Use of thermogravimetric analyzer and high temperature furnace as an alternative to the coke reactivity index test and study on effect of binders in metallurgical coke making

by

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ABSTRACT

Metallurgical coke, a porous carbon material produced by carbonization of coking coal at high temperature, generally above 900 °C, is an integral part of iron-making in the blast furnace. During iron making, coke serves several important roles in the blast furnace such as a source of energy, as a reducing agent, to provide a permeable bed for gas flow and provides enough strength to sustain the load of the charge within the furnace. A coke is said to be of good quality if the CRI is lower and CSR is higher. Reaction of coke with carbon dioxide increases the porosity of the coke and, hence, the coke strength decreases. However, tests involving CRI and CSR are very laborious and time-consuming; this study aims to propose TGA and HTF experiments as an alternative for the CRI test.

In the first part of this study, a series of Thermo-gravimetric analysis (TGA) and high temperature furnace (HTF) experiments with various cokes was conducted in CO_2 atmosphere to observe kinetics of the CO_2 gasification; in particular, the mass loss during the isothermal period at 1100 °C. The results from TGA and HTF showed a linear relation with the actual CRI values. The results from this study were helpful to predict the reactivity of the cokes and to decide the quality of different cokes. In a wider perspective, this study has high potential in assessing the reactivity index of the metallurgical cokes for iron-making industry.

Another part of this study describes the attempts to produce the carbonization products from different bituminous coals and a sub-bituminous coal by adding binders such as petcoke and a blend of petcoke and asphaltene. Also, a study was conducted by adding minerals such as calcite, siderite, magnesite and dolomite. Coking experiments were carried out in a lab-scale horizontal tube furnace at a temperature of about 900 °C in an inert atmosphere (N_2). The effect on carbonization products by addition of binders to the coal samples was studied. Porosity of the produced cokes was determined using optical microscopy by obtaining the 2D stitched images. Raman spectroscopy was used to determine the amount of graphitic carbon and disorientated carbon, which was used to determine the extent of graphitization. Further, Thermo-Gravimetric Analysis (TGA) in CO_2 atmosphere was also conducted to observe kinetics of the CO_2 gasification in terms of Coke Reactivity Index (CRI) - mass loss during isothermal period at 1100 °C for two hours. This study suggests the potential usage of petcoke as binder to bituminous coals and blend of asphaltene and petcoke as binder to improve the quality of cokes from sub-bituminous coals.

Keywords: *Coke, carbonization, binders, minerals, CRI, reactivity, porosity, graphitization*

PREFACE

Part of the research conducted for this thesis is part of MITACs accelerate research project with Teck Metals Ltd. led by Dr. Qun Zhang, Senior research engineer, Teck Metals and by Professor Dr. Rajender Gupta, University of Alberta. The experiments, the data analyses, the conclusive analysis in chapter 3 and chapter 4 along with the literature review of chapter 2 are originally my work under the supervision of Dr. Rajender Gupta.

To my Parents and Teachers

“The little boy you know,

If not for your sacrifices,

If not for your affection,

Wouldn’t have had these wings to fly”

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Sanat, Hemant, Rahul, Sruthi, Gokul, Anjana, Dhanvini, Anuja, Simona, Gowtham, Amritha, Akash, Sahil, Tejal, Kaushik, Sowmya, Sumanth...(Sorry! If I missed anyone) for making Edmonton "a home away from home". For all my friends at university and also everyone back home;

"In the sea of gratitude, Shall I send my ships of thank you,
To all my friends in deed, to my angels in disguise,
Thanks turned out to be such a short word… "

Last but not the least, I would like to express my thanks and love to my parents, my dear brother Gokul and my family. Paati and Late Taatha, the word "thank you" wouldn't suffice and mere words aren't enough to describe for all that you have done to me so far! It's a LOVE you, from the bottom of my heart! Thanks for all your support!

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CRI - Coke Reactivity Index

CSR - Coke Strength

TGA - Thermogravimetric Analyzer

HTF - High Temperature Furnace

PC10 - Petcoke 10wt%

PC20 - Petcoke 20wt%

PC30 - Petcoke 30wt%

P5A5 - Petcoke 5 wt% and Asphaltene 5 wt%

P10A10 - Petcoke 10 wt% and Asphaltene 10 wt%

P15A15 - Petcoke 15 wt% and Asphaltene 15 wt%

1. INTRODUCTION

The iron and steel industry is one of the most important industrial sectors in the world with the industry significantly contributing to the development of many countries. The Global steel production in 2018 was 1689 Million tonnes with China producing 49.2% followed by EU, and Japan. Figure 1.1 shows the steel production in various countries in 2018.

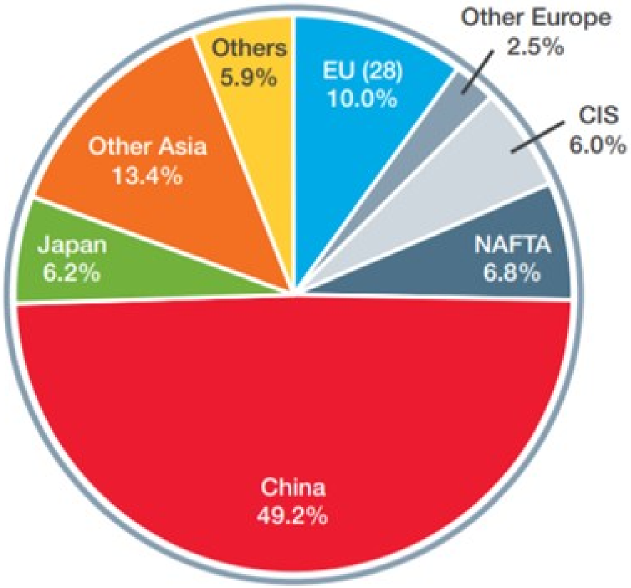


Figure 1.1 Global steel production in 2018 [World steel 2018]

The steel making process is a multi-stage process and yields a large number of by-products. The process involves complex heterogeneous reactions, high temperature operations, gas and solid handling systems along with solid transport systems. There are several technologies available with variations in the operating conditions and process for making iron and steel. Steel is ideally produced from three major processes:

- Blast furnace
- Direct Reduced Iron- Electric Arc Furnace
- Direct Reduced Iron- Electric Induction Furnace

Production of iron and steel in blast furnace is the highest with it contributing to 71.5% of the world production [Owais, 2018]. China produces 91% of its steel from the blast furnace route which accounts to 756 Million tonnes of the world production. The blast furnace route heavily relies on the use of coking coal for its production. Coking coal is used as a fuel and to produce coke which is the chief reducing agent to produce pig iron. Cokes produced from high quality coking coals have high quality which increases the productivity of blast furnace performance for iron making. Hence, lots of researches have been carried out to produce a high quality coke to increase the blast furnace performance.

The world demand for coking coal is on the increase with China, India, Japan, Russia and Ukraine accounting for 74% of the demand [World Coal Institute 2009]. The demand for Prime grade coking coal is currently met by China and Australia. China is the highest producer of coking coal followed by Australia, USA, Russia and India. China satisfies its domestic demand for the production of steel after which only about 18% is available for its exports. Figure 1.2 shows the major coking coal exporting countries over the last decade. Australia leads the way for the coking coal exports with the country exporting more than 140 Million tonnes. Canada is the third major coking coal exporter of the world.

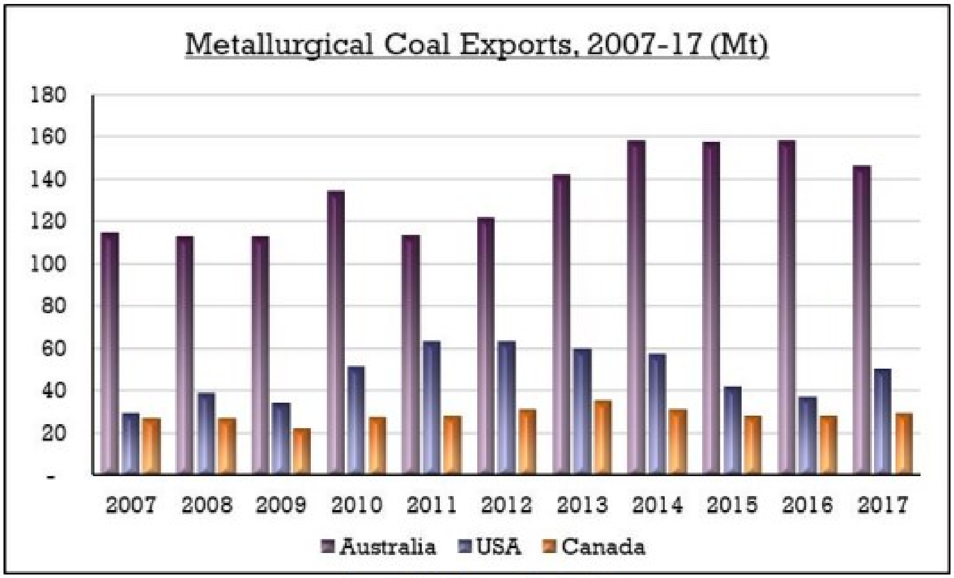


Figure 1.2 Major coking coal exporters from 2007-2017[Commodity insights report 2018]

The production of crude steel has grown at a Compounded Annual Growth Rate (CAGR) of 5% over the past decade. With 71% of the demand currently being met by blast furnace route and with a lack of prime grade coking coal, there warrants an alternative in the process. One such process is the use of Direct Reduced Iron (DRI) to produce steel. This technique is widely used in India, with India producing 62% of its sponge iron from this process. However, only 28% of the world demand is satisfied by the DRI process. This would necessitate a rapid increase in the number of DRI plants being set up. However, a rapid growth in the DRI units would render the blast furnace plants obsolete. This would turn detrimental for the iron and steel manufacturers relying on the blast furnace for the production of steel.

On the other hand, G7 leaders insisted on phasing out thermal coal by 2100 due to the adverse effect on extreme climate change as a result of excessive emissions of greenhouse gases by combustion of coal [Connolly 2015]. Thermal coal can be also used to produce cokes with the addition of binders. Annual world steel demand is expected to grow from approximately 1,410 million tonnes (Mt) of crude steel in 2010 to approximately 2200 Mt in 2050 [China Energy Group, 2018] . Due to the high growth in demand of steel production and limited resources of coking coal in the world, researches have been carried out to study the potential usage of cokes produced by blending coking coals with additives and/or with non-coking coals [Díez, 2002][Krzesińska, 2009].

Thus, this research focusses on the study of potential usage of cokes from low quality coking coal and non-coking coals with the addition of binders.

1.1. Research objectives

Coke is considered to be of good quality if the Coke Reactivity Index (CRI) is low and Coke Strength after Reaction (CSR) is high. The first part of this study focusses on the gasification behaviour of the industrially produced cokes. The second part focusses on the study of preparation of metallurgical coke in a lab scale with the addition of binder. The research objectives are as follows:

1. TGA and HTF as an alternate to CRI test
    - To study CO_2 gasification behaviour of industrially produced cokes.
    - To propose High Temperature Furnace (HTF) or Thermogravimetric Analysis (TGA) as an alternative to the actual CRI test.
    - To relate the results of laboratory tests with CRI of cokes.
2. Use of binders in metallurgical coke making
    - To study the effect in coke properties with addition of minerals such as dolomite, siderite, calcite, magnesite.

- To study the effect of petcoke addition in coke properties.
- To study the effect of blend of petcoke and asphaltene in coke properties.

1.2. Source of coal and coke

Metallurgical coals and cokes used in this study originate and were obtained from the mines in British Columbia. The thermal coal used in this study was obtained from mine in Alberta. The asphaltene and petcoke which has been used as a binder was collected from by-product of oil-sand mine in Northern Alberta.

1.3. Thesis outline

The thesis is organized in five chapters. The content of each chapter is described briefly below.

Chapter 1 has briefly introduced the global demand of coking coal, iron and steel. This chapter also explains the motivation for this research, the research objectives, and the layout of the thesis.

Chapter 2 reviews the literature related to the present research. This chapter gives an overview of coal and elaborates on metallurgical coke, and importance of coke in blast furnace, along with the brief explanation of blast furnace operation. Also, the theory behind coal carbonisation and coke formation are discussed. Past researches related to lab-scale production of coke and researches related to addition of binders in coke are presented.

Chapter 3 includes the details of the investigated samples and the details of experimental and characterisation techniques used in TGA and HTF. It explains the results of the coke gasification with carbon dioxide, in thermogravimetric analyser and in high temperature furnace. This chapter compares the results of both (TGA and HTF) to correlate with the actual CRI values of the coke.

Chapter 4 explains coke preparation in a lab scale furnace and different characterization techniques employed to study the effect of binders on coke properties. It discusses the results of characterization of cokes carbonized in a lab-scale horizontal tube furnace with addition of binders such as petcoke, blend of petcoke and asphaltene and minerals such as calcite, magnesite, dolomite and siderite.

Chapter 5 provides the conclusion remarks of this study along with suggestions for future research.

2. LITERATURE REVIEW

2.1. Coal and its uses- an overview

Coal is a combustible black or dark brown rock which mainly consists of carbonized plant materials, buried underground over the ages. In other words, coal is described as the altered remains of prehistoric vegetation that gets accumulated in peat, lowlands and swamps. The combustible organic segment of coal is primarily composed of carbon, hydrogen, oxygen and little amounts of nitrogen and sulphur [ASTM D3176-15].

Coal can be classified based on their fixed carbon and gross calorific value as Lignite, Sub-bituminous, Bituminous, Semi-anthracite and Anthracite. Anthracite being a high-rank coal and lignite being a low-rank coal, the fixed carbon value and gross calorific value increases with a decrease in volatile matter from Lignite to Anthracite [ASTM D388-15][Saxena and Tiwari, 2015].

In spite of many uses, coal is most significantly used in electricity generation and steel production. Thermal coals, also known as steaming coals, are generally burnt to produce steam required to run the turbines and generate electricity, while on the other hand, coking coals, also known as metallurgical coals, are used to produce metallurgical coke, a potential raw material for blast furnace operation to produce iron. However, not all coals can be used to produce coke. It is the unique thermo-plasticity nature of the bituminous coals that make them suitable for coke production. The chemical structure of the bituminous coal is shown in Figure 2.1.

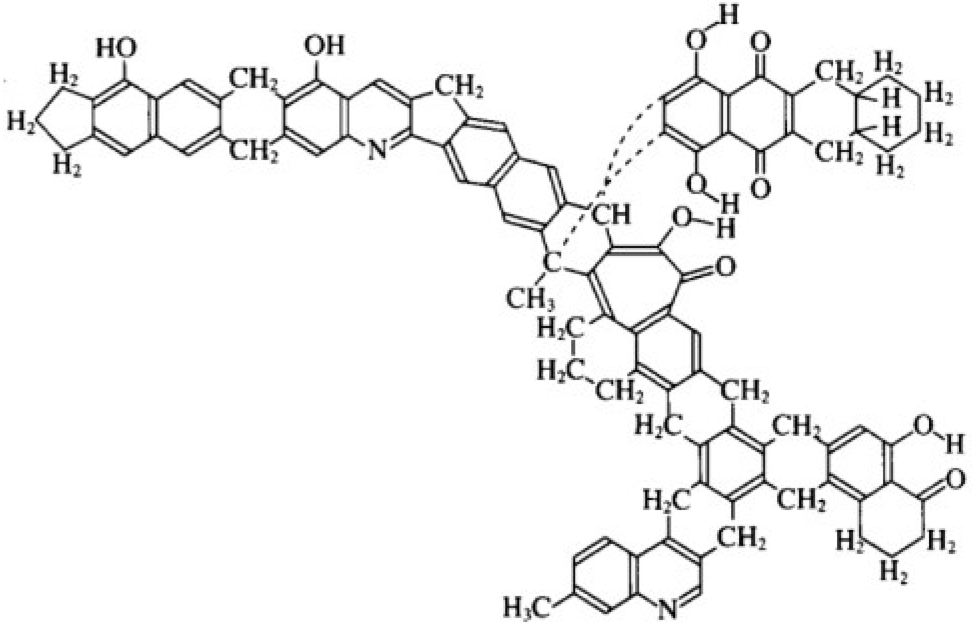


Figure 2.1Structure of a bituminous coal [Given, 1960]

2.2. Overview of iron – making

Iron-making is a process of converting iron ores into metallic iron. Blast furnace operation is the primary source of steelmaking accounting for about 60% of worldwide steel production [Ishii, 2000]. The blast furnace is essentially a countercurrent reactor process in which solid raw materials are placed into the furnace from the top in alternating layers and the liquid products are drawn from the bottom of the furnace.

The iron ore, mostly in the form of hematite is continuously charged from the top of the furnace with metallurgical coke in an alternate layers and as the charge travels down the furnace, it is heated and at a temperature of around 500^{o}C, indirect reduction of the ore by the carbon monoxide (CO) occurs. As the charge travels further down and is heated to around 900-950^{o}C, reduction of the iron oxide by solid coke occurs. The cross-sectional schematic of the blast furnace is given in Figure 2.2.

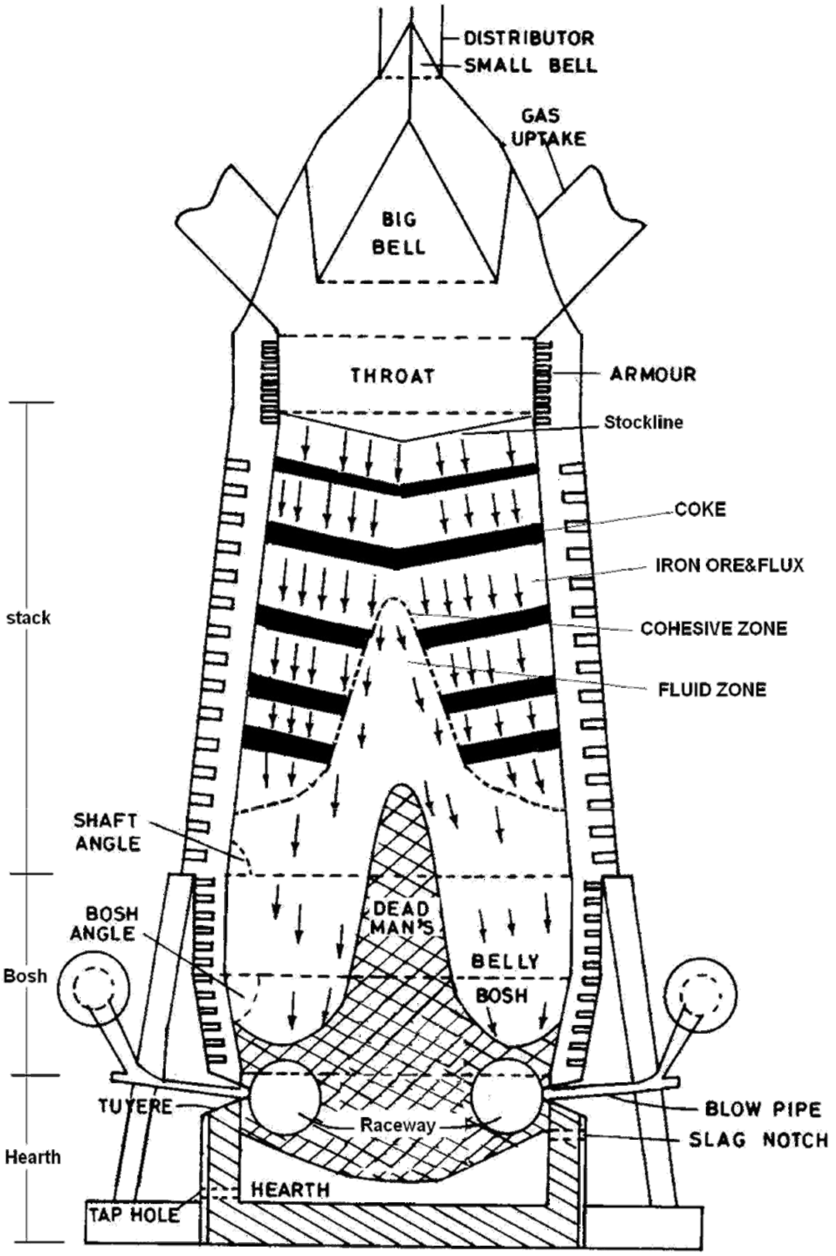


Figure 2.2 Cross-sectional schematic diagram of blast furnace [Biswas, 1981]

The iron oxides are transformed by reduction into a hot metal and are melted towards the lower part of the furnace. The reduction is achieved with carbon monoxide (CO) which is generated by the coke. The reactions are as follows [Biswas, 1981];

$3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2$ ----------------------- (1)

$Fe_3O_4 + CO \rightarrow CO_2 + 3FeO$ ------------------------ (2)

Indirect reduction: $FeO + CO \rightarrow CO_2 + Fe$ ----------------------- (3)

Direct reduction: $FeO + C \rightarrow Fe + CO$ ----------------------- (4)

2.3. Role of coke in the blast furnace

In 1709, Abraham Dorby invented the use of coke as a fuel in the blast furnace to produce iron. Metallurgical coke, a porous carbon material produced by carbonization of coking coal at high temperature, generally above 900 °C, is an integral part and one of the most important raw materials for iron-making in the blast furnace. It has a strong influence on the efficiency of the process and the quality of the hot metal. Coke is the only raw material that remains in the solid state at a high temperature at the lower zone of the blast furnace.

Coke has many important roles in the blast furnace, of which three major ones are discussed as follows [Díez, 2002]. In the blast furnace, coke acts as a fuel to supply heat for the endothermic chemical reactions. It acts as a chemical reducing agent by reducing carbon dioxide to carbon monoxide which is required to reduce iron oxides. It also acts as a permeable support for the hot gas to flow upwards and for providing enough strength to sustain the load of the charge within the furnace. Role of coke as a fuel and as a reducing agent in blast furnace can be substituted by the use of other materials like plastics, coal, oil but no other materials can substitute the metallurgical coke's role as a permeable support in the blast furnace [Díez, 2002] [Hilding, 2005].

Coke undergoes degradation in blast furnace due to thermal stress, mechanical stress, and also due to its properties. If the coke reacts with carbon dioxide excessively, coke will become weak and will degrade into smaller particles, which causes permeability reduction and reduce the performance of blast furnace [Ishii, 2000]. Metallurgical coke has many quality requirements such as chemical composition, reactivity, thermal stability, strength etc. It is very important to understand the properties of coke and select a good quality coke for blast furnace operation as quick degradation of the coke is undesirable.

2.3.1. Coke Reactivity Index (CRI) and Coke Strength after Reaction (CSR)

A coke is said to be of good quality if the Coke Reactivity Index (CRI) is lower and Coke Strength after Reaction (CSR) is higher. The reaction of coke with carbon dioxide increases the porosity of the coke and, hence, the strength of the coke decreases and it degrades. However, the tests involving CRI and CSR are costly, laborious and time-consuming.

Coke reacts with carbon dioxide to produce carbon monoxide which in turn reduces the iron oxides. The porosity of coke increases due to its reactivity with CO_2 and the mass loss occurred due to reaction with carbon dioxide for a stipulated period of about 2 hrs is termed as CRI. Measurement of CRI using ASTM D5341[ASTM D5341] is described as follows;

In an inert (N_2) atmosphere, 200 g of coke samples in the size range of -22.4 + 19 mm is heated up to 1100 ^{o} C. Once the sample is heated to 1100 ^{o} C, the N_2 gas flow is turned off and the sample is maintained isothermally at 1100 ^{o} C with continuous flow of Carbon dioxide (CO_2).

Then the sample is cooled with the help of N_2 gas and weighed. The percentage of mass loss of coke refers to CRI and it can be given by the equation [ASTM D5341];

$$CRI = \frac{200 - Final\ mass\ after\ reaction}{200}\ X\ 100$$

For CSR test, a known weight of coke lumps reacted with carbon dioxide is placed in a tumbler and then rotated at 20rpm for 30 minutes. Once the 600th revolution is completed, the sample is then sieved using a mesh size of 9.5 mm. Particles less than 9.5 mm are discarded and greater than 9.5 mm are weighed. CSR can be determined by the following equation [ASTM D5341];

$$CSR = \frac{+9.5\ mm\ fraction}{Mass\ after\ reaction\ with\ CO2}\ X\ 100$$

Therefore, lower the reactivity of coke with Carbon di-oxide, higher is the CSR and better is the coke quality.

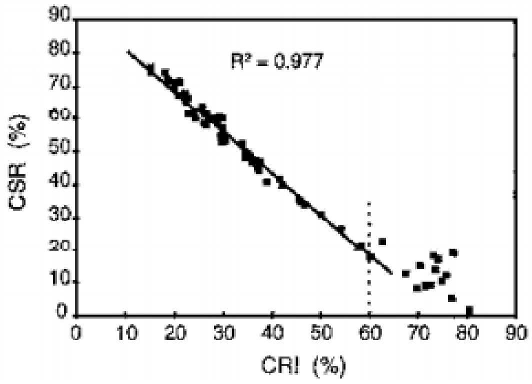


Figure 2.3 Relationship CSR and CRI[Menéndez, 2013]

Figure 2.3 shows the relationship between CSR and CRI determined for a series of more than 60 cokes produced from single coals of different origin [Menéndez, 2013]. It has been observed that an inverse linear correlation exists between CRI and CSR indices obtained from the method developed by Nippon steel co. (NSC).

2.4. Manufacturing of coke

2.4.1. History of coke manufacturing

The evolution of beehive oven dominated the coke production during the nineteenth century. Beehive oven is a circular vaulted fire bricked chamber with an opening at the top through which coal is charged and an arched door at the bottom where the products would be withdrawn. The arched door is bricked during the coking procedure. The schematic diagram of typical beehive oven for coke making is shown in Figure 2.4.

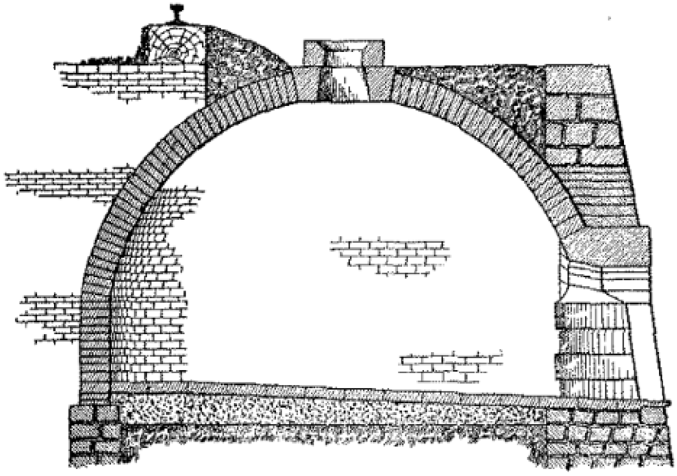


Figure 2.4 Beehive oven – schematic [Belden, 1913]

In beehive oven, coking proceeds from top to bottom of the oven and as the amount of volatile matter decreases, the heat required is regulated by adjusting the air opening. Once the coking is over, the final coke product is watered and then drawn out [Belden, 1913]. This method has no recovery of by-products and also consumes more time [Burger and John, 1979]. Beehive ovens dominated the coke production sector until the coke oven with by-product recovery was introduced [Belden, 1913].

Otto Hoffman's by-product oven method of producing metallurgical coke has high thermal efficiency. This method also reduces the time of carbonization compared to beehive oven method and by-products such as coal tar, ammonia, sulphur, benzene, naphthalene etc. are recovered. The schematic diagram of Otto Hoffman by-product oven is given in Figure 2.5.

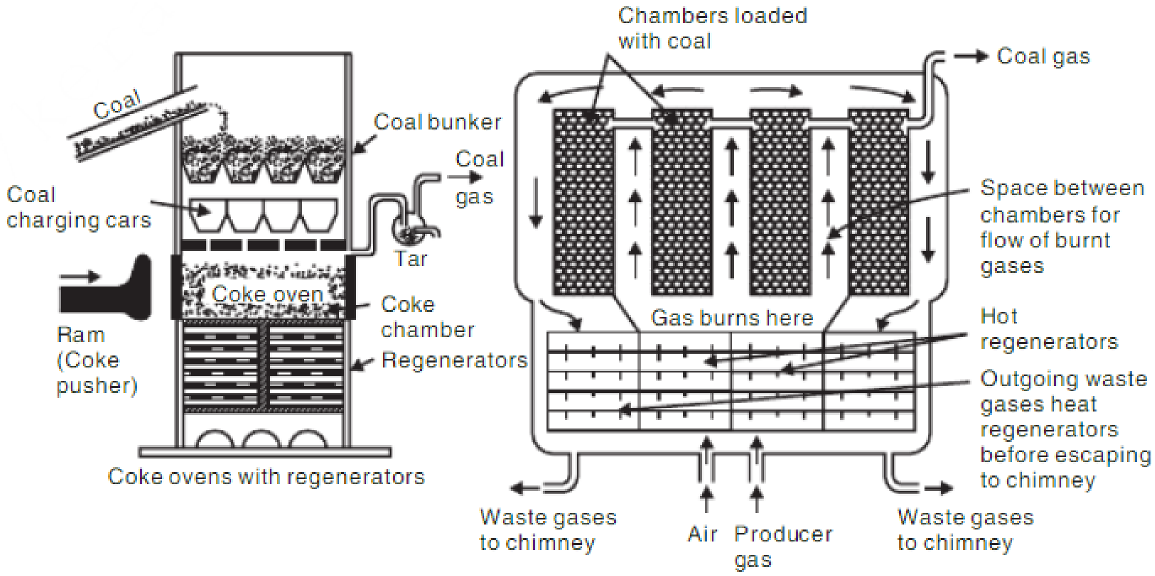


Figure 2.5 Otto Hoffman's by-product oven [Jain, 1976]

Otto Hoffman's oven consists of narrow silica chambers which are tightly closed so that no air is admitted. The chamber has three holes through which the coal is charged, a gas off-take to carry out the volatile matter and a refractory iron door at each end to discharge the coke. In this method, coal is charged into the chamber and it is closed. Heat is supplied by the hot flue gases produced by combustion. Once the carbonization is complete, the doors are opened and the hot coke is taken out and quickly quenched by spraying water. Dry quenching can also be performed by passing flue gases over hot coke and waste heat boilers can be run by using these hot gases.

2.4.2. Coal carbonization

Coal carbonization is usually studied by heating the coal in an inert atmosphere using gases like Nitrogen, Argon etc. Coal undergoes several physical and chemical changes when it is heated in an inert atmosphere. The three main stages of coal carbonization are; pre-plastic stage, plastic stage, and post-plastic stage.

Pre-plastic stage: is generally the stage below 350 °C. During this stage, coal loses its moisture content and the volatile matter starts evolving.

Plastic stage: When the coal is heated between 350 °C and 500 °C, rapid de-volatilization of coal occurs and the coal softens and become plastic in nature.

Post-plastic stage: When the coal is further heated at high temperatures, plasticity nature begins to decrease and at 600 °C, it begins to harden to form a solidified mass called as semi-coke.

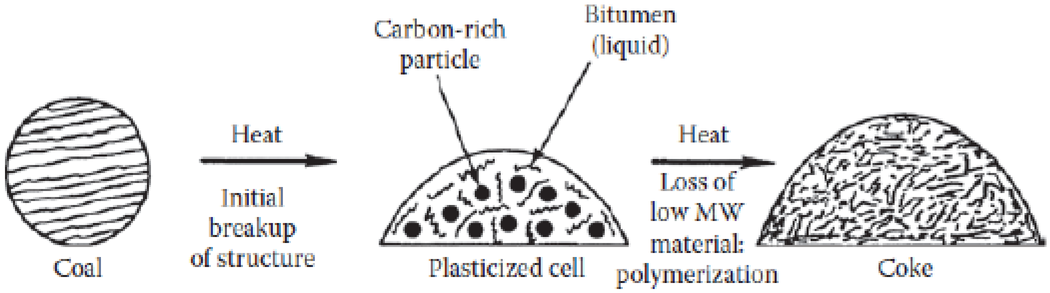


Figure 2.6 Behaviour of coal during carbonization [Speight, 2012]

As it is further heated at high temperatures, further de-volatilization occurs and finally the semi-coke will be transformed into a solid grey mass called coke. The behaviour of coal during the three stages of carbonization is shown in Figure 2.6.

According to Fitzgerald (1956) and Chermin and Van Krevelen (1957), the stages of coal carbonization can be denoted into three successive reactions as the formation of intermediate metaplast and transformation of metaplast into semi-coke and into coke [Saxena and Tiwari, 2015]

$$coal \overset{k1}{\rightarrow} metaplast \qquad \text{------------------ (5)}$$

$$metaplast \overset{k2}{\rightarrow} semi-coke + primary\ volatiles \qquad \text{------------------ (6)}$$

$$semi-coke \overset{k3}{\rightarrow} coke + secondary\ volatiles \qquad \text{------------------ (7)}$$

2.4.3. Coke production in laboratory

Research is being performed by varying operating conditions to produce a good quality coke in a lab scale. Some of the attempts are discussed briefly below.

In 1976, Hays et al. [Hays, 1976] studied the carbonization of eleven single coals by employing vertically heated walls in sole-heated oven developed by Ritter and Juranek. In their study, 400 g of coal with a particle size less than 3 mm; approximately 50% greater than 1 mm and 12% finer than 0.12 mm was used. The sample was first air dried and later loaded with a packing density of 820kg/m^3 in an asbestos- paper box with the dimensions of 70 x 70 x 90 mm. The asbestos-paper box was kept in the oven and silica-sheathed thermocouples were inserted into the coal charge in such a way that it was parallel to the heated walls. During carbonization, the box was purged with pure nitrogen and the rate of heating was maintained at 3K/min. Once the carbonization was done, the box containing coke was withdrawn from the heated walls and then allowed to cool naturally.

Grigore et al. [Grigore, 2006] studied the carbonization of four Australian bituminous coals in a cylindrical retort with the capacity of 9 kg electrically heated furnace. Coals were first crushed to a size less than 6 mm and were dried. Once the temperature of the furnace wall reached 1050 °C, the cylindrical retort with coal charge was inserted into the furnace. When the temperature at the centre of coal charge was recorded 900 °C, the cylindrical retort with the coal charge was kept in the furnace for 50 minutes to increase the temperature at the centre to 1050 °C. Then, the retort with final product was removed from the furnace and was cooled in a nitrogen atmosphere. The coke produced was then crushed to a size less than 1 mm to carry out the characterization tests.

Alvarez et al. [Álvarez, 2007] had studied the carbonization of coals to a semi-industrial scale using a 6-tonne capacity oven with the dimensions 2.8 x 0.45 x 6.5 m. In this study, 22 bituminous coals were chosen and loaded with a packing density of 705±25kg/m^3. After 18 hours of coking, the final coke products were pushed from the oven and were water quenched. Alvarez et al. stated that the results obtained from this study could be directly applied to an industrial scale coke production.

Koszorek et al. [Koszorek, 2009] performed the carbonization of coals in Jenkner's retort as shown in Figure 2.7. The coal samples used in this study were first air dried and then crushed to a size less than 3 mm. The coal blends, after manually mixing 1000g of each coal manually were stacked in four layers in Jenkner's retort. The retort was then placed in the furnace and

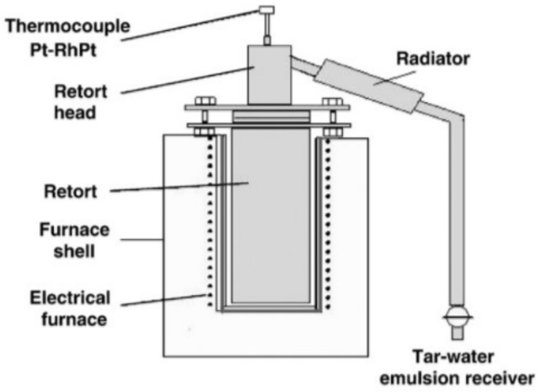


Figure 2.7 Schematic diagram of Jenkner's retort [Koszorek, 2009]

heated at 25 ° C/min until the temperature of the furnace reached 1000 ° C. The retort was kept isothermal at 1000 ° C for about an hour and then the retort was removed from the furnace. The coke was taken out by dismantling the retort after cooling it to room temperature for about 12 hours.

Grigore et al. [Grigore, 2012] studied the carbonization of four Australian bituminous coals of different ranks by preparing a semi-coke first and later calcined to coke at 1050 ° C in a horizontal tube furnace. For carbonization, 70 g of the prepared coal blends were loaded in the retort with a packing density that ranged between 0.68 and 0.80 g/cm^3 and the retort was placed in an oven which was preheated to 300° C. Continuous flow of nitrogen was maintained in order to avoid oxidation of the sample. When the centre of the coal charge reached 300 ° C, the coal charge was heated at a constant rate to 470 ° C and kept isothermal for about 2 hours. The semi-coke obtained was cooled down in a nitrogen atmosphere. The produced semi-coke samples were then taken in alumina crucibles and then placed in a horizontal tube furnace. Under continuous flow of high purity nitrogen, the furnace was heated at 1 ° C/min to 500 ° C and then it was heated at 10 ° C/min to 1050 ° C by purging high purity argon. Once the calcination was completed, the coke samples were cooled down in an argon atmosphere to 500 ^{o}C and then the argon gas was replaced by nitrogen while cooling down the samples to room temperature.

Tiwari et al. [Tiwari, 2013] performed the carbonization tests at the laboratory using a 7 kg electrically heated carbolite oven of dimensions; 370 mm length, 115 mm width, 305 mm height. The coal samples were stacked in the carbolite oven at a packing density of 800 kg/m^3 and then heated to 1000 ^{o}C. The total carbonization time was 5 hours.

Zhong et al. [Zhong, 2013] prepared coke using a vertical tube-type resistance furnace. 85% of the mass of samples used in this study was less than 3 mm in size. During the coking process, 20 g of dried coal was taken in a circular mould of 90 mm diameter and placed in the furnace. The furnace was then heated at the rate of 3 ^{o}C/min up to 800 ^{o}C with a continuous nitrogen flow of 700 mL/s from the bottom of the furnace.

MacPhee et al. [MacPhee, 2013] prepared coke in two steps; semi-coke preparation and heat treatment. For preparing semi-coke, 12 kg of the sample was charged into the chambers of 280 x 280 x 280 mm double chambered oven. A constant load was applied on the surface of coal in the oven using a weighted piston. Using sole plate set initially at 554 ^{o}C, the coal bed in the oven was heated from below up to 950 ^{o}C. After 6 to 7 hours, when the temperature at the top surface of the coal reached 500 ^{o}C, the coke was pushed out from the oven. Then the semi-coke was water quenched and was dried overnight in an oven at 120 ^{o}C. 9 kg of produced semi-coke was placed in pieces in a stainless steel box with a hole at top centre for venting hot gases. The box was then heated in a muffle furnace at the rate of 5 to 10 ^{o}C/min to 1100 ^{o}C for 2 to 3 hours. At 1100 ^{o}C, the coke was kept isothermal for an hour and then it was cooled to 100 ^{o}C with a continuous flow of nitrogen.

Mollah et al. [Mollah, 2015] studied the carbonization of coal in a muffle furnace. Samples were loaded in an alumina crucible and then inserted into the muffle furnace. It was then carbonized at a heating rate of 2 ° C/min to 500 ° C and at 5 ° C/min to 950 ° C with a continuous flow of nitrogen at the rate of 400 L/h. The sample was then kept isothermal in the furnace at 950 ° C for 2 or 5 hours and it was cooled overnight with a continuous flow of nitrogen.

Nomura et al. [Nomura, 2016] prepared coke in an electrically heated pilot-scale oven of dimensions; 420 mm width, 600 mm length, 400 mm height. In this study, 5 coals were used and the samples were crushed to less than 3 mm in size. Coal samples were charged in a steel box which was then inserted into the oven and carbonized. The total time of carbonization was about 18.5 hours.

Li et al. [Li, 2017] used a quartz reactor shown in Figure 2.8 to perform the carbonization experiment. The reactor was first heated to 900 ° C with the help of an external electrical furnace.

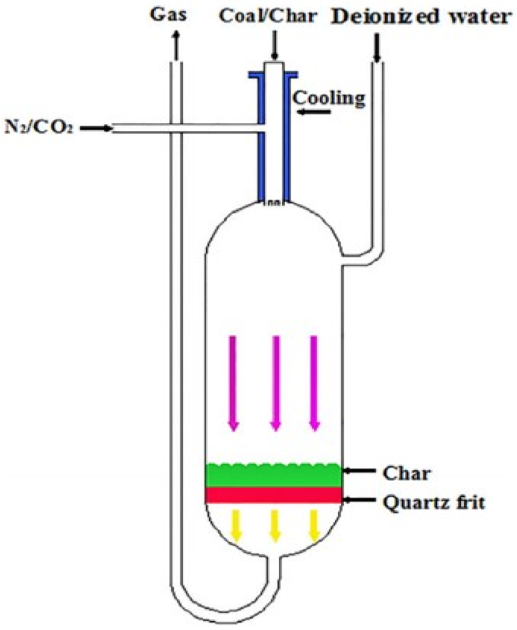


Figure 2.8 Schematic of the quartz reactor [Li, 2017]

The temperature in the reaction zone was monitored with the help of a thermocouple. After 20 minutes of the isothermal period at 900 ^{o} C, 4 g of coal samples was dropped into the reactor with a continuous flow of nitrogen at 0.75 L/min. The samples were kept in the reactor for about 30 minutes and the reactor was taken out from the furnace, allowing it to cool down to room temperature in nitrogen atmosphere.

2.5. Use of binders in coal carbonization

Cokes produced from coking coals show excellent strength which determines its usability in the blast furnace operation. The strength of the coke produced from low-quality coking coals or from a higher fraction of non-coking coal is less and do not qualify for blast furnace operation. However, the price of the coking coal is increasing and the resources of metallurgical coke are limited. Hence, researches have been going on to produce coke using binders to the non-coking coal or low quality coking coal to maintain the coke strength suitable for blast furnace [Nomura, 2017].

2.5.1. Waste tire

Fernandez et al. [Fernández, 2015] had used recycling tyre wastes as an additive to assess the influence of the additives on the thermoplastic properties of coal in coke making. In this study, two coal blends, two wastes; tyre crumbs and fibres obtained as a waste from scrap tyres were selected. These wastes were added to the coal blends at different ratios (98:2 and 95:5). The experiment was carried out in a 17 kg capacity movable wall oven with the dimensions of 270 mm L x 165 mm W x 790 mm H. The coal samples were charged when the oven reached 1100 ^{o}C and the total coking time was about 3.5 hours. Quality of the cokes produced was evaluated by measuring their reactivity and post-reaction strength. It has been observed that the addition of fibres increases the ash content resulting in a poor quality coke and the addition of tyre crumbs in 2 Wt% results in a negligible increase in ash content. This study concluded that the addition of tyre crumbs in a proportion of 2 Wt% is a considerable option for obtaining acceptable quality coke and a good performance in the blast furnace.

Silva et al. [Silva, 2016] had used the waste tire as a binder in coal. The experiment was carried out with blends prepared using coal with waste tires in weight percentages of 1, 3, 5 and 10%. Samples were then heated to 1000 $^{\circ}$C in an electrical furnace. This study has shown that cokes produced from coal-tire mixture showed lower ash content than cokes produced from only coal. They also showed that when waste tire added up to 3%, remarkable CSR values could be obtained in the resulting cokes.

2.5.2. Organic binders

Benk et al. [Benk, 2008] had used two types of phenolic resin as a binder for making coal briquettes for coke and found that the strength of cokes increased significantly when a blend of both of the resins was used.

Makgato et al. [Makgato, 2013] studied the effect of coke oven tar additions to coal for coke making. They used the coke oven tar obtained from tar decanters in coking plant by- product section. The moisture content of coke oven tar was varied in 1 wt%, 3 wt% and 6 wt% in order to investigate and evaluate the effect on carbonization of coal. The test was carried out in a 350 kg capacity pilot plant oven with the dimensions of 915 mm length x 455 mm width x 1015 mm height. The oven temperature was controlled by a programmable controller and the coking time was about 19 hours. It has been observed in the study that moisture content of 3 wt% with a coke oven tar addition of 6 wt% in coal blend was optimum to obtain a good coke yield with a good quality. The results of this study concluded that coke oven tar addition leads to improved coke quality and is a feasible option based on the economic factors.

Nag et al. [Nag, 2017] had investigated the effect of phenolic resin, as a binder in coke making. The carbonization experiments were conducted in 7 kg carbolite test oven using a standard procedure established at R&D, Tata Steel. The coal samples were crushed to a fineness of 90% below 3.2 mm and the blends were prepared by adding the additive. The carbonization time was about 5 hours and the hot coke was pushed out and quenched with water. Then, the coke samples were tested for ash, CRI and CSR. It has been observed that the addition of resin improves coke quality in terms of its strength. This study concluded that 0.3% of phenolic resin is the optimum amount to be added along with coal samples to yield better quality coke.

Zhu et al. [Zhu, 2016] had studied the effect of additives from low-grade biomass on coke making. In this study, two extracts, the feasibility of two extracts; low (called as soluble) and high molecular weight extract (deposit) as additives in coking coal blends was investigated. In the study, 100 g samples were used for each run and the carbonization tests were carried out in a lab-scale crucible coking oven. It has been observed in the study that the re-solidification temperature and plastic range increased, thus improving the thermoplastic properties of the coal blends, especially due to the addition of soluble and deposit obtained at a higher temperature. The results also indicated that the addition of deposits and soluble also enhanced the quality of coke with reduced CRI and increased CSR. It has been concluded from this study that addition of soluble and deposit is a most viable option compared to raw biomasses addition due to significantly higher carbon content and extremely lower ash content in the extracts.

2.5.3. Asphaltene

McCandless and Blake [McCandless, 1970] studied the use of asphaltene, a petroleum residue as a binder in metallurgical coke making from a low rank coal chars. During the study, it was observed that with increasing content of asphaltene in the coal, the strength of the coke briquettes produced was considerably increased and the mass losses decreased.

Paul et al. [Paul, 2002] performed carbonization of coal using asphaltene as a binder. The strength of the briquettes produced was increased with the addition of asphaltene. The coke briquettes were found to have maximum strength when more than 20 wt% asphaltenes were added to the coal.

2.5.4. Petroleum coke

Menendez et al. [Menéndez, 1996] studied the ability of petroleum coke to be used as an additive in metallurgical coke making through its optical texture, FTIR analysis, thermogravimetric analysis, hydrogen donor ability and thermoplastic properties of blends made with coals. The results from this study suggested the potential selection of petroleum coke as a binder for coking process.

Phani et al. [Phani, 2013] had studied the effect of the use of petroleum coke as an additive in metallurgical coke making. The carbonization was carried out in 120 kg capacity electrically heated pilot oven at R&D centre in JSW (Jindal South West) Steel Ltd., India. Blends of three different coals with petroleum coke at varying percentages from 5 to 20% with low sulphur pet coke up to 20% and high sulphur pet coke up to 10% were used in this study and a sample of coal blend without petroleum coke was used as a reference. The coking period was about 24 hours and the coke was water quenched after being pushed out from the oven. Metallurgical coke thus obtained was characterized in terms of physical, chemical properties i.e. CSR, CRI etc. It has been observed from the study that the addition of pet coke resulted in a significant reduction of coke ash and increase in coke yield.

2.5.5. Minerals

Longbottom et al. [Longbottom, 2012] developed a coke analogue to determine the effects of minerals on reactivity of coke. The coke analogue with no mineral matter was prepared by firing mixtures of differently sized graphite particles and the phenolic resin to 1600 ^{o} C. Also, analogues with different types and amounts of mineral matter such as silica, sodium as sodium carbonate and magnesia were prepared at the same conditions. The reactivity was carried out in a TGA by using ASTM D5341 method. During the pseudo-CRI test, the samples were reacted with carbon dioxide at a constant temperature, 1000 ^{o} C. In this study, it was observed that increasing the addition of silica, decreased the reactivity whereas increasing the amount of sodium in the coke analogue increased the coke reactivity. With the increase in addition of magnesia, no effect on reactivity of coke analogue was observed.

Reid et al. [Reid, 2014] studied the effect of minerals on coke reactivity of coke analogues produced in the laboratory. Coke reactivity was measured in a high temperature thermogravimetric analysis system. During the test, each coke analogue weighing 8 g approximately, was taken in a perforated alumina crucible and heated to 1373 K in an argon atmosphere with flow rate of 1 L/min. Upon reaching 1373 K, the gas flow was switched with CO_2 and maintained isothermal for 2 hrs at 1373 K and the reactivity was reported based on mass loss of the sample. From this study, it was reported that the reactivity of coke increased with minerals such as calcite, pyrite, siderite, magnetite and hematite.

3. Use of TGA and HTF as an alternative to the CRI test

3.1. Materials

Six industrially produced coke samples C1, C2, C3, C4, C5 and C6 with known CRI values were used for the experiments. The CRI values of the samples are given in the Table 3.1.

Table 3.1 Samples and CRI values

Samples	***CRI***
C1	18.5
C2	20.1
C3	28.2
C4	28.9
C5	30
C6	38

3.2. High temperature furnace (HTF)

High temperature furnace experiments were carried out in an electrically heated vertical furnace housing a mullite tube as shown in Figure 3.1. The temperature of the furnace was fixed and controlled using three Omron E5CK proportional-integral-derivative temperature controllers at the top, middle and bottom of the reactor.

50 g of coke chunks were taken in a sample holder up to half of its length and the rest half was filled with 1 cm diameter zirconia balls. Zirconia balls were used to retain the temperature of the samples at 1100 °C under CO_2 atmosphere. The sample holder was made up of mullite tube with a honeycomb at the base for gas to pass through the sample effectively. The sample holder was

then placed in the middle of the furnace and ASTM D5341 was followed to measure the reactivity of coke under CO_2 atmosphere. The sample was heated up to 1100°C with Nitrogen gas. K-type thermocouples were used to control the temperature in the furnace. Upon reaching 1100°C, Nitrogen gas was replaced with carbon dioxide flowing at 5 L/min and temperature was kept isothermal for two hours and then cooled down. The mass loss during isothermal period is directly proportional to the CRI value and can be mathematically given as;

$$Mass\ loss\ \%\ (\alpha) = \frac{m_i - m_f}{m_i}\ X\ 100$$

Where, m_i = initial mass of the sample and m_f= final mass of the sample

Figure 3.1 Electrically heated high temperature furnace

The schematic representation of the experimental setup is given in Figure 3.2. Coke chunks, zirconia balls and honeycomb used in the experiment were shown in Figure 3.3.

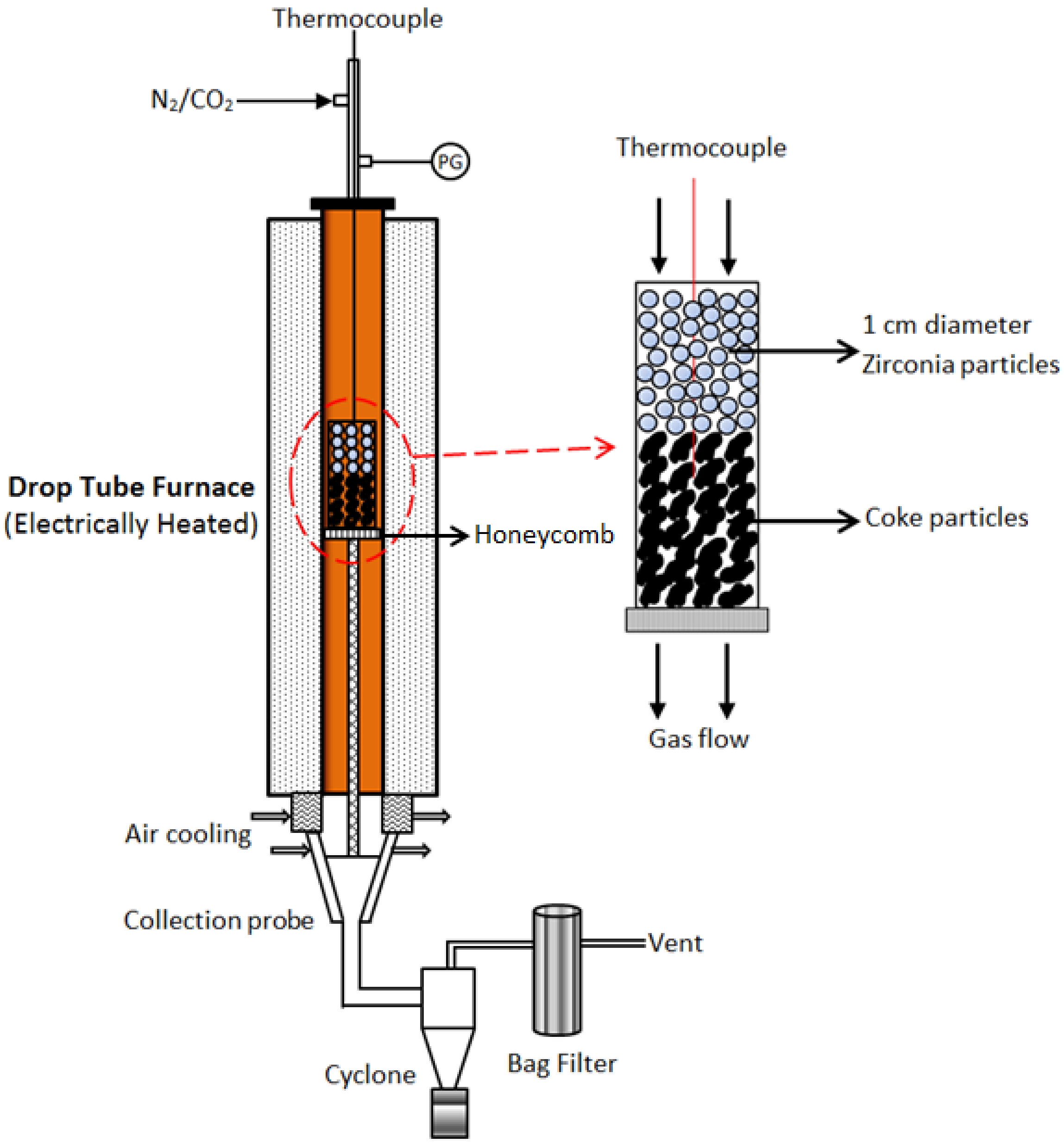
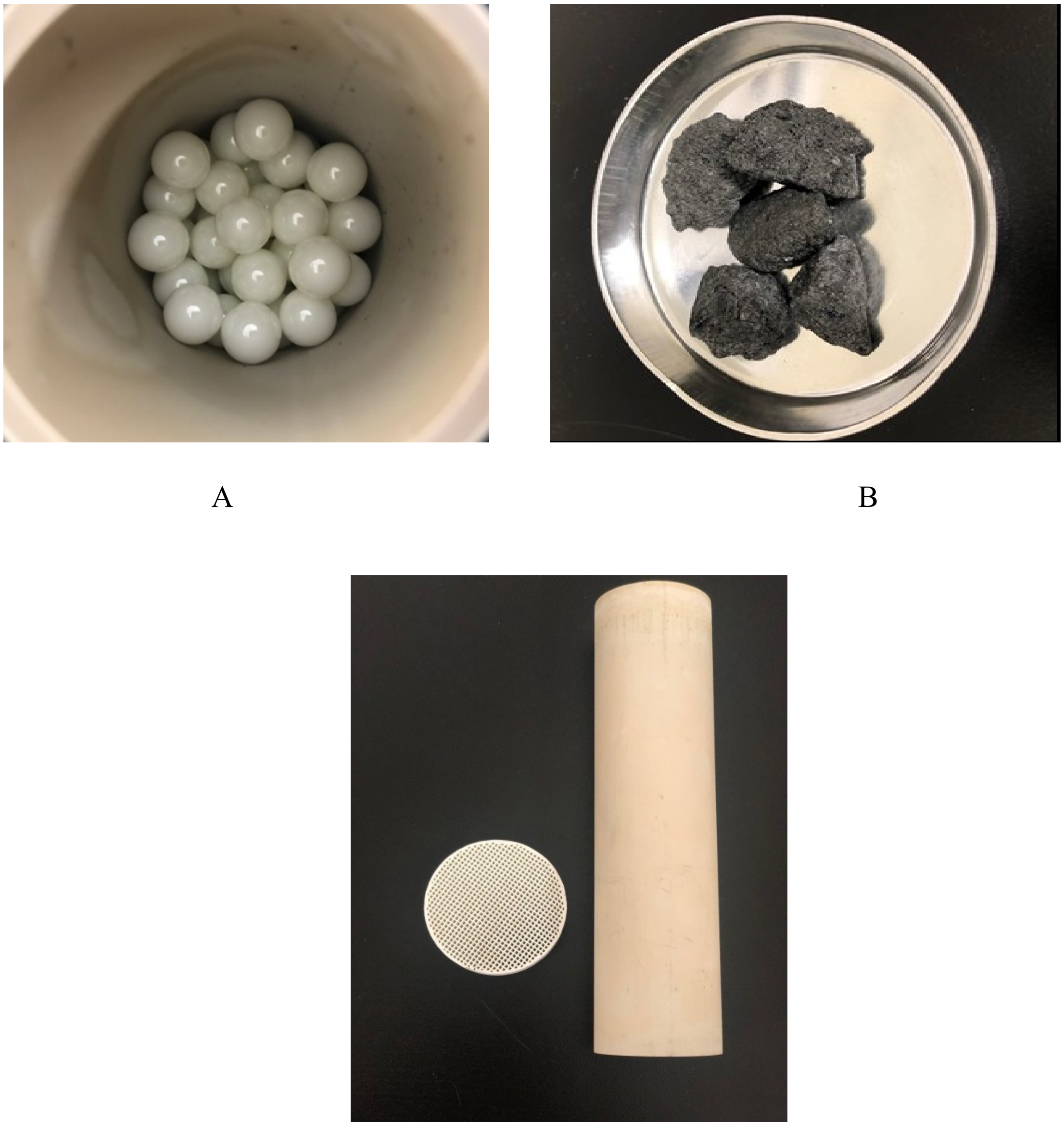


Figure 3.2 Schematic diagram of the experimental setup



A B

C

Figure 3.3 A) Zirconia balls B) Coke chunks C) Sample holder with honeycomb

3.3. Thermogravimetric Analysis

The thermogravimetric analysis experiments were carried out using SDT Q600, TA instrument, as shown in Figure 3.4.

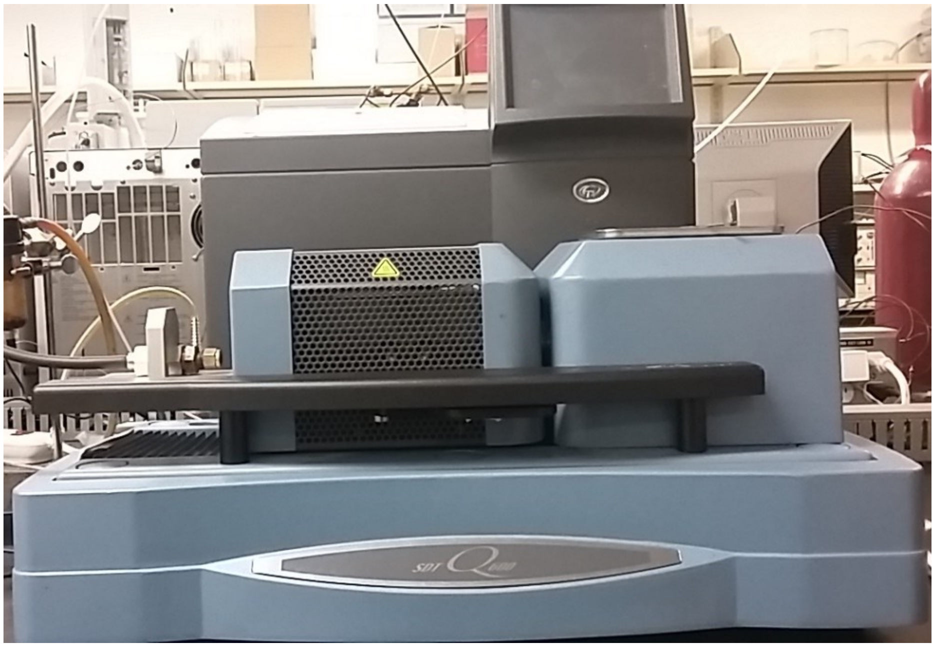


Figure 3.4 Thermogravimetric analyzer SDT Q600, TA Instruments

Samples were prepared by crushing coke to -0.25mm size and approximately 40mg sample was loaded in an alumina crucible. Coke reactivity using TGA was measured using ASTM D5341. With the continuous flow of Nitrogen at 100 mL/min, samples were heated at the rate of 10°C/min up to 1100°C. Then, the Nitrogen gas was replaced with carbon dioxide and temperature was kept isothermal at 1100°C for two hours and then cooled down. The resulting mass loss during isothermal period is directly proportional to the Coke Reactivity Index (CRI) value and the mass loss can be calculated using the formula;

$$Mass\ loss\ \%\ (\alpha) = \frac{m_i - m_f}{m_i}\ X\ 100$$

Where, m_i = mass of sample when temperature reaches 1100°C (i.e. beginning of isothermal period) and m_f= mass of sample after 120 minutes.

3.4. Results and discussions

In order to measure the coke reactivity index, the 6 industrially produced cokes were subjected to gasification in carbon dioxide atmosphere in both TGA (SDT Q600, TA Instruments) and high temperature furnace using the ASTM standard method for CRI test (ASTM D5341). An earlier study was carried out in our laboratory to study the gasification behaviour of cokes in CO_2 atmosphere in TGA (SDT Q600, TA Instruments) [Basher, 2017]. It was found from the study that the mass loss % in TGA correlated with the actual CRI values of the coke samples and TGA can be widely used to study the coke reactivity.

3.4.1. Mass loss in thermogravimetric analysis

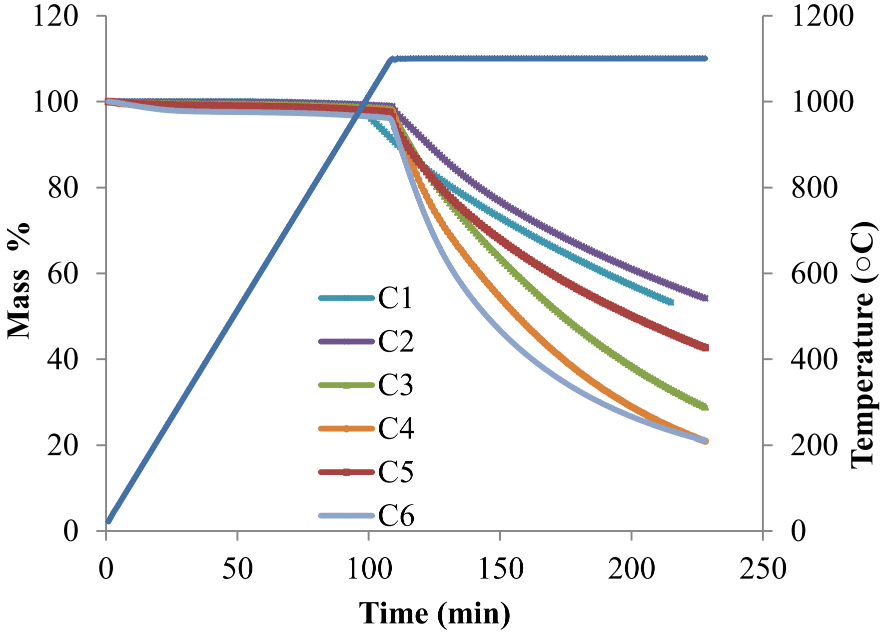


Figure 3.5 Mass Vs Time

Figure 3.5 shows the plot of mass of all 6 coke samples vs. time using ASTM D5341 method. It has been observed that the coke samples with higher CRI values have higher mass loss when compared to the other. It has also been observed that the mass loss of C1 and C2 are lower than the other coke samples. Coke sample C6 has a higher mass loss rate compared to the other coke samples.

The mass loss during the isothermal period at 1100°C was calculated by using the following formula,

$$Mass\ loss\ (\alpha)\ = \frac{m_i - m_f}{m_i}$$

Where, m_i = mass of sample when temperature reaches 1100°C (i.e. beginning of isothermal period) and m_f = mass of sample after 120 minutes. The mass loss of the coke samples along with the actual CRI values is given in Table 3.2.

Table 3.2 Mass loss % in TGA at isothermal period and CRI values of coke

Sample	***Coke Reactivity Index, CRI***	***Mass loss during isothermal period, α (%)***	***Standard Deviation***
C1	18.5	46.4	0.57
C2	20.1	45.2	1.20
C3	28.2	70.5	0.57
C4	28.9	78.6	0.64
C5	30	55.8	0.21
C6	38	77.9	0.85

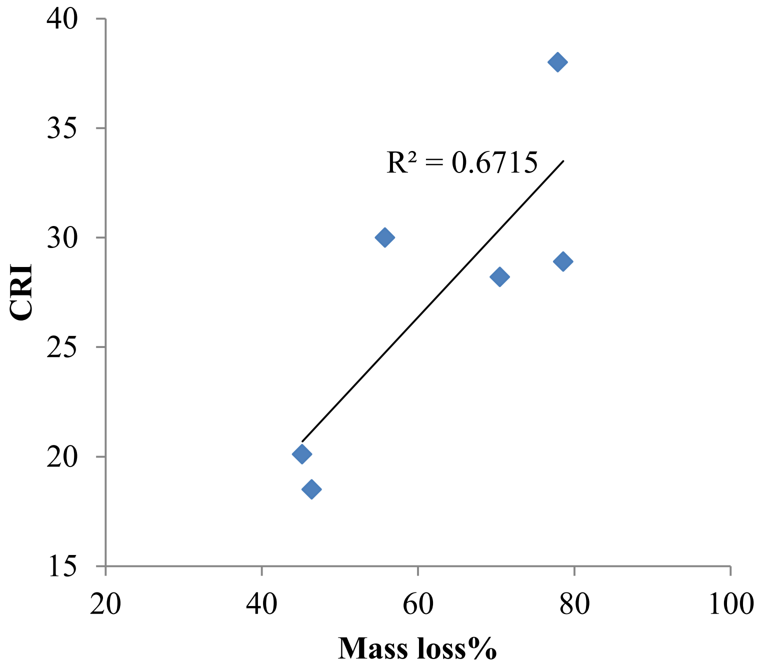


Figure 3.6 Mass loss% in TGA vs CRI

Figure 3.6 shows the plot of mass loss of the coke samples during isothermal period at 1100 ° C against their respective CRI values. The samples with higher CRI values have the higher mass loss % during the isothermal period. It has been observed the mass loss % of the coke samples at isothermal period at 1100 ° C has a significant linear relation with the actual CRI values of the coke samples.

3.4.2. Mass loss in high temperature furnace

The mass loss of the coke samples during the isothermal period at 1100 ° C was calculated by using the same formula as given above and is given in Table 3.3.

Table 3.3 Mass loss % in HTF at isothermal period and CRI values of coke

Sample	***Coke Reactivity Index, CRI***	***Mass loss during isothermal period, α (%)***	***Standard Deviation***
C1	18.5	19.58	1.86
C2	20.1	17.74	0.06
C3	28.2	21.83	1.46
C4	28.9	25.53	1.15
C5	30	21.77	0.74
C6	38	30.77	1.65

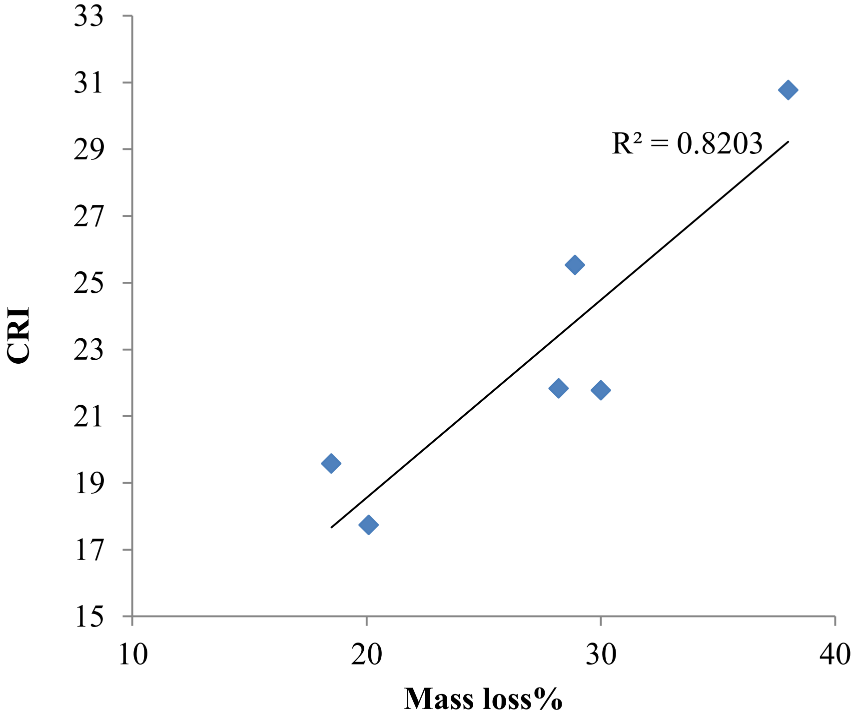


Figure 3.7 Mass loss% of coke in HTF vs CRI

The mass loss of the coke samples in the high temperature furnace during isothermal period at 1100 °C against their respective CRI values is plotted in Figure 3.7. It has been observed the mass loss % of the coke samples during the isothermal period at 1100 °C has a linear relation with the actual CRI values of the coke samples. The mass loss % of the coke samples at isothermal period is very much comparable and close to the actual CRI values.

3.5. Conclusion

- During the isothermal period in carbon dioxide atmosphere at 1100°C, the mass loss (%) in TGA is found to have some significant linear relation with the actual CRI values. The mass loss estimated in TGA is found to be very high, as the tests are carried out with only 40 mg of sample with particle size of 0.25 mm; higher surface area, higher the reactivity. Hence, TGA could be a helpful tool to screen out the coke samples before carrying out the real CRI test, which is expensive.
- Since, coke chunks are used to carry out the high temperature furnace experiments, the mass loss (%) during the isothermal period at 1100°C is very much comparable and close to the actual CRI values of the coke samples. Hence, High temperature furnace can be used as an alternative to predict the CRI of cokes.

4. Effect of binders in metallurgical coke making

4.1. Materials

Four coking coals of bituminous rank (MC, EC, DC and CC), a coal of sub-bituminous rank were used to prepare metallurgical coke. The properties of these parent coals are given in the below Table 4.1.

Table 4.1 Properties of parent coals

Coal sample	***Moisture content (%)***	***Volatile matter (%)***	***Fixed carbon db (%)***	***Ash content db (%)***
MC	0.72	19.19	70.42	10.4
EC	0.7	19.72	67.58	12.7
DC	0.76	19.68	64.93	15.39
CC	0.65	22.21	67.84	9.73
GC	6.73	34.11	57.9	5.53

Db: dry basis

For carbonization, the coal samples (MC, EC, DC, GC) and binders such as asphaltenes, petroleum coke were crushed to less than 2mm size and were mixed well in desired ratio by tumbling. The amount of binders was varied between 0% and 30% in total weight % of the sample. In addition, 1 wt% of minerals such as calcite, dolomite, siderite and magnesite were added to CC coals to prepare the samples.

4.2. Coal carbonization in a tube furnace

Figure 4.1 Thermolyne 79300 tube furnace

The coal carbonization experiments were carried out in a Thermolyne 79300 tube furnace shown in Figure 4.1, which comprises of a control unit, a tubular heating chamber (furnace chamber) and a pyrometer. The furnace chamber consists of a mullite tube with the dimensions of 5.9 cm diameter and 80 cm length. Metallic coils embedded in a rigid refractory material are used to heat the furnace chamber. K-type thermocouple is used to measure the temperature of the furnace and the temperature can be controlled using the control unit. In order to minimize the heat losses, the exposed ends of the tube are well insulated using K-wool and fibrefrax materials. Cole-Parmer rotameter was used to regulate the gas flow and to prevent excessive pressure build up within the furnace; a pressure release value is installed at the exit of the furnace. For carbonization experiments, around 7.5gm of coal with or without binder was taken in a crucible and placed inside the tube furnace. To remove any reactive species in the furnace, it was purged with Nitrogen gas at the rate of 10 mL/min for 15 minutes. With continuous flow of Nitrogen at the rate of 10 mL/min, the furnace was heated to 300°C at the rate of 10°C/min. Then, with increased flow of nitrogen at the rate of 25 mL/min, the furnace was heated up to 500 °C at the rate of 2.5°C/min allowing effective de-volatilization of volatile matters present in the coal. Volatile matters evolved were passed through water-based scrubbing solution. Upon reaching 500°C, the samples were then heated to 900°C at the rate of 10°C/min with nitrogen flow rate at 10 mL/min. The samples were kept isothermal at 900°C for 12 hours. Then, with continuous flow of nitrogen, the furnace was cooled down at the rate of 2°C/min and the samples were taken out. The schematic diagram of the experimental setup is given in Figure 4.2.

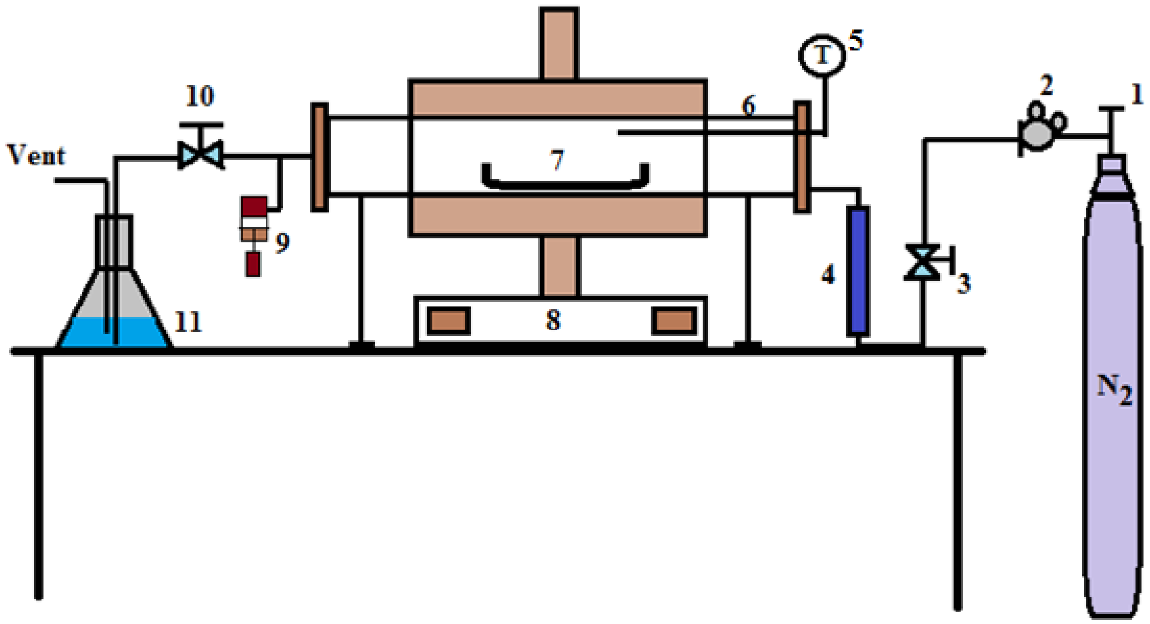


Figure 4.2 Schematic diagram of experimental set-up

1) Gas cylinder 2) gas regulator 3) valve 4) rotameter 5) thermocouple 6) Mullite tube 7) sample holder 8) control box 9) pressure release valve 10) valve 11) Scrubbing Solution

4.3. Thermogravimetric analysis

Thermogravimetric analysis was carried out in SDT Q600, TA instrument (shown in Figure 3.4) for measuring the reactivity of the produced cokes with CO_2. The experimental procedure followed was same as described in Section 3.3.

4.4. Optical Microscopy

Keyence VHX-S90BE Automated Microscope used in the study to obtain optical images shown in Figure 4.3. The thin section samples were prepared in thin section laboratory, University of Alberta. The coke samples for optical microscopy were prepared by subjecting them to vacuum pressure impregnation with blue dyed resin. A very thin slice of coke of about 30 microns was cut and mounted on a glass. These thin sections were then placed on the microscope stage and auto-focused by the microscope. 2-Dimensional image stitching of the samples were carried out at 250X magnification to obtain optical image of larger area at a higher resolution.

Figure 4.3 Keyence VHX-S90BE automated microscope

The porosity was calculated by processing the optical images obtained from the microscope in MATLAB. By thresholding, these images were converted into binary images which were then used to calculate the total area of the coke. Then the total void space was calculated by subjecting these binary images to inverse of color.

The porosity was then calculated using the formula

$$Porosity = 100 * A/(A + B)$$

Where,

A = total surface area of the coke

B = total surface area of the pores.

4.5. Raman Spectroscopy

The polished thin section slides of the coke samples were used to determine the extent of graphitization using Raman spectroscopy shown in Figure 4.4.

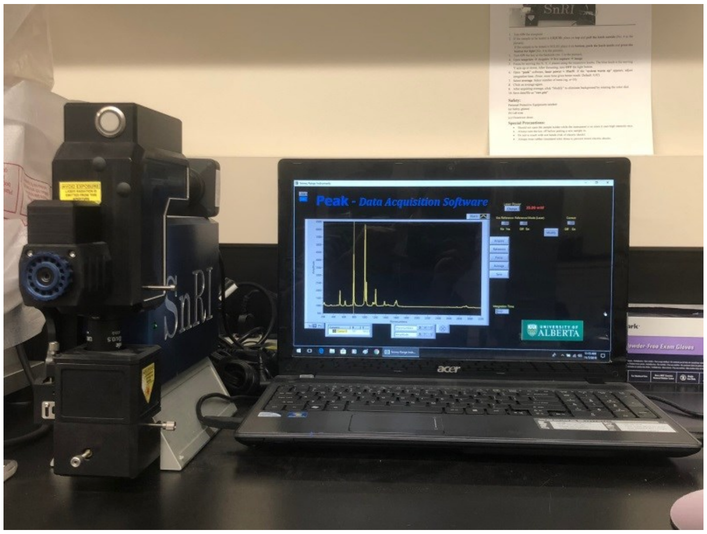


Figure 4.4 Raman spectroscopy

The thin section slides were first placed in the chamber. Using an in-built camera with low magnification, location with least pores was chosen in the sample and was focused using the Toupview software. Then, by passing the laser beam on the surface of the sample, an average spectrum was obtained by using Peak software. The extent of graphitization was then calculated from the obtained average spectrum using the formula given below;

$$\text{Extent of graphitization} = \frac{A_g}{A_g + A_d}\ X\ 100$$

Where, A_g = Area under G peak

A_d = Area under the D peak

4.6. Results and discussions

Metallurgical cokes were prepared using various binders in lab scale in Thermolyne 79300 tube furnace (horizontal tube furnace). An earlier study using asphaltene and ash free coal as binders was carried out in our laboratory where it was found that ash free coal has some potential to improve the quality of coke produced from bituminous coal [Basher 2017]. The quality of the produced coke samples was examined by using various characterization techniques described above and the results are discussed below.

4.7. Effect of petcoke addition

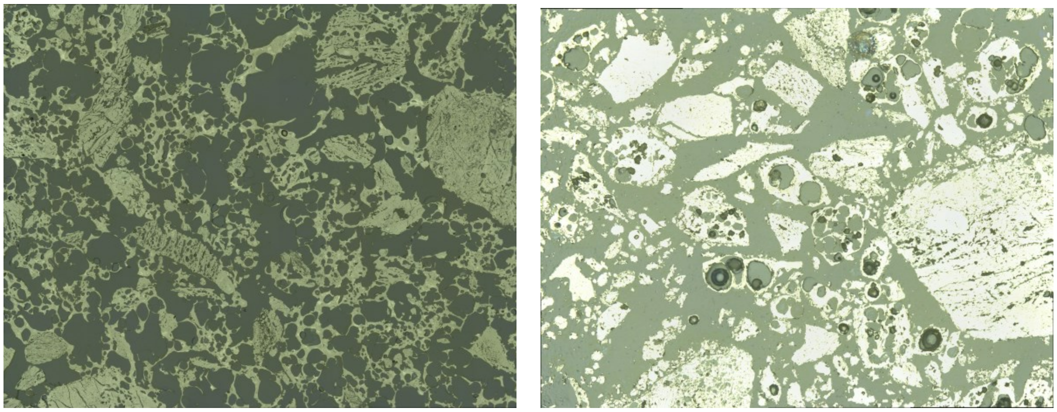
Petroleum coke or petcoke is a by-product obtained from the refining of crude. Petcoke is chosen as additive in this study as it is highly rich in carbon. The coke samples were prepared by adding pet coke as a binder to three types of bituminous and a sub-bituminous coal. The low ranking bituminous coal and the sub-bituminous coal used in the study did not form a good solid coke and it crumbled into pieces. So, different characterization techniques were performed only for the cokes formed from the other two bituminous coals and are discussed below. The summary of the samples with the binder is given in Table 4.2.

Table 4.2 Summary of samples with addition of binders

Name of Sample	***Type of coal***	***Amount of petcoke (%)***	***Amount of coal (%)***
MC100	Bituminous	0	100
MC90PC10	Bituminous	10	90
MC80PC20	Bituminous	20	80
MC70PC30	Bituminous	30	70
EC100	Bituminous	0	100
EC90PC10	Bituminous	10	90
EC80PC20	Bituminous	20	80
EC70PC30	Bituminous	30	70

4.7.1. Porosity by image analysis

Porosity of the cokes was calculated by processing the 2D stitched microscopic images obtained from the optical microscopy in MATLAB as described in chapter 3.The microscopic images of the coke samples produced are shown in Figure 4.5.



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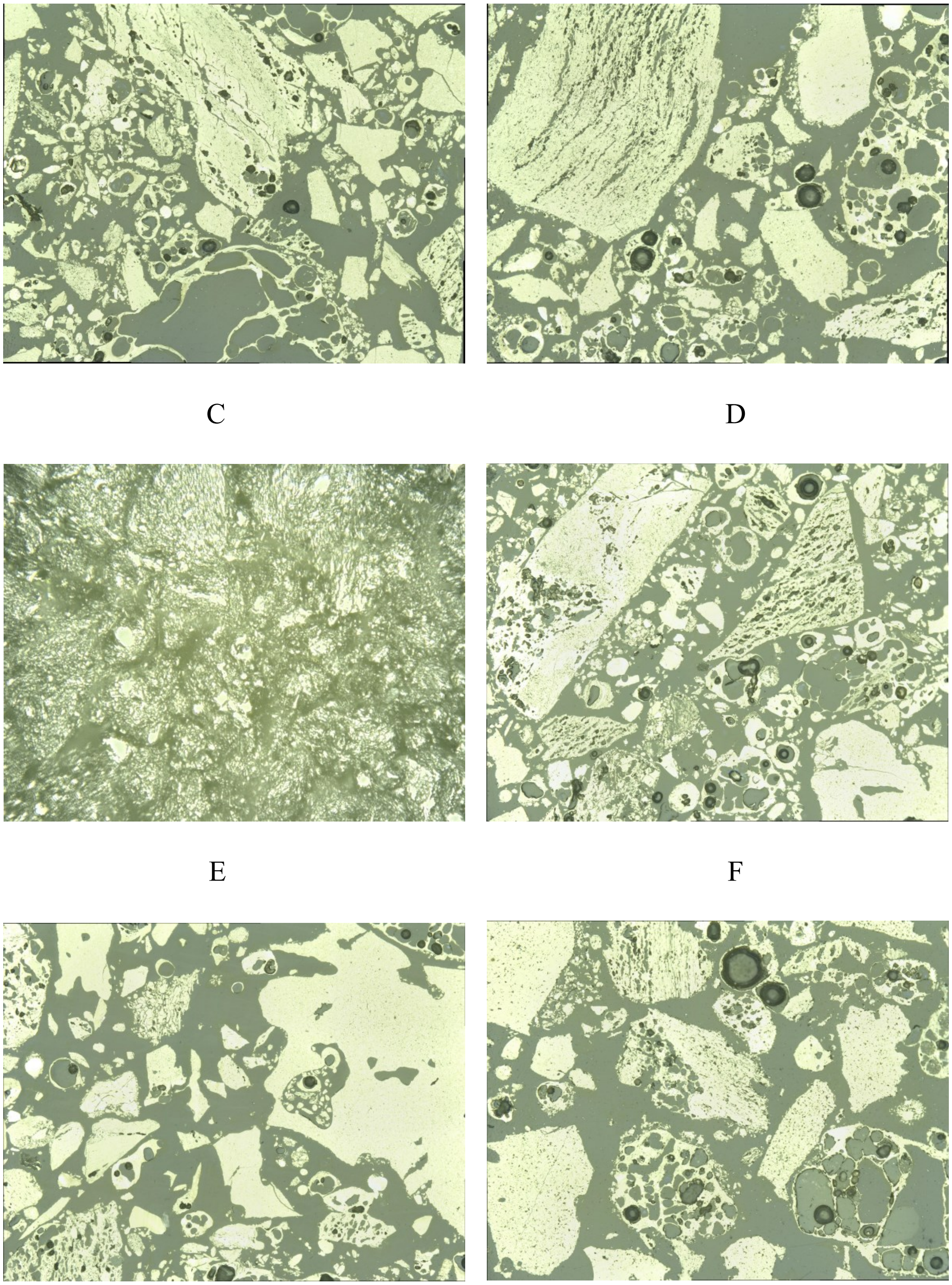


C

D

E

F

G

H

Figure 4.5 2D stitched images of A) MC100 B) MC90PC10 C) MC80PC20 D) MC70PC30 E) EC100 F) EC90PC10 G) EC80PC20 H) EC70PC30 (250X)

The porosity (%) of the cokes produced with petcoke is given in Table 4.3 and the effect of petcoke on porosity is shown in Figure 4.6.

Table 4.3 Effect of petcoke addition on porosity

Sample	***Average porosity (%)***	***Standard Deviation***
MC100	60.89	0.37
MC90PC10	55.63	0.21
MC80PC20	54.63	1.32
MC70PC30	48.6	0.6
EC100	54.29	1.04
EC90PC10	48.04	0.39
EC80PC20	48.14	0.21
EC70PC30	56.34	1.01

From the Figure 4.6, it was observed that the porosity of the MC cokes decreased with the increase in addition of petcoke. It could also be observed that the porosity of EC cokes decreased with the addition of 10 wt% and 20 wt% of petcoke but slightly increased with 30 wt% of petcoke as binder. This suggests that petcoke has a significant contribution in reducing the porosity of the cokes produced from bituminous coals and can be used as a binder.

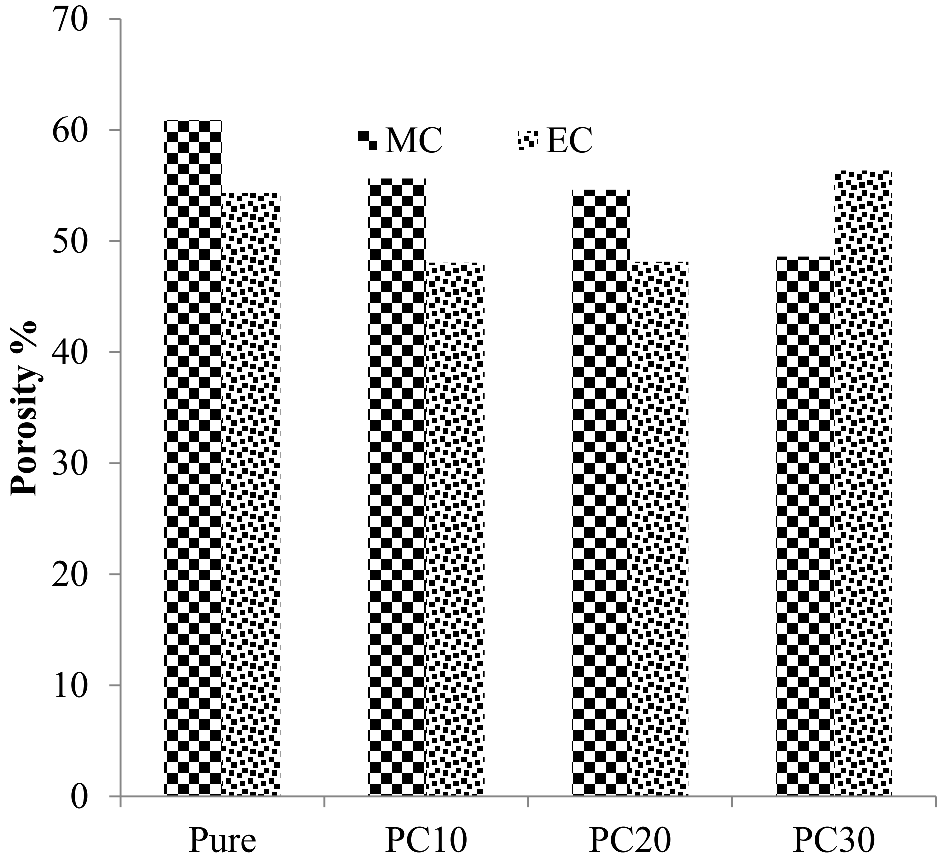


Figure 4.6 Effect of petcoke on porosity

4.7.2. Coke reactivity

The produced coke samples were subjected to gasification in CO_2 atmosphere in Thermogravimetric analyzer to measure the reactivity as discussed in chapter 3. The mass loss (%) of the coke samples during the isothermal period at 1100 °C is mentioned in Table 4.4.

Table 4.4 Effect of petcoke addition on coke reactivity

Sample	***Mass loss during isothermal period, α (%)***
MC100	57.6
MC90PC10	53.2
MC80PC20	58.7
MC70PC30	60.73
EC100	68.1
EC90PC10	65.9
EC80PC20	72.4
EC70PC30	69.52

Figure 4.7 shows the effect of petcoke addition on coke reactivity. It was observed that the reactivity of MC and EC cokes decreased with the addition of 10 wt% of petcoke and increased with the increase in the amount of petcoke as suggested in the literature [Phani 2013]. This reflects that 10 wt% of petcoke is the optimal amount to reduce the reactivity of the cokes produced from bituminous coals.

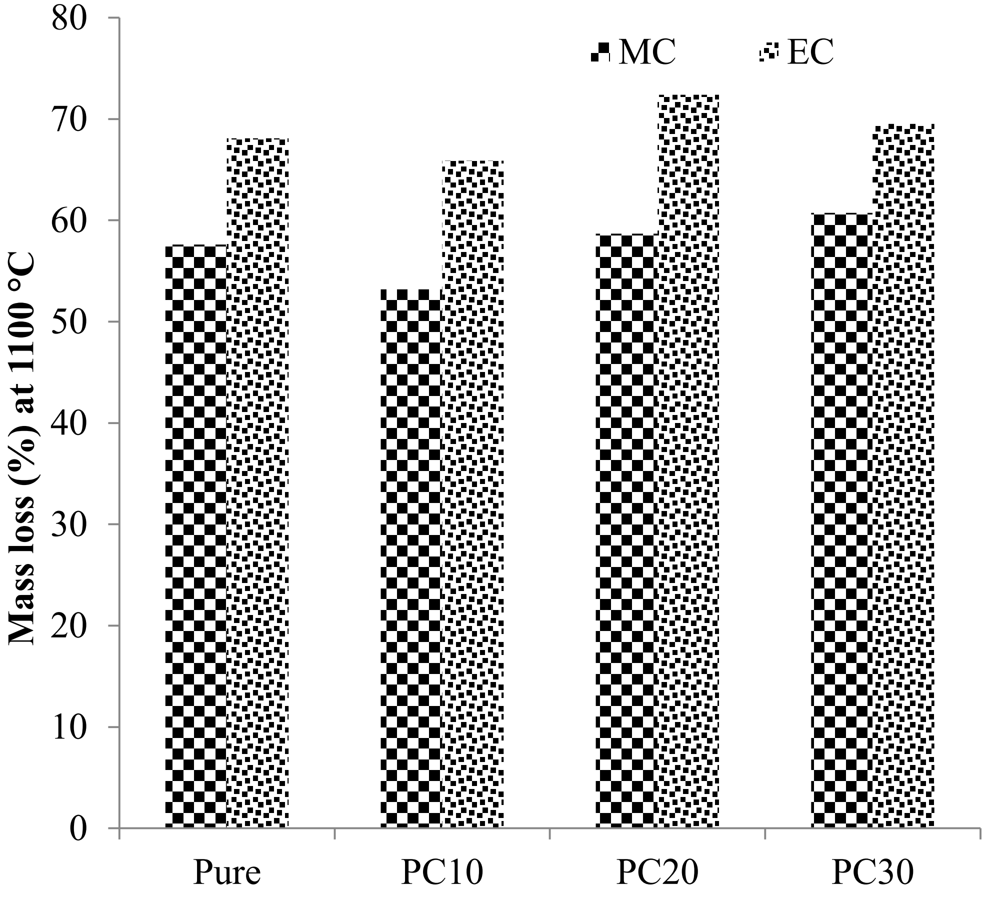


Figure 4.7 Effect of petcoke addition on coke reactivity

4.7.3. Effect of graphitization

Raman spectroscopy was carried out to calculate the extent of graphitization as described above. Two distinct peaks obtained at around 1300cm^{-1} and 1600cm^{-1} was observed in the spectrum as expected from the literature [Mennella, 1995]. Figure 4.8 shows the spectrum of MC sample and similar plots were obtained for other samples.

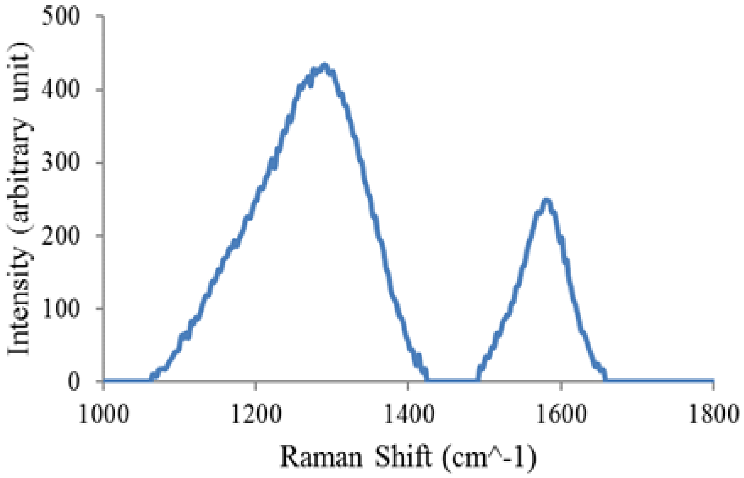


Figure 4.8 Raman spectrum of DC

The extent of graphitization of the cokes produced with was calculated by using the ratio of area under the two curves and is given in Table 4.5.

Table 4.5 Effect of petcoke addition on extent of graphitization

Sample	***Extent of graphitization***	***Standard Deviation***
MC100	0.23	0.004
MC90PC10	0.24	0.007
MC80PC20	0.21	0.003
MC70PC30	0.21	0.021
EC100	0.24	0.001
EC90PC10	0.23	0.008
EC80PC20	0.21	0.019
EC70PC30	0.22	0.003

Figure 4.9 shows the effect of petcoke on extent of graphitization. It was observed that the extent of graphitization of MC cokes increased with the addition of 10 wt% of petcoke as binder and decreased with increase in the amount of petcoke. It was also observed that addition of 10 wt% of petcoke had negligible effect on EC coke and the extent of graphitization of EC cokes decreased with increase in the amount of petcoke.

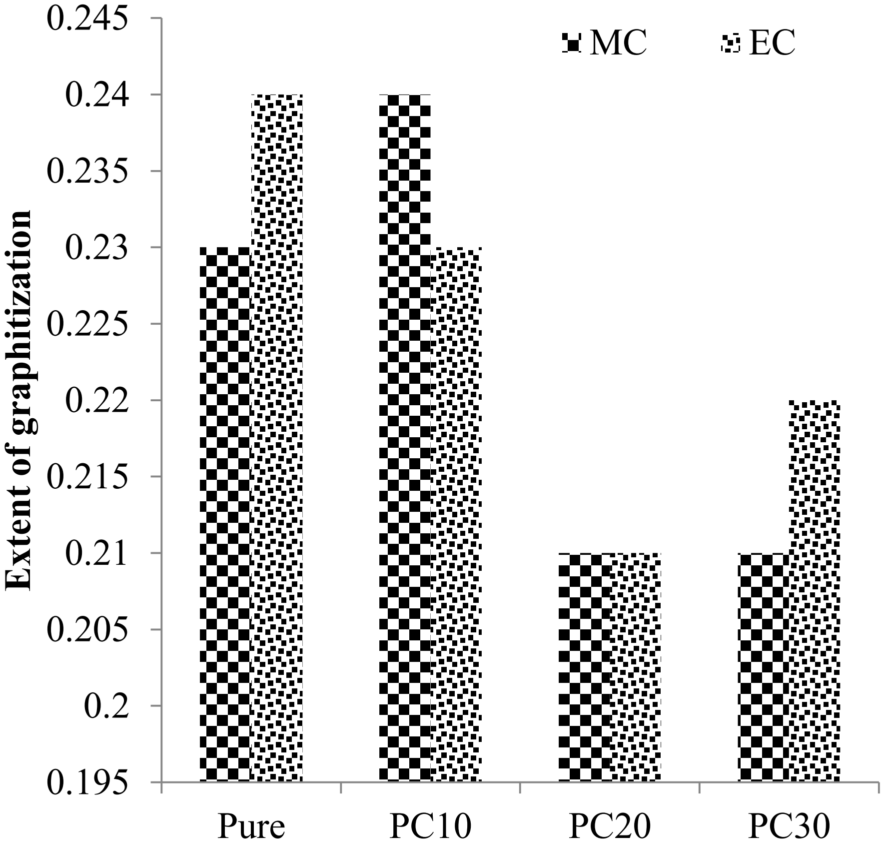


Figure 4.9 Effect of petcoke addition on extent of graphitization

4.8. Effect of petcoke and asphaltene

The low quality bituminous coal and the sub-bituminous coal used in the study could not form a good solid coke with pet coke as, the carbonization experiments were carried out with the blend of pet coke and asphaltene as binder. The summary of the samples with the binder is given in Table 4.6.

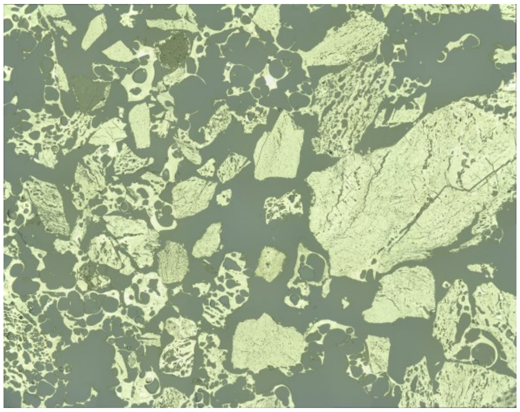
Table 4.6 Summary of samples with addition of binders

Name of Sample	***Type of coal***	***Amount of asphaltene (%)***	***Amount of pet coke (%)***	***Amount of coal (%)***
DC100	Bituminous	0	0	100
DC90P5A5	Bituminous	5	5	90
DC80P10A10	Bituminous	10	10	80
DC70P15A15	Bituminous	15	15	70
GC100	Sub-Bituminous	0	0	100
GC90P5A5	Sub-Bituminous	5	5	90
GC80P10A10	Sub-Bituminous	10	10	80
GC70P15A15	Sub-Bituminous	15	15	70

Different characterization techniques were performed for the cokes produced and are discussed below.

4.8.1. Porosity by image analysis

2D stitched microscopic images obtained from the optical microscopy were processed in MATLAB to calculate the porosity as described in section 4.4. The microscopic images of the coke samples produced are shown in Figure 4.10.



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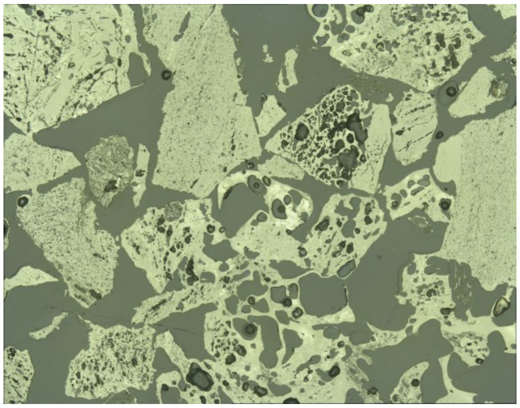

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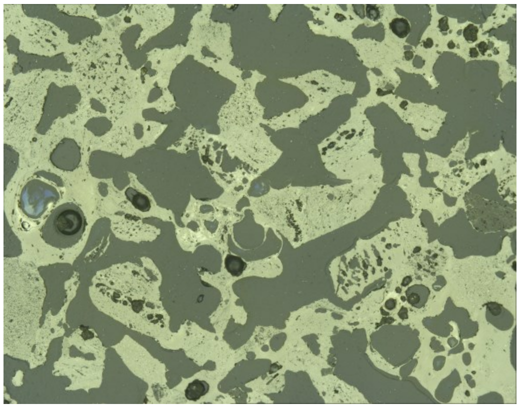

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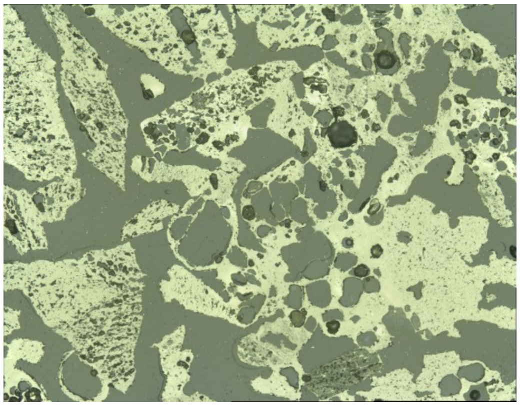

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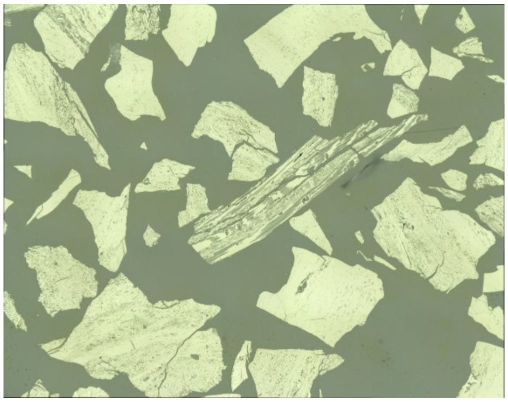

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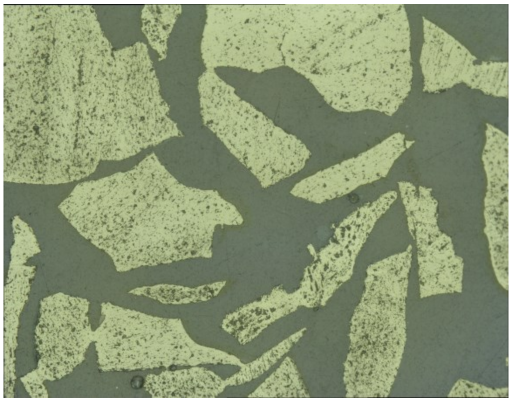

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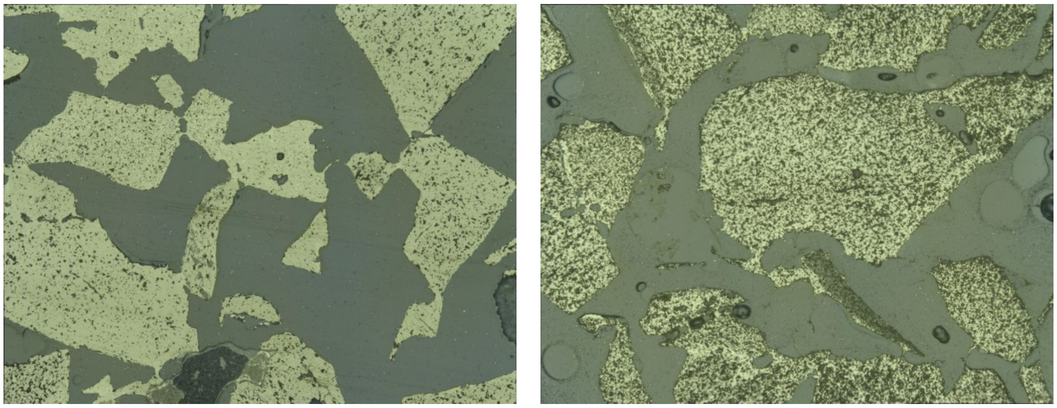


G H

Figure 4.10 2D stitched images of A) DC100 B) DC90P5A5 C) DC80P10A10 D) DC70P15A15 E) GC100 F) GC90P5A5 G) GC80P10A10 H) GC70P15A15 (250X)

The porosity values of the coke samples are given in Table 4.7.

Table 4.7 Effect of petcoke and asphaltene addition on porosity

Sample	***Average porosity (%)***	***Standard Deviation***
DC100	62.9	0.2
DC90P5A5	57.12	0.71
DC80P10A10	57.79	0.09
DC70P15A15	79.18	0.63
GC100	58.07	1.34
GC90P5A5	58.84	0.1
GC80P10A10	55.39	0.66
GC70P15A15	53.82	0.9

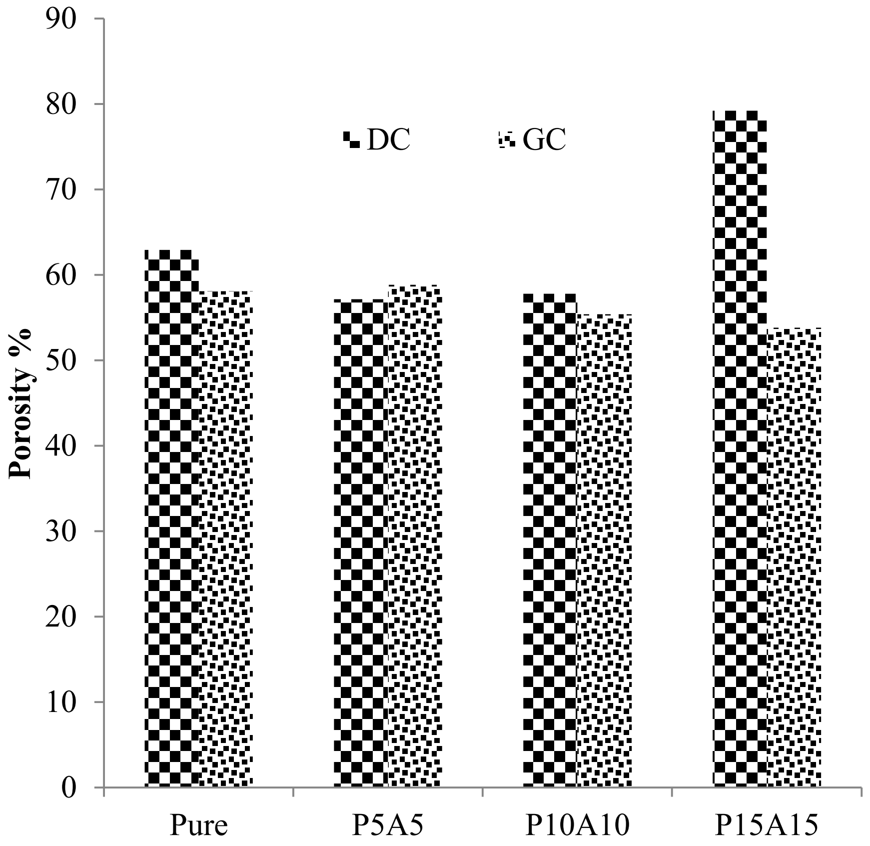


Figure 4.11 Effect of petcoke and asphaltene addition on porosity

The effect of petcoke and asphaltene on porosity of the cokes is shown in Figure 4.11. It was observed that the porosity of DC cokes decreased with the addition of 10 wt% of binder (5 wt% of petcoke + 5 wt% of asphaltene) and 20 wt% of binder (10 wt% of petcoke + 10 wt% of asphaltene). Upon addition of 15 wt% of petcoke and 15 wt% of asphaltene, the porosity of DC coke increased. The porosity of the GC cokes decreased with the increase in the addition of petcoke and asphaltene. This suggests that petcoke and asphaltene has a significant contribution in decreasing the porosity of cokes prepared from sub-bituminous coal.

4.8.2. Coke reactivity

The reactivity of the produced coke samples was measured by subjecting to gasification in CO_2 atmosphere in Thermogravimetric analyzer as discussed in chapter 3. The mass loss (%) of the coke samples during the isothermal period at 1100 °C is mentioned in Table 4.8.

Table 4.8 Effect of petcoke and asphaltene on coke reactivity

Sample	***Mass loss during isothermal period, α (%)***
DC100	62.1
DC90P5A5	63.5
DC80P10A10	69.91
DC70P15A15	70.2
GC100	98
GC90P5A5	92.5
GC80P10A10	92.7
GC70P15A15	92.1

Figure 4.12 shows the effect of petcoke and asphaltene on coke reactivity. It was observed that the reactivity of the DC cokes increased with the increase in addition of petcoke and asphaltene. it could also be observed that asphaltene and petcoke addition had little effect on the cokes of the sub-bituminous coal, GC and most of the mass had been consumed within 2 hrs in CO_2 atmosphere as given in the literature [Ye, 1998]. However, the porosity of the GC cokes decreased slightly with the addition of petcoke and asphaltene as binder.

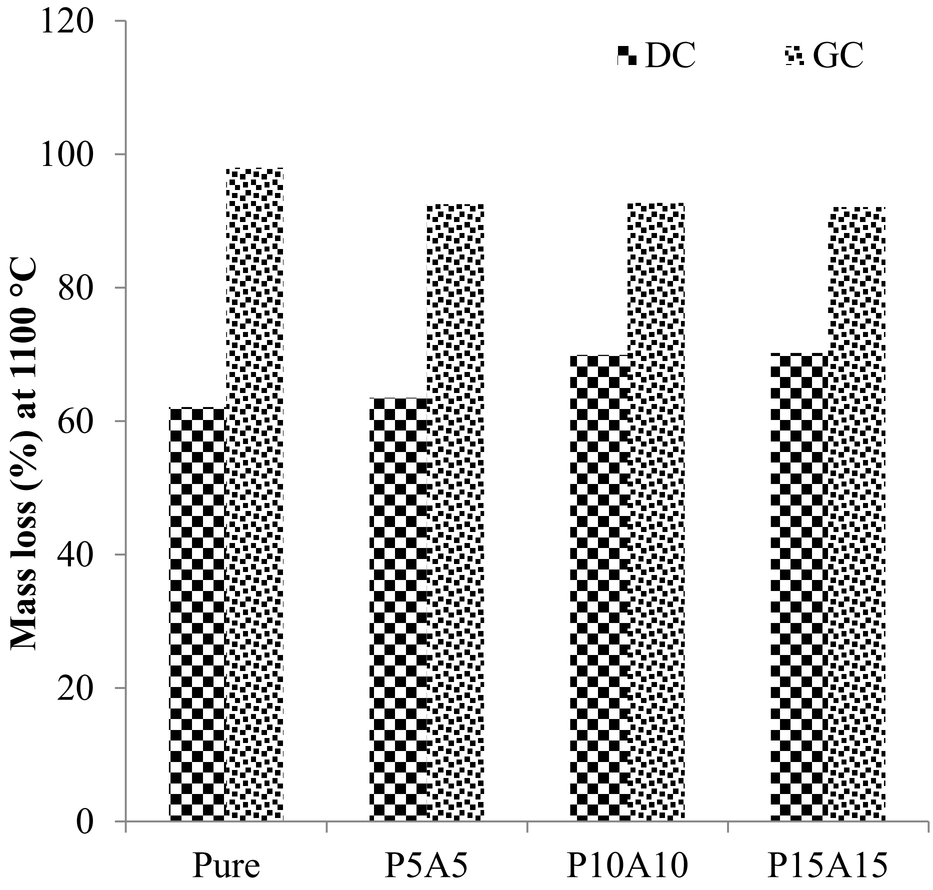


Figure 4.12 Effect of petcoke and asphaltene addition on coke reactivity

4.8.3. Effect on graphitization

The coke samples were subjected to Raman spectroscopy to calculate the extent of graphitization as described in section 4.5. Two distinct peaks obtained at around 1300cm^{-1} and 1600cm^{-1} was observed in the spectrum as expected from the literature [Mennella, 1995]. Figure 4.13 shows the spectrum of DC sample and similar plots were obtained for other samples.

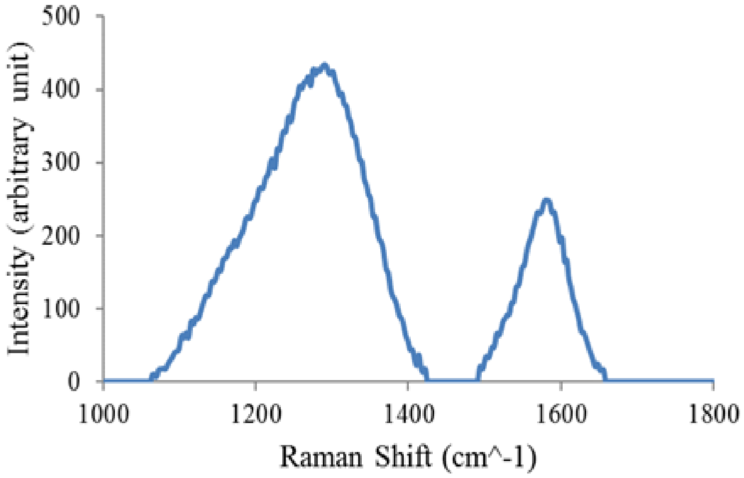


Figure 4.13 Raman spectrum of DC

The extent of graphitization of the cokes produced with petcoke and asphaltene addition was calculated by using the ratio of area under the two curves. The effect of petcoke and asphaltene on extent of graphitization is given in Table 4.9 and is shown in Figure 4.14.

Table 4.9 Effect of petcoke and asphaltene addition on extent of graphitization

Sample	***Extent of graphitization***	***Standard Deviation***
DC100	0.224	0.02
DC90P5A5	0.28	0.005
DC80P10A10	0.27	0.003
DC70P15A15	0.23	0.003
GC100	0.22	0.005
GC90P5A5	0.26	0.009
GC80P10A10	0.23	0.002
GC70P15A15	0.22	0.014

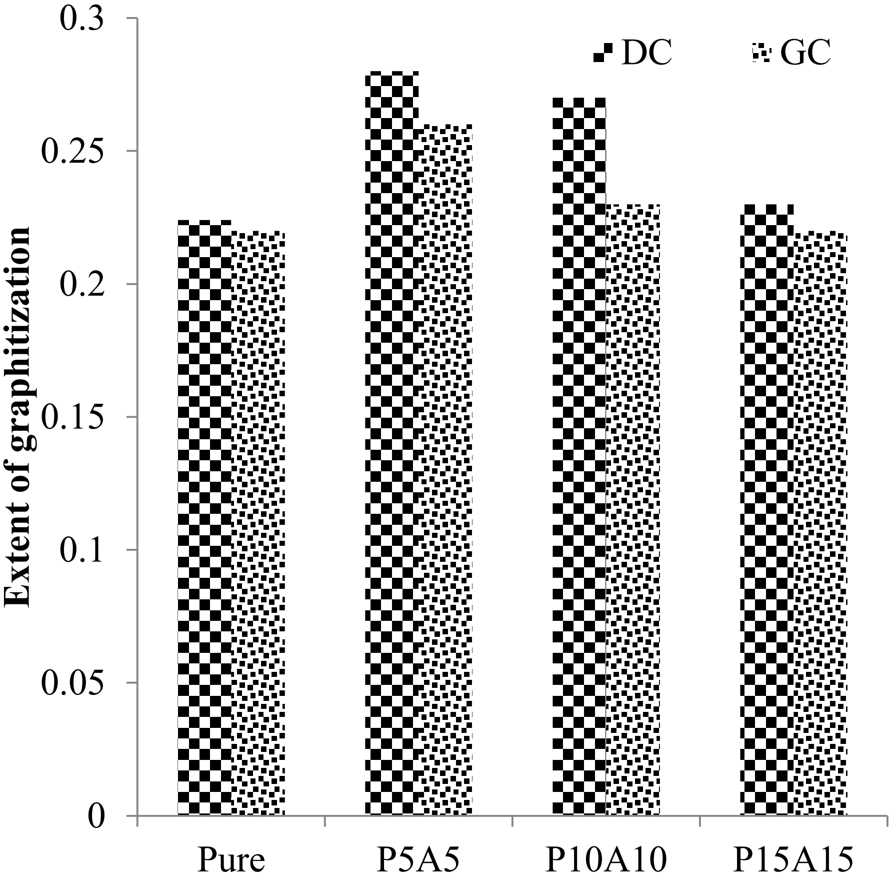


Figure 4.14 Effect of petcoke and asphaltene addition on extent of graphitization

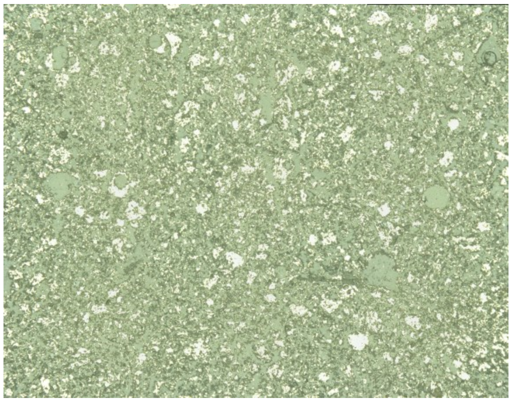
It was observed from the figure that the extent of graphitization of the DC cokes increased with the addition of 10 wt% of binder (5 wt% of petcoke + 5 wt% of asphaltene) and 20 wt% of binder (10 wt% of petcoke + 10 wt% of asphaltene) and the extent of graphitization of GC coke increased with the addition of 5 wt% of asphaltene and 5 wt% of petcoke. This occurred as asphaltene can yield up to 47% of coke [Trejo, 2010]. However, the effect on graphitization was lower for higher amount of binder on DC coke. It was also observed that petcoke and asphaltene on higher amounts (higher than 10 wt% of each) had negligible effect on GC cokes.

4.9. Effect of Minerals

The coke samples were prepared by adding 1 wt% of calcite ($CaCO_3$), magnesite ($MgCO_3$), siderite ($FeCO_3$), and dolomite ($Ca.Mg\ (CO_3)_2$), individually to the total wt % of the CC coal sample. Minerals were added in coarse form and also as fines. Different characterization techniques were carried out and the characterization results are discussed below.

4.9.1. Porosity by image analysis

The porosity was calculated by image processing the 2D stitched images obtained from the optical microscopy as discussed in chapter 3. The 2D stitched microscopic images of the coke samples with minerals coarse and minerals fines are shown in Figure 4.15. The porosity (%) of the samples is mentioned in Table 4.10.



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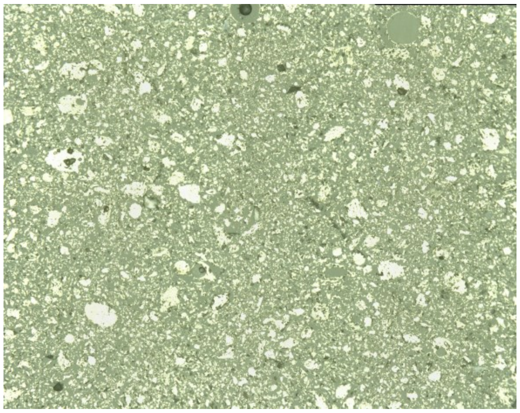

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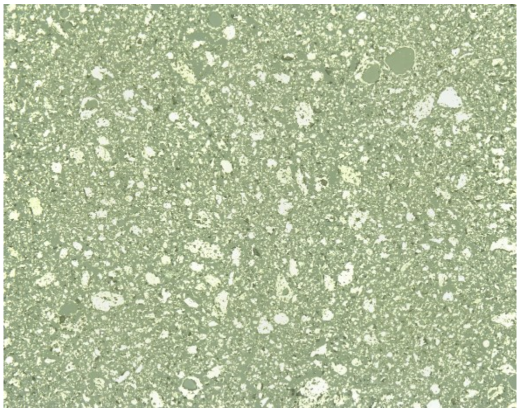

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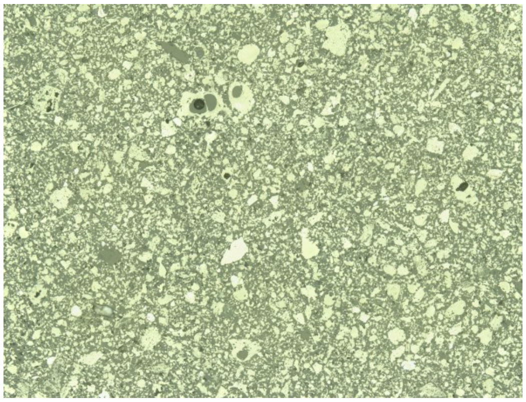

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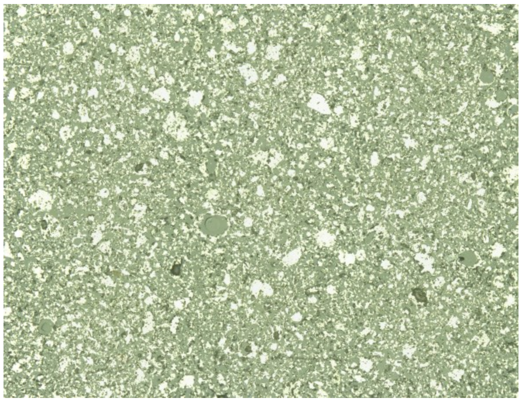

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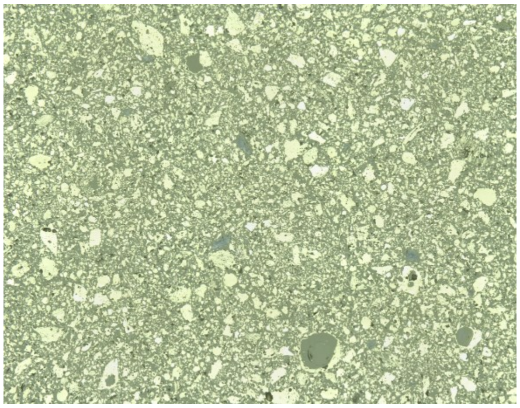

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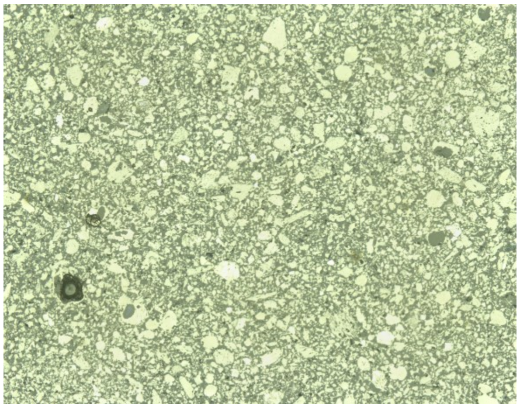

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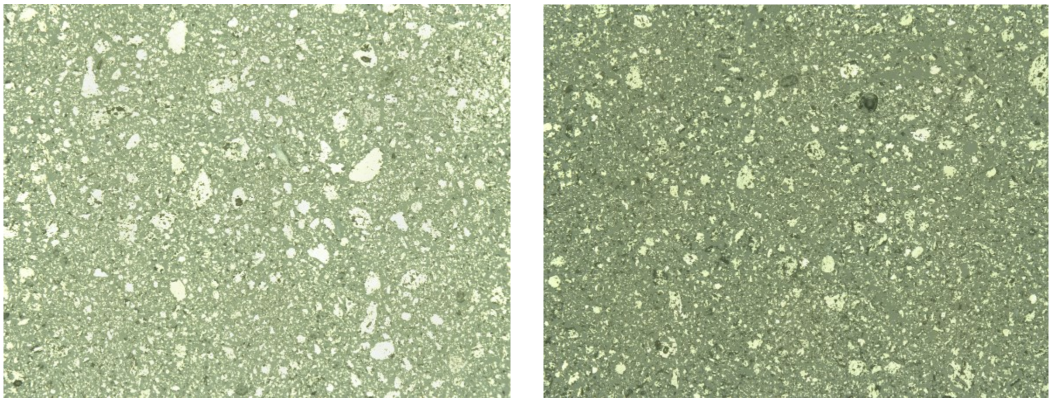

H I

Figure 4.15 2D stitched images of CC A) Raw B) with calcite coarse B) with calcite fines C) with magnesite coarse D) with magnesite fines E) with siderite coarse F) with siderite fines G) with dolomite coarse I) with dolomite fines(250X)

Table 4.10 Effect of minerals on porosity

Sample	***Average porosity (%)***	***Standard Deviation***
CC	78.8	1.24
CC with Calcite coarse	63.3	1.09
CC with Calcite fines	71.8	0.93
CC with Magnesite coarse	61.5	1.02
CC with Magnesite fines	68.1	0.45
CC with Siderite coarse	71.36	1.82
CC with Siderite fines	89.26	0.06
CC with dolomite coarse	64.52	1.19
CC with dolomite fines	59.52	1.55

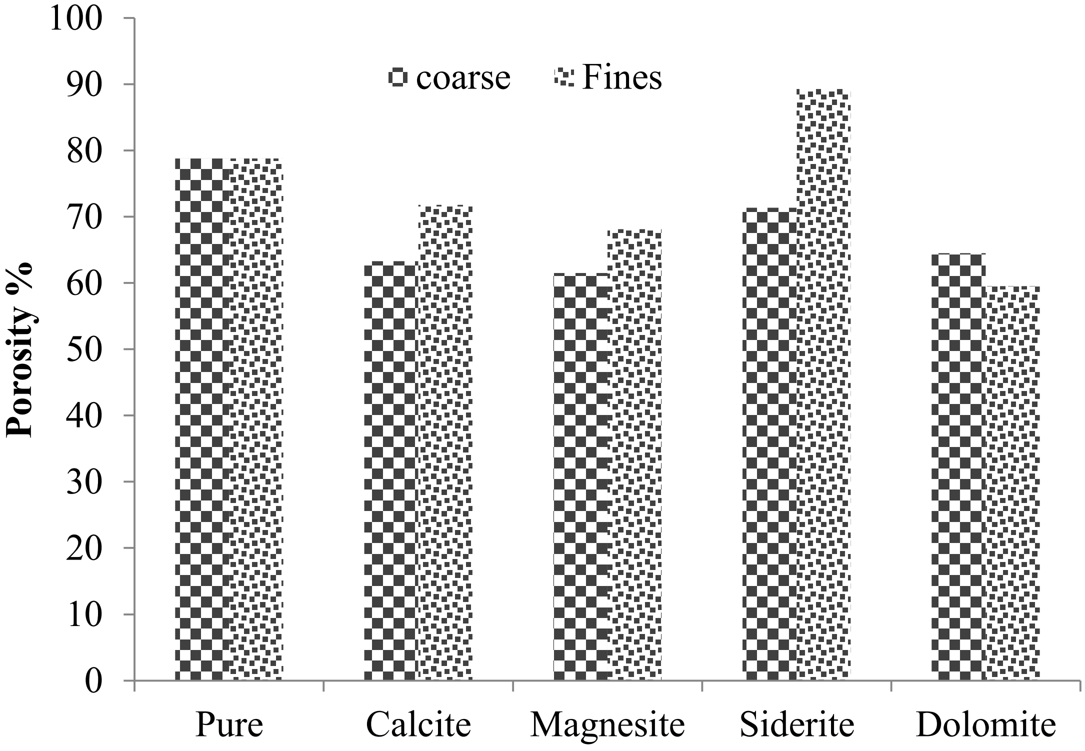

Figure 4.16 Effect of minerals on porosity

The effect of minerals on porosity is given in Figure 4.16 . It has been observed that the porosity of the coke samples decreased with the addition of calcite coarse, siderite coarse, dolomite coarse and decreased more than 15% with the addition of magnesite coarse to CC. The porosity slightly decreased with the addition of siderite calcite fines, magnesite fines, dolomite fines but increased with the addition of siderite fines. Also, the porosity is found to be lower when the minerals were added in coarse form.

4.9.2. Coke reactivity

To measure the reactivity, the produced coke samples were subjected to gasification in CO_2 atmosphere in Thermogravimetric analyzer as discussed in chapter 3. The mass loss (%) of the coke samples during the isothermal period at 1100 °C is mentioned in Table 4.11.

Table 4.11 Effect of minerals on coke reactivity

Sample	***Mass loss % at 1100°C***
CC	68.5
CC with Calcite coarse	75.8
CC with Calcite fines	78
CC with Magnesite coarse	71.5
CC with Magnesite fines	69.4
CC with Siderite coarse	79.4
CC with Siderite fines	82.5
CC with dolomite coarse	77.17
CC with dolomite fines	78.77

The effect of minerals on coke reactivity is shown in Figure 4.17. It has been observed from the above figure that the reactivity of the coke samples increased with the addition of minerals coarse and also with the addition of minerals fines to the CC coal. The results align with the literature where Reid et al. [Reid, 2014], studied the effect of minerals on coke reactivity and found that the addition of calcium increased the reactivity of coke and magnesium had negligible effect on reactivity of cokes.

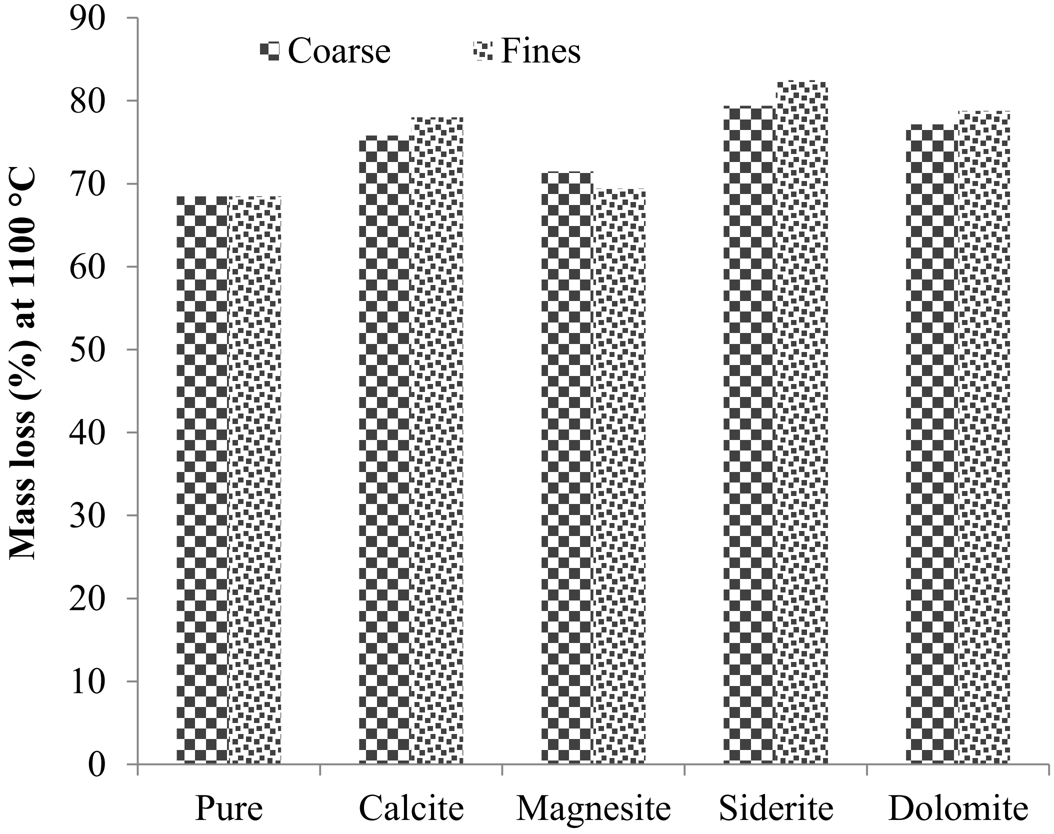

Figure 4.17 Effect of minerals on coke reactivity

4.9.3. Extent of graphitization

The extent of graphitization was calculated by using the Raman spectrometer as described above. Figure 4.18 shows the Raman spectrum of CC coke sample. It was observed from the spectrum that two distinct peaks were obtained at around 1300cm^{-1} and 1600cm^{-1} as expected from the literature [Mennella, 1995]. Similar plots were obtained for other samples with minerals coarse and fines.

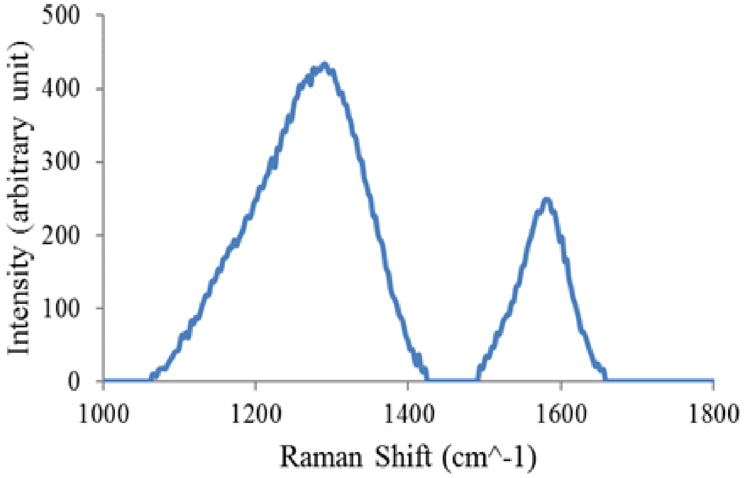

Figure 4.18 Raman spectrum of CC

The extent of graphitization calculated by using the ratio of area under two curves and is given in Table 4.12. The effect of calcite on extent of graphitization is shown in Figure 4.19.

Table 4.12 Effect of minerals on extent of graphitization

Sample	***Extent of graphitization***	***Standard Deviation***
CC	0.27	0.007
CC with Calcite coarse	0.26	0.001
CC with Calcite fines	0.22	0.003
CC with Magnesite coarse	0.27	0.003
CC with Magnesite fines	0.25	0.005
CC with Siderite coarse	0.21	0.009
CC with Siderite fines	0.22	0.002
CC with dolomite coarse	0.29	0.014
CC with dolomite fines	0.22	0.005

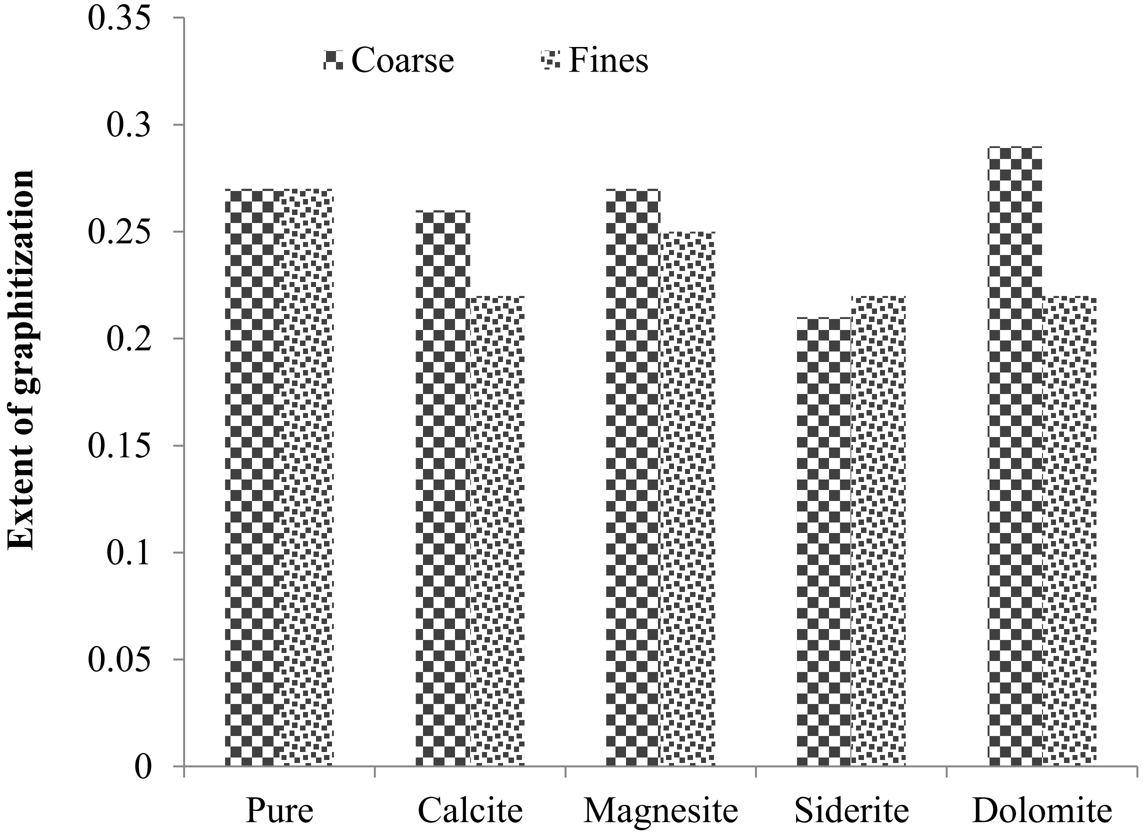

Figure 4.19 Effect of minerals on extent of graphitization

From the figure, it was observed that the addition of calcite coarse and magnesium coarse had negligible effect on extent of graphitization. The extent of graphitization decreased further upon the addition of siderite coarse and increased with the addition of dolomite coarse. The extent of graphitization decreased with the addition of minerals fines.

4.10. Conclusion

- *Effect of Calcite addition:* Reactivity of the cokes produced with addition of 1 wt% of calcite coarse and 1 wt% of calcite fines increased. However, with the addition of 1 wt% of calcite coarse, the total porosity decreases and the extent of graphitization increases, resulting in a slightly improved coke.
- *Effect of Magnesite addition*: Addition of magnesite to CC coal shows no improvement in the reactivity and the extent of graphitization of the produced cokes. However, the total porosity of the coke decreased with 1 wt% of magnesite coarse.
- *Effect of Siderite addition*: Siderite caused higher reactivity and decreased the extent of graphitization of the cokes and had no significant contribution in improving coke quality.
- *Effect of Dolomite addition*: Dolomite decreases the total porosity and increases the extent of graphitization of the cokes produced from CC coal. However, the reactivity of the coke sample increases with the addition of dolomite. Further study is required in this area for getting conclusive remarks on these mineral additives.
- *Effect of Petcoke*: The total porosity of cokes produced from bituminous coals decreases with the increase in the addition of pet coke. But the reactivity increases and the extent of graphitization have a negligible effect when more than 10 wt% of petcoke is used as binder. Hence, 10 wt% of petcoke is the optimal amount of binder that can be used to improve the quality of cokes to be prepared from bituminous coals.
- *Effect of blend of petcoke and asphaltene*: The total porosity of the cokes produced from bituminous coal decreases with the addition of blend of petcoke and asphaltene as binder but increases with more than 15 wt% of asphaltene and 15 wt% of petcoke. However, the reactivity of cokes from bituminous coal increases with increase in the addition of petcoke

and asphaltene. Hence, bituminous coal with addition of asphaltene and petcoke as binder is not suitable for blast furnace. With increase in the addition of petcoke and asphaltene to the sub-bituminous coal, the total porosity and the reactivity of the coke produced decreases and the extent of graphitization increases. This suggests that the blend of petcoke and asphaltene can be used as binder to improve the quality of the coke from sub-bituminous coal.

5. CONCLUSION AND FUTURE WORK

5.1. Conclusion

5.1.1. Use of TGA and HTF as an alternative to the actual CRI test

- Reactivity of coke measured in TGA was correlated with the actual CRI values of the coke samples and a significant linear relation was observed. However, the reactivity measured in TGA at 1100°C was very high as the samples were crushed to -0.25 mm, giving higher surface area and only 40 mg of sample was used to study the gasification behaviour. In high temperature furnace, the reactivity estimated at 1100°C was close enough and approximately equal to the actual CRI values of the coke samples. This is because, in high temperature furnace the coke chunks were used and also, the exact conditions of real CRI test were reflected. High temperature furnace experiments also eliminate the usage of 200 g of coke in CRI test by using only 50 g of the sample. Hence, TGA can be widely used to screen the samples before carrying out the real CRI test if large number of samples is provided and HTF can be widely used as an alternative to predict the CRI of the cokes.

5.1.2. Effect of binders in metallurgical coke making

- *Effect of mineral addition:* Addition of magnesite was found to have negligible effect on coke reactivity and the extent of graphitization. Siderite addition had a negative impact on the coke quality. Addition of dolomite and calcite decreased the total porosity and increased the extent of graphitization resulting in a slightly improved coke. However, the reactivity of cokes increased with the addition of dolomite and calcite making them not suitable to increase the quality of the coke. Further study is required in this area for getting conclusive remarks on these mineral additives.

- *Effect of addition of petcoke*: When petcoke was used as a binder, the cokes produced from sub-bituminous coal and a low quality bituminous coal crumbled making it not suitable to be used for the blast furnace operation. With the increase in addition of pertcoke as a binder with bituminous coals decreased the total porosity of cokes produced. The reactivity of the cokes increased and the extent of graphitization had a negligible effect beyond 10 wt% of petcoke as binder. Hence, 10 wt% of petcoke can be used as a binder with bituminous coals to improve coke quality.
- *Effect of addition of blend of petcoke and asphaltene*: When the blend of petcoke and asphaltene was used as a binder with the low quality bituminous coal, the total porosity of the cokes produced decreased but increased beyond the addition of 15 wt% of asphaltene and 15 wt% of petcoke. However, the reactivity of cokes increased with increase in the addition of petcoke and asphaltene making it not for blast furnace. With increase in the addition of petcoke and asphaltene to the sub-bituminous coal, the total porosity and the reactivity of the coke produced decreases and the extent of graphitization increases. This suggests that the blend of petcoke and asphaltene has some potential to be used as binder to improve the quality of the coke from sub-bituminous coal.

5.2. Future work

- Cokes can be produced in lab scale and the reactivity can be measured using the high temperature furnace.

- Reactivity of large variety of cokes can be measured in high temperature furnace with more repeatability tests to develop a model to predict CRI of cokes, provided a large number of cokes are used in the work.
- Effect of other minerals such as quartz, alumina, and kaolinite on coke quality can be studied.
- Study on removal of SO_2 from asphaltene and petcoke can be studied.

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