3
	362	404	482	29.4	47.2
8 wt.% Tar	372	417	474	27.8	55.1
	374	419	472	27.7	55.0

T_1 = Softening Temperature; T_2 = Maximum Contraction Temperature; T_3 = Maximum Dilatation Temperature; Max C = Maximum Contraction; Max D = Maximum Dilatation

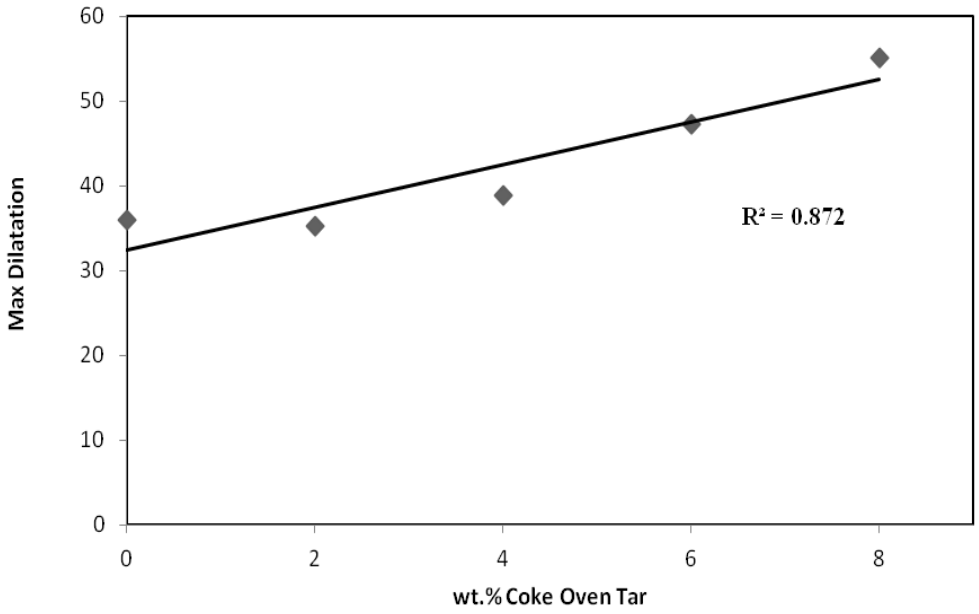

Figure 5.2: Relationship between Maximum Dilatation and coke oven tar addition

The G factor is one of the predicting tools for coke quality. Revisiting Equation 2.2, G values were calculated as shown in the example below. For example, G value for 0 wt.% coke oven tar addition was calculated as follows:

$$G = \left(\frac{T_1 + T_3}{2} \right) \times \left(\frac{C + D}{C \times T_3 + D \times T_1} \right) \tag{2.2}$$

Example: G value calculation for 0 wt.% coke oven tar addition

$$G = \left(\frac{T_1 + T_3}{2} \right) \times \left(\frac{C + D}{C \times T_3 + D \times T_1} \right)$$

$$G = \left(\frac{381 + 426}{2} \right) \times \left(\frac{27.5 + 36.0}{27.5 \times 426 + 36 \times 381} \right)$$

$$G = 1.01$$

Similarly, all the other G - values were calculated using Table 5.3 above as an input data and results are recorded as shown in Table 5.4. According to Collin and Bujnowaska (1994), prime coking coals have G values between 1.02 and 1.1 for 2 – 4 wt.% coke oven tar. At 6 and 8 wt.% coke oven tar, caking capacity slightly improved from 1.01 to 1.03 and 1.04 respectively. The effect of coke oven tar addition on G values is shown in Table 5.4. Collin and Bujnowaska (1994)'s results are in good agreement with the results of this study when comparing Roga values at Fig. 4.3 and 10 times G values.

Table 5.4: G values

Coal	**0 wt.% Tar**	**2 wt.% Tar**	**4 wt.% Tar**	**6 wt.% Tar**	**8 wt.% Tar**
G value	1.01	1.01	1.01	1.03	1.04
	1.01	1.01	1.01	1.03	1.04

5.6 Effect of coke oven tar addition on Free Swelling Index

Therefore, Free Swelling Index (FSI) test is a very simple test used to determine the agglomeration or swelling properties of coal. As already said, FSI indicates caking ability through swelling behaviour. However, FSI is not additive for coal blend. The effect of coke oven tar addition on G values is shown in Table 5.5. FSI is reported in whole or half units. As shown on Table 5.5 below, FSI did not deteriorate with coke oven tar addition in overall. At 2 wt.%, FSI did not change. However, at 4 – 6 wt.%, FSI increases slightly by 0.1 followed by 0.2 increase at 8 wt.%. Generally, FSI greater than 4 means good coking coals and FSI greater than 7 indicates high quality coking coal. According to Collin and Bujnowaska (1994), as a rule of thumb, Roga Index is about 10 times higher than that of Swelling Index.

Table 5.5: G and FSI values

Coal	0 wt.% Tar	2 wt.% Tar	4 wt.% Tar	6 wt.% Tar	8 wt.% Tar
G value	1.01	1.01	1.01	1.03	1.04
	1.01	1.01	1.01	1.03	1.04
FSI	8	8	8	8	8
	8	8	8	8	8

5.7 Effect of coke oven tar addition on coal particle sizes

Coal size acts on the bulk density. According to Yu *et al.* (1995), bulk density is strongly affected by the particle size distribution. Therefore in order to quantify the effect of the moisture content on bulk density, the particle size distribution of coal was determined. Table 5.6 shows the effect of coke oven tar addition on particles size distribution. For each sample, these size results are percentages and on a cumulative basis. It is important to note that -0.106 mm decreases with an increase in coke oven tar addition. This is a desirable result because more fines results in high Quinoline Insoluble in coke oven tar due to carry over during coking process. Also, at 2, 6 and 8 wt.% coke oven tar, S_m of 2.0, 2.0 and 1.9 was achieved respectively against a target of 2.1 – 2.9. Therefore, coke oven tar addition decrease mean size (S_m). However, there is no significant change. All

values can be considered identical and within analytical reproducibility. The results are in good agreement with Leibrock and Petak (1983) who reported a case where finer grinding lead to a decrease in the bulk density. However, according to Leibrock and Petak (1983), fine crushing has a negative effect on the substantive strength of the coke. On the other hand, fines have an adverse effect on dust emission during charging, carry-over or enhancement of carbon deposition. Nakagawa *et al.* (1998) suggests that fine particles generated during the charging of coal are the cause of increased carbon deposits. In the context of this research and its objectives, increase in coke oven tar suppresses the fines and therefore reduces dust emissions during charging.

Table 5.6: Coal screen analysis

Coal Screens	**0 wt.% Tar**	**2 wt.% Tar**	**4 wt.% Tar**	**6 wt.% Tar**	**8 wt.% Tar**
+10 mm	0	0.3	0	0	0
+8 mm	2.0	1.2	2.0	1.8	1.3
+6.3 mm	6.6	5.4	6.7	6.2	4.7
+5 mm	12.7	10.3	12.0	11.3	9.4
+4 mm	17.6	15.6	16.4	16.9	14.0
+3.35 mm	23.1	20.4	22.5	20.4	18.8
+2 mm	37.3	34.7	38.1	35.1	33.8
+1 mm	55.1	54.4	58.3	54.9	54.6
+0.5 mm	69.6	69.9	71.6	69.7	69.9
-0.5 mm	30.4	30.1	28.4	30.3	30.1
+0.212 mm	80.7	84.8	85.5	84.3	84.6
+0.150 mm	87.5	88.3	88.9	88.3	88.1
+0.106 mm	91.0	91.6	91.7	91.3	92.0
-0.106 mm	9.0	8.4	8.3	8.7	8.0
S_m	2.1	2.0	2.1	2.0	1.9
Total - 3.35 mm	76.9	79.6	77.5	79.6	81.2

5.8 Effect of coke oven tar addition on coal blend moisture

Figure 5.3 depicts the relationship of coal blend moisture and coke oven tar. As coke oven tar addition increased, coal blend total moisture increased correspondingly, arising from the moisture content in the coke oven tar. The addition of coke oven tar containing a range of moisture contents changes the heat

transfer through the coal mass significantly. According to Krebs *et al.* (1996), two effects could be responsible for these modifications. The first is a physical effect in which coke oven tar plays the role of a vehicle for the volatiles by penetrating the porous structure of the coal and accelerating the desorption of low-molecular-weight compounds trapped within the macro-molecular network. The second effect is a chemical one, the coke oven tar partially depolymerizing the coal network to release low-molecular-weight components with similar sizes but different compositions. High moisture content is less desirable in a coal blend because it translates to high energy consumption due to the additional energy required to drive off the moisture in the coal blend. In addition, studies of the effect of water on carbon formation have shown that water (as moisture) in the coal charge can play the role of an inhibitor in the formation of carbon deposits during the carbonization process (Krebs *et al.*, 1996).

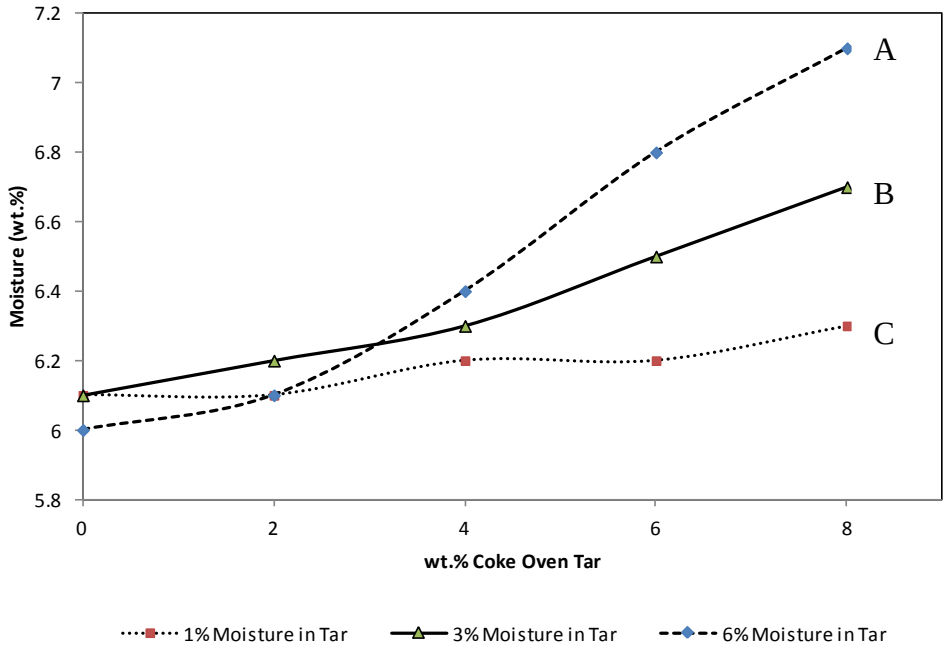

Figure 5.3: Dependence of coal blend moisture on coke oven tar addition

5.9 Effect of coke oven tar addition on bulk density

The bulk density was determined by measuring the height of the sample charged in a cold steel box having the same size as the movable wall oven. Figure 5.4 depicts the correlation between bulk density of coal blend and coke oven tar

addition. As shown in Figure 5.4, the bulk densities increased from 810 to 870 kg/m^3 and from 810 to 835 kg/m^3 over the 0 – 8 wt. % coke oven tar addition range using *1%* (A) and *3%* (B) *moisture content* in coke over tar respectively. In contrast, bulk density decreased from 813 to 760 kg/m^3 over the 0 – 6 wt.% coke over tar addition range, then started to increase at 8 wt.% coke oven tar addition when using coke oven tar with *6% moisture content* (C).

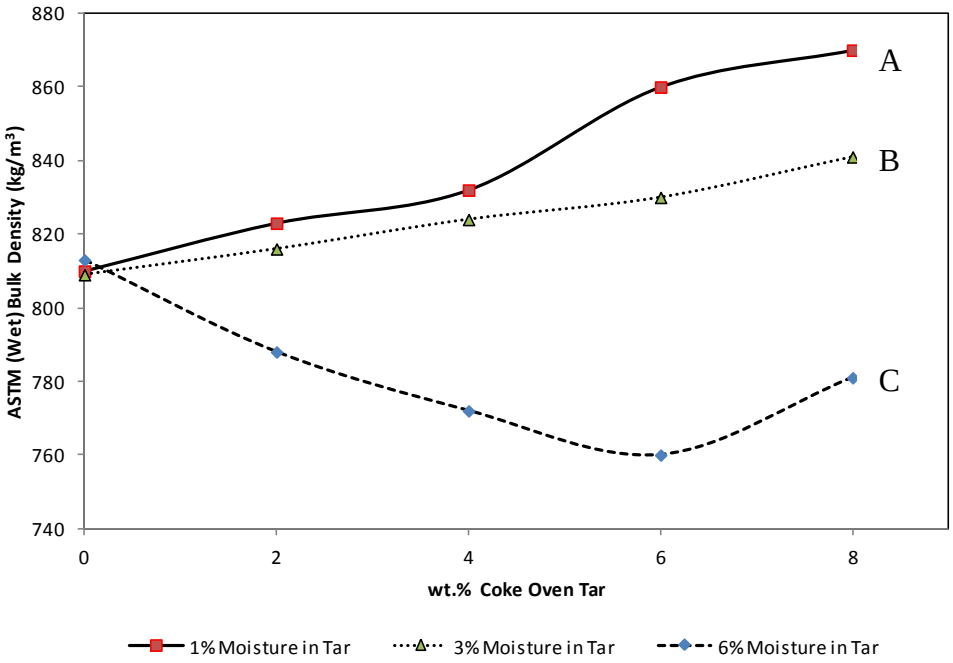

Figure 5.4: Relationship between bulk density and coke oven tar addition

Decrease in bulk density is attributed to agglomeration. Agglomeration occurs when liquid-like coke oven tar is added to a coal blend charge. Bulk density is the parameter usually used to describe coal compactness. Therefore, if coal is compacted, bulk density increases. On the other hand, the increase in bulk density can also be attributed to an increase in moisture content of the coal charge. The bulk density-moisture content relation may be governed by a number of factors such as particle size distribution, interparticle friction and particle deformation under given agglomeration and packing conditions. Various authors have shown that bulk density is influenced by the moisture content of the coal and the use of additives such as oil (Chatterjee, and Prasad, 1982; Standish *et al.*, 1991; Yu *et al.*,

1995). Yu *et al.* (1995) considered interporosity and intraporosity. These are also contributing to agglomeration as the major influence to the overall bulk density of a coal packing system.

The results in this study are in good agreement with the findings of Chatterjee and Prasad (1982) who reported bulk density improvement from 768 and 803 kg/m^3 with tar addition. Chatterjee and Prasad (1982) also added 0.2% of light diesel oil (LDO) in a coal blend with equal beneficial effect on bulk density. However, although those authors emphasized that the addition of 0.2% LDO or 0.4% furnace oil to the coal charge did not affect coke quality at levels of 5 – 6% moisture content, the cost of LDO would be the drawback and this cannot be underestimated.

The current study reveals that the level of moisture content in coke oven tar does influence bulk density. Chatterjee and Prasad (1982) did not highlight this aspect in their findings. However, this is clearly confirmed in the current study. Furthermore, in Chatterjee and Prasad (1982)'s study, prime and medium coking coal constituents were used in the blend as opposed to soft coking coal used in large proportion in the current study.

5.10 Effect of moisture content in coal blend on bulk density

The effect of coal blend moisture on bulk density was studied as a function of moisture content in coke oven tar addition and the results are depicted on figures 5.5 to 5.7. As shown on the Figure. 5.5 below, as coal blend moisture increases from 6.0 to 6.7 wt.%, bulk density decreases from 813 to 760 kg/m^3. This is only true for moisture less than 6.7%. However, at moisture of 7%, bulk density started to increase to 781 kg/m^3. Therefore, an increase in coal moisture leads to a decrease in coal bulk density in the coke oven chamber in moisture content less than 6.7%. The reason for decrease and increase in bulk density as moisture content increases is explained by Yu *et al*. (1995). According to Yu *et al*. (1995), the mixture of coal blend with insufficient liquid or less than 6.7 % moisture content forms loose aggregates, or 'crups' in which the void space between the

coal particles is only partially filled with liquid. This forms the bridges between individual particles and result in bulk density decreases. In another case, Fröhlichovà *et al*., (2010) elaborated that the reason for the decrease in bulk density caused by the charge moisture content is the influence of the surface tension of water on the surface contacts of coal grains, where the formation of agglomerates prevents the charge from a higher thickening. The effect increases with grinding fineness (Fröhlichovà *et al*., 2010). A decrease in coal moisture leads to a decrease in coal bulk density in the coke oven chamber as shown in Fig. 5.5.

However, with moisture content above 6.7%, the particles in the agglomerate are closer hence an increase in bulk density. The results are supported by Nomura *et al.*, (2003) who mentioned that a decrease in coal moisture leads to an increase in coal bulk density in the coke oven chamber. It is considered that an increase in coal blend moisture above 7.5% affects coal flow.

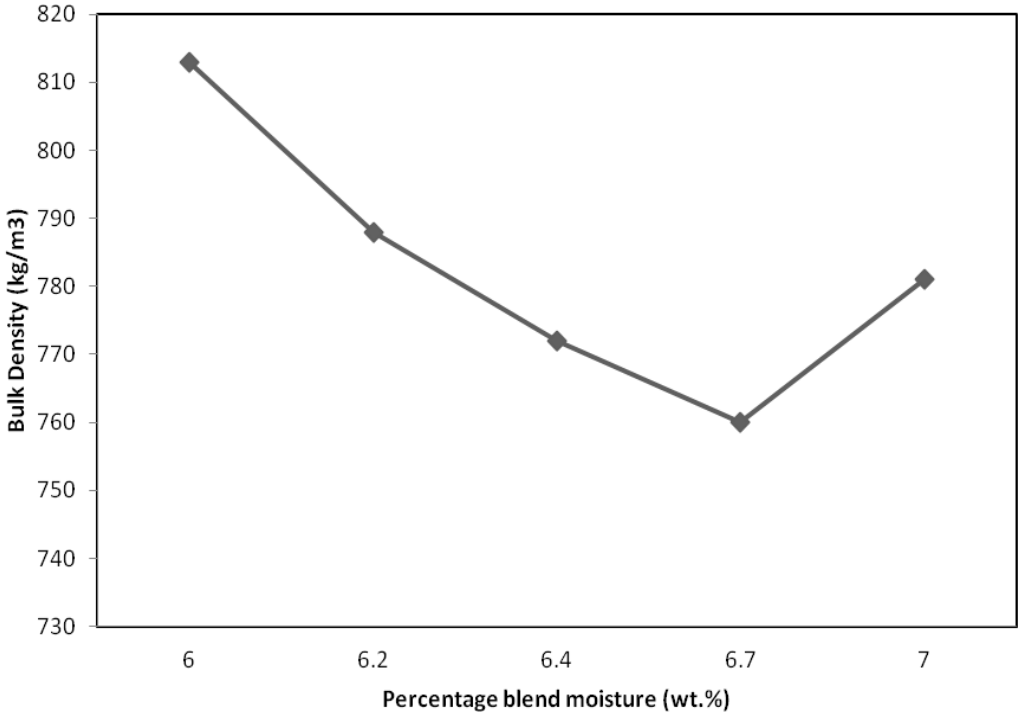

Figure 5.5: Relationship between bulk density and moisture content of blend coal due to 6% moisture content in tar

The bulk density versus coal blend moisture figure shown above looks exactly like the figure reported by Sundholm *et al.*, (1999). Therefore the effect of decrease in bulk density appears not to be due to coke oven tar but due to moisture content in coke oven tar. To further confirm that moisture content in coke oven tar was indeed responsible for the decrease in bulk density, various amount of coke oven tar with lower moisture content (1 and 3%) were used in the coal blend charge and the results are shown in figures 5.6 and 5.7 below. Figure 5.6 shows that as coal blend moisture increases from 6.08 to 6.33 wt.%, bulk density increases from 810 to 870 kg/m^3. Correlation of up to 81% was achieved due to coke oven tar addition. This is considered a good correlation.

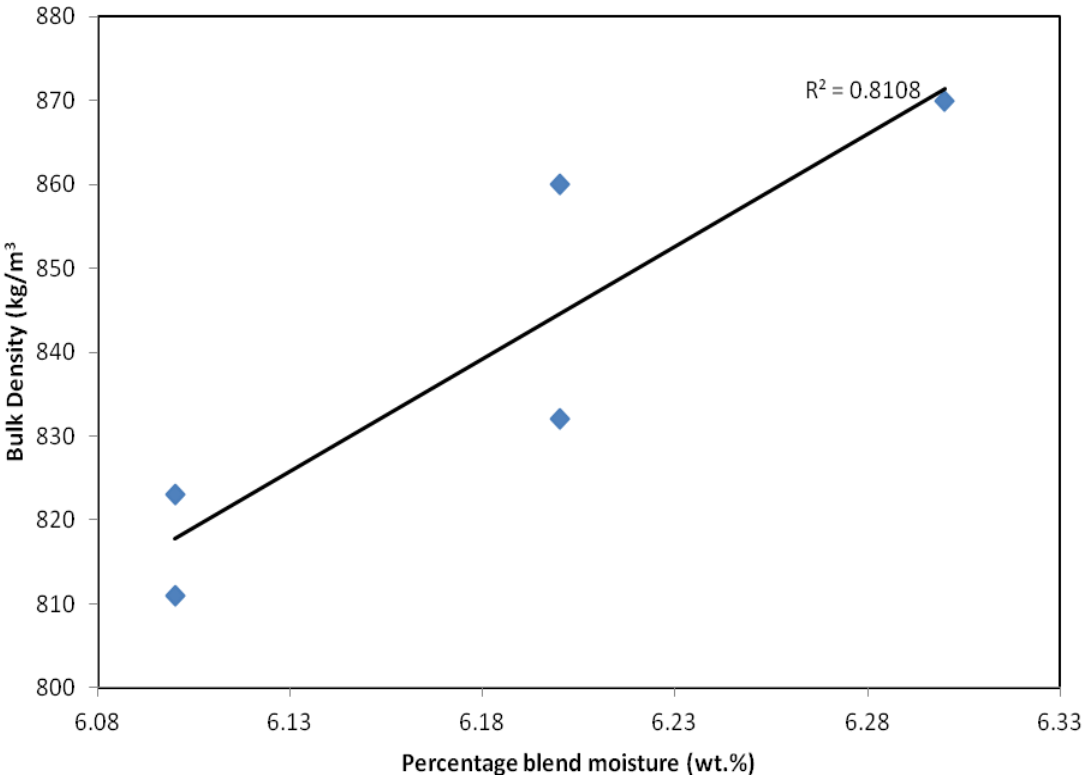

Figure 5.6: Relationship between bulk density and moisture content due to 1% moisture in tar

Figure 5.7 shows that as coal blend moisture increases from 6.08 to 6.68 wt.%, bulk density increases from 809 to 841 kg/m^3. Correlation of up to 97.8% was achieved due to coke oven tar addition. This is considered an excellent correlation.

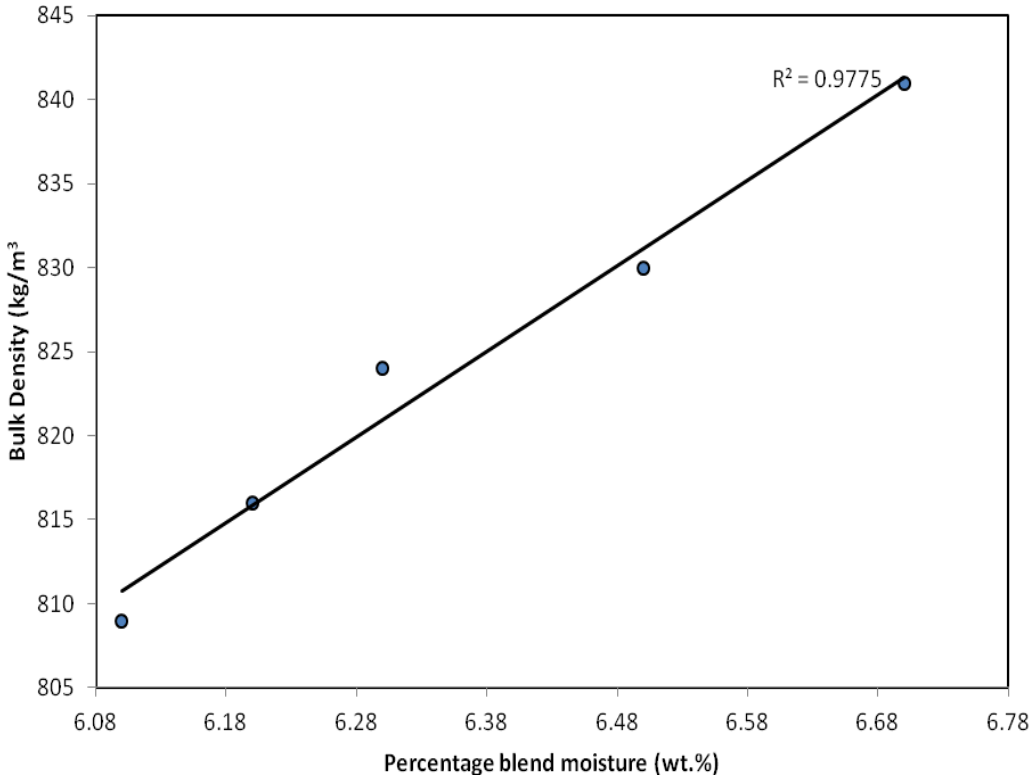

Figure 5.7: Relationship between bulk density and moisture content due to 3% moisture content in tar

5.11 Effect of coke oven tar addition on plasticity and fluidity

The fluidity of coal is an important parameter affecting coke stability by providing bonding to various coal components. In order to ensure optimum coal particle interaction, it is important that the temperature intervals of the plastic state for coals constituting a blend should overlap. Effect of tar addition on plasticity and fluidity was investigated over coke oven tar addition range of 0 – 8 wt.%. Table 5.7 shows the details of the results obtained. Coke oven tar increased the fluidity of the coal blends from 466 at 0 wt.% to 491 at 8 wt.%. All these results are consistent with the view that during heating through the thermoplastic range, the development of Gieseler fluidity is strongly dependent on a source of transferable hydrogens to cap radical species and thereby generate the low molecular weight 'solvating' species favourable to fluidity development (Tiwari *et al.*, 2013).

The plasticity of coal charge during heating is the major factor in coke production. The results obtained by Gieseler plastometer shows a positive effect on coal plasticity with addition of coke oven tar addition. Table 5.7 clearly show that as coke oven tar increases, plastic temperature range increases. However, the plasticity characteristics of coal blends were seen to be proportional to the plasticity characteristics of the individual coals used in the blends (see Table 4.4). However, this relation cannot be generalized to other coals or blends. Phenomena occurring in the plastic stage are influenced by coke oven tar and are indicated by an increase in the maximum fluidity and plastic temperature range.

Table 5.7: Plasticity and fluidity values

Plasticity	**0 wt.%**	**2 wt.%**	**4 wt.%**	**6 wt.%**	**8 wt.%**
Max Fluidity (ddpm)	466	476	488	489	491
	467	475	484	493	494
Max Fluidity Temp. ºC	357	360	367	388	397
	358	362	369	390	395
Plastic Range ºC	78	81	84	86	90
	75	82	85	88	87

5.12 Effect of coke oven tar addition on carbonisation properties

During the carbonization tests, the temperature of the wall was kept constant at 1200 °C and the coking time was targeted at 19 h. Table 5.8 shows the relationship between coke oven tar addition and carbonization conditions. It can be seen from Table 5.8 that as coke oven tar increases, the coke rate to 900°C/h decreased from 15.80 at 0 wt.% to 13.95 at 8 wt.%.

Table 5.8: Carbonization properties of various coke oven tar addition

Properties	**0 wt.% Tar**	**2 wt.% Tar**	**4 wt.% Tar**	**6 wt.% Tar**	**8 wt.% Tar**
Plastic Zone (474^{o}C) /Hours	14.35	13.75	12.60	12.65	11.50
	14.20	12.99	12.43	12.76	12.00
Plastic Zone target to 474°C	14.2	14.2	14.2	14.2	14.2
	14.2	14.2	14.2	14.2	14.2
Coke Rate to 900°C/Hours	15.80	15.85	15.35	15.20	13.95
	15.77	15.82	15.30	15.22	14.00
Coke Rate target to 900°C	16.3	16.3	16.3	16.3	16.3
	16.1	16.4	16.1	16.3	16.4
Total Coking Cycle / Hours	17.15	19.55	18.30	17.80	18.45
	17.20	19.60	18.33	17.75	18.49
Oven Start Temperature (°C)	870	870	870	870	870
	870	870	870	870	870
Oven End Temperature (°C)	1200	1200	1200	1200	1200
	1200	1200	1200	1200	1200
Coke End Temperature (°C)	1051	1048	1051	1051	1051
	1055	1051	1051	1053	1051

The maximum coking temperature increased by about 2 °C and remained constant over a coke oven tar addition of 2 – 8 wt.% range. According to Amamoto (1997), the quality of the coke produced from a conventional coal blend has been recognised to be influenced by the heating rate as well as the maximum coking temperature. In coke making, coke rate is related to the initial temperature and the heat capacity of the oven on charging, oven temperature increment per unit of time and the thermal conductivity of both the coal charge and the progressive developing of the coke zone.

Total coking cycle per hour increased with coke oven tar addition. The increase in total coking cycle per hour can be attributed to increase in additional mass of coal charged meaning less time was required to complete carbonisation process. These results are supported by another case reported by Leibrock and Petak (1983) who mentioned that without changing the other coking conditions, an increase in the density of the oven charge requires a long coking time.

5.13 Effect of coke oven tar addition on coking pressure

Generally, coking pressure is defined as the force per unit wall area. Melendi *et al.* (2011) defined coking pressure as the force generated by the charge on the oven walls during the process of transformation of coal to coke. This force has a major impact on the life of the conventional slot coke oven. Fernández *et al.* (2012) mentioned that the most important variables that affect the generation of coking pressure are the characteristics of the coal blend and bulk density. According to Nomura and Thomas (1996), the origin of wall pressure during carbonization is the gas pressure developed in the plastic layer.

In order to investigate the effect of coke oven tar addition on coking pressure during carbonization, the charged coal was carbonized in the pilot plant oven and the changes in the coking pressure during carbonization was monitored. Figure 5.8 depicts the variation in coking pressure over 0 – 8 wt.% coke oven tar addition. With 1% moisture content (A) in coke oven tar, coking pressure increased from 1.75 to 2.88 kN, mainly due to an increase in bulk density. At 6% moisture content (C) in coke oven tar, coking pressure remained constant at 2 and 4 wt.% coke oven tar addition and then decreased to 1.25 kN with 8 wt% coke oven tar addition resulting in a noticeable decrease in bulk density. Finally, with 3% moisture content (B) in coke oven tar, coking pressure increased from 2.0 to 2.17 and remained relatively constant between 2 wt.% to 8 wt.% coke oven tar addition. The high coking pressures such as generated by coal blends with 2 – 4 wt.% coke oven tar addition containing 1% and 6% moisture contents are likely to shorten the life of the coke oven's lifespan and operational problems such as stickers and heavy pushes may arise causing deterioration of the bricks of the coke oven walls and a consequent shortening of the coke oven's life span. These statements are supported by Fernández et al. (2012) who stated that the most important variables that affect the generation of coking pressure are the characteristics of the coal blend and bulk density.

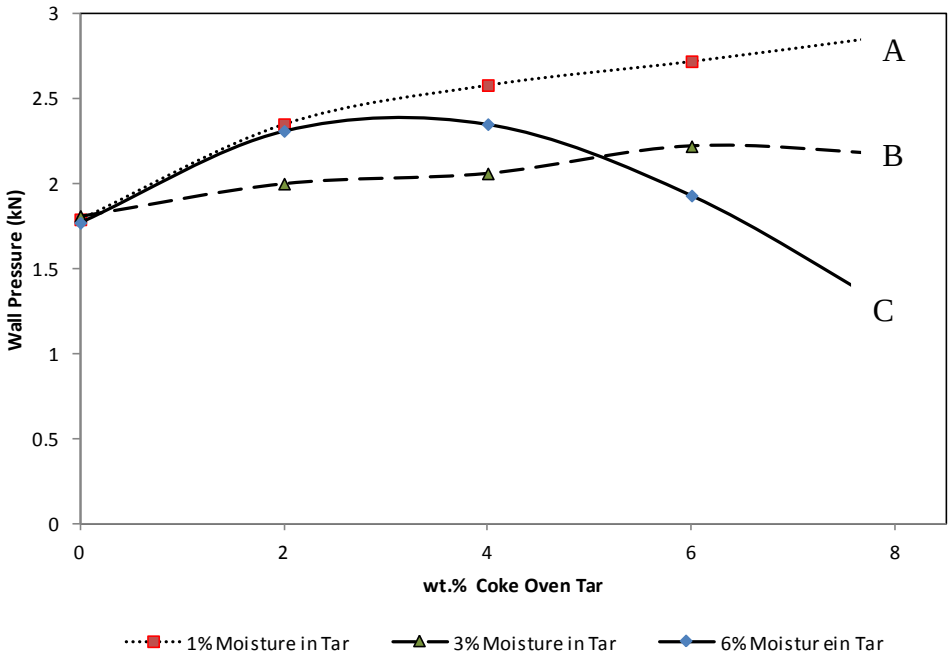

Figure 5.8: Variation of wall pressure with coke oven tar addition

The pressure developed in a coke oven depends on the bulk density of the coal in the oven and additional parameters such as the permeability of plastic layers (Jackman and Helfinstine, 1970). These authors have shown that the permeability of plastic layers increases with increasing coke oven tar addition. According to Jackman and Helfinstine (1970), loosely packed coal tends to develop low pressure during carbonization. These findings are supported by a further case reported by Melendi *et al.* (2011) who mentioned that coal - tar mixtures increased coking pressure.

Coke shrinkage needs to be considered as a further factor that may affect wall pressure. Shrinkage is sometimes related to the volatile matter of the coal. However, despite significant differences in volatile matter content in the current suite of coals (see Table 4.1 on coking coals origin and properties), the shrinkage characteristics of the coals (results are shown in Table 4.4) and their blend were very similar, indicating that this was not a factor contributing to the differences in wall pressure observed for the coal blend studied.

When the coking pressure generated by a coal or coal blend is relatively high (See Fig. 5.8A), the life of the oven may be shortened and operational problems such as stickers and heavy pushes may arise causing deterioration of the bricks of the coke oven walls and a consequent shortening of the coke oven's life span (Nomura *et al.,* 2003; Melendi *et al.,* 2011; Fernández *et al.,* 2012). According to Barriocanal et al. (2009), coking pressure is related to gases formed during pyrolysis and their escape through the different layers formed in the oven due to the lateral heating applied in coke ovens. It is established that some coals can damage coke oven walls because of either excessive pressure developed during carbonization or insufficient coke contraction at the end of the coking process (Menendez and Alvarez, 1989).

Coking pressure has been studied extensively during the last few years in an attempt to find the mechanism that controls the development of excessive coking pressure during coking and identify the factors that determine its development and also to try to monitor it accurately and to reduce its generation and undesirable effects (Fernández *et al.,* 2012). According to Fernández *et al.,* (2012), the most important variables that affect the generation of coking pressure are the characteristics of the coal blend and bulk density. The bulk density of the coal charge has a significant effect on the coking pressure because as the bulk density increases, there is more coal per cubic foot of oven volume which means coal is packed tighter in the oven (Gray *et al.,* 1978). On the other hand if the bulk density is too low, the quality of the coke will be poor due to over-firing and it will not possess sufficient strength for the subsequent operations of the steel making process (Kestner *et al.,* 1981). Therefore it is quite important to control coking pressure in the coal charging processes in order to prolong the life of the coke oven.

5.14 Effect of coke oven tar addition on pushing energy

The effect of pushing energy due to coke oven tar addition on the coal blend was studied and the results are depicted in Figure 5.9. The results indicate that 1% moisture content (A) in coke oven tar is characterized by hard pushes (39 to 53

kW/h) at all levels of tar addition. At 3% moisture content (B) in coke oven tar, hard pushes (36 to 39 kW/h) were observed only at 6 and 8 wt.% coke oven tar addition; these values are lower than those in the 1% moisture content in coke oven tar. At 6% moisture content (C) in tar, pushing energy is found to be consistently below 40 kW/h, with only a minor increase at 4 wt.% coke oven tar addition (37 kW/h).

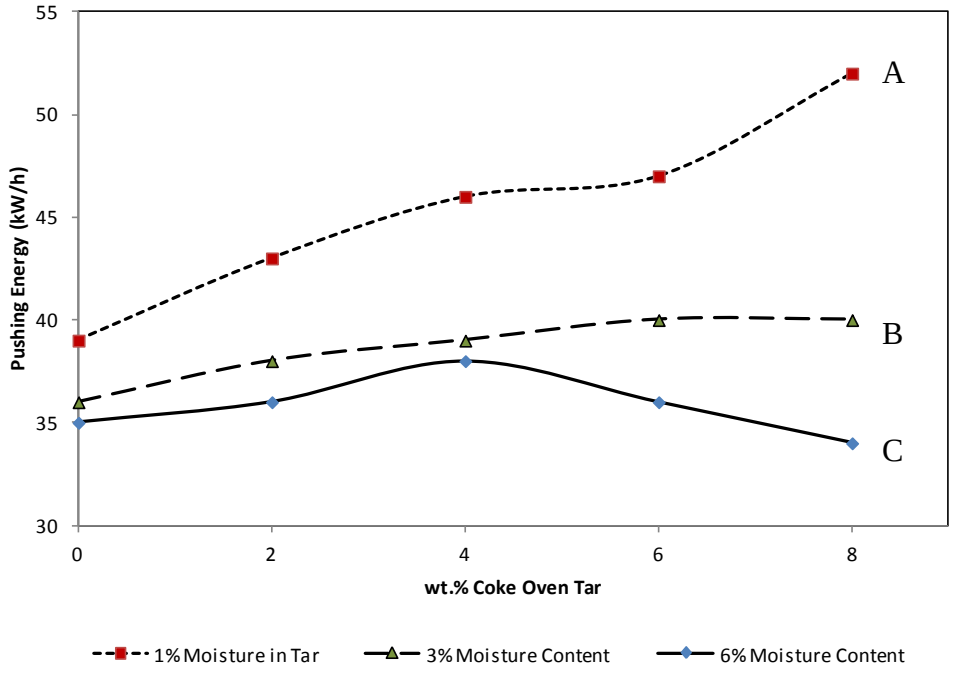

Figure 5.9: Relationship between pushing energy and coke oven tar addition

The increase in pushing energy on wall pressure would therefore appear to be attributed to the effect of coke oven tar addition on the wall pressure. Namely, higher pressures occur with the addition of coke oven tar in the amounts of 2 – 4 wt%, with 1 and 6% moisture contents in the coke oven tar. Lower pressures occur with the addition of coke oven tar of any proportion up to 6 – 8 wt%, but where coke oven tar has moisture contents of less than 6%.

Another factor affecting pushing energy is bulk density. A decrease in bulk density results in less coke throughput which means less pushing energy is required. Possibly as the bulk density decreases, the tunnel head space increases,

resulting in carbon deposition which could lead to an increase pushing energy. The difference in energy needed to push the coke oven tar with lower moisture content as opposed to coke oven tar with higher moisture content can be explained in terms of the extra mass of coal loaded into the ovens. However, an increase in pushing force is less desirable since it leads to the physical deterioration of the condition of the coke oven batteries. This is a definite risk which may lead to premature capital expenditure in the mid to longer term

5.15 Effect of coke oven tar addition on coal to coke yield

The yield of coke produced from carbonization of the coal blend with coke oven tar addition is given in Table 5.9. Considering the optimum condition of 6 wt. % coke oven tar addition, at 1% moisture content in coke oven tar, coke yield increased by marginal change of 1%. At 3% moisture content in coke oven tar, coke yield decreased by 2%. Furthermore, at 6% moisture content in coke oven tar, coke yield decreased by up to 4%.

Coal to coke transformation is known to be influenced by coal moisture, coal grind, oven charging, oven charge density and oven filling levels because these factors affect the quantity of coal in an oven. Although the 3% moisture in coke oven tar resulted in bulk density increase, coke yield decreased confirming that bulk density is not the primary factor involved. Other factors to be considered are the effective heating rate of the coal charge, the rate of contraction, the final temperature gradient and finishing temperature as these also play significant roles in coke yield. In the current case, it would appear that the decrease in coke throughput is a result of deteriorated heat transfer mechanism due to lower packing density. This means that the lower homogeneity of coal blend density over the height of the oven and oven length brings a further decrease in oven productivity. In addition, it is generally expected that as the surface moisture of the coal increases, throughput decreases.

According to Kestner *et al.* (1981), when fuel oil just like tar is added to coking coal with high moisture content, although the coking characteristics of that coal

are improved, the addition of fuel oil generally aggravates the lessened throughput characteristics produced by the surface moisture. The coke yield data presented here provides evidence supporting synergistic interaction between macerals in different coals during carbonization. Having said that, a yield of coke of 69% is possible for a coal blend with 30% volatile matter. This is known to be an acceptable norm in industry.

Table 5.9: Coke yield as a function of coke oven tar addition

Description	1% Moisture in Tar	3% Moisture in Tar	6% Moisture in Tar
0 wt.% Tar	69.2	69.0	69.1
	68.8	69.1	69.3
2 wt.% Tar	69.4	68.2	66.5
	69.6	68.3	66.7
4 wt.% Tar	70.1	69.1	65.1
	69.8	69.3	65.3
6 wt.% Tar	70.1	67.0	65.3
	69.9	67.2	65.1
8 wt.% Tar	70.5	69.0	68.0
	70.8	69.3	68.2

Figures 5.10 to 5.12 depict the relationship between pushing energy and coke yield as a function of coke oven tar with 6% moisture content in tar. Coke oven tar addition with 1% moisture content in tar gave high pushing energy while coke oven tar with 6% moisture content in tar had acceptable pushing energy although had fluctuations. Lastly, coke oven tar with 3% moisture content in tar had acceptable stable pushing energy. This is quite acceptable norm in industry. The pushing energy is influenced by coking pressure, carbon deposits and bulk density.

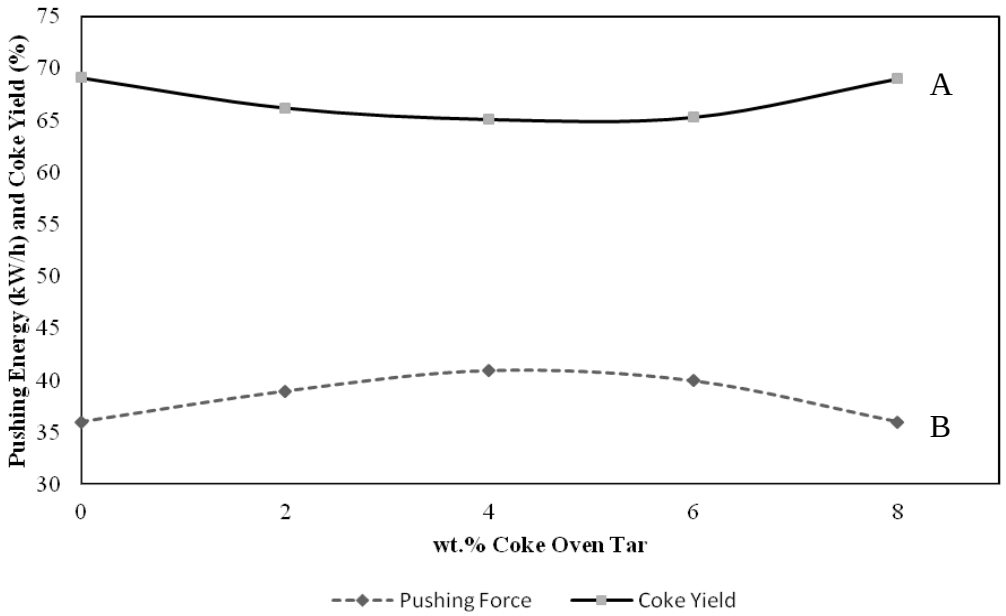

Figure: 5.10 Pushing energy and coke yield as a function of coke oven tar with 6% moisture content in tar.

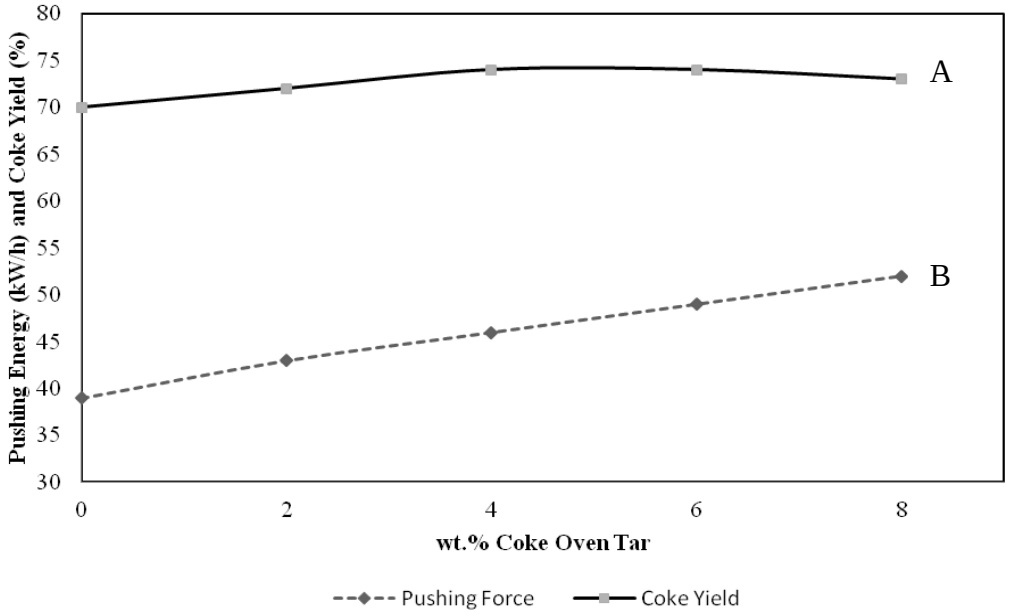

Figure: 5.11 Pushing energy and coke yield as a function of coke oven tar with 1% moisture content in tar.

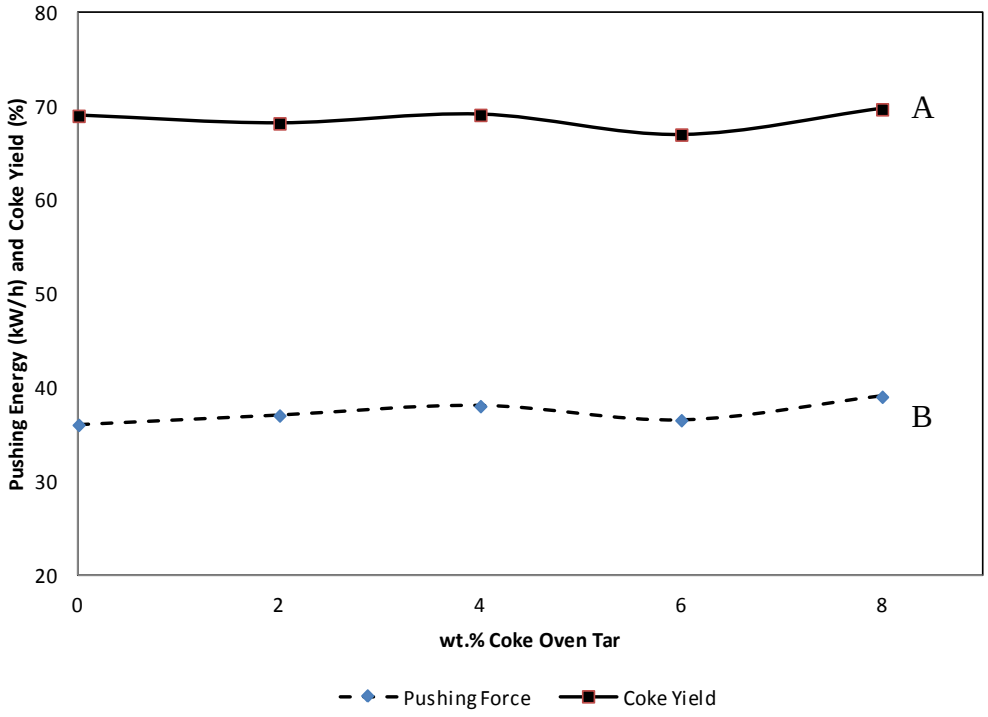

Figure: 5.12 Pushing energy and coke yield as a function of coke oven tar with 3 moisture content in tar.

5.16 Effect of coke oven tar addition on ash composition in cokes

Table 5.10 below list all chemicals composition that were identified in ash in the coke. Table 5.10 shows that there was insignificant change in iron with coke oven tar addition. However, there has been an increase in iron from the parent coal blend (average 0.60) to the iron in coke (average 0.96). The main reason is explained by Sakurovs (2003) who indicated that iron may occur in the parent coal either as pyrite, siderite or iron-rich clays such as chamosite. According to Sakurovs (2003), during coking process at 1200 °C, this could break down and react with other minerals to form species such as pyrrhotite, magnetite, iron silicates, cementite and metallic iron. Therefore, the amount of each that is formed depends on the maximum temperature the coke is exposed to, the heat treatment conditions and the conditions under which the coke was cooled after heat treatment. There was no change in other chemicals due to coke oven tar addition.

Table 5.10: Ash composition in cokes (wt.%)

Blending	Na_2O	MgO	Al_2O_3	SiO_2	P	Fe	K_2O	CaO	TiO_2	Mn
0 wt.% Tar	0.01	0.1	2.7	7.3	0.032	0.9	0.17	0.3	0.25	0.001
	0.02	0.1	2.8	7.0	0.030	0.7	0.18	0.3	0.24	0.001
2 wt.% Tar	0.03	0.1	3.0	7.0	0.027	1.0	0.17	0.3	0.25	0.001
	0.03	0.1	2.9	7.3	0.025	1.1	0.17	0.2	0.25	0.001
4 wt.% Tar	0.02	0.1	3.1	7.2	0.026	1.1	0.17	0.3	0.26	0.001
	0.03	0.1	3.1	7.2	0.026	1.2	0.17	0.2	0.24	0.001
6 wt.% Tar	0.02	0.1	3.0	7.0	0.026	1.0	0.17	0.2	0.24	0.001
	0.02	0.1	2.9	7.0	0.026	1.1.	0.18	0.2	0.25	0.001
8 wt.% Tar	0.02	0.1	2.8	7.0	0.025	0.8	0.17	0.3	0.24	0.001
	0.03	0.1	2.9	7.2	0.027	0.7	0.17	0.3	0.24	0.001

5.17 Effect of coke oven tar on phosphorus in coke

As shown in Table 5.10 above, Phosphorus decreases from 0.032 with coke oven tar and stays uniform at 0.026. The result is excellent as coke oven tar helps reducing phosphorus to an acceptable target of < 0.028. These results are supported by Díez *et al.* (2002) who singled out that impurities such as phosphorus affect coke performance in the blast furnace by decreasing its role as permeable support. Therefore their levels have to be kept as low as possible. High phosphorus contents create brittleness in steels and alloys. CaO and Al_2O_3 stabilises the slag in the blast furnace. Coke oven tar addition did not affect CaO and Al_2O_3. The range 2.7 - 3.1 reported for Al_2O_3 is well within analytical reproducibility.

5.18 Effect of coke oven tar on catalytic Index

Basicity Index within the ash is defined as the ratio of the sum of the fraction of the basic compounds in the ash (CaO, MgO, K_2O, Na2O and Fe_2O_3) to the fraction of the acidic compounds (SiO_2 and Al_2O_3) in the ash. Alternatively, basicity Index is the ratio of basic and acidic oxides used in coke quality prediction formulas. Hattingh *et al.* (2011) however report the catalytic efficiency of the ash as the ratio of non-catalytic constituents, i.e.: Al_2O_3 to SiO_2 present in the ash. Using Hattingh *et al.* (2011) relationship, Catalytic Index was calculated using information provided on Table 5.10 above and the values were compared

with the one obtained using Eq. 5.1 below. As shown on Table 5.11, Basicity Index (BI) decreased from 0.35 to 0.26 at 2, 4 and 6 wt.% Tar and stays uniform at 8 wt.%. This is good results because catalytic index has significant influence on the coke quality. Therefore, the lower BI, the better. However, Hattingh *et al.* (2011) relationship showed that BI values are essentially the same meaning that coke oven tar addition didn't influence BI. The reason is because Hattingh *et al.* (2011) relationship is just an indication and is not comprehensive as Eq. 5.1.

$$CI = \left(\frac{Fe_2O_3 + CaO + MgO + K_2O + Na_2O}{SiO_2 + Al_2O_3} \right) \tag{5.1}$$

Table 5.11: Basicity Index versus Coke oven tar addition

Coal Tar	Eq. 5.2 CI	Hattingh *et al.* BI
0 wt.% Tar	0.35	0.37
	0.34	0.40
2 wt.% Tar	0.26	0.43
	0.27	0.40
4 wt.% Tar	0.26	0.43
	0.26	0.43
6 wt.% Tar	0.25	0.43
	0.28	0.41
8 wt.% Tar	0.34	0.40
	0.33	0.40

5.19 Effect of coke oven tar addition on sulphur content of cokes

Table 5.12 shows coke sulphur as a function of coke oven tar addition. In the entire blend studied, sulphur content of cokes didn't change with coke oven tar addition. The constant sulphur content in the coke with an increasing coke oven tar addition is attributed to no increase of organic sulphur in the parent coal blend. It is an established fact that that coke sulphur content is dependent upon sulphur content of the precursor coal blend as revealed in revisited Eq. 2.3 which shows

the empirical relationships between sulphur content of cokes and those of precursor coals:

Coke Sulphur = 0.66 (Coal Sulphur) + 0.184 (2.3)

When coal sulphur was applied on Eq. 2.3, Ndaji & Imobighe Model gave errors as shown in the Table 5.12 below. These errors as shown in Table 5.12 are insignificant and well within the reproducibility range.

Table 5.12: Coke sulphur as a function of tar addition

	Coal Sulphur (wt.% db)	Coke Sulphur (Actual)	Coke Sulphur (Ndaji & Imobighe Model)	Error
0 wt.% Tar	0.87	0.90	0.76	0.14
	0.88	0.87	0.76	0.11
2 wt.% Tar	0.99	0.89	0.84	0.05
	0.97	0.88	0.82	0.06
4 wt.% Tar	0.98	0.87	0.83	0.04
	0.99	0.85	0.84	0.01
6 wt.% Tar	0.97	0.91	0.82	0.09
	0.97	0.94	0.82	0.12
8 wt.% Tar	0.99	0.89	0.84	0.05
	0.98	0.92	0.83	0.09

db: dry basis

5.20 Effect of coke oven tar addition on ash content of cokes

Table 5.13 shows ash content of cokes over a range of 0 – 8 wt.% coke oven tar addition. The ash content of cokes decreased from 12.5 to 12.3 at 2 wt.% and decreased further to a constant of 11.8 over 4 – 8 wt.% coke oven tar addition range. Due to ash reproducibility limits of 4% of the mean of values, therefore no significant change was noticed. In the case of 11.8 and 12.5, it is mean 12.2% plus or minus 0.5% (*i.e* 11.8 and 12.7 are acceptable limits). It is an established fact

that that coke ash content is dependent upon ash content of the precursor coal blend as revealed in revisited Eq.2.4 which shows the empirical relationships between ash content of cokes and those of precursor coals:

$$\text{Coke Ash} = 1.32\ (\text{Coal Ash}) + 0.53 \qquad (2.4)$$

When coal ash was applied on Eq. 2.4, Ndaji & Imobighe Model gave error as shown in the Table 5.13 below. These errors can be attributed to the different in qualities of individual coals used in the blend.

Table 5.13: Ash content of cokes with coke oven tar addition

	Coal Ash	Coke Ash	Coke Ash (Ndaji & Imobighe Model	Error
0 wt.% Tar	9.2	12.5	12.6	0.10
	9.0	12.3	12.4	0.10
2 wt.% Tar	8.5	12.3	11.8	-0.50
	8.6	12.5	11.9	-0.60
4 wt.% Tar	8.6	11.8	11.9	0.10
	8.6	11.9	11.9	0.00
6 wt.% Tar	8.6	11.8	11.9	0.10
	8.4	11.8	11.6	-0.20
8 wt.% Tar	8.6	11.8	11.9	0.10
	8.6	11.9	11.9	0.00

5.21 Discussion Summary: Coke properties

The following sections describe the relationship between CRI and CSR, coke hot and cold strength properties at 1, 3, and 6% moisture content in coke oven tar.

5.21.1 Relationship between CRI and CSR

Figure 5.13 depicts the relationship between CSR and CRI of cokes produced from pilot plant scale oven. Low CSR of 58.7 against a target of ≥ 60 was achieved at 8 wt.% coke oven tar addition as opposed to CSR of 65.4 at 6 wt.%.

The reason for a low CSR at 8 wt.% coke oven tar is because as more water is driven off, that increases coke porosity which decreases mechanical strength. The higher the coke porosity, the less the CSR. Therefore, the coke from coke oven tar addition follows the general trend observed for the CRI and CSR of the blast-furnace cokes: i.e. the lower the CRI, the higher the CSR index. Fig. 5.13 shows a good correlation of R^2 = 0.986 due to coke oven tar. This is considered a good correlation. The correlation between CRI and CSR indices for different cokes produced from single coals of different rank and geological origin were reported by Diez *et al.* (2002) as R^2 = 0.946. The correlation between CRI and CSR in the current study outperformed that of single coals. Therefore, the following results show a definitive and consistent improvement in the CSR and CRI values achieved with coke oven tar addition.

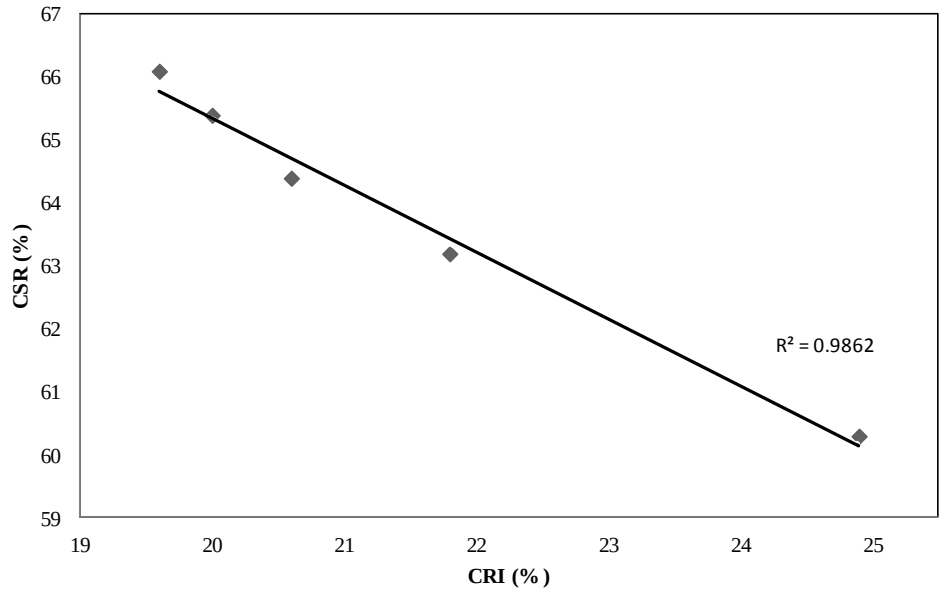

Figure 5.13: Relationship between CRI and CSR

5.21.2 Coke Hot and Cold strength properties: 1% moisture content in tar

Table 5.14 shows coke properties as function of 1% moisture content in coke oven tar addition. Coke oven tar addition decreased both I10 and M10. I40 decreased with an increasing coke oven tar addition. The lowest I40 of 42.9 was achieved at 6 wt.% coke oven tar addition. M30 for 4 wt.% tar and 6 wt.% tar results are essentially the same indicating the effect of coke oven tar addition. Hardness and

S_m improved with coke oven tar addition. Low Stability of 50.3 against a target of ≥52 was achieved at 6 wt.% coke oven tar addition.

Table 5:14 Coke Hot and Cold strength properties: 1% moisture content in tar

Properties	**Target**	**0 wt.% Tar**	**2 wt.% Tar**	**4 wt.% Tar**	**6 wt.% Tar**	**8 wt.% Tar**
M40	≥ 60	63.2	66.4	65.1	68.1	69.1
		65.0	66.8	65.4	67.3	68.7
M30	≥ 95	96.4	98.3	97.1	97.1	96.2
		96.8	98.6	97.4	97.5	96.0
M10	≤ 7.2	5.8	5.6	7.0	6.1	6.9
		6.2	5.8	6.7	6.0	7.2
I40	≥ 43	46.0	47.4	44.2	42.9	45.3
		46.3	48.2	45.0	43.7	46.4
I30	≥ 68	68.7	69.7	71.2	70.3	68.3
		68.4	69.9	71.5	69.7	68.7
I20	≥75	78.7	79.1	77.3	79.3	78.2
		77.5	78.8	77.0	80.2	77.9
I10	≤ 20	20.1	19.1	17.4	16.5	17.3
		19.7	19.4	17.3	17.0	16.9
CRI	≤22.9	21.0	22.1	20.3	19.2	23.5
		20.9	22.4	20.6	20.4	23.1
CSR	≥ 60	64.6	61.0	68.0	66.6	60.5
		65.0	61.5	67.9	67.0	61.2
S_m	≥ 53	56.1	58.2	61.0	59.3	61.2
		56.4	58.6	59.8	59.4	60.9
ASTM Stability	≥52	53.2	52.8	54.1	50.3	51.1
		53.4	53.2	54.3	51.0	52.8
Hardness	≥65	65.1	67.2	68.1	67.0	65.1
		65.5	66.9	67.6	67.3	65.3

5.21.3 Coke Hot and Cold strength properties: 3% moisture content in tar

Table 5.15 presents a summary of the coke properties as a function of coke oven tar addition for 3% moisture content in tar. Coke oven tar addition reduced the abrasion resistance and M10. I10 increased at 2 wt.% and decreased at 4 – 8 wt.% to an average of 18.5 against a target of ≤ 20 I10. In terms of coke fragmentation,

M40 increased with increased coke oven tar addition. I40 also increased with increasing coke oven tar addition. The highest I40 of 50.9 was achieved at 6 wt. % coke oven tar addition.

These results are supported by studies reported by Collin and Bujnowaska (1994) who confirmed that coke properties improved with coke oven tar addition. The results are also in good agreement with the results reported by Chatterjee and Prasad (1982) who stated that the mechanism involved in the improvement in coke strength is due to the fact that coke oven tar increases the amount of liquid phase which is essential for the formation of an adequately bonded structure during carbonization. It is this material which provides the "glue" and thereby improves coke strength.

It is well known that coke size depends on fissures occurring in coke and that coke oven flue temperatures and the addition of inert substances are further factors controlling coke size (Nomura, and Arima, 2013). However, as the latter factors were not considered variables in the current tests, the results relate more to the impact of coke oven tar addition and moisture content. The results for coke mean size (S_m), measured as the +35 mm fraction are significant and positive. The S_m also considerably improved with coke oven tar addition.

Other coke properties such as stability and hardness as a function of coke oven tar addition were also studied. The hardness factor indicates the tendency of the coke to abrade into fines upon handling and the stability factor indicates the tendency of the coke to break upon handling on impact (Gray *et al.*, 1978). As shown in Table 5.15, hardness was not affected by coke oven tar addition (it remained constant through all levels of coal tar addition) and stability increased with 2 wt.% and 6 wt.% coke oven tar addition. The results are in good agreement with DuBroff *et al.* (1985) who mentioned that the stability index of between 50 to 60 is preferred for an acceptable strength metallurgical coke. The stability results of 52 to 56 in the current set of tests, using a *3% moisture content* coke tar addition falls well within this prime metallurgical coke category.

Table 5:15 Coke Hot and Cold strength properties: 3% moisture content in tar

Properties	**Target**	**0 wt.% Tar**	**2 wt.% Tar**	**4 wt.% Tar**	**6 wt.% Tar**	**8 wt.% Tar**
M40	≥ 60	64.4	65.8	64.0	66.9	68.5
		64.8	66.0	64.6	66.2	68.4
M30	≥ 95	97.1	97.9	96.7	96.4	95.3
		97.0	97.7	96.5	96.4	95.1
M10	≤ 7.2	6.1	6.7	6.9	7.0	7.1
		6.0	6.7	6.7	7.0	7.0
I40	≥ 43	45.0	44.6	45.6	50.9	47.9
		45.2	43.0	45.4	51.0	48.0
I30	≥ 68	69.3	69.3	69.3	69.3	66.4
		69.0	69.2	69.3	69.2	66.1
I20	≥75	78.4	77.9	78.9	79.7	77.9
		78.2	77.5	79.1	79.4	77.9
I10	≤ 20	19.0	20.3	18.9	18.7	18.4
		18.9	20.0	18.7	18.5	18.2
CRI	≤22.9	20.6	24.9	19.6	20.0	22.8
		20.4	25.1	19.8	20.4	22.5
CSR	≥ 60	64.4	60.3	66.1	65.4	57.8
		64.0	60.6	66.4	65.0	59.4
S_m	≥ 53	59.3	59.5	60.5	58.4	62.8
		59.0	59.8	60.1	58.1	62.4
ASTM Stability	≥52	52.8	56.1	52.2	56.1	52.2
		52.6	56.0	52.0	56.0	52.4
Hardness	≥65	65.3	66.3	66.2	66.5	66.2
		65.3	66.5	66.0	66.4	66.1

5.21.4 Coke Hot and Cold strength properties: 6% moisture content in tar

Table 5.16 shows summary of coke properties as function of 6% moisture content in coke oven tar addition. Coke oven tar addition increased the abrasion resistance and M10. I10 decreased with coke oven tar addition and was within the range of ≤ 20 target. In terms of coke fragmentation, M40 increased with increased coke oven tar addition. I40 decreased with an increasing coke oven tar addition but was within acceptable range. The lowest I40 of 44.1 was achieved at 6 wt.% coke oven tar addition. Stability, Hardness and CRI improved with coke oven tar addition.

However, CSR of 60.3 at 6 wt.% coke oven tar was the main concern due to being on the boarder line of the target values.

The results for coke mean size, measured as +35 mm fraction are influentially positive. The mean coke size is however very much increased by 0.3, 2.2, 1.2, 1.9, and 0.9 at 2, 4, 6, and 8 respectively. According to (Nomura and Arima, 2013), there is no clear relationship between mean coke size and coal blending in literature. Other reports shows that mean coke size decreases with increasing volatile matter content and other mention that no correlations exist between volatile matter and mean coke size (Nomura and Arima, 2013). The results from 6 wt.% moisture content in coke oven tar reveals that mean coke size decreases with increasing volatile matter content. Although Nomura and Arima (2013) further highlighted that coke oven flue temperature and addition of inerts substances are other factors controlling coke size, this was not applicable in the case discussed.

Table 5:16 Coke Hot and Cold strength properties: 6% moisture content in tar

Properties	**Target**	**0 wt.% Tar**	**2 wt.% Tar**	**4 wt.% Tar**	**6 wt.% Tar**	**8 wt.% Tar**
M40	≥ 60	64.7	65.7	64.8	67.2	70.2
		64.1	66.3	64.5	67.3	69.5
M30	≥ 95	96.9	98.8	98.2	97.0	94.2
		97.2	98.4	98.5	96.8	94.7
M10	≤ 7.2	5.9	6.1	6.6	6.8	7.0
		6.1	6.4	6.9	6.9	7.4
I40	≥ 43	45.9	43.2	45.7	44.1	43.5
		45.1	44.4	46.1	44.7	43.2
I30	≥ 68	68.9	69.4	71.0	69.9	67.1
		69.2	69.2	69.7	69.6	67.5
I20	≥75	78.2	78.3	76.2	80.4	75.8
		78.9	78.7	75.9	79.7	75.5
I10	≤ 20	19.5	19.5	17.6	17.6	19.4
		20.0	19.9	18.0	17.9	20.1
CRI	≤22.9	20.5	19.7	21.0	21.3	22.6
		20.8	21.3	21.5	21.8	23.9
CSR	≥ 60	64.7	61.2	62.4	60.3	60.9
		64.3	60.9	62.0	58.7	59.2
S_m	≥ 53	53.6	55.2	54.2	52.9	53.9
		54.1	53.2	53.2	51.3	52.5
ASTM Stability	≥52	53.2	55.6	54.1	55.3	54.1
		53.4	55.7	54.3	54.0	53.8
Hardness	≥65	66.3	65.6	66.7	65.9	66.1
		65.9	65.1	65.4	66.7	64.9

5.22 Economic evaluation of coke oven tar addition

In order to assess the economics of coke oven tar addition, the cost of imported coals were weighed against the coke yield. It is shown in this study that the optimum condition achieved, coke yield decreased by 2%. Table 5.17 shows the details of the business case. Prices quoted for coals A to D are as delivered at the works, whereas the price quoted for coke are that ex-works (i.e. free on truck, excludes transport. Therefore major savings have risen as a result of coke oven tar addition to coal blend. In addition, it is expected that maximum of up to 50% of

coke oven tar added be recovered after carbonization. Recovering up to 50% of the total tar added is a bonus from the economics point of view.

Table 5: 17: Business case for coke oven tar addition to coal blend

Coal Prices	**R/Ton**	**0 wt.% Tar**	**6 wt.% Tar**
Coal B	1,850	8	7.3
Coal C	1,800	38	34.5
Coal D	1,750	19	17.2
Coal A	0,950	35	35
Blend Cost R		1,721,550.00	1, 597,982.50
Blend Saving		-	123, 567.50
Coke Yield		69%	67%
Coke R	1,900	1,805,000.00	1,768,900.00
Coke saving lost		-	36,100.00
Overall Savings (per day)		-	**87, 602.50**

Assumptions:

Based on 50 ovens of 23 tons charged coal each per day = 1150 tons

Coke in each oven weigh = 19 Ton

Coal C= 92 Tons (base) and 83.95 Tons (6%)

Coal B = 437 Tons (base) and 396.75 Tons (6%)

Coal D = 218.5 Tons (base) and 197.8 Tons (6%)

Coal A = 402.5 Tons (base) and 402.5 Tons (6%)

Coke oven tar addition results in savings of R87, 602.50 x 30 = R2, 628, 075.00 per month. The profit is made due to the difference in blend saving and coke throughput.

5.23 Summary

The variation in moisture content in coke oven tar has demonstrated to impact on coal blend bulk density. Therefore the nature of interaction between coke oven tar and coal blend is moisture in coke oven tar dependent. With 1% moisture content in coke oven tar of 6 wt.% in the coal blend, coke yield increased by 1% and low I40 of 42.9, CRI of 19.2, CSR of 66.6, hardness of 67.0 and Stability of 50.3 were

achieved. Also, addition of coke oven tar with 1% moisture content directly to coal blend can be prohibited by its high viscosity. In addition, the latter process was characterized by excessive increased in wall pressure and pushing energy. Both wall pressure and pushing energy increase are less desirable due to their detrimental effect on the physical condition of the oven walls.

At 3% moisture content in coke oven tar addition of 6 wt.% in the coal blend, coke properties improved, coke yield showed up to 2% decrease and coke properties such as I40 of 50.9, CRI of 20.9, CSR of 65.4, hardness of 66.5 and Stability of 56.1 were achieved. Comparatively, at 6% moisture content in coke oven tar addition of 6 wt.% in the coal blend, coke properties improved, coke yield showed up to 4% decrease and coke properties such as I40 of 44.1, CRI of 21.3, CSR of 60.3, hardness of 65.9 and Stability of 55.3 were achieved. Therefore, the optimum moisture content in coke oven tar was found to be 3% with a coke oven tar addition of 6 wt.% in the coal blend. At 3% moisture content in coke oven tar addition of 6 wt.% in the coal blend, coke properties improved. When the amount of coke oven tar was increased to 8 wt.%, coke yield was not affected but low CSR of 57.8 against a target of ≥60 was achieved as opposed to CSR of 65.4 at 6 wt.%. Also, coke stability of 52.2 at 8 wt.% as opposed to 56.1 at 6 wt.% was achieved. Moreover, the highest I40 of 50.9 was achieved at 6 wt.% whereas with 8 wt.% coke oven tar, I40 of 47.9 was achieved.

Factors associated with the improvement of coke quality following coke oven tar addition are due to increase in bulk density, maximum fluidity and fine crushing. By adding coke oven tar to the coal blend, decrease of the surface tension of water is reached which causes the spontaneous charge thickening during pouring. The optimum condition was achieved in order to get coke oven tar uniformly mixed with coal blend. Specialised or coke oven tar resistant conveyor belt were used to transport mixed coal blend with coke oven tar to the test bunkers.

CHAPTER 6: CONCLUSIONS

The purpose of this research was to establish the potential and feasibility of substituting fractions of imported coking coals with coke oven tar whilst maintaining or improving coke quality. Based upon the results, the following conclusions can be drawn:

- Moisture content in coke oven tar was found to influence coke qualities.
- High moisture content in coke oven tar reduced bulk density while low moisture content in coke oven tar increased bulk density, wall pressure and pushing energy.
- Optimum moisture content in coke oven tar was found to be 3% with a 6 wt.% coke oven tar addition.
- High wall pressure generated by coke arising from a coal blend low with low moisture in the coke oven tar is less desirable because the life of the oven may be shortened and operational problems such as stickers and heavy pushes may arise causing deterioration of the bricks of the coke oven walls and a consequent shortening of the coke oven's life span.
- Coke properties improved with coke oven tar addition. Following tests using 0-8 wt% coke tar addition in optimum moisture content in coke oven tar, it was established that coke oven tar of 6 wt.% proved to be the most beneficial proportion to maintain coke quality.
- However, when adding 6 wt.% coke oven tar, up to 2% decrease in coke yield was observed but without showing any deterioration in coke quality.
- Despite this 2% decrease in coke yield, coke oven tar addition is still a viable option based upon economic factors (*i.e.* reduced quantity and cost of imported coking coal whilst achieving a similar or better final coke product).
- Preliminary constituents of coke oven tar were confirmed with GC-MS.
- The results from this study are the first steps in the development of improving coke quality through the addition of coke oven tar for the iron and steel industry where prime coking coal availability and costs are of

great concern. Coke producers could benefit from the adoption of coke oven tar addition for production of metallurgical coke especially in countries where large proportions of imported coking coals are included in the base blend.

- Flow characteristics of coal blend and coke oven tar mixture should be investigated after allowing the mixture to stay for about a week and more. There are usually unplanned delays in operations and it is of paramount importance to establish if coke oven tar addition will accommodate such cases and to what extent.
- In conclusion, it must be stated that, whilst all the objectives in this research were accomplished, there is further work to be undertaken in up-scaling this process for commercial purposes. It is the intention of the author to continue further in this regard.

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