TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

This chapter provides an introduction to the anode production in primary aluminum industry, the role of calcined coke as well as the desulfurization of petroleum coke for anode production. The statement of the problem and the objectives of the research project as well as the general methodology used to reach the objectives are outlined in the following sections.

1.1 Background

The production of aluminum is carried out by means of the electrolysis of alumina (Al_2O_3) in molten cryolite (Na_3AlF_6) called the Hall-Heroult process. This electrolytic process is represented by the following reaction [1]:

$$2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2 \qquad (1.1)$$

In the electrolysis cell, aluminum ions within Al_2O_3 are reduced to Al in its metallic form which accumulates below the electrolyte in liquid form at temperatures around 950°C. CO_2 is produced as a result of the reaction of oxide ions with the carbon [1, 2]. Carbon anodes are immersed in the molten electrolyte during electrolysis and are consumed by the electrochemical reaction [1, 3-5]. The anode life in a modern electrolysis cell is between 20 and 30 days, and this duration is directly related to the quality of anode [6]. Secondary reactions increase the carbon consumption and consequently greenhouse gas (GHG) emissions [4, 7]. Low quality anodes lead to high energy consumption during the electrolytic process, which is directly related to environmental emissions [8, 9]. Thus, the anode quality is highly important for an efficient, economic, and environmentally-sound aluminum production [1, 4].

Typically, prebaked anodes consist of approximately 65% calcined petroleum coke, 15% coal tar pitch, and 20% recycled anodes and butts [1, 10]. The anode production comprises of the following steps: preparation of green paste from raw materials (coke, pitch, butts, rejected anodes), forming of green paste block either by vibro-compaction or hydraulic pressing, cooling and storage of obtained green anodes, baking of green anodes in the furnace at temperatures around 1100°C, and finally rodding prior to their use in the electrolysis cell [1, 11]. To carry out an efficient electrolysis process, the anodes need to have appropriate properties such as high electrical conductivity, high thermal shock resistance, high mechanical strength, low CO_2 and air reactivities as well as good homogeneity [1, 11].

It has been shown that the influence of calcined coke properties on anode quality is significant [12]. Therefore, attention should be paid to the quality and the properties of petroleum coke used in the production of carbon anodes for the aluminum industry [13]. These properties include chemical composition (sulfur, sodium, vanadium, etc.), porosity, density, reactivity, etc. Coke morphology plays an important role as well [14].

Calcined coke, which is one of the main raw materials for carbon anodes, is produced from green petroleum coke by the calcination process. The rising demand for aluminum results in higher demand for green petroleum coke in order to produce calcined coke for carbon anode fabrication [15]. However, the availability of the type of green petroleum coke, which is suitable for the production of high quality calcined coke, has been decreasing during recent years [10]. This latest trend comes about from the significant increase in sour crude oil usage in refining industry due to economic reasons. Sour crude oil leads to the production of high sulfur green coke, [16] and aluminum industry uses such cokes by blending with low sulfur cokes. However, calcined coke which is produced from high sulfur petroleum coke has a negative impact on environment and anode quality, which is undesirable for primary aluminum industry [17, 18]. This master project addresses the problem of sulfur content in coke and its removal with an objective to reduce its impact on environment.

1.2 Statement of the Problem

The growing demand on aluminium requires the increase in the production of carbon anodes [19] and consequently calcined coke. Green petroleum coke, the source of calcined coke, is produced from the heavy residual fractions of petroleum (or crude oil) [20]. The quality of the anode-grade coke widely depends on the raw material used in the petroleum refining as well as the operating conditions during refining, coking, and calcination [1]. Today’s petroleum industry uses crude oil sources containing higher sulfur and impurity levels and produces cokes with higher sulfur content and metal impurities than before [10, 16]. Today, smelters are using more of high sulfur cokes in blends to satisfy the demand for aluminum metal production [21, 22].

A certain amount of sulfur is needed in calcined coke to reduce anode reactivity [11, 23]. However, using calcined coke with a sulfur content higher than necessary in carbon anodes would have a number of adverse effects on environment. High-sulfur anode use in electrolysis results in increase in emissions such as H_2S, COS, CS_2, and SO_2, which are at the heart of environmental problems such as acid rain and GHG. High sulfur content in anodes may also cause sulfur removal during anode baking if the baking is continued above a certain temperature. This would increase anode porosity and specific electrical resistivity, and decrease anode baked density. Such anodes have shorter lives and increase the energy consumption and environmental emissions during electrolysis, which is undesirable for the aluminum industry.

There are several methods for removing sulfur from petroleum coke. Solvent extraction uses chemical solvents [24, 25]. This method is not suitable for the treatment of petroleum coke used in anode manufacturing since it contaminates the coke. Its complexity and its impact on the environment are also part of its unsuitability. Thermal desulfurization must meet several criteria (specific heating rate, maximum temperature, residence time) without affecting the quality of coke [26, 27]. The economic and environmental aspects should not be neglected either. Also, in thermal desulfurization, coke has to be calcined at higher temperatures than that is normally used by the industry, which increases the energy consumption and results in a porous coke structure. Hydrodesulfurization consists of subjecting the coke to a heat treatment (using a suitable heating rate, maximum temperature, and residence time) during calcination in a medium of hydrogen gas or steam, which reacts with sulfur in the coke. This method seems promising for reducing the high sulfur content in green coke to acceptable levels and adds value to high-sulfur green coke by making its utilization possible in the manufacture of carbon anodes [22, 28].

1.3 Objectives

The main objective of this study is to investigate the simultaneous calcination and hydrodesulfurization of high-sulfur containing sources of green coke to produce low-emission, anode-grade coke that will allow a smelter to maintain anode quality as well as respect environmental regulations. To attain this objective, the effects of various experimental conditions (water injection temperature, water flow rate, etc.) on sulfur removal have been studied. The results will open the way to the utilisation of high sulfur green coke in anode production.

This work aims to develop a method for combining the hydrodesulfurization and calcination of green petroleum coke through an experimental study. The application of this method in a vertical shaft furnace might allow the production of calcined and desulfurized coke with desired quality and appropriate sulfur level for anode fabrication.

1.4 Methodology

Normally, simultaneous hydrodesulfurization and calcination would be carried out in a vertical shaft furnace where coke would be in contact with one or more of the following gases: water gas ($CO+H_2$), CO_2, volatiles, and sulfurous gases such as H_2S. The vertical shaft furnace is one of the most common technologies used by calcination industry in order to produce calcined coke.

Many phenomena occur simultaneously during the combined hydrodesulfurization and calcination process. A fundamental investigation of the hydrodesulfurization conditions has to be carried out in order to find the favorable conditions to obtain calcined coke with a desired sulfur content and suitable structure. Thus, in the current study, coke was subjected to different water injection conditions during its calcination. To achieve the specified objectives, the work included the following steps:

Hydrodesulfurization of high sulfur petroleum coke was carried out in an electrically heated furnace with a thin layer of particles to ensure their contact with water vapor. During the experiments, tap water was injected into the sample holder at different temperatures and flow rates for different period of times. The contact between the water vapor and the green coke with high sulfur content results in the reaction products H_2S, COS, etc. The effect of contact time of green coke with water, quantity and temperature of water injected on the desulfurization has been studied.

Prior to and following the experiments, the sulfur content of the coke and its properties (density, porosity, surface functionality) were measured. These data were correlated with the experimental conditions in order to understand the fundamental processes taking place.

In order to compare the effect of two different desulfurization methods on the removal and the structure of coke, thermal desulfurization of high sulfur green petroleum coke was carried out using a thermogravimetric analyser (TGA) heated by induction. The weight loss of cokes during the experiments was measured with a balance, and the sulfur contents were measured before and after the experiments.

Weight loss and final sulfur content results were compared with the results of hydrodesulfurization.

This study was carried out in the UQAC laboratories. The equipment used for the detailed analysis of coke is as follows: Scanning Electron Microscope (SEM) for surface imaging, Energy-Dispersive X-ray Spectroscopy (EDX) for chemical analysis of surface, X-ray Photoelectron Spectroscopy (XPS) and Fourier Transform Infra-Red (FT-IR) spectroscopy to determine chemical composition of surfaces, X-ray Powder Diffraction to determine the crystallinity of coke samples, helium and water pycnometers for real density and apparent density measurements, respectively.

1.5. Scope

The thesis is organized in five chapters as follows:

Chapter 1 presents a summary of the role of carbon anodes in the production of primary aluminum, the problem of high-sulfur content in petroleum cokes and its usage in carbon anodes, desulfurization methods as a solution to this problem as well as a general introduction of this research work including the research objectives, the methodology, and the scope.

Chapter 2 provides a review of the available literature and the background information on different green petroleum cokes available in industry, sulfur in green petroleum coke, and the use of high-sulfur petroleum coke in carbon anodes, the calcination process as well as different desulfurization methods to solve the sulfur problem in coke such as solvent extraction, thermal desulfurization, and hydrodesulfurization. The concepts and explanations provided in this chapter make it possible to understand the principles of the tests and the reasons for choosing hydrodesulfurization method in this research. This chapter also summarizes previous studies and results obtained related to the topic of desulfurization.

Chapter 3 explains the experimental procedures for thermal desulfurization and hydrodesulfurization of high-sulfur green petroleum coke. It also provides a description of the facilities and techniques used for the characterization of coke samples, e.g., Scanning Electron Microscope (SEM), Energy-Dispersive X-ray Spectroscopy (EDX), X-ray Photoelectron Spectroscopy (XPS), Fourier Transform Infra-Red (FT-IR) spectroscopy, helium and water pycnometer, etc.

Chapter 4 presents the experimental results obtained from the thermal desulfurization and hydrodesulfurization of high sulfur petroleum coke as well as the characterization of coke samples before and after the treatment. Sulfur removal and weight loss results obtained after the treatment under different conditions are discussed in detail in this chapter. The changes in coke structure are presented and compared to understand the effects of two different desulfurization methods.

Chapter 5 gives the general conclusions as well as recommendations for future works based on this research study.

Appendix A includes the characterization results of different high sulfur green petroleum cokes and the application of thermal desulfurization method on these cokes under different conditions.

CHAPTER 2

LITERATURE REVIEW

2.1 Green Petroleum Coke and Its Use in Aluminum Industry

Green coke, which is one of the raw materials of carbon anodes, is produced from the heavy residual fractions of petroleum (crude oil) by a process known as delayed coking [23]. The quality of anode-grade coke widely depends on the feed material used in petroleum refining as well as the operating conditions of refining, coking, and calcination processes. Structure, density, and volatile matter content can vary significantly as can the sulfur, metals, and ash contents [1, 11].

The origin of the crude oil determines its composition which could vary significantly from one region to another. For instance, the crude oil from North America typically contains high S and is known as sour whereas in North Africa crude oil with low sulfur is called sweet crude [1, 11]. Four different kinds of products, gas, naphtha, gas oil and green coke, are produced by delayed coking process. One of the uses of green coke fraction is the production of carbon anodes for aluminum smelting. The production of different sorts of coke is influenced by the unit feedstock and operating conditions [11, 23].

The main types of green delayed petroleum coke can be classified as shot coke, sponge/fuel coke, sponge/honeycomb coke (also called anode-grade coke), and needle coke [11, 29]. They are explained in the following paragraphs.

Shot coke which is currently used as a fuel is a form of isotropic coke which shows identical properties in all directions [23, 30]. It is obtained from highly asphaltenic coker feedstock. It has a fine texture with uniform properties, and the shape of particles tend to be spheroidal with sizes ranging from buckshot to basketballs. The structure can also be layered like an onion. The aluminum industry has avoided using highly isotropic cokes, especially shot cokes, because of their high coefficients of thermal expansion (CTE) and low open porosity [11, 31].

Fuel grade cokes have a less optimal macrostructure and a high coefficient of thermal expansion. Millions of tonnes of these cokes are burned directly for power generation and cement production. Sponge (honeycomb) coke has a heterogeneous, porous, and amorphous structure with a mixture of coarse and fine textures. It contains 10 to 15 percent of volatile hydrocarbons together with impurities such as sulfur, vanadium, nickel, and nitrogen. If green coke contains sufficiently low levels of sulfur and metals, it may be suitable for calcination to produce feedstock for carbon anodes for aluminum smelters. This higher quality green sponge coke is often described as anode-grade coke. Its pore structure is more prominent, and the coefficient of thermal expansion is lower compared to that of fuel coke. [11, 16, 23, 27, 29, 30].

While sponge coke is used in aluminum industry, needle coke is a premium product for steel industry [16, 23]. It seems similar to sponge coke in terms of porosity and has a characteristic layered structure which is referred to as anisotropic in general. It is chemically produced through cross linking of condensed aromatic hydrocarbons during coking reactions. The use of needle coke in steel industry is in graphite electrodes for electric arc furnaces. It has a low sulfur content (<0.5%) and a low coefficient of thermal expansion [16, 23, 29, 30]. The surface structures of four different types of cokes are given in Figure 2.1.

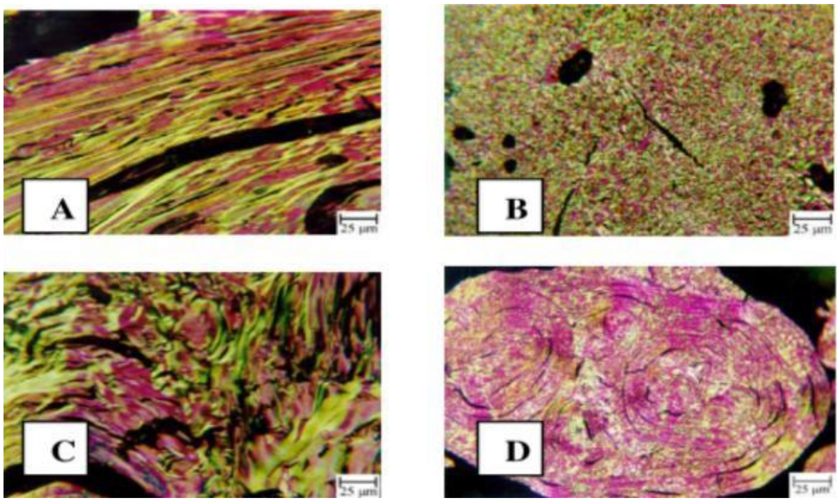


Figure 2.1 Coke structures under polarized light A) needle coke, B) isotropic coke, C) sponge coke D) shot coke [27]

Global aluminum production has increased by about 10 million tonnes since 2009 and is estimated to reach about 61 million tonnes per year by 2016. The increase in aluminum production has increased the demand for anode-grade coke. The calcination industry is trying to produce the required quality of calcined coke to meet this demand. However, due to crude oil and refinery economics, the production of coke with higher sulfur and metal contents has been increasing. Refineries use heavy, sour crudes and produce coke with higher sulfur and metal (Ni, V) contents. Although light, sweet crudes are easier to process and give higher proceeds of liquid fuels, elevated price of light sweet crude drives refineries to process cheaper crudes and adapt their technologies accordingly. This results in a general shortage of low sulfur coke. The needs of aluminum industry for low sulfur coke due to environmental reasons are not necessarily supported by the refining industry. Cokes, considered as inconvenient for anode production in the past, are being used regularly in blends at varying levels today, and this trend is likely to continue [16, 31]. This has been also the subject of several papers and presentations since 2001 [32-34].

The difference in the sulfur level of cokes used in classical anode blends by smelters has not increased significantly due to environmental constraints. However, broader range of cokes is being used in anode blends today. The greater range particularly applies to sulfur and vanadium levels. For instance, a sulfur level of 1-2% may be blended with cokes with sulfur levels up to 4-6% to achieve a smelter anode coke specification of 2.5-3.0%. A good illustration of the range of S and V in green petroleum cokes (GPC) supplied by Rain CII for anode blends from 2000 to 2011 is given in the Figure 2.2 [16, 27, 35].

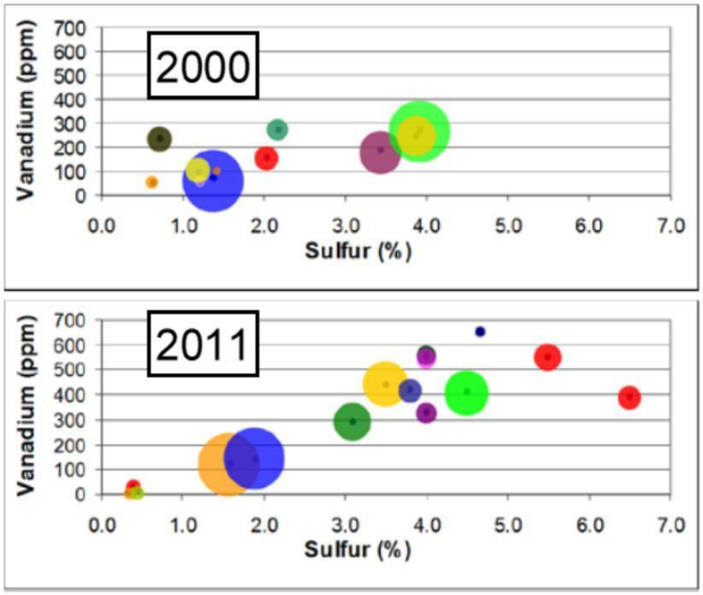


Figure 2.2 S and V level of GPC Sources in 2000 and 2011 [16]

2.2 Sulfur in Petroleum Coke

Sulfur is recognized as the most tightly bound to green coke among the four elements (H, O, N, S) and is released in large quantities above 1400°C [36]. The sulfur content of green petroleum coke is a good indicator of its properties, which is important for its application. It can vary from less than 0.5% to more than 10% and mainly depends on the sulfur content of the feedstock [37]. Sulfur in the petroleum coke is a function of sulfur in the charge as well as the origin of crude oil from which the coker feedstock is prepared. Sulfur can be present in the petroleum coke in different forms [38]:

- It can be attached to the aromatic skeleton between the aromatic rings.
- It can be present on the surface of the structure, but attached to the aromatic skeleton.
- It can be in lateral chains.

It was reported that it is more difficult to remove the first two forms of sulfur than the last one [38].

It was demonstrated by several authors that the nature of sulfur in green petroleum coke is mostly organic [39-41]. Specifically, sulfur may exist in the form of aromatic and aliphatic sulfides, thiophenes, and mercaptans [26, 41-43]. According to some works, sulfur can also be present as sulfates and pyritic sulfur. Elemental sulfur may occasionally be present, too [26, 44].

Although the exact form of organic sulfur in a petroleum coke is difficult to determine, according to the literature, thiophenes appear to be the most common forms of sulfur present in these cokes. It was reported that since thiophenes are stable compounds, the thiophenic form of sulfur in petroleum coke is difficult to remove without selectively breaking the C-S bonds, which may necessitate thermal, chemical, or thermochemical treatments [42].

The work of Hay et al. (2004) [45] deserves a special mention as they studied sulfur specification in petroleum cokes and aluminum smelter anodes. XANES (X-ray absorption near-edge structure) spectroscopy was used to determine the sulfur species in different petroleum cokes from major suppliers and anodes with different thermal histories. It was found that organic sulfur comprising of five- and six-membered ring structures were the dominant sulfur species in these cokes. These species were stable during anode baking and usage. In addition to the dominant existence of thiophenic and other cyclic sulfur, small quantities of sulfoxides and elemental sulfur were also detected by semi-quantitative analysis in some samples. Lesser amounts of inorganic sulfides (S^{2-}) and sulfates were usually detected in the petroleum cokes. It was also reported that organic sulfur ring structures were the dominant sulfur species in petroleum cokes from different sources with slight variations from one supplier to the next.

2.3. Effects of Sulfur on Environment and Anode Properties

The general specification for the sulfur content of petroleum coke used in carbon anode production is around 2.5-3%. Today's aluminum industry uses blends of high and low sulfur cokes to obtain a suitable sulfur level for carbon anodes. The background of this application was explained in the first section.

The presence of high amounts of sulfur in carbon anodes used in alumina reduction cells negatively affects the performance of the electrolysis process. It was mentioned by many authors that carbon anode consumption during electrolysis increases with increasing anode sulfur content [17, 18, 46, 47]. It was reported that net anode consumption increases 2-3% per S% in the anode between 1-4% total sulfur [46]. Sulfur in anodes also results in a significant loss of current efficiency in the electrolysis cell [18, 47] as well as an increase of emissions such as hydrogen sulfide (H_2S), carbonyl sulfide (COS), carbon disulfide (CS_2) and sulfur dioxide (SO_2) which can create significant environmental problems [17, 46, 48]. High sulfur content in anodes also causes loss of sulfur during the baking step if it reaches a certain temperature resulting in an increase in anode porosity and a decrease in baked anode density. Less dense anodes will reduce the efficiency of electrolysis cell operation and increase the environmental emissions, which are not desired by the aluminum industry [49].

2.4. Coke Calcination

Calcination is a heat treatment process during which green coke is heated to a specific temperature in order to remove moisture, drive off volatile matter, and produce anode-grade coke at the desired level of real density with the highest purity, high physical strength and electrical conductivity, minimum porosity and reactivity [50-53]. It was stated that the degree of coke calcination influences chemical, physical, and mechanical properties of carbon anodes [51]. Calcination is carried out at temperatures up to 1200-1400ºC, and the contact time varies from 0.5 h to 48 h, depending on the nature of the petroleum coke and the process. The calcination process also enables the arrangement of coke structure, i.e. transformation of the amorphous structure into a crystalline structure [53]. These properties along with low metal and ash contents make calcined petroleum coke the best material presently available for making carbon anodes for the production of aluminum [52].

Calcination process is important for the production of good quality anodes. There are three kinds of primary processes for the continuous calcination of petroleum coke: rotary kiln, rotary hearth and vertical shaft furnace. Rotary kiln and vertical shaft furnace processes will be explained in more detail.

2.4.1. Rotary Coke Calcining Kiln

Rotary kiln calciners are widely used for calcined petroleum coke production in the world while the vertical shaft calciners are used mostly in Chinese calcined petroleum coke plants [54]. In a rotary kiln, enough heat is provided to solids to raise their temperatures to desired level and to promote an efficient mixing of these solids in order to ensure uniformity of heat transfer [53]. The rotary kiln is a long cylinder rotating about its axis and operating basically as a counter-current heat exchanger. The cylinder is slightly tilted along its axis by an angle of about 2-5° to facilitate the axial motion of the coke bed along the kiln by means of gravity, and the rotary action of the cylindrical walls helps increase the solid-gas contact while the hot gas flows upwards. A typical kiln is 60 m in length, 2-3 m in diameter and rotates at 2 to 4 rpm. A typical green coke contains 8-12 wt% moisture and about the same weight percentage in volatiles [55-57]. Figure 2.3 gives a schematic description of the kiln.

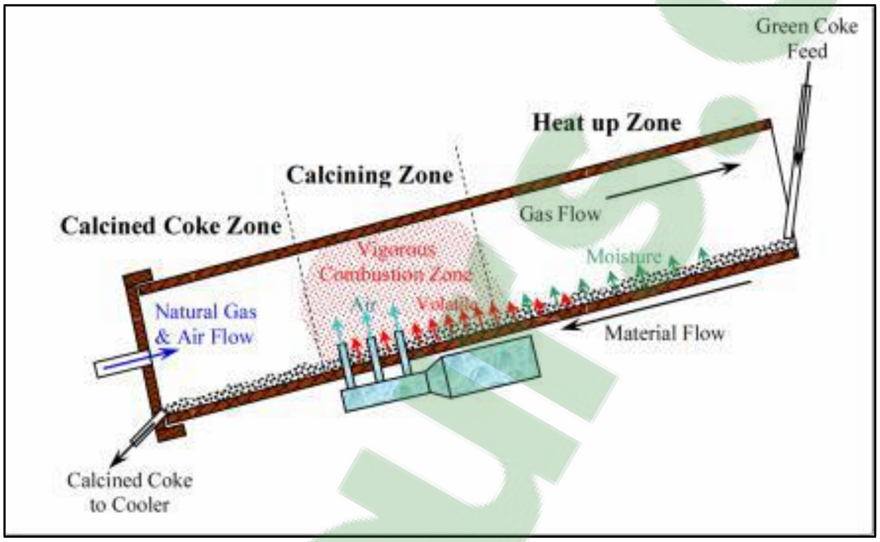


Figure 2.3 A schematic description of the rotary kiln [52]

In the calcination process, first green coke is fed to the system. As the coke flows down the kiln countercurrent to the hot combustion gases, the temperature increases to a maximum value that is reached around 13 to 20 m before the discharge end of the kiln. In the first zone of the kiln, which is called “Heat-Up Zone”, moisture is driven off from the coke structure at temperatures between 25-400°C. Devolatilization takes place mostly between 400°C and 1000°C in the “Calcining Zone”. Further dehydrogenation, desulfurization, and shrinkage of coke structure (densification) occur in the “Calcined Coke Zone” from 1000 to 1400°C [52].

Air (primary and secondary) for combustion is injected through the burner at the coke discharge end of the kiln. A tertiary air is injected into the calcining zone to burn the volatiles evolving from the bed in that section [53].

The necessary energy for the calcination process is provided by the partial combustion of volatile compounds and coke dust. As a result, the system is energy self-sufficient under normal conditions [56].

2.4.2. Vertical Shaft Calciner

A shaft calciner has multiple vertical refractory shafts surrounded by flue walls. The green coke is continuously fed on the top and travels down through the shafts by gravity and exits through water cooled jackets at the bottom. The process is illustrated in Figure 2.4. The movement of coke is controlled by the opening of a slide gate or a rotary valve at the bottom to discharge a small amount of coke. The discharge is intermittent (~every 20 min) and green coke is added to the top to maintain the feed. The volatile matter (VM) in a shaft furnace travels up through the coke bed and enters flue wall cavities at the top of the furnace. It is mixed with air at this point and then drawn down through a set of horizontally orientated flues. VM is combusted inside the flue walls and heat is conducted to the coke indirectly from the flue walls in a manner similar to an anode baking furnace [58]. The residence time of coke in shaft furnace is 24 to 36 h, resulting in a heating rate of ~1°C/min (compared to about 40-50°C/min in a rotary kiln). Due to this very slow heating rate, green coke with high VM (12 – 16%) can be calcined, and anode-grade coke with desired properties can be produced [59].

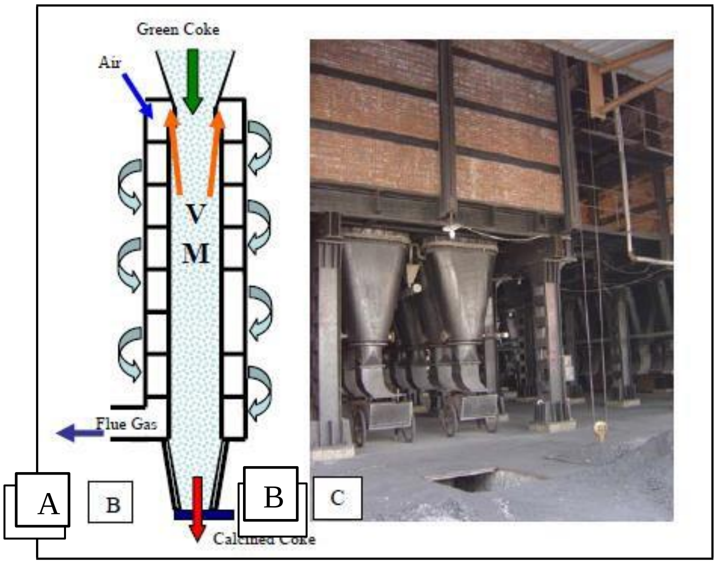


Figure 2.4 Shaft calciner a) Cross section b) Shaft outlets [60]

Green coke (crushed to size < 70 mm) primarily passes through the preheating zone in order to remove moisture and some part of the volatiles during the calcination process in the shaft calciner. Devolatilization takes place between about 400°C and 1000°C. In the calcining zone, where the highest temperatures in the flue reaches 1250 – 1400°C, further dehydrogenation, some desulfurization, and coke shrinkage (densification) occurs**.** The coke moves through the heated part of the calciner in 18 – 30 h and finally reaches the cooling zone. In the cooling zone, a coke discharge temperature of 60°C is reached with indirect water cooling [59]. Figure 2.5 shows the zones of calcination process in a vertical shaft calciner.

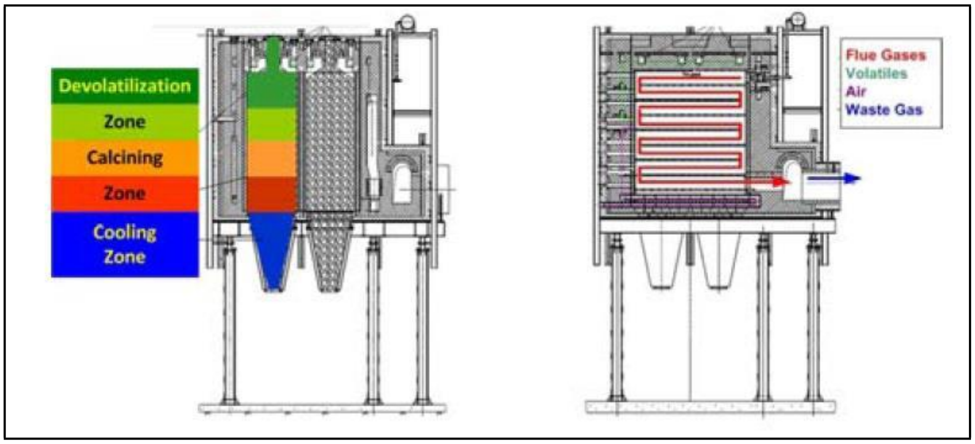
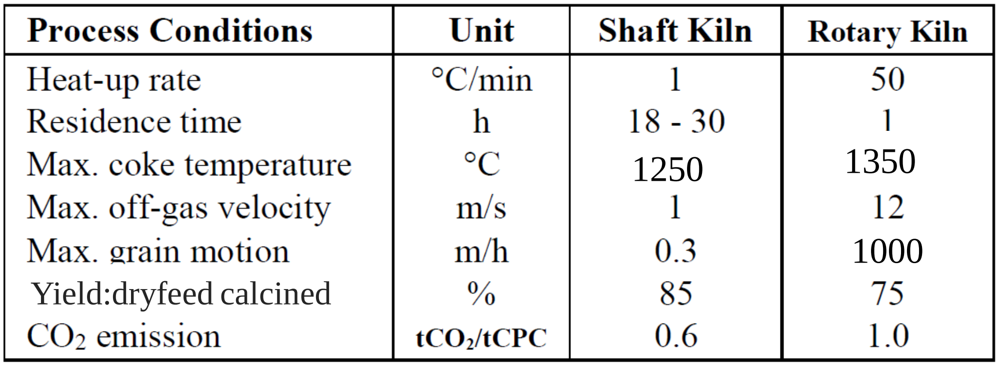


Figure 2.5 Shaft furnace concept [59]

The differences between two processes have a significant impact on some calcined coke quality parameters. The most universally reported difference is the higher bulk and apparent density achieved with a shaft calciner. This is due to the slower heat up rate of green coke. The loss of VM creates porosity in coke. Lower VM gives lower porosity (and higher density) so lower VM green coke is always preferred. Porosity is also a function of the heat-up rate of the coke. Faster heat-up rates create higher porosity and lower bulk density [15, 58, 60]. Shaft-calcined coke has high levels of -75 μm fines. This can result in significant dusting problems. It also necessitates high refractory volume and mass, which results in higher refractory cost. The level of automation is one of the advantages of rotary kilns. Labor requirement is higher for shaft calciner operation [60]. In Table 2.1 the major process parameters of a shaft kiln are compared with those of a rotary kiln.

Table 2.1 Comparison of typical calcination conditions of a shaft kiln and a rotary kiln [59]



Process Conditions	**Unit**	**Shaft Kiln**	**Rotary Kiln**
Heat-up rate	°C/min	1	50
Residence time	h	18 - 30	1
Max. coke temperature	°C	1250	1350
Max. off-gas velocity	m/s	1	12
Max. grain motion	m/h	0.3	1000
Yield:dryfeed calcined	%	85	75
CO_2 emission	$tCO_2/tCPC$	0.6	1.0

2.5. Desulfurization

It is known from the previous studies that the temperatures at which the calcination of high-sulfur green petroleum coke is traditionally carried out are not sufficient to reduce the sulfur content of coke to an acceptable value for aluminum smelters. Hence, the desulfurization of high sulfur coke is necessary [61]. The process which involves the breaking of C-S bonds in organic groups and the subsequent separation of sulfur is called desulfurization, and this can be achieved in several ways: calcination at higher temperatures, hydrodesulfurization, and chemical treatment with different agents, solvents, and acids [43].

2.5.1. Solvent Extraction

In solvent extraction, coke is treated with different solvents to selectively dissolve sulfur. Based on the fact that similar chemical structures have greater tendency to be reciprocally soluble in one another, solvents including aromatic and similar organic compounds might be used for the extractive desulfurization of petroleum cokes where the sulfur is mostly in organic form and exists as thiophenes [62]. Extractive desulfurization experiences with coal showed that weak organic acids like phenols are more effective than other organic solvents [63].

Many studies have been carried out on solvent extraction of petroleum coke by a large variety of solvents by several researchers [64-68]. It was found that while no sulfur removal was seen with the use of petroleum ether, dioxane or hydrochloric acid; o-chlorophenol, pyridine, phenol, furfural, chlorex, aqua regia, molten NaOH, naphthalene, p-cresol, xylene, benzene, nitrobenzene, ethanolamine, toluene, and acetone led to 1-25% sulfur removal from the petroleum coke [39, 66, 67, 69]. The two highest sulfur removals of 20% and 19% were found at 160°C in 2 h with the use of o-chlorophenol and pyridine as solvent, respectively. It was observed that sulfur removal increased with extraction temperature and time while it decreased with increasing coke particle size [69].

Agarwal et al. (2011) [42] applied the organodesulfurization technique using a potential solvent system of N-methyl-2-pyrolidone (NMP) containing small amounts of ethylenediamine (EDA). They also used morpholine, o-chlorophenol, and several other solvents for the desulfurization of petroleum coke. When high sulfur coke sample was subjected to organorefining using N-methyl-2-pyrolidone (NMP) containing small amounts of ethylenediamine (EDA), almost 34-41% sulfur removal was found within 2 h extraction time at room temperature. With the separate treatment of o-chlorophenol, tetrachloroethylene, trichloroethylene, and morpholine solvents, almost 28-50% of sulfur was removed from the coke structure in an optimum extraction time of 2 h. Among these solvents, trichloroethylene was found to be the most effective. Morpholine is also known to be used to remove organic S from coal or oil. It gave more than 40% desulfurization in 2 h with petroleum coke [42].

When ferric chloride and benzene were used consecutively, more than 35% sulfur removal was obtained by Aly et al. (2003) [37]. In this work, Egyptian petroleum coke was treated with ferric chloride and benzene one after another, and more than 35% desulfurization was achieved. It was found that when the concentration of ferric chloride increases, desulfurization degree increases up to a certain residence time which was found as 45 min. Effect of solvent-to-feed ratio (S/F) and coke particle size on sulfur removal was also examined in this work. It was observed that the desulfurization increases with increasing S/F ratio and decreasing particle size [37].

Pre-oxidation and chemical oxidation treatments were applied to petroleum cokes prior to solvent extraction by Ibrahim (2011) [62] and Philips et al. (1977) [69]. It was reported that pre-oxidation at a moderate temperature (327°C) and chemical oxidation make petroleum coke more suitable for solvent extraction. O-chlorophenol and pyridine solvents were used to extract sulfur, and 76% and 69% desulfurization were achieved, respectively. It was found that, with oxidation, the coke porosity and surface area of coke increased due to the creation of micro and macro porosity [62]. In the work of Philips (1977) [69], about 40% sulfur removal was obtained when coke was treated consecutively with nitric acid and o-chlorophenol. When the order of these two treatments was reversed, about 35% sulfur removal has been achieved [69]. Extraction of sulfur in petroleum coke using a large variety of solvents, which were done by different workers, was summarized in Table 2.2.

Table 2.2 Previous works on the desulfurization of petroleum coke by solvent extraction

Solvent	**S (wt %) in coke**	**Solution-to-coke ratio (vol:wt)**	**Reaction time (min)**	**Reaction Temperature (°C)**	**Particle size (μm)**	**Max desulf. (%)**	**Reference**
Air oxidation+ o-chlorophenol	7.8	N/A	15-120	327-25	-250	76	Ibrahim (2011) [62]
Air oxidation+ pyridine	7.8	N/A	15-120	327-25	-250	69	Ibrahim (2011) [62]
N-methyl-2-pyrrolidone + ethylenediamine	6.8	17:1	120	25	-250+125	41.4	Agarwal et al. (2011) [42]
Trichloroethylene	6.8	17:1	120	25	-250+125	41	Agarwal et al.(2011) [42]
Morpholine	6.8	17:1	120	25	-250+125	40	Agarwal et al. (2011) [42]
Tetrachloroethylene	6.8	17:1	120	25	-250+125	35	Agarwal et al. (2011) [42]
Ferric chloride+ benzene	5-5.2	10:1	45	80	100-200	35	Aly et al. (2003) [37]
Nitric acid+ o-chlorophenol	7.5	N/A	N/A	N/A	-55	40	Philips et al. (1977) [69]

Solvent	S (wt %) in coke	Solution-to-coke ratio (vol:wt)	Reaction time (min)	Reaction Temperature (°C)	Particle size (μm)	Max desulf. (%)	Reference
Nitric acid (HNO_3-14%) + N-methyl-2-pyrrolidone+ ethylenediamine	6.8	N/A	N/A	25	-250+125	38.5	Agarwal et al. (2011) [42]
Nitric acid	7.5	6 N of Nitric acid	240	102	-55	30	Philips et al. (1977) [69]
o-chlorophenol	6.8	17:1	360	25	-250+125	28.5	Agarwal et al. (2011) [42]
	7.5	5:1	120	160	-55	19	Philips et al. (1977) [69]
NaOH-10% aq.	6.8	N/A	360	522	-250+125	26.74	Agarwal et al. (2011) [42]
Nitric acid (HNO_3-14%)	6.8	N/A	360	25	-250+125	25.5	Agarwal et al. (2011) [42]
Molten NaOH	1.26	N/A	90	25	-250+210	24	Sabott (1952) [67]
Pyridine	1.26	N/A	240	25	-250+210	19	Sabott (1952) [67]
	5.8	250 ml of solvent	2880	25	-841+177	8.8	Parmar et al. (1977) [66]
Aqua regia	1.26	-	120	25	-250+210	14	Sabott (1952) [67]
Molten phenol	1.26	-	120	25	-250+210	14	Sabott (1952) [67]

Solvent	S (wt %) in coke	Solution-to-coke ratio (vol:wt)	Reaction time (min)	Reaction Temperature (°C)	Particle size (μm)	Max desulf. (%)	Reference
Furfural	1.26	-	240	25	-250+210	14	Sabott (1952) [67]
	5.8	250 ml of solvent	120	25	-841+177	5.2	Parmar et al. (1977) [66]
Chlorex	1.26	-	240	25	-250+210	13	Sabott (1952) [67]
Molten naphthalene	1.26	-	120	25	-250+210	13	Sabott (1952) [67]
p-Cresol	5.8	250 ml of solvent	2880	25	-841+177	8.8	Parmar et al. (1977) [66]
Xylenes	5.8	250 ml of solvent	2880	25	-841+177	8.6	Parmar et al. (1977) [66]
Nitrobenzene	5.8	250 ml of solvent	2880	25	-841+177	7.4	Parmar et al. (1977) [66]
Benzene	1.26	250 ml of solvent	360	25	-250+210	1	Sabott (1952) [67]
	5.8	250 ml of solvent	2880	25	-841+177	7.2	Parmar et al. (1977) [66]
Toluene	5.8	250 ml of solvent	2880	25	-841+177	5	Parmar et al. (1977) [66]

Despite promising results for chemical desulfurization, this method is not practical for petroleum cokes that are used for anode production. It is a costly process which requires a considerable amount of solvent consumption and may leave residues in coke that are not removable even after washing.

2.5.2. Thermal Desulfurization

During the calcination process, the sulfur content of green petroleum coke decreases due to heat treatment and is referred to as thermal desulfurization [27]. Many studies have been done on this method [26, 27, 39, 40, 43, 50, 70-73].

In thermal desulfurization, green coke is directly heated in a single stage to a specific temperature above the calcination temperature and kept at that temperature for a certain period of time [61]. It was reported that desulfurization could be an added asset to the petroleum coke calcination if it can be shown to occur to a significant degree within the temperature range of calcination. The desulfurization efficiency is not only affected by the maximum temperature to which the coke is heated, it also depends on other factors such as initial sulfur and impurity contents of the coke, particle size, rate of heating, gas atmosphere, and soaking time at the maximum temperature [39, 74]. The amount of sulfur removal with thermal desulfurization and its effects on coke density and porosity appear to be directly related to the sulfur and volatile matter contents in green coke as well as the coke structure [74, 75].

Previous works divided the calcination and thermal desulfurization process into two stages, which is explained by the following phenomena [38, 39, 72, 73, 76]:

The initial stage starts at temperatures between 100-200°C with the removal of moisture (dehydration) [73, 77, 78]. Reactions begin at temperatures close to those for coke production (460-480°C) [77]. Sulfur bound on the coke surface and in the coke pores starts to evolve around 500°C [38, 39, 73]. With devolatilization, the release of condensable hydrocarbons from coke occurs between 450 and 700°C. Non-condensable compounds are released from coke between 600 and 1200°C [80]. Figure 2.6 shows the evolution of volatiles for uniform heating (up to 1000°C) of a high sulfur coke produced from delayed coking.

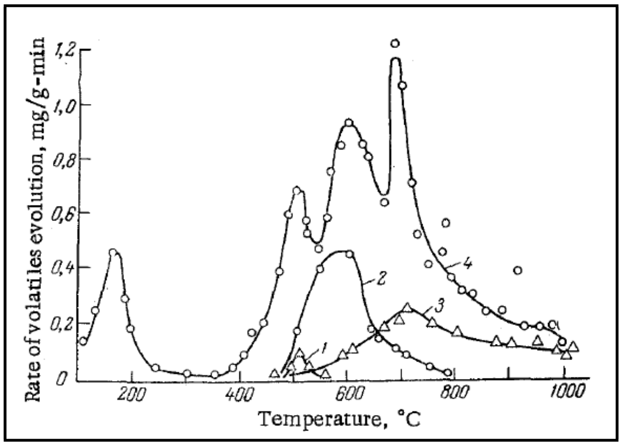


Figure 2.6 Evolution of volatile matter from high sulfur coke (heating rate 4°C/min): 1) ethane+ethylene; 2) methane; 3) hydrogen; 4) total [77]

Simultaneously with the devolatilization reactions at higher temperatures (700-1000°C), the cracking of side chains of aromatic hydrocarbons including some sulfurous hydrocarbons take place; and with further reactions, stable compounds such as CH_4, C_2H_6, C_3H_8, H_2, and H_2S are produced. The probability of each chain being detached is determined by the stability of its bond with the coke molecules. The results from previous studies demonstrate that sulfur is separated in the form of CS_2, COS, H_2S, and RSH (mercaptans; R represents alkyl or aryl group) in this step [38, 73, 77].

Sulfur which is found on the coke surface or in the coke pores bound by capillary condensation, adsorption or chemisorption is the greater part of sulfur separated at this stage. Furthermore, the sulfur that remains evolves in the form of H_2S and RSH, which are produced by the cracking of acyclic sulfur-hydrocarbon compounds. As a result of the separation of sulfur bonds mentioned above, the initial phase of the thermal treatment enables the reduction of total sulfur content of petroleum coke [73].

The final phase occurs in the temperature range of 1000-1400°C. In this stage, the separation of sulfur is observed in the form of CS_2 and elemental sulfur. H_2S and SO_2 are also formed in this temperature range. It can be stated that the second phase of the calcination process is characterized by a rapid rise in desulfurization for all types of petroleum coke samples that are exposed to thermal treatment [73]. This is due to the fact that the available energy becomes sufficiently high for the decomposition of stable sulfur-hydrocarbon constituents up to those of thiophene structure [39].

From the previous findings, it can be concluded that the amount of sulfur in calcined coke depends on hydrocarbon-sulfur as well as metal-sulfur and sulfur-metal-hydrocarbon constituents that exist in coking feedstock as well as those generated in the course of coking or calcining process. Metal content in petroleum coke may create organometallic complexes which are basic refractory sulfur-metal-hydrocarbon structures and do not change during calcination [73, 79].

El-Kaddah et al. (1973) [26] and Hussein et al. (1976) [40] investigated the thermal desulfurization of coke and obtained 91% and 80% sulfur removal at 1600ºC and 1500ºC, respectively. Paul et al. (2001) [71] obtained around 91% desulfurization with the calcination of sponge coke at 1649ºC with 1 hour soaking time. Sulfur decreases with increasing temperature as given in Figure 2.7. It was observed that shot coke was slightly more resistant to desulfurization up to 1467ºC, but beyond 1538ºC, showed a similar trend to that of sponge coke.

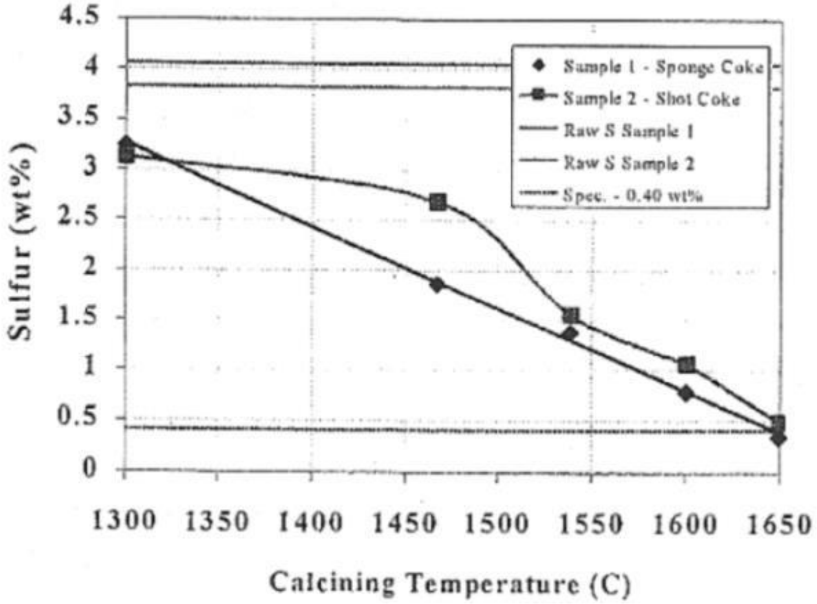


Figure 2.7 Sulfur remaining in coke as a function of calcination temperature [71]

It is stated that at temperatures above 1300ºC, the desulfurization can increase dramatically [27, 72, 73]. These temperatures are high enough for the decomposition of sulfur-hydrocarbon compounds like thiophene. The sulfur loss at different calcination temperatures is given in Figure 2.8 for different initial sulfur contents of coke [27].

In the work of Chen et al. (2008) [50], calcination was performed in the temperature range of 900-1600ºC with a holding time of 60 min. They obtained the same sharp increase in desulfurization after 1300ºC as Edwards et al. (2007) [27]. They also indicated that the desulfurization increases quickly with an incremental increase in the calcination temperature when it surpasses 1400ºC. A desulfurization ratio of 85% had been achieved when the temperature reached 1600ºC (Figure 2.9). In the work of Ibrahim (2005) [80], high sulfur petroleum coke with particle size range of 0.85-1.60 mm was desulfurized from 300 K (7°C) to 1700 K (1437°C) with a heating rate of 3.5°C/min. The residence time at maximum temperature was 180 min. Sulfur content of coke decreased remarkably starting from 1100 K. 46.75%, 58.44% and 80.5% sulfur removal was obtained at 1177°C, 1277°C and 1377°C, respectively (Figure 2.10). Figure 2.9 and Figure 2.10 show the change in desulfurization ratio at different temperatures.

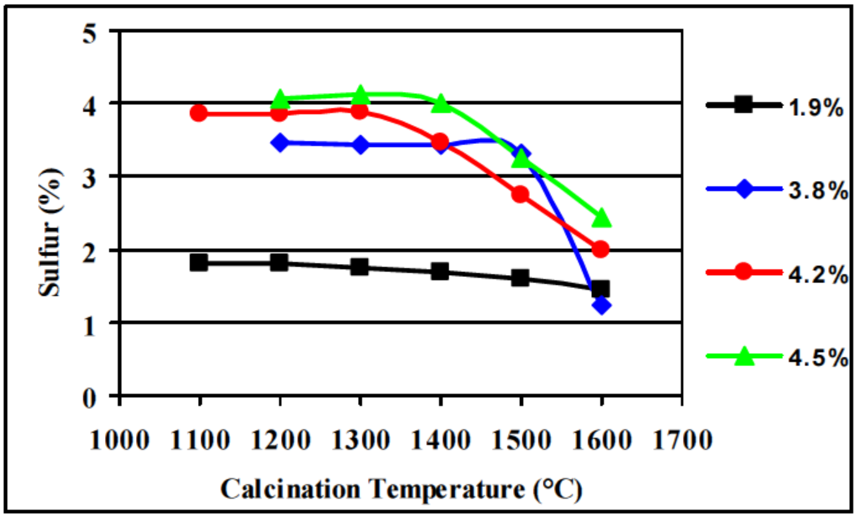


Figure 2.8 Sulfur removal at different calcination temperatures for cokes with various initial S% [27]

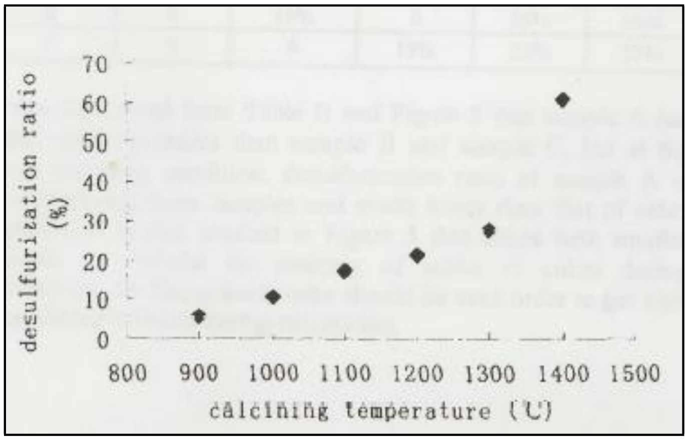


Figure 2.9 The change in desulfurization ratio at high calcination temperatures [50]

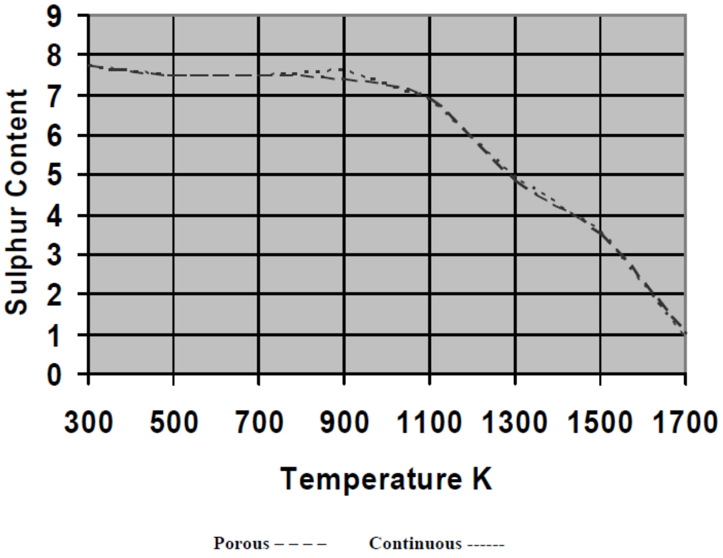
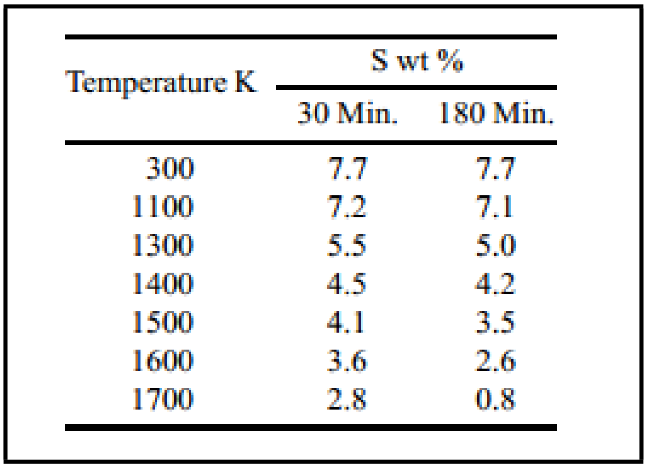


Figure 2.10 The change in coke sulfur content during thermal treatment [80]

Residence (holding) time at maximum temperature has also an influence on the thermal desulfurization. Ibrahim et al. (2004) [76] examined the effect of residence time at the maximum temperature and found that increasing the residence time from 30 to 180 min had remarkably improved the desulfurization efficiency, particularly in the temperature range 1327-1527ºC. In the work of Chen et al.(2008) [50], it was found that the extent of desulfurization increases with longer holding time at temperatures of 900-1300ºC. The same tendency has been observed in the work of

Vrbanovic (1980) [73]. It was shown that the effect of increasing residence time on sulfur removal is more significant for the desulfurization temperatures above 1300ºC. The impact of holding time on the desulfurization level is given in Figure 2.11 and Figure 2.12 [73, 76].



Temperature K	S wt %	
	30 Min.	180 Min.
300	7.7	7.7
1100	7.2	7.1
1300	5.5	5.0
1400	4.5	4.2
1500	4.1	3.5
1600	3.6	2.6
1700	2.8	0.8

Figure 2.11 The effect of residence time on the desulfurization [76]

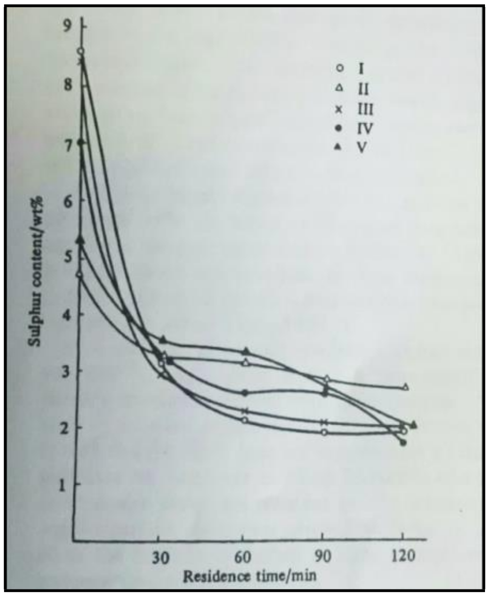


Figure 2.12 Sulfur content versus residence time for several cokes calcined at 1400ºC. Particle size 1 mm [73]

Thermal desulfurization of petroleum coke has been investigated by many researchers under several different conditions and for different coke types. Table 2.3 present a summary of these studies.

Table 2.3 Previous works on thermal desulfurization of petroleum coke

Temperature/holding time	**Heating rate**	**Initial S in coke (wt %)**	**Particle Size (mm)**	**Max desulf. (%)**	**Reference**
1277ºC / 3 h 1427ºC / 3 h	3.5ºC/min	8	Coke fines	62.02 89	Ibrahim (2014) [81]
1300ºC / 5 min	50ºC/min	3.61-Anisotropic	-0.3	8.5	Gagnon et al. (2013) [82]
1400ºC / 5 min	50ºC/min	3.61-Anisotropic	-0.3	8.5	
1500ºC / 5 min	50ºC/min	3.61-Anisotropic	-0.3	16.8	
1300ºC / 5 min	50ºC/min	5.37-Isotropic	-0.3	16.2	
1400ºC / 5 min	50ºC/min	5.37-Isotropic	-0.3	21.8	
1500ºC / 5 min	50ºC/min	5.37-Isotropic	-0.3	33	
1300ºC / 5 min	50ºC/min	3.8-Anisotropic	-0.3	9.2	
1400ºC / 5 min	50ºC/min	3.8-Anisotropic	-0.3	13.1	
1500ºC / 5 min	50ºC/min	3.8-Anisotropic	-0.3	23.6	
1300ºC / 1 h	N/A	2.59	0-4	27.9	Chen et al. (2008) [50]
1400ºC / 1 h	N/A	2.59	0-4	60	
1500ºC / 1 h	N/A	2.59	0-4	75	

Temperature/holding time	**Heating rate (ºC/min)**	**Initial S in coke (wt %)**	**Particle Size (mm)**	**Max desulf. (%)**	**Reference**
1600ºC / N/A	N/A	4.5	N/A	52.4	Edwards et al. (2007) [27]
1177 ºC / 180 min	3.5	7.7	0.85–1.60	46.75	Ibrahim (2005) [80]
1277 ºC / 180 min	3.5	7.7	0.85–1.60	58.44	
1377 ºC / 180 min	3.5	7.7	0.85–1.60	80.5	
1427ºC / 180 min	3.5	7.7	0.85–1.60	88	
1227ºC / 180 min	3.5	7.7	0.85–1.60	54.5	Ibrahim et al. (2004) [76]
1327ºC / 30 min	3.5	7.7	0.85–1.60	53.2	
1327ºC / 180 min	3.5	7.7	0.85–1.60	66.2	
1427ºC / 30 min	3.5	7.7	0.85–1.60	63.6	
1427ºC / 180 min	3.5	7.7	0.85–1.60	90	
1300ºC / 30 min	55	4.05	-6.73	19.75	Paul et al., (2001) [71]
1538ºC / 30 min	55	4.05	-6.73	65.9	
1650ºC / 1 h	55	4.05	-6.73	91	
1200-1500ºC	N/A	4.2	-6.73	48	Hardin et al. (1994) [75]
1200-1500ºC	N/A	4.1	-6.73	60	

Temperature/holding time	Heating rate (ºC/min)	Initial S in coke (wt %)	Particle Size (mm)	Max desulf. (%)	Reference
1400ºC / 1 h	N/A	4.9	N/A	59.2	Nadkarni and Rhedey (1986) [83]
1400ºC / 1 h	N/A	4.9	N/A	75.5	
1200ºC / 30 min	N/A	6	1-3	14	Vrbanonic (1983) [72]
1200ºC / 3 h	N/A	6	1-3	18.16	
1400ºC / 30 min	N/A	6	1-3	28.7	
1400ºC / 3 h	N/A	6	1-3	61.3	
1400ºC / 1 h	N/A	8.6	1	75.2	Vrbanonic, (1980) [73]
1400ºC / 2 h	N/A	8.6	1	77	
1400ºC / 1 h	N/A	7.01	1	62.5	
1400ºC / 2 h	N/A	7.01	1	75.6	
1400ºC / 1 h	N/A	8.6	1	75.2	Vrbanonic, (1980) [73]
1400ºC / 2 h	N/A	8.6	1	77	
1400ºC / 1 h	N/A	7.01	1	62.5	

Temperature/holding time	Heating rate (ºC/min)	Initial S in coke (wt %)	Particle Size (mm)	Max desulf. (%)	Reference
1400ºC / 1 h	30	3.44	N/A	53.5	Akhmetov et al. (1980) [44]
1400ºC / 2 h	30	3.44	N/A	73.8	
1400ºC / 3 h	30	3.44	N/A	78.2	
1450ºC / 1 hour	30	3.44	N/A	65.1	Akhmetov et al. (1980) [44]
1450ºC / 2 h	30	3.44	N/A	80.8	
1450ºC / 3 h	30	3.44	N/A	82.8	
1500ºC / 1 h	30	3.44	N/A	73.8	Akhmetov et al. (1980) [44]
1500ºC / 2 h	30	3.44	N/A	82.8	
1500ºC / 3 h	30	3.44	N/A	85.75	
1500ºC /4 h	N/A	5.51	+1.676	71	Hussein et al. (1976) [40]
1400ºC / 4 h	N/A	5.51	+1.676	51	
1400ºC / 1 h	N/A	8.83- Delayed coke	-1	44.3	El-Kaddah et al. (1973) [26]
1400ºC / 3 h	N/A	8.83- Delayed coke	-1	88.8	
1600ºC / 15 min	N/A	8.83- Delayed coke	-1	91	

1350ºC / 145 min	N/A	4.6	N/A	32.6	Syunyaev et al. (1967) [79]
1350ºC / 370 min	N/A	4.6	N/A	60.9	
1450ºC / 50 min	N/A	4.6	N/A	50	Syunyaev et al., (1967) [79]
1450ºC / 90 min	N/A	4.6	N/A	63	
1450ºC / 300 min	N/A	4.6	N/A	76.1	

The high temperatures required for the thermal desulfurization result in structural changes in petroleum coke during sulfur evolution. The sudden irreversible thermal expansion, called “puffing” takes place in the range 1400-1800°C [84]. This phenomenon has been studied comprehensively by many researchers [85-88]. The release of sulfur from petroleum coke at certain temperatures has a detrimental effect on the coke structure. Puffing or popcorn effect occurs due to sulfur outbreak which results in increased porosity, reduced apparent density, and increased air reactivity. Puffing also causes lower mechanical strength, electrical and thermal conductivity as well as crack formation [75, 84, 89]. Puffing is more likely to occur in high-sulfur petroleum cokes. Moreover, the extent of changes is influenced by the structure of green coke. More isotropic cokes physically degrade less during thermal desulfurization. However, highly isotropic cokes typically contain high Ni and V impurities and have quite high coefficients of thermal expansion. Such characteristics usually disqualify these kinds of thermally-desulfurized cokes for aluminum smelting use [90]. Rhedey (1988) [91] has examined the change in porosity expressed in volume percent with calcination temperature for two types of coke. The result is illustrated in the Figure 2.13.

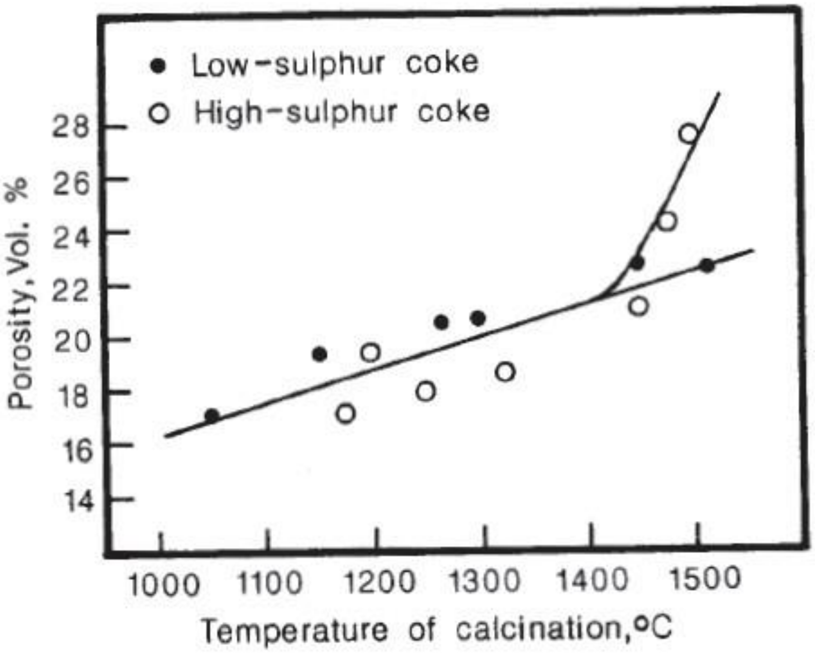


Figure 2.13 Coke porosity change as a function of calcination temperature [91]

As a result, it was shown by many studies that while this procedure effectively reduces the sulfur content of the coke, many physical properties substantially deteriorated during the heat treatment process in comparison with the coke properties after calcination at typical temperatures. Therefore, pure thermal treatment at high temperatures is not a suitable method for the desulfurization of high-sulfur petroleum coke in order to generate anode-grade calcined coke. It is also an energy–intensive and costly method with limited capacity which is difficult to apply at the industrial level.

2.5.3. Thermochemical Desulfurization

Thermochemical desulfurization is one of the desulfurization methods of petroleum coke. In this method, first, a chemical reagent is mixed with coke either in solid phase or by adding the solution of the reagent to coke which is followed by stirring and drying. After this, the chemically impregnated coke sample is heated to moderate temperatures (500-1000°C) in an inert atmosphere with subsequent water leaching and drying.

A variety of substances such as NaOH, Na_2CO_3, Na_2S, K_2CO_3, KOH, Na_2SO_4, and $NaHCO_3$ have been examined for thermochemical desulfurization. Wang et al. (2014) [92] obtained 91% sulfur removal from coke by NaOH addition in a reagent-coke mass ratio of 2 and calcination up to 500°C for 2 h. Hall et al.(1982) [93] and George (1977) [94] used NaOH-coke mass ratio of 0.18 and obtained 91% desulfurization at 760°C in 1 hour. Under the same conditions except by using 0.31 reagent-coke ratio, Lukasiewicz and Johnson (1960) [95] obtained 79% sulfur removal. George et al. (1978) [96] got 90% desulfurization at 850°C in 4 h with a NaOH-coke ratio of 0.4. It has been stated that as the temperature, the ratio of alkali to coke, and the reaction time increased, the desulfurization level of petroleum coke increased up to a certain point and reached optimum conditions [92]. The summary of the papers on the calcination of chemically impregnated cokes is given in Table 2.4.

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Table 2.4 The list of the works on thermochemical desulfurization available in the literature

Reagent	**Initial S % in coke**	**Reagent-to-coke ratio (wt)**	**Reaction time (h)**	**Reaction Temperature (°C)**	**Particle size (μm)**	**Max desulf (%)**	**Reference**
Addition of NaOH +calcination	6.5	2	2	500	N/A	98.1	Wang et al. (2014) [92]
Na_2CO_3 (salt roasting) + H_2O leach + HCl	4.03	6:1 + 3M reactant	3 + 24 + 72	450 + 70 + 70	-300	13	Gagnon et al. (2013) [82]
Na_2CO_3(salt roasting) + H_2O leach+ NaOH	4.03	6:1 + 3M reactant	3 + 24 + 72	450 + 70 + 70	-300	12	Gagnon et al. (2013) [82]
Na_2CO_3(salt roasting) + H_2O leach + Na_2CO_3	4.03	6:1 + 3M reactant	3 + 24 + 72	450 + 70 + 70	-300	10	Gagnon et al. (2013) [82]
Na_2CO_3(salt roasting) + H_2O leach + H_2SO_4 leaching	4.03	6:1 + 3M reactant	3 + 24 + 72	450 + 70 + 70	-300	1	Gagnon et al. (2013) [82]
Addition of Na_2CO_3+calcination	6.8	1	0.5	522	-250+125	56.68	Agarwal et al. (2011) [42]
Addition of Na_2CO_3+calcination	6.8	0.5	0.5	522	-250+125	46.94	Agarwal et al. (2011) [42]

Reagent	Initial S % in coke	Reagent-to-coke ratio (wt)	Reaction time (h)	Reaction Temperature (°C)	Particle size (μm)	Max desulf (%)	Reference
Molten caustic leaching (NaOH)	fluid coke-7.01 delayed coke-6.22	2	0.5	400	-250+149 -400+250	80	Ityokumbul (1994) [97]
Impregnation K_2CO_3 + calcination	5.8 (delayed coke)	1	1	870	-841+177	93	Hall et al. (1982) [93]
Impregnation Na_2S + calcination	5.8 (delayed coke)	0.18	2	800	-841+177	91.3	Hall et al. (1982) [93]
Impregnation NaOH + calcination	5.8 (delayed coke)	0.18	1	760	-841+177	91.3	Hall et al. (1982) [93]
Impregnation KOH + calcination	5.8 (delayed coke)	1	1	870	-841+177	90	Hall et al. (1982) [93]
Impregnation Na_2SO_4+calcination	5.8 (delayed coke)	0.33	2	800	-841+177	91.3-60	Hall et al. (1982) [93]
Impregnation NaOH + calcination	6 (fluid coke)	0.15	2	700-800	-400+250	41.6	Hall et al. (1982) [93]
Impregnation Na_2S+calcination	8.2 (fluid coke)	0.2	2	700-900	-250+177	39-27	Hall et al. (1982) [93]
Addition of Na_2CO_3+calcination	5.8 (delayed coke)	0.25	2	900	-841+177	93	George (1977) [94]

Reagent	Initial S % in coke	Reagent-to-coke ratio (wt)	Reaction time (h)	Reaction Temperature (°C)	Particle size (µm)	Max desulf (%)	Reference
Impregnation NaOH +calcination	5.8 (delayed coke)	0.176	1	760	-841+177	91	George (1977) [94]
Impregnation NaOH +calcination	8.2 (fluid coke)	0.4	4	850	-250+177	90	George (1977) [94] George et al. (1978) [96]
Addition of NaOH +calcination	5.64	0.31	1	760	-250+149	79	Lukasiewicz et al (1960) [95]
Addition of K_2CO_3 + calcination	5.64	0.31	1	760	-250+149	67	Lukasiewicz et al (1960) [95]
Addition of trona +calcination	5.57	0.2	1	760	-250+149	64	Lukasiewic et al (1960) [95]
Addition of $NaHCO_3$ + calcination	5.64	0.31	1	760	-250+149	51	Lukasiewicz et al (1960) [95]
Addition of Na_2CO_3 +calcination	7.01 5.64	0.2	1	760	-250+149	50	Lukasiewicz et al (1960) [95]
Addition of NaCl + calcination	5.64	0.31	1	760	-250+149	10	Lukasiewicz et al (1960) [95]

2.5.4. Hydrodesulfurization

Hydrodesulfurization is a widely used process by refineries to remove sulfur (S) from natural gas and refined petroleum products; but, it has not been applied yet to petroleum coke in industrial scale. The advantage of hydrodesulfurization compared to thermal desulfurization is that it allows sulfur removal in moderately high temperatures without affecting the petroleum coke properties. In hydrodesulfurization, green petroleum coke is heated in a fixed bed under a hydrogen or steam atmosphere, and it forms H_2S with sulfur present in coke. More efficient contact between hydrogen and coke can improve the sulfur removal [39].

The mechanism of hydrodesulfurization of coke can be described by the following steps: first hydrogen diffuses into the pores of coke particles and then reacts with sulfur compounds to form H_2S which can be described by the following reaction:

$$(\mathrm{C\text{-}S})_{\mathrm{solid}} + \mathrm{H_2} \leftrightarrow \mathrm{C_{solid}} + \mathrm{H_2S} \qquad (2.1)$$

After H_2S is formed, it diffuses from the pores to the outside of coke particles and from the surface of the particles to the fluid stream through the surrounding film layer. At high temperatures, H_2S reacts with coke particles and forms new stable carbon-sulfur compounds. The last two steps probably control the overall rate of desulfurization [64, 98].

It is indicated in the literature that a gas-solid reaction takes place during the hydrodesulfurization of fluid coke. First, methane and ethane form by thermal cracking, and then they react with hydrogen to produce hydrogen sulfide via the chemical reaction shown below:

$$B_2S(s) + 2H_2(g) \rightarrow 2BH(s) + H_2S(g) \qquad (2.2)$$

where B is any hydrocarbon group with which sulfur may be bonded [98].

Sulfur atoms in the coke structure can be placed at three different locations: on the outer surface of coke, on the walls of pores and cracks, and inside the coke surrounded by the dense wall. The degree of desulfurization obtained within a certain period of time depends mainly on the accessibility of sulfur to hydrogen or effective surface area available in addition to the fact that the desulfurization is strongly dependent on the temperature [99].

Hydrodesulfurization with Steam (H_2O)

Hydrodesulfurization with steam can be assumed to occur according to the following reaction:

$$CxSy + n\ H_2O \rightarrow y\ H_2S + (n/2)\ CH_4 + n\ CO + (x\text{-}3n/2)\ C \qquad (2.3)$$

where carbon monoxide and methane can react to produce more complex hydrocarbons [40]. The liberated hydrogen from the reaction shown below increases the reaction rate of the desulfurization process [40].

$$C + H_2O \rightarrow H_2 + CO \qquad (2.4)$$

The degree of sulfur removal from coke by hydrogen or steam was found to be strongly affected by the desulfurization temperatures [74]. Hussein et al. (1976) [40] carried out hydrodesulfurization of high sulfur coke in a steam atmosphere up to 1500ºC. It was found that sulfur removal up to 1300ºC is considerably more than that observed under only nitrogen or CO_2 atmospheres. When temperature was increased to 1400ºC, significant desulfurization took place. A maximum of 87% desulfurization was observed at 1500ºC with very fine particles. The dependence of sulfur removal on reaction temperature is given in Figure 2.14. It is indicated that the desulfurization by steam occurs only in the temperature range where the water-gas reaction becomes active and is accompanied by significant gasification of the coke [66].

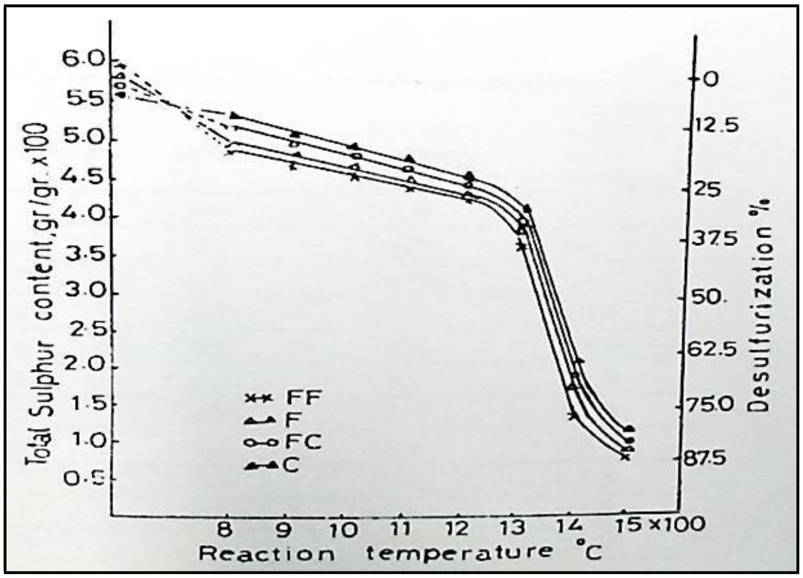


Figure 2.14 Effect of temperature on the sulfur removal from coke during hydrodesulfurization with steam [40]

Mason (1959) [100] and Parmar et al. (1977) [66] found 32.8% and 20% sulfur removal during hydrodesulfurization with steam. Reaction temperatures were 816ºC and 871ºC, and reaction times were 2 h and 4 h, respectively. Figure 2.15 shows the sulfur removal as a function of time at different temperatures for -20 +80 mesh (-0.841 mm +0.177 mm) particle size [66].

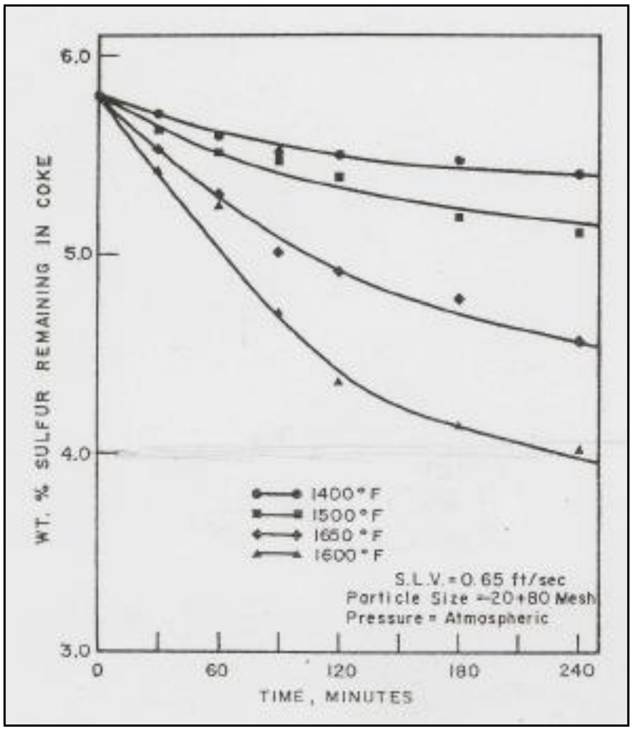


Figure 2.15 Variation of sulfur content of coke with time at different temperatures [66]

Table 2.5 gives a summary of works on hydrodesulfurization of petroleum coke by steam.

Table 2.5 Previous works on hydrodesulfurization of petroleum coke by steam

Reaction gas	**S % in coke**	**Particle size (µm)**	**Flow rate (ml/min)**	**Holding time (h)**	**Reaction T (°C)**	**Max desulf (%)**	**Reference**
Steam	5.96	+1676	420	0.5	1400 1500	71 80	Hussein et al. (1976) [40]
Steam	5.8	-841+177	-	4	871.11	32.8	Parmar et al. (1977) [66]
H_2+Steam	7	-500+250	150 H_2 +30 steam	2	815-915	20	Mason (1959) [100]

Hydrodesulfurization with Hydrogen

In several works, maximum desulfurization achieved under hydrogen atmosphere at low temperatures (800ºC and 850ºC) for reaction times of 2.5 h, 1.5 h, 160 min, and 2 h was 75%, 86.6%, 54%, and 87%, respectively [64, 98, 101, 102]. It was also reported by George (1975) [64] that more than 80% desulfurization was achieved at 700ºC with a 72 h reaction time while 62% desulfurization was achieved at 850ºC for the same period. 50% desulfurization was achieved at 850ºC in 2.5 h, which were the optimum conditions of the reported study [64]. Mahmoud et al. (1968) [65] achieved 93% desulfurization at 600ºC in 40 h in a fluidized bed. However, static bed desulfurization resulted in only 28% of sulfur removal at the maximum temperature of 600ºC in 4 h [65]. The effect of temperature on hydrodesulfurization reported by two previously mentioned works [64, 65] is given in Figure 2.16 and Figure 2.17. Figure 2.16 also shows the effect of particle size on the desulfurization of coke.

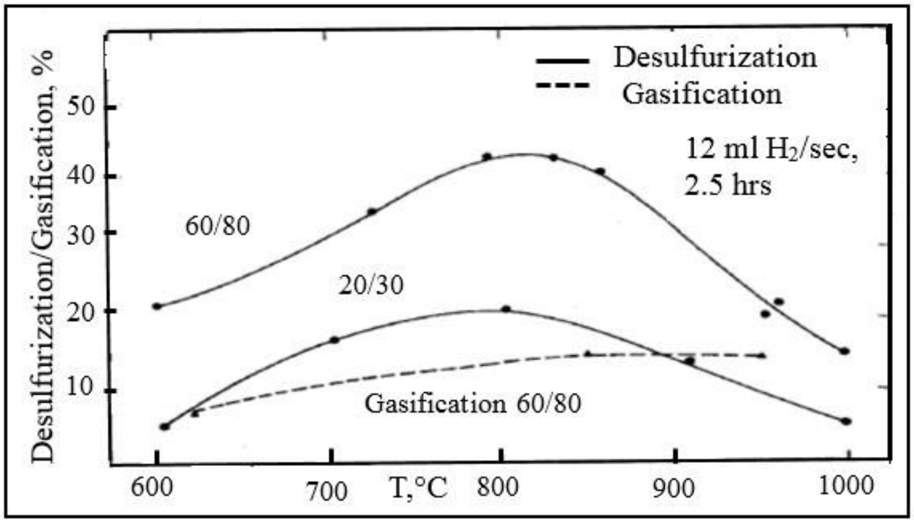


Figure 2.16 The effect of temperature on hydrodesulfurization for 60/80 mesh particles and the effect of particle size on hydrodesulfurization at 850ºC [64]

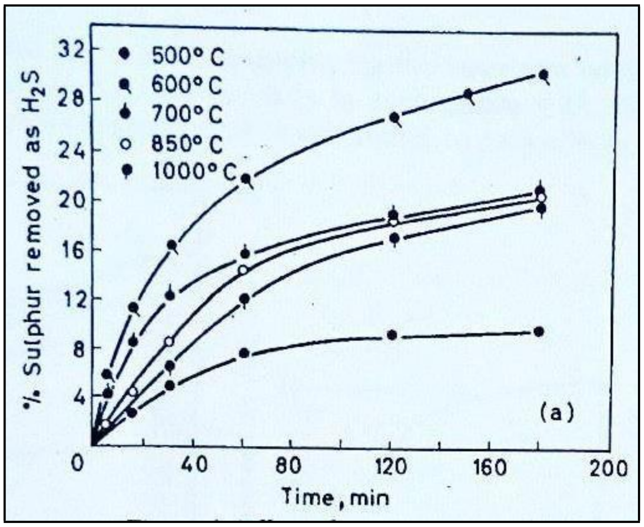


Figure 2.17 Effect of temperature on hydrodesulfurization in a static bed with H_2 [65]

The reason given for the highest sulfur removal observed at maximum temperatures of 600ºC [64] and 850ºC [65] is the occurrence of sintering above these temperatures. The agglomeration of the particles reduces the external surface area of the coke resulting in a decrease in rate of diffusion of hydrogen towards the interior of the coke particle and that of H_2S out of the particle [64, 65]. Another reason for the observation of such a maximum is based on the net rate of desulfurization, which is the consequence of two competing reactions. These are the rate of removal of unstable sulfur by hydrogen and the thermal fixation of sulfur by the reverse reaction to produce a more stable form of sulfur. It is possible that the latter reaction occurs more rapidly at higher temperature leading to such a maximum [64].

Mochida and his coworkers carried out the hydrodesulfurization of anode-grade petroleum coke in a hydrogen flow at temperatures of 650ºC, 750ºC, and 850ºC, and obtained 90%, 70%, and 45% desulfurization, respectively, in a 6 h desulfurization period with 10-150 µm size particles [103]. Desulfurization profiles of petroleum coke at different temperatures are given in Figure 2.18.

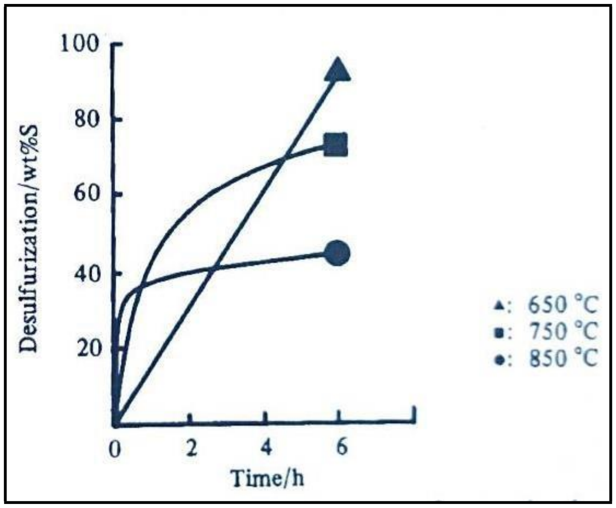


Figure 2.18 Hydrodesulfurization of coke at various temperatures [103]

Mochida and his coworkers also carried out hydrodesulfurization of needle coke which had a sulfur content of 0.6% and was in the form of lump and ground coke. Ground coke which had a diameter smaller than 74 μm was almost completely desulfurized after 6 h at 700ºC while 23% of sulfur in lump coke was removed at 700ºC after 10 h. At 650ºC and 750ºC, for lump needle coke, desulfurization reduced significantly to 10%. It is reported that the desulfurization of needle coke is much more difficult than regular-grade petroleum coke with high sulfur content [104]. Hydrodesulfurization of petroleum coke deposited on iron ores was studied in the temperature range of 650ºC to 900ºC to reduce the sulfur content suitable for direct reduction of iron ores, and 83% desulfurization occurred at 950ºC [99].

Different levels of desulfurization at different temperatures were explained in terms of variable extents of crack development because of the thermal expansion and shrinkage at the reaction temperature. This has been clearly indicated in Figure 2.19 which shows SEM microphotographs of coke surfaces before and after the hydrodesulfurization at two different temperatures [99]. It can be seen from this figure that the desulfurization induced many cracks on the surface. The number and size of cracks were strongly dependent on the desulfurization temperature: a higher temperature induced more cracks of larger width and length. The important factor is to increase the accessibility of gas to sulfur bound to coke. Both grinding and heat treatment in an inert atmosphere resulted in an increase in the extent of the desulfurization of coke, giving similar results at 750ºC and 950ºC. Partial gasification can be considered as another approach to increase the accessibility [99].

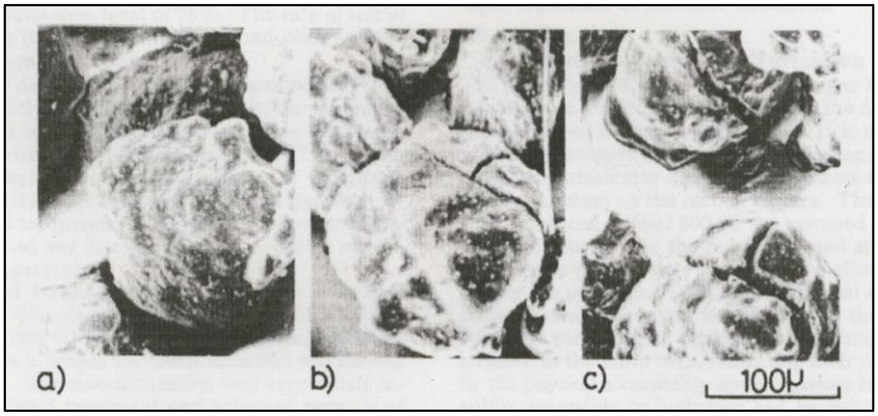


Figure 2.19 Microphotographs of coke surfaces: a) green coke, b) desulfurized coke at 650ºC, c) desulfurized coke at 950ºC [99]

Residence time of gas during hydrodesulfurization has a significant influence on sulfur loss from coke. It was observed in several studies that the higher the holding time is, the higher the desulfurization is. However, an optimum holding time have to be determined. George (1975) [64] who carried out several experiments using -250 µm +177 µm particles and 12 ml/s of H_2 for different periods of time, 25 min to 17 h, indicated that a substantial portion of the total desulfurization was achieved in 2.5 h. Figure.2.20 shows the dependence of desulfurization on the holding time.

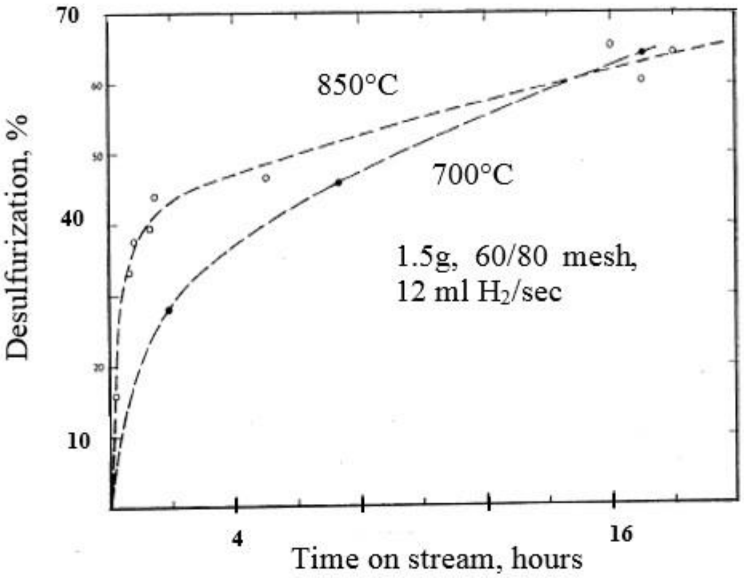


Figure.2.20 Influence of holding time on hydrodesulfurization at 850ºC and 700ºC [64]

The effect of particle size on the extent of desulfurization is quite significant. The increase in the level of desulfurization with the use of smaller particle sizes shows that the diffusion of H_2S out of the pores of the particle limits the desulfurization [64]. It can be seen from Figure 2.21 that reducing the particle size increases the level of desulfurization of oil sands coke. This might be due to (a) an increase in the external surface area by opening the previously unexposed pores and (b) a decrease in the resistance of the pore diffusion path [65, 66].

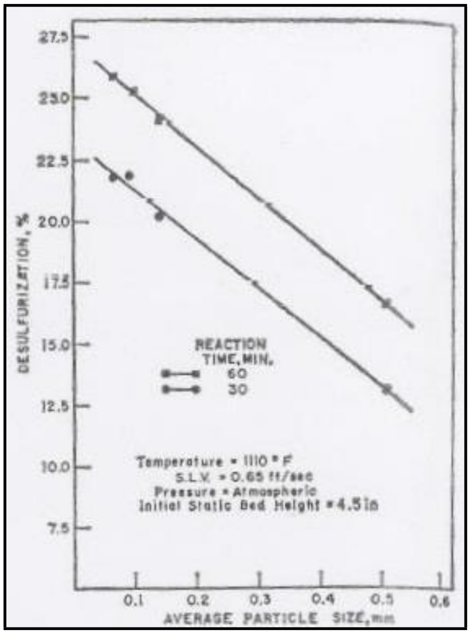


Figure 2.21 Effect of particle size on hydrodesulfurization [66]

Saha et al. (1995) [98] observed a small variation in the extent of desulfurization while working with three different samples with small particle sizes of -44 µm, -53 µm +44 µm, and -74 µm +53 µm. Figure 2.22 shows the variation of desulfurization with particle size and hydrogen flow rate for this study.

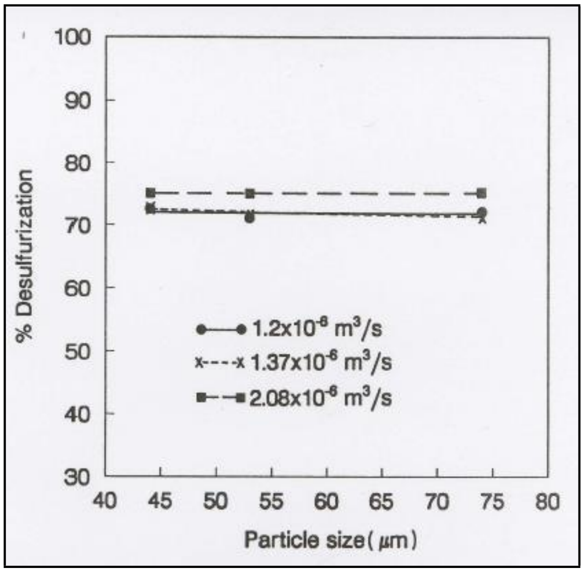


Figure 2.22 Influence of particle size and hydrogen flow rate on % desulfurization at 750ºC for 90 min experiments [98]

It has been found by many researchers that the rate of desulfurization increases with the hydrogen flow rate [64, 65, 100]. The effect of hydrogen flow rate on hydrodesulfurization at different temperatures and particles sizes is illustrated in Figure 2.23.

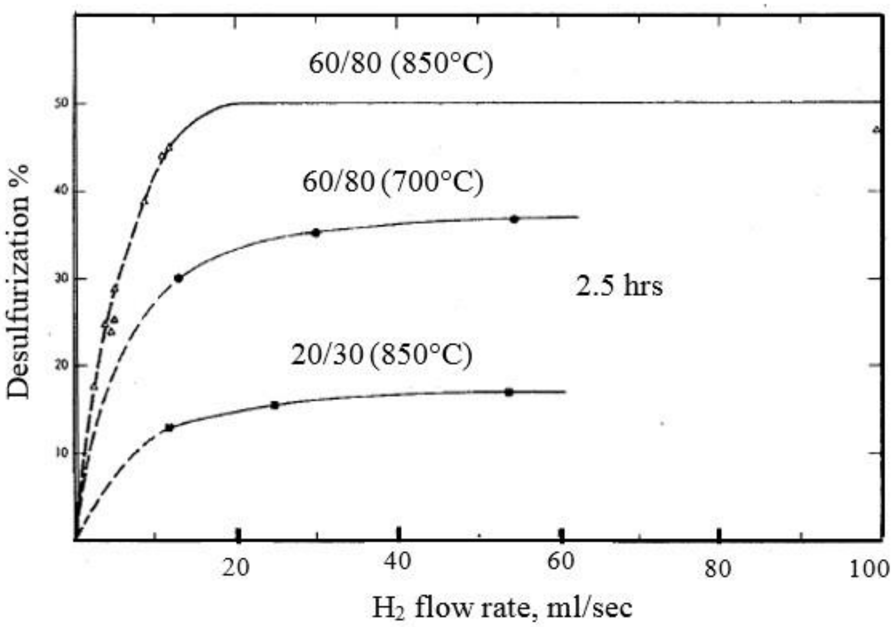


Figure 2.23 Effect of hydrogen flow rate on hydrodesulfurization at 850 and 700ºC for 60/80 mesh particles and the influence of particle size at 850ºC (2.5 h): 1st curve, 60/80 mesh - 850ºC; 2nd curve, 60/80 mesh - 700ºC; 3rd curve 20/30 mesh - 850ºC [64]

Saha and Tollefson (1995) [98] examined the effect of H_2 flow rate at different reaction temperatures. Three different flow rates ranging from 1.2×10^{-6} m^3/s (72 ml/min) to 2.1×10^{-6} m^3/s (150 ml/min) were used in the temperature range of 973 K (700ºC) to 1073 K (800ºC). At 998 K (725ºC), desulfurization increased from 65.6% to 69.1% as the gas flow rate was increased from 1.2×10^{-6} m^3/s (72 ml/min) to 2.1×10^{-6} m^3/s (150 ml/min) whereas desulfurization varied from 75.8% to 78.8% at

1048 K (775ºC) over the same gas flow increase. The effect of flow rate on percent desulfurization at different temperatures can be seen in Figure 2.24.

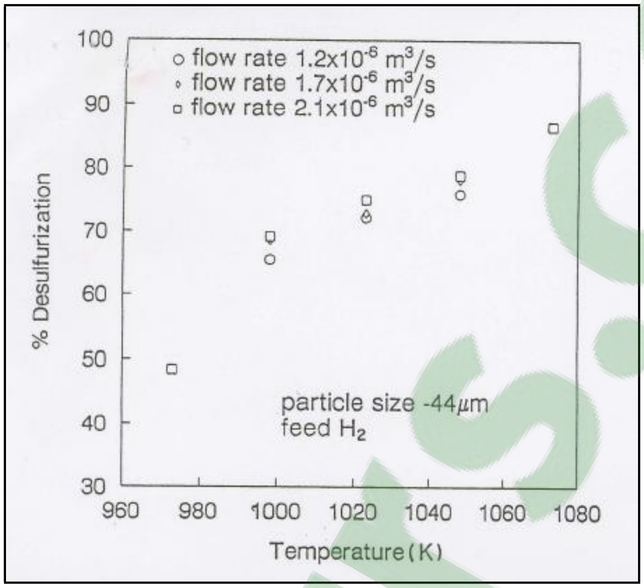
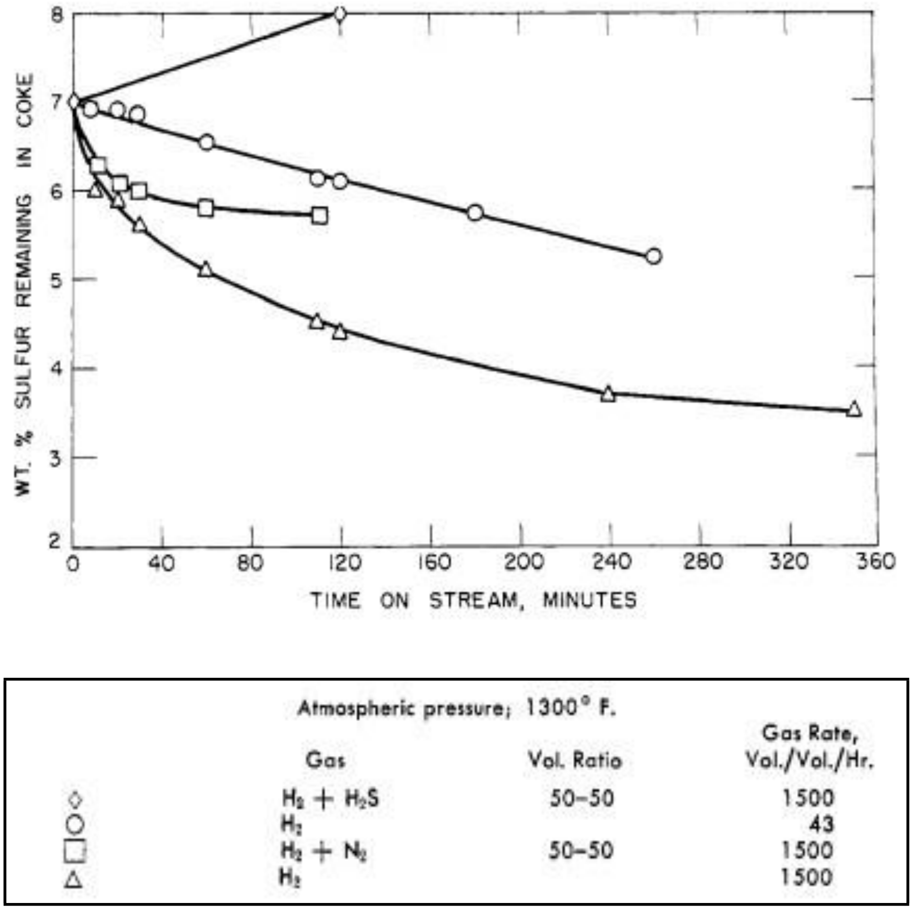


Figure 2.24 Effect of temperature and flow rate on % desulfurization for 90 min [98]

The adverse effect of hydrogen sulfide during hydrodesulfurization was determined by several researchers [64, 100]. It has been stated that as the partial pressure of H_2S was increased, desulfurization decreased and the sulfur level had increased by the occurrence of following reverse reaction between coke and H_2S.

$$H_2S + C \rightarrow C\text{-}S + H_2 \qquad (2.5)$$

where reaction product is new stable compounds with (C-S) bond [64]. The effect of H_2S on the sulfur content of coke during desulfurization is given in Figure 2.25.



Atmospheric pressure; 1300° F.

	Gas	Vol. Ratio	Gas Rate, Vol./Vol./Hr.
◇	$H_2 + H_2S$	50–50	1500
○	H_2		43
□	$H_2 + N_2$	50–50	1500
△	H_2		1500

Figure 2.25 Adverse effect of added H_2S to petroleum coke during desulfurization [100]

The list of the works on hydrodesulfurization of petroleum coke and their experimental conditions are given in Table 2.6.

Table 2.6 Previous works on Hydrodesulfurization of petroleum coke by hydrogen

Reaction gas	S % in coke	Particle size (µm)	Gas flow rate (ml/min)	Holding time (hour)	Reaction Temperature (°C)	Max desulf. (%)	Reference
H_2	5.98	10-150 (mean particle size: 60)	48	6	650	90	Mochida et al (1987) [103]
				6	750	70	
				6	850	45	
H_2	5.5	375	0.5 L/min	40	600	93	Mahmoud et al. (1968)[65]
		-200+125	1 L/min	4	600	28	
H_2	7.7	200	10 L/h (10 kg/cm^{2}G)	2	800	87	Takanari et al. (1973) [102]
H_2	7.68	-44	126	1.5	800	86.6	Saha et al. (1995) [98]
H_2	2.6	70-230	48	2	950	77	Mochida et al. (1986)[99]
				10	850	60	
				28	650	37	
H_2	2.6	10-100	48	1	850	72	Mochida et al. (1986)[99]
				3	750	75	
				10	650	75	

H_2	5.4	250/177	720	2.5	850	75	George (1975) [64]
H_2	5.98	Lump coke (1-2-1 cm^3) *	48	20 10	650 850	60 20	Mochida et al. (1987) [103]
H_2	1.9	-210+50	1 atm- 2 L/g coke/h 6.5 atm- 20.5 L/g coke/h	2.67	450-850	45.7 91.5	Sef (1960) [101]
H_2	0.5	0.8-2.8 mm <74 µm	48 48	10 6	700 700	50 99	Mochida et al. (1988) [104]
H_2	7	-500+250	1500 vol/vol/h	5.8	704	50	Mason (1959) [100]
H_2	5.8	-841+177	N/A	4	598.9	27	Parmar et al. (1977) [66]
H_2	7.3	-420+250	120	2	700	31	George et al. (1982)[105]
H_2	0.5	Lump coke (1-2-1 cm^3)*	48 48	10 6 6	700 750 650	23 10 10	Mochida et al. (1988) [104]

Hydrodesulfurization of Chemically Treated Coke

The hydrodesulfurization of petroleum coke with alkaline reagents has been investigated in several studies. Hall et al. (1982) [93] achieved high sulfur removal such as 90% and 80% with the hydrodesulfurization of NaOH impregnated delayed and fluid coke, respectively. After impregnation of NaOH into delayed and fluid coke with NaOH/coke ratios of 0.038 and 0.06, respectively, hydrodesulfurization was carried out by hydrogen or hydrogen and steam at atmospheric pressure and 700ºC for 2 h followed by cooling and leaching with water. George et al. (1982) [105] obtained similar results to those of Hall and his coworkers under similar experimental conditions. They obtained 90% of desulfurization with NaOH-impregnated fluid coke (NaOH/coke ratio: 0.04) at 700ºC in 2 h. Parmar et al. (1977) [66] used Na_2CO_3 as chemical reagent with the Na_2CO_3/coke ratio of 0.05. After hydrodesulfurization with steam at 871ºC for 3 h, they obtained 19% sulfur removal. The summary of the papers on hydrodesulfurization of chemically impregnated cokes is given in Table 2.7. Although this method of hydrodesulfurization gives high sulfur removal, it is not suitable for petroleum cokes used for anode production. It requires a considerable amount of alkaline solvent consumption and may leave residues in coke that are not removable even after washing.

Table 2.7 Previous works on Hydrodesulfurization of chemically treated petroleum coke

Additional Treatment	**Reagent-to-coke ratio (mass)**	**Reaction gas**	**Gas flow rate**	**Particle size (μm)**	**Temperature /holding time**	**Initial S % in coke**	**Max desulf (%)**	**Reference**
Impregnation of NaOH before HDS	0.038	H_2	30 ml/g.min	-707+177	700ºC / 2 h	5.8 (delayed coke)	90	Hall et al. (1982) [93]
Impregnation of NaOH before HDS	0.04	H_2	120 ml/min	-400+250	700ºC / 2 h	7.3 (fluid coke)	90	George et al.(1982) [105]
Impregnation of NaOH before HDS	0.06	H_2+Steam	24 ml/g.min H_2 15 kPa steam pressure	-400+250	700ºC / 2 h	6 (fluid coke)	80	Hall et al. (1982) [93]
Impregnation of NaOH before HDS	0.06	H_2	30 ml/g.min	-400+250	700ºC / 2 h	6 (fluid coke)	60	Hall et al. (1982) [93]
Impregnation of NaOH before HDS	0.038	H_2	24 ml/g.min	-400+250	700ºC / 2 h	6 (fluid coke)	42	Hall et al.(1982) [93]
Impregnation of Na_2CO_3 before HDS	0.05	Steam	-	-841+177	871ºC / 3 h	5.8 (delayed coke)	19	Parmar et al. (1977) [66]

Hydrodesulfurization of Pre-oxidized/ Pre-heated Coke with Hydrogen

Parmar et al. (1977) [66] and Mason (1959) [100] examined the hydrodesulfurization of coke with pre-oxidation treatment. First, they treated coke with hydrogen and steam and obtained 20-30% sulfur removal. After the pre-oxidation of coke under suitable conditions, they achieved a significant level of desulfurization with H_2. It was found that pre-oxidized coke is not as sensitive to hydrodesulfurization temperatures as untreated coke, so higher temperatures were effectively used [100].

In the work of Mochida et al. (1987) [103], hydrodesulfurization of high sulfur petroleum coke was carried out at atmospheric pressure over the temperature range of 650 to 850ºC. The hydrodesulfurization of lump coke at 650ºC for 20 h gave the highest desulfurization for this coke as 60%. Grinding the coke enhanced the sulfur removal at both 650ºC and 750ºC to 90 and 70%, respectively, in 6 h. The cycles of desulfurization at 750ºC and then cooling to room temperature also increased the desulfurization of the lump coke to 60 %. Preheating the coke to 650ºC for 2 h which is followed by hydrodesulfurization at 750ºC for 2 h resulted in 80% sulfur removal. Preheating treatment was more efficient at 650ºC than at 850ºC for the same period of time. The lump coke which was exposed to preheating at 650ºC gave higher sulfur removal (80%) compared to that without preheating. When air oxidation treatment (gasification) was applied to the lump coke at 350ºC for 65 min followed by one stage hydrodesulfurization, 31% sulfur removal was obtained. The combination of air oxidation with cooling to room temperature after the first hydrodesulfurization of 2 h followed by 8 h of second desulfurization at 750ºC in 20 h of total residence time resulted in a sulfur removal of 65%. The experimental conditions and results of related works is given in Table 2.8. Although hydrodesulfurization with pre-heating and pre-oxidation gave high sulfur removal, it was found that these treatments increase the surface area of coke by opening micropores which result in structural change in the coke matrix [66]. Thus, these methods do not provide a suitable structure for petroleum cokes which are utilized in anode production.

Table 2.8 Previous works on Hydrodesulfurization of pre-treated petroleum coke

Additional Treatment	**Treatment conditions**	**Reaction gas**	**Gas flow rate (ml/min)**	**Particle size (µm)**	**Temperature /holding time**	**Initial S % in coke**	**Max desulf (%)**	**Reference**
Preheating + HDS+ cooling	Preheating-650ºC /2 h- 2 h of HDS - Cooling to room temperature - HDS	H_2	48	Lump coke 1-2-1 cm^3 *	750ºC / 20 h	5.98	80	Mochida et al. (1987) [103]
Preheating at N_2 atmosphere + HDS	1000ºC / 10 min 900ºC / 10 min 900ºC / 60 min	H_2	48	10-100	750ºC / 10 h	2.6	78 60 68	Mochida et al. (1986) [99]
Preoxidation + HDS	400ºC / 4.5 h	H_2	1500 vol/vol/h	500-250	760ºC / 5.8 h	7	77	Mason, (1959) [100]
Preoxidation + HDS	276ºC / 8 h	H_2	-	-841+177	650ºC / 8 h	5.8	75	Parmar et al. (1977) [66]
Airoxidation + HDS + cooling	Air oxidation 350ºC 65 min + 2 h HDS+ Cooling to room temperature+ 8 h HDS	H_2	48	Lump coke 1-2-1 cm^3 *	750ºC / 20 h	5.98	65	Mochida et al. (1987) [103]

Cooling to room temperature during HDS	Cooling after 8 h and 12 h of HDS + HDS	H_2	48	Lump coke 1-2-1 cm^3 *	750ºC / 20 h	5.98	60	Mochida et al. (1987) [103]
Cooling to room temperature during HDS	Cooling after 8 h and 12 h of HDS + HDS	H_2	48	Lump coke 1-2-1 cm^3 *	750ºC / 16 h	5.98	60	Mochida et al. (1987) [103]
Preheating+ HDS	650ºC / 2 h	H_2	48	Lump coke 1-2-1 cm^3 *	750ºC / 2 h	5.98	55	Mochida et al. (1987) [103]
Preheating+ HDS+ cooling	Preheating 850ºC/ 2 h+ 2 h HDS+ Cooling to room temperature+ HDS	H_2	48	Lump coke 1-2-1 cm^3 *	750ºC / 10 h	5.98	38	Mochida et al. (1987) [103]
Preoxidation + HDS	276ºC / 8 h	Steam	-	-841+177	885ºC / 4 h	5.8	34	Parmar et al. (1977) [66]
Air oxidation + HDS	Air oxidation 350ºC / 65 min	H_2	48	Lump coke 1-2-1 cm^3 *	750ºC / 2 h	5.98	31	Mochida et al. (1987) [103]
Preheating + HDS	Preheating 850ºC / 2 h	H_2	48	Lump coke 1-2-1 cm^3 *	750ºC / 2 h	5.98	24	Mochida et al. (1987) [103]

* The lump coke has a cuboid shape whose dimensions are 1 cm - 2 cm- 1 cm

2.6. Conclusions

Several methods which have been reported in the literature so far on petroleum coke desulfurization are presented in this chapter. Solvent extraction, chemical treatment with different agents and acids, thermochemical treatment, calcination at higher temperatures, hydrodesulfurization with steam and hydrogen combined with some additional treatments such as air oxidation, preheating or cooling to room temperature are the methods which were found in the literature and are explained in detail in this section. Chemical treatment with organic solvents, acids or other agents results in high percentage of sulfur loss from petroleum coke. Nevertheless, this method not only contaminates the coke, but also changes the coke structure which is not practical for petroleum cokes that are used in anode fabrication. Calcination at high temperature, which is called thermal desulfurization, was found to remove high quantity of sulfur from coke. This method is also not suitable for high sulfur cokes that are aimed for use in anode production due to the fact that it creates undesirable porosity in coke structure. It also requires high energy consumption which is not desirable in industry. Thermochemical desulfurization enables the desulfurization at lower temperatures by means of a chemical agent. However, it results in the contamination of coke as well as structural changes which disqualify such coke from use in anode making. The hydrodesulfurization method uses steam or hydrogen during calcination. According to the literature, it is possible to reduce the sulfur content of coke by this method at moderately high temperatures. Although many of the possible desulfurization methods found in the literature are not suitable for anode-grade coke production, hydrodesulfurization seem to offer possibility for such use of cokes in practice. As a result, hydrodesulfurization was chosen for the desulfurization of petroleum coke and was investigated in this master project.

CHAPTER 3

EXPERIMENTAL SET-UP AND TEST PROCEDURES

Based on the previous works related to desulfurization of petroleum coke and in order to achieve the objectives of the study, different sets of experiments were carried out systematically on thermal and hydrodesulfurization of green petroleum cokes. The sulfur content as well as the morphology of coke samples were analyzed using surface analysis and characterization techniques, which are explained in this chapter. The objective of this chapter is to introduce and discuss in detail the experimental conditions and systems used in the current study for desulfurizing and characterizing different petroleum coke samples. It consists of four sections: materials, sample analysis and characterization, thermal and hydrodesulfurization of green petroleum coke including the explanation of methods and principles for each case.

3.1. Materials

In this study, industrial high-sulfur green petroleum cokes from the same supplier with different sulfur contents have been used. Cokes A, C, and D are anisotropic sponge cokes whereas coke B has an isotropic structure. The hydrodesulfurization experiments were conducted only with coke D since this coke was received in large amounts. Although thermal desulfurization of all cokes and their characterization before and after thermal treatment were carried out, only the results with coke D are given in the results and discussion section. The rest of the results is presented in Appendix A. Physical and chemical properties of green petroleum cokes are given in Table 3.1. The real density and the proximate analysis of green coke D are given in Table 3.2.

Table 3.1 Physical and chemical properties of green coke A, B, C and D

Properties	**Green Petroleum Coke**			
	Coke A (sponge coke)	Coke B (isotropic coke)	Coke C (sponge coke)	Coke D (sponge coke)
Elements (wt%)				
Carbon	88.74	88.80	88.68	88.17
Sulfur	6.44	5.64	5.03	6.87
Hydrogen	3.85	3.77	3.75	3.87
Nitrogen	1.00	1.42	1.45	0.97
Impurities (ppm)				
Ni	126	252	208	122
Fe	401	592	381	319
V	361	535	431	362
Si	418	180	175	419
Ca	102	133	136	19
Na	127	131	116	142
P	10	13	9	1
Volatile content (%)	12.9	10.8	10.9	12.3

Table 3.2 Real density and proximate analysis of green petroleum coke D (air dried basis)

Ash content (%)	1.34
Water content (%)	0.29
Fixed carbon (%)	82.0
Volatile matter content (%)	12.3
Real density (g/cc)	1.39

3.2. Sample Analysis and Characterization

In this work, sulfur analysis, helium and apparent coke density measurements, and surface characterization of green coke D sample were carried out with a C-S analyzer, helium and water pycnometer, SEM/EDX, FT-IR and XPS, respectively. Helium density can be considered as the real density since the particles are crushed to -45 µm; thus, almost all closed pores are eliminated. Final sulfur content, porosity, and surface morphology of thermally desulfurized and hydrodesulfurized coke D samples were also analyzed.

3.2.1. Sulfur Analysis

The sulfur content analysis of green, thermally, and hydrodesulfurized coke samples were done in the Earth Materials Laboratory of the Geology Module of the Department of Applied Science at UQAC. Sulfur and carbon analyses were done based on infrared light absorption during combustion in oxygen flow, also called High-Temperature Tube Furnace Combustion Method with Infrared Absorption (ASTM D5016). A mixture of a petroleum coke sample and an accelerator (Fe, Sn, W) is put into a porcelain crucible, which is heated in the induction furnace. The sample reacts with oxygen, and, consequently, the carbon is transformed to CO_2 and CO, whereas the sulfur is transformed to SO_2. During the analysis, water could be released (H_2O or H_2). As this water is considered to be a contaminant, it is eliminated by dehydration with $Mg(ClO_4)_2$. The oxygen flow is then regularized and passed through an infrared detector. The sulfur and carbon concentrations are obtained from the CO, CO_2, and SO_2 detector [106].

3.2.2. Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray Spectroscopy (EDX)

SEM/EDX was utilized to study the morphology and the microstructure of several samples such as green, hydrodesulfurized, and calcined cokes. Samples (+1 mm –2 mm) were vacuum-dried for one day at room temperature prior to SEM analysis. Each coke sample was then sputtered with gold–platinum coating using a plasma current of 10 mA, a chamber pressure of 6 x 10^{-2} mbar, and a sputtering time of 140 s with a Polaron Range sputter coater. The SEM analysis was done using JEOL-JSM-6480LV with secondary electron scattering and with a voltage of 20 kV and WD of 16 mm.

3.2.3. Fourier Transform Infrared Spectroscopy (FT-IR)

The chemical structure of green coke D samples was examined with FT-IR spectroscopy at room temperature. The main objective was to identify the surface functionalities of different green petroleum coke samples. The IR spectra were collected in the wavenumber range of 500–4000 cm^{-1}, and the entire spectra were recorded using 4 cm^{-1} resolution. Each time, 20 scans were carried out prior to the Fourier transformation. All spectra were collected using the DRIFTS (Diffuse Reflectance Infrared Fourier Transform Spectroscopy) technique (Perkin Elmer Instrument, Spectrum one), and each result is the average of four experimental runs. The DRIFTS technique was used with an aperture mask of 2 mm-diameter and a reflector angle of 16°. All spectra were analyzed using the Spectrum-version 5.0.1 software. The effective depth of the surface scanning is 0.5–5 µm.

3.2.4. X-Ray Photoelectron Spectroscopy (XPS)

Different green, hydrodesulfurized, and thermally desulfurized coke samples were studied with AXIS Ultra XPS spectrometer (Kratos Analytical) using Mono-chromate Al

K[α] (hν = 1486.6 eV) source at a power of 210 W at the Alberta Centre for Surface Engineering and Science (ACSES), University of Alberta. The working pressure in the analytical chamber was lower than 2 x 10^{-8} Pa. The resolution function of the instrument for the source in hybrid lens mode was calibrated at 0.55 eV for Ag 3d and 0.70 eV for Au 4f peaks. The photoelectron exit was along the normal of the sample surface with an analysis spot of 400 x 700 μm^2. During the analysis, a separate charge neutralizer was used to compensate for sample charging. Survey spectra were scanned from 1100 to 0 eV of binding energy and collected with an analyzer, pass energy (PE) of 160 eV and a step of 0.35 eV. For the high-resolution spectra, the PE of 20 eV with a step of 0.1 eV was used. The XPS spectra fitting and quantitative analysis were performed using the CasaXPS 2.3.16 software at UQAC. The peak areas corresponding to different elements were evaluated using the “find peaks” option of the“element library” module of CasaXPS software, and scaled to the instrument’s sensitivity factors after a linear background was subtracted from each peak. All binding energies were referenced against a C1s peak at 284.3 eV. High-resolution spectra were used to carry out the spectra fitting and the component analysis. The analyzed surface depth of the sample was 2–5 nm.

3.2.5. X-ray Diffraction (XRD) Analysis

X-ray diffraction (XRD) measurements were conducted on the coke samples after thermal and hydrodesulfurization treatments using a diffractometer (Bruker D8 discover) available in CURAL laboratories of UQAC which uses Cu anode with the Kα wave length of 1.5406 Å. Measurements were made in a step scan mode with a step size of 0.05^o over the 2θ range from 3^o to 70^o. A scan time of 0.5 s was used for each step. Samples were ground to -125 µm by using a mortar prior to analysis.

3.2.6. Density and Porosity Analyses

Real and apparent densities of green, hydrodesulfurized, and thermally desulfurized samples were measured with helium pycnometer and water pycnometer, respectively. Real density analyses with helium pycnometer were done at COREM, Quebec according to ASTM D2638-10 standard. Apparent densities of samples were measured in UQAC carbon laboratory according to ASTM D854–14 standard. The porosities of samples were calculated based on real and apparent densities with the equation (3.1):

$$Porosity\ (\%) = \frac{Real\ density - Apparent\ density}{Real\ density} \times 100 \tag{3.1}$$

3.3. Thermal Desulfurization

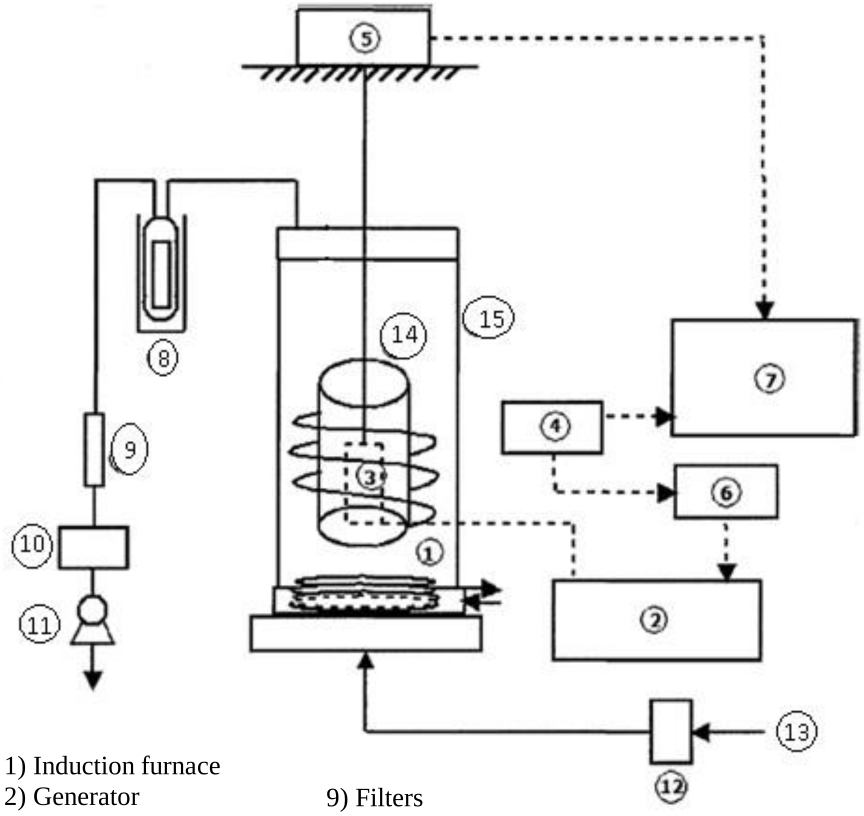
In the context of petroleum coke thermal desulfurization, various experiments were conducted using green cokes A, B, C, and D at different maximum temperatures. The details about the experimental set-up and the procedure for thermal desulfurization experiments are given below.

3.3.1. Experimental Set-up

Thermal desulfurization experiments were carried out using the thermogravimetric experimental set-up located in the UQAC carbon laboratory. Thermogravimetry is an analysis technique which is used to determine the mass change of a sample as a function of temperature and time. A schematic diagram of the experimental system is shown in Figure 3.1.

The experiments were done with perforated graphite crucibles which can hold 20 to 30 g of 1 mm coke particles. The geometry of the crucible is given in Figure 3.2. The crucible was suspended with a wire (Kanthal-A1 (FeCrAl alloy) or tantalum) from a balance (Mettler Toledo XS205), which measures the weight loss during the experiment. The weight loss data were taken at every 30 seconds. The measured data were exported simultaneously to the LabX Balance program.

The sample was heated via an induction furnace (Taylor Winfield 5 kilowatts) controlled by a temperature controller (Micristar) with an infrared sensor (OMEGA OS1200), which measures the temperature starting from 300°C. The temperature data was recorded with InfraWin Version 4.14b program.



1) Induction furnace
2) Generator
3) Sample
4) Infra-red pyrometer
5) Balance
6) Temperature controller
7) Computer
8) Condensator
9) Filters
10) Flow-meter
11) Pump
12) Flow-meter
13) N_2 gas
14) Isolator
15) Quartz tube

Figure 3.1 Experimental system for calcination and thermal desulfurization

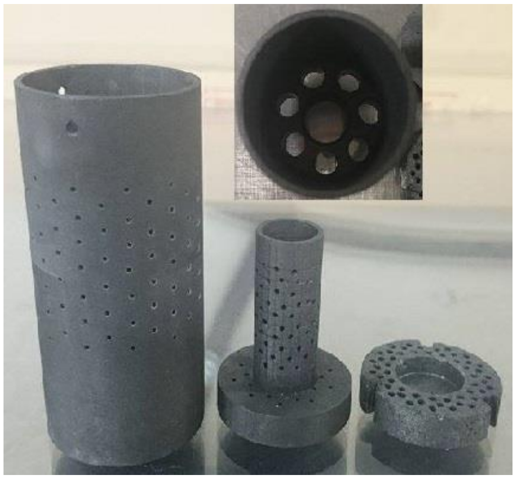


Figure 3.2 Graphite crucible

3.3.2. Experimental Procedure

As explained previously, experiments were carried out using 20 g to 30 g of coke samples with -2 mm +1 mm particle size placed in a graphite crucible. The crucible was heated by induction at a heating rate of 40°C/min to 1200°C, and then kept at this temperature for 15 min (soaking time) with the objective of using conditions similar to those of a rotary industrial calciner. Experiments were performed using four different maximum temperatures (1080°C, 1200°C, 1300°C, 1400°C) at the same heating rate and soaking time. Insulation was placed around the induction coil to reduce the heat losses from the crucible. Nitrogen was used as the inert gas at a flow rate of 10 L/min at constant pressure (1 atm). The heating profile for 1200ºC maximum temperature is given in Figure 3.3.

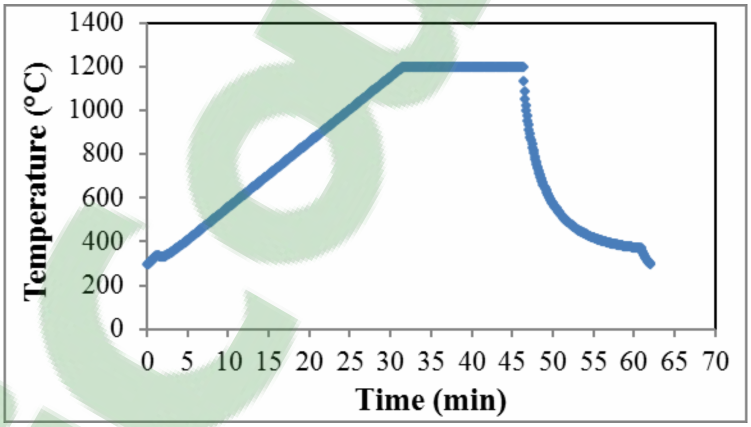


Figure 3.3 Heating profile used in thermal desulfurization experiments with induction furnace

3.4. Hydrodesulfurization

Hydrodesulfurization experiments were carried out with different experimental set-ups under different experimental conditions in order to determine the most favorable conditions such as water injection temperature, water injection duration and flow rate as well as particle size to remove as much sulfur as possible. Green coke D sample which was received in large quantities was used for all the hydrodesulfurization experiments. These experimental systems along with the specific experimental conditions are explained below.

3.4.1. First Experimental Set-up and Procedure

Hydrodesulfurization experiments were carried out in an electrically heated Pyradia (ALC 182412) furnace controlled by a PID controller (Omega CN 7800) and a maximum temperature controller (Omega CN355). The equipment is located in the UQAC carbon laboratory. The experiments were conducted under N_2 atmosphere with a flow rate of 1 L/min. A sample of 95 g coke with -2 mm +1 mm particle size was packed in an alumina crucible with perforated plates at both ends. The purity of N_2 used was 4.8 (99.998%). Gas flow rates were controlled using OMEGA gas flow-meters. The water flow was controlled by an Omega water flow-meter. A diagram of the experimental system is shown in Figure 3.4.

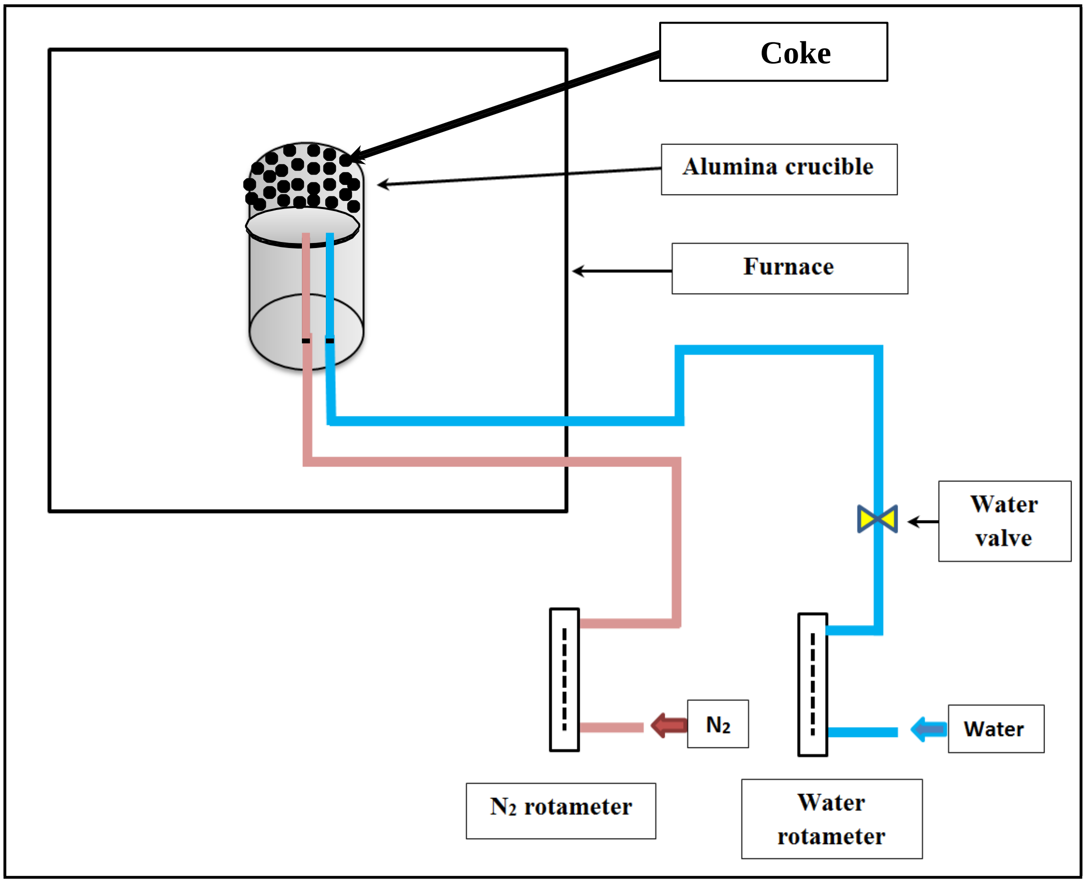


Figure 3.4 First experimental set-up for hydrodesulfurization

The experimental conditions of hydrodesulfurization (HDS) tests which were done with the 1st set-up are shown in Table 3.3. They are numbered in sequence as HDS-1, HDS-2, HDS-3, etc. The experiments were conducted at a heating rate of 50°C/h and up to 1080°C maximum temperature under inert gas atmosphere. N_2 was used as the inert gas. The tap water which was controlled via a water flow-meter was injected into the system at a specific temperature in each run in order to determine suitable temperatures in terms of sulfur removal. Water was passed through the coke for 1 h at 40 ml/min flow rate in all experiments.

Table 3.3 Experimental conditions for the experiments with the 1st set-up

Experiment	**HDS-1**	**HDS-2**	**HDS-3**	**HDS-4**
Heating rate (°C/h)	50	50	50	50
$T_{maximum}$ (°C)	1080	1080	1080	1080
$T_{H2O\ injection}$ (°C)	600-650	700-750	808-858	900-950
Duration of water injection (min)	60	60	60	60
Water flow rate (ml/min)	40	40	40	40

The possibility of oxygen infiltration led to the modification of this set-up. Presence of oxygen influences the removal of sulfur and the weight loss of coke. The details of the 2nd set-up and the experimental conditions are explained in the next part.

3.4.2. Second Experimental Set-up and Conditions

In the 2nd set-up, hydrodesulfurization experiments were carried out in the same electrically-heated Pyradia (ALC 182412) furnace controlled with a PID controller (Omega CN 7800) and a maximum temperature controller (Omega CN355) as in the 1st set-up. However, the design of crucible was modified. The experiments were conducted under N_2 gas, at a flow rate of 1 L/min, passing through the coke bed (-2 mm +1 mm particle size) placed inside the crucible. Also N_2 gas with a 3.5 L/min flow rate was passed from outside of the crucible and inside a steel box. The purity of N_2 used was 4.8. OMEGA gas and water flow meters were used to control the gas and water flow rates.

The experiments were done in a fire brick crucible which was mainly made of alumina (Al_2O_3), silica (SiO_2), and small amounts of other oxides. A hole with a certain volume was created in the middle of the brick in order to place the coke sample. The entire brick was coated with refractory cement and baked at high temperature. This crucible could hold 95 g of -2 mm +1 mm size coke sample. After the placement of coke sample into the crucible, the hole was closed by a stainless steel circular cover which was coated with boron nitride in order to prevent any contact between water and stainless steel cover. The crucible brick is placed in a rectangular steel box also coated with boron nitride and was covered in order to avoid the air infiltration. A schematic diagram of the 2nd set-up, the design of the crucible and the steel box are given in Figure 3.5 and Figure 3.6, respectively.

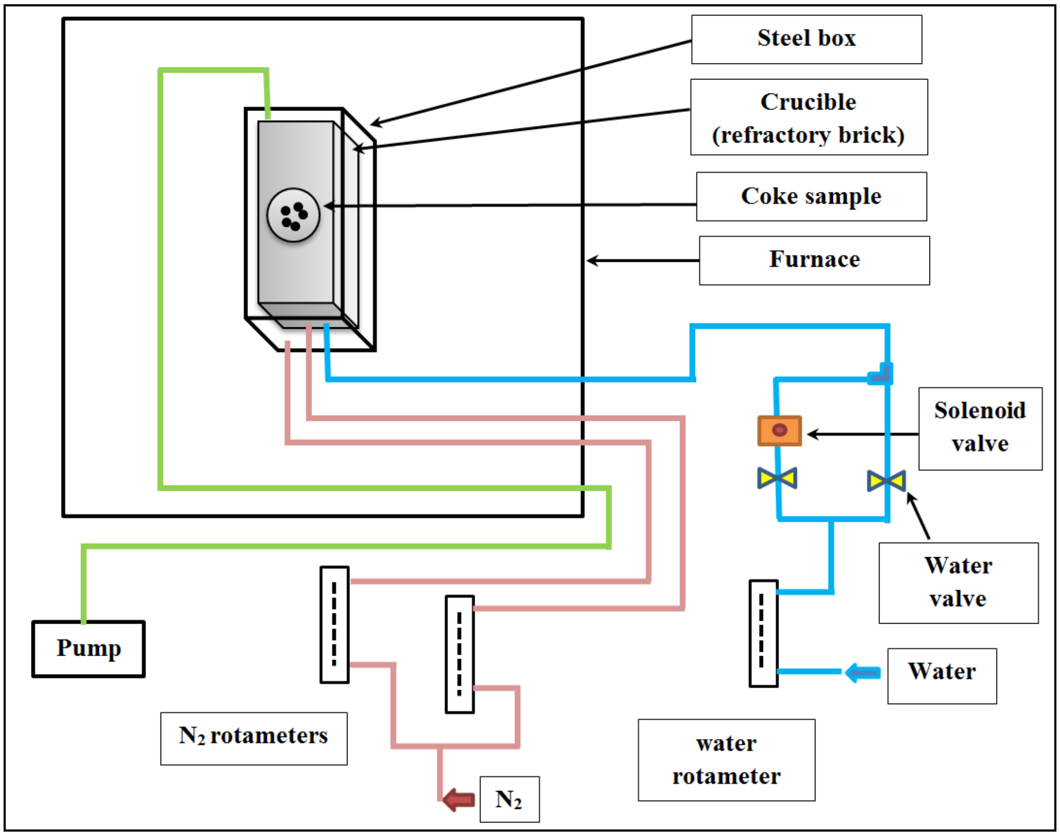


Figure 3.5 Second experimental set-up for hydrodesulfurization

Figure 3.6 Crucible

Based on the sulfur removal results of first set of hydrodesulfurization tests as well as the observations during those experiments, new conditions were determined for the experiments with the 2nd set-up. The water injection temperatures were chosen as 700-750°C. Various modifications have been tried in these tests such as injecting water during the cooling step after calcination was completed, continuous water flow during calcination, application of suction at the gas exit, discontinuous injection of water (pulse) and their combinations. The experiments were conducted at 50°C/h heating rate and up to 1080°C maximum temperature under inert gas atmosphere. N_2 was used as the inert gas. N_2 gas was passed through the coke sample as well as between the crucible brick and the steel box simultaneously during the experiments as it was explained in the previous part. Both flows were controlled by two gas flow meters which were connected to N_2 gas bottles. Water was injected to the coke for 1 h at 40 ml/min flow rate in all experiments. The conditions for each test are given in Table 3.4.

Table 3.4 Experimental conditions for the experiments with the 2nd set-up

Experiment	**Heating rate (°C/h)**	**T_{max} (°C)**	**T_{H2O} (°C)**	**Duration of water injection (h)**	**Water flow rate (ml/min)**	**Details**
HDS-5	50	1080	700-750	1	40	Suction at the outlet
HDS-6	50	1080	700-750	1	40	Suction + pulse
HDS-7	50	1080	750-647	1	40	H2O during cooling + suction
HDS-8	50	1080	750-650	1	40	H2O during cooling + pulse+ suction
HDS-9	50	1080	700-750	1	40	Pulse
HDS-10	50	1080	400-1080	13.5	40	Continuous H2O + suction
HDS-11	50	1080	500-1080	11.5	40	Continuous H2O + pulse+ suction
HDS-12	50	1080	700-750	1	40	No suction, no pulse

Since no significant sulfur removal was observed from the set of experiments with the 2nd set-up except the one with continuous water injection (high amount of coke was lost during this test), the reason for the low sulfur removal were investigated further. It was found that there was a 150-200°C temperature difference between the furnace temperature and the sample temperature due to the low thermal conductivity of the crucible material. To overcome this, a thermocouple was placed inside the sample and the furnace was controlled with respect to the sample temperature in order to get the desired sample temperatures.

3.4.3. 2nd Experimental Set-up Coupled with Gas Chromatography (GC)

After eliminating the temperature gap between the crucible and the coke sample, a hydrodesulfurization experiment and a thermal desulfurization experiment were done with the 2nd set-up with which two different types of gas chromatograph were used. GC (Varian 3800) equipped with a TCD (thermal conductivity detector) was used to determine H_2 and CH_4 in the outlet gas. GC (Agilent 7890B) equipped with a PFPD (pulsed flame photometric detector) was used to detect the presence of sulfur compounds in the reaction medium during thermal and hydrodesulfurization tests. During these two desulfurization tests, S, H_2 and CH_4 peaks were determined with two GCs within a temperature range. For the thermal desulfurization test, the data were collected between 400-1080°C. For the hydrodesulfurization test, water was injected to the system continuously at 4 ml/min flow rate for 8 h 15 min between 618-1000°C, and data were collected simultaneously during this water injection period. The details of these tests are given in the following sections.

GC-TCD (Thermal Conductivity Detector)

GC (Varian 3800) was equipped with a thermal conductivity detector. The nitrogen gas was used as the carrier gas for the GC analysis. Compressed air was used for the injection valve operation. A known volume of sample gas was stored in the injection loop and was injected into the column with the help of this valve. Injector type 1061 was used. The column was packed with 5A molecular sieve. This type of column can separate hydrogen and methane well. After the injection, the column adsorbs all the gases and desorbs each gas separately. The thermal conductivities of the sample gas mixture are compared with that of the carrier gas which flows on the reference side of the detector. The Wheatstone bridge arrangement is used for the TCD measurements. Table 3.5 shows the details of GC conditions for gas analysis. Figure 3.7 shows the gas chromatograph coupled with a TCD.

Table 3.5 The GC analysis conditions for hydrogen and methane

Gas Chromatography	Varian 3800
Detector	TCD
Column	Molecular sieve 5A 8 ft long - 1/8 inch internal diameter
Analysis conditions	
Column temperature	50°C
Injector temperature	120°C
Detector temperature	120°C
Filament temperature	250°C
Volume of sample loop	3 ml
Carrier gas and flow rate	Nitrogen-20 ml/min
Injector	Continuous injection

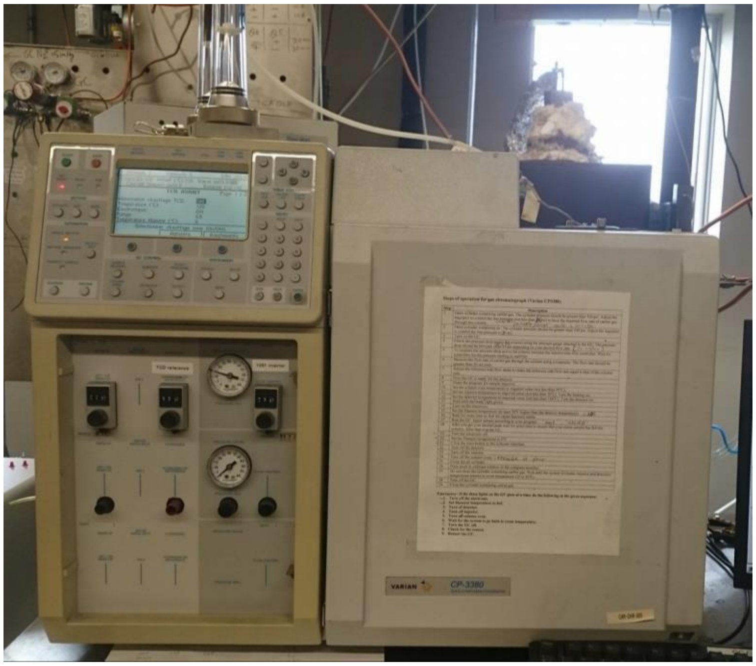


Figure 3.7 Gas chromatograph equipped with a thermal conductivity detector (GC-TCD)

GC-PFPD (Pulsed Flame Photometric Detector)

An Agilent 7890B Gas Chromatograph equipped with an OI 5380 pulsed flame photometric detector (PFPD) and a J&W GasPro column was used to analyze the sulfur compounds in the hydrodesulfurization gas. The PFPD is ideal for analyzing sulfur compounds such as hydrogen sulfide (H_2S), carbon sulfide (COS), carbon disulfide (CS_2), mercaptan (RSH), and thiophene at low ppm to 50 ppb in light hydrocarbon matrices like propylene or natural gas [107]. During the hydrodesulfurization experiments, the sulfur compounds present in the reaction medium at different temperatures were observed qualitatively by GC-PFPD which is shown in Figure 3.8.

Figure 3.8 Gas chromatograph equipped with a pulsed flame photometric detector (GC- PFPD)

Agilent 7890B GC was equipped with a PFPD and volatiles interface (VI). The inlet gas containing volatiles was connected directly to a six-port gas sampling valve (GSV). SilcoNert 2000-treated tubing including the sample loop was used for all lines that come in contact with the sample. It is extremely important that all lines in contact with the sample should be inert for successful detection of sulfur compounds at low levels [107]. Sample loop size was typically 1.0 ml to maximize sensitivity. All GC gas flows and pressures were controlled electronically. Agilent ChemStation software was used to operate and adjust the parameters and temperatures of GC-PFPD. The sample was introduced directly to the capillary column using an automated 6-port Valco gas sampling valve [108]. Table 3.6 shows the operation conditions of GC-PFPD equipment.

Table 3.6 Typical GC conditions

Technique	GC-PFPD
Column	Agilent J&W Capillary GasPro Column 30 m length x 320 µm internal diameter
Oven temperature	200°C isotherm
Inlet	200°C, split ratio 15:1
Carrier gas	Nitrogen, constant flow, 1.2 ml/min
Sample loop	1 mL
Injection	Gas sampling valve
PFPD Settings	Temperature: 250°C H_2 fuel flow: 14 ml/min Air flow (utility flow): 14.5 ml/min Make up flow (N_2): 12.5 ml/min CMT: 550 V Ignitor current: 2.8 mA Triger level: 400 mV

The PFPD is an ideal detector for analyzing sulfur compounds at low ppm to 50 ppb levels. It houses two chambers. Ignition from a continuous igniter filament takes place in the ignition chamber and the flame propagates to a quartz tube in the combustion chamber to which a light aperture, a photomultiplier tube, and a filter is connected. Hydrogen and air flow to the PFPD should be such that a continuous flame is sustained at about 2-4 pulses per second. During each pulse background, chemiluminescent emissions associated with the hydrogen rich flame emit over a period of only 3-4 milliseconds while emissions from the sulfur species emit from about 4 to 16 milliseconds. This delayed emission is monitored by a delayed electrometer gate where gate delay and width are optimized for the sulfur emissions. Since the flame background is significantly eliminated, the sulfur signal is optimized. A detectivity of 1 pgS/s and a selectivity of 10^6 S/C are obtained, and equimolar response is obtained irrespective of sulfur compound identity [108].

3.4.4. Third Experimental Set-up and Conditions

After the set of experiments with the 2nd experimental set-up, the quantity of coke was reduced from 95 g to about 10 g to have one layer of coke particles for good contact between gas and coke. In a packed-bed, it is challenging to have a good contact between water-gas and coke particles.

Based on certain observations which were obtained from the experiments with the previous two systems, a different experimental set-up was constructed for the next set of hydrodesulfurization experiments. In this set-up, the emphasis was on good contact between the coke particles and steam. Some head space was maintained to arrange the release of hydrogen sulfide gas from the system. Another bed of coke particles was used outside the system to eliminate oxygen infiltration. These coke particles reacted with any oxygen infiltrated into the furnace and thus did not let any oxygen reach the actual system.

A new crucible was fabricated which contained 6 separate sample holders each of which had a diffuser plate for a uniform steam distribution and 10 g of coke sample. Each sample holder on the crucible had a separate water connection which was controlled by a water flow meter (Omega FL-1443-G and FL-1444-G). The crucible was made of a refractory board material provided by Pyrotek. The tubes for water connections were chosen as stainless steel. This arrangement, given in Figure 3.9, and Figure 3.10, made the application of different conditions to different samples possible during the same test.

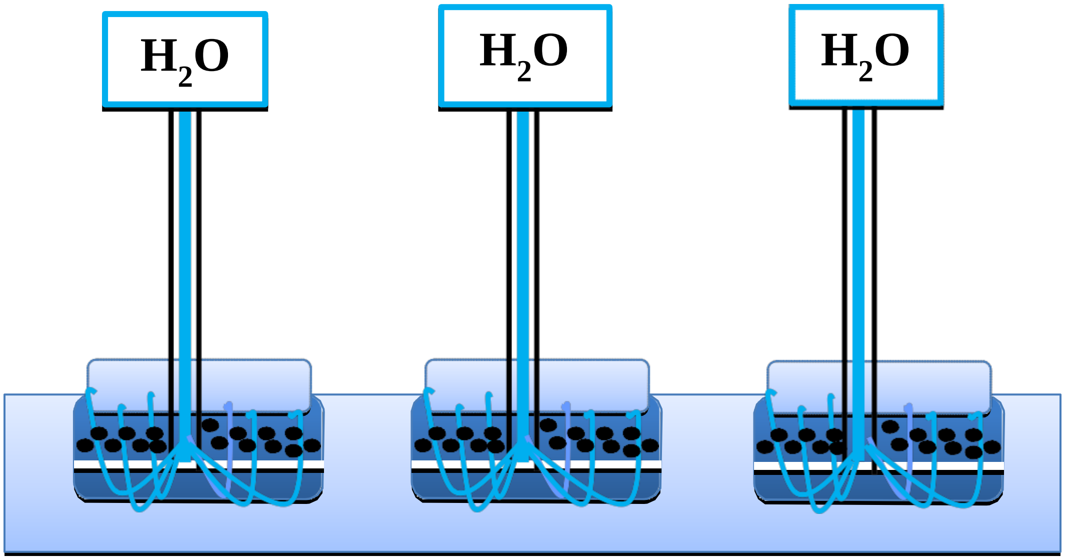


Figure 3.9 Vertical cross section of the crucible during water injection

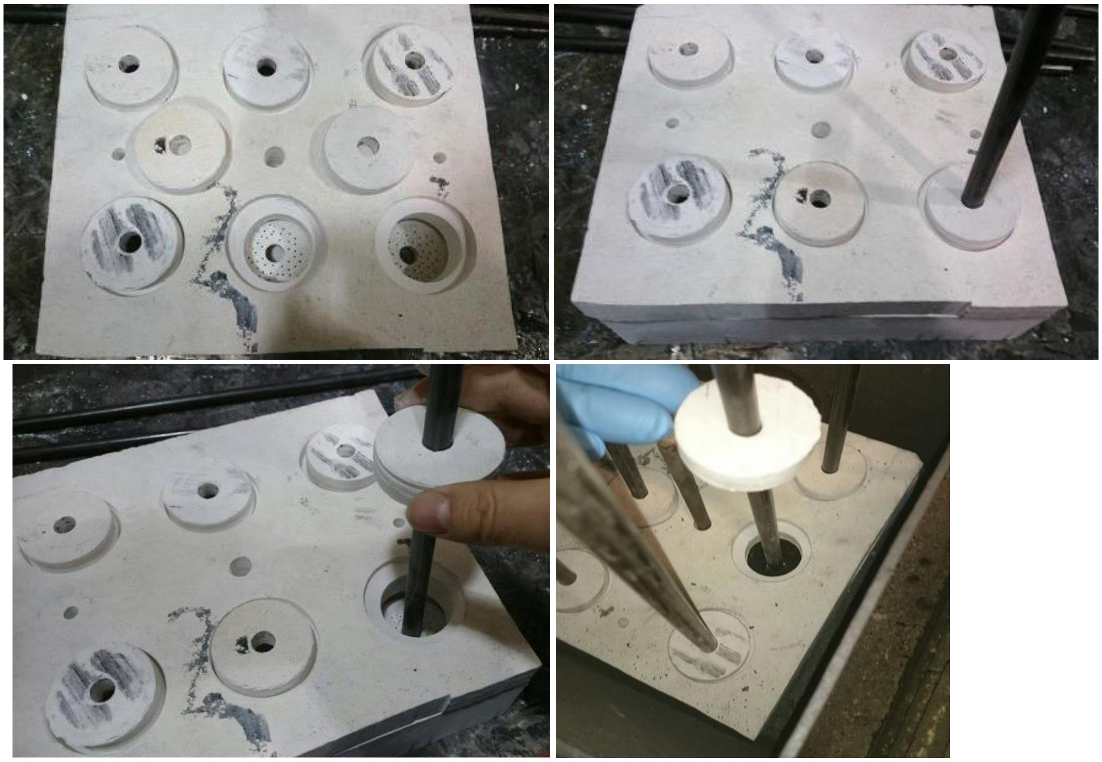


Figure 3.10 The new crucible with 6 sample holders and water connections

The furnace in which the new crucible was installed is an electrically-heated Pyradia furnace controlled by a PID controller (Omega CN 7800) and a maximum temperature controller (Omega CN 740) available in the UQAC carbon laboratory. The operating temperature was controlled within ±20°C. The experiments were conducted under N_2 atmosphere flowing at 4 L/min outside of the crucible. The N_2 flow rate was controlled using an OMEGA gas flow meter. After the installation of crucible into the furnace, the furnace was filled with packing coke in order to prevent air infiltration. When the coke reached the desired temperature, tap water at room temperature was injected to the system until the preset period ended. The furnace continued heating at the adjusted heating rate during the water injection. After the water flow was stopped, coke was heated up to 1080°C maximum temperature in all runs. Normally, in order to simulate a standard calcination, one should go up to about 1200°C. However, due to the furnace limitations, all hydrodesulfurization experiments were carried out up to 1080°C. The particle size of green coke samples for most of the experiments was -2 mm +1 mm. In order to study the particle size effect on hydrodesulfurization, some coke samples with fine and coarse particles were also used. Several hydrodesulfurization experiments were carried out at different water injection temperatures in the range of 650-950°C. The influence of water injection temperature, water flow rate, and injection duration as well as particle size of coke on the desulfurization was examined. A schematic diagram of the 3rd set-up is given in Figure 3.11. The pictures of the crucible and water assembly inside the furnace as well as the complete set-up are given in Figure 3.12 and Figure 3.13, respectively.

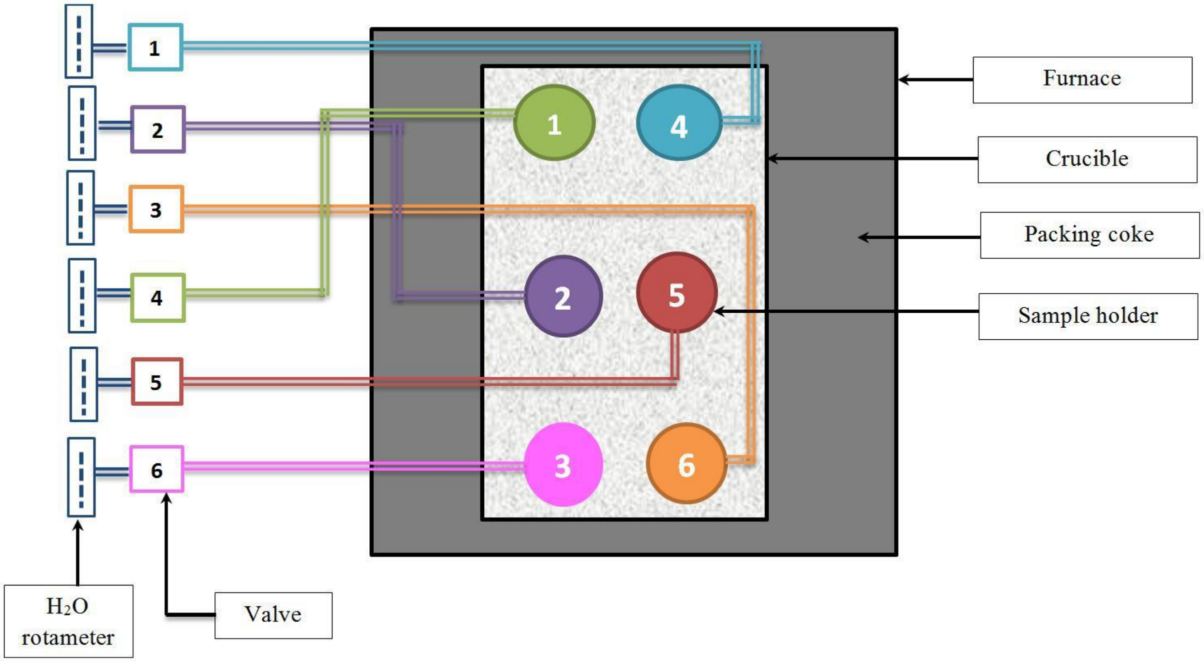


Figure 3.11 Schematic representation of the third experimental system including crucible with multiple sample holders and water connections

Figure 3.12 The furnace and the third experimental system including crucible with multiple sample holders and water connections

Figure 3.13 The third experimental system

The experimental conditions that were applied to hydrodesulfurization experiments using the 3rd experimental system are given in Table 3.7.

Table 3.7 Experimental conditions for the hydrodesulfurization experiments with the 3rd set-up using green coke D

Water injection temperature (ºC)	Water injection period (min)	Water flow rate (ml/min)	Particle size (mm)
650-670	8	6	1
	37	1	1
	60	1	1
	100	1	1
750-770	8	6	1
	37	1	1
	60	1	1
	100	1	1

850-870	8	6	1
	37	1	1
	37	4	1
	37	1	0.1
	60	1	1
	60	1	0.1
	100	1	1
	141	1	1
950-970	8	6	1
	37	1	1
	60	1	1
	100	1	1
1020	60	1	1

After the experiments which were carried out under different conditions, the effect of granulometry on hydrodesulfurization was studied using 850°C water injection temperature, 37 min water injection time and 1 ml/min water flow rate. The granulometry that was used in these experiments was as follows: -16 mm +12.5 mm, -12.5 mm +8 mm, -8 mm +6.3 mm, -6.3 mm +4 mm, -4 mm +2 mm, -2 mm +1 mm. In order to increase the coke-water contact, the diffuser plates inside the sample holder were modified. Horizontal groves were added to each diffuser plate as shown in Figure 3.14. The purpose of this modification was to provide a better contact between water and coke by minimizing the contact area between the particles and the diffuser plate.

Figure 3.14 Diffuser plate with horizontal grooves

The same experimental set-up and the test procedure as those of the experiments carried out with the 3rd set-up were used in the hydrodesulfurization tests with different granulometries. One experiment was done with a standard sample of 10 g while in the second experiment the sample amount was reduced to have a single layer of particles in this system as shown in Figure 3.15. The effect of this change on the extent of hydrodesulfurization for different granulometries was also investigated. The experimental conditions of these experiments are given in Table 3.8.

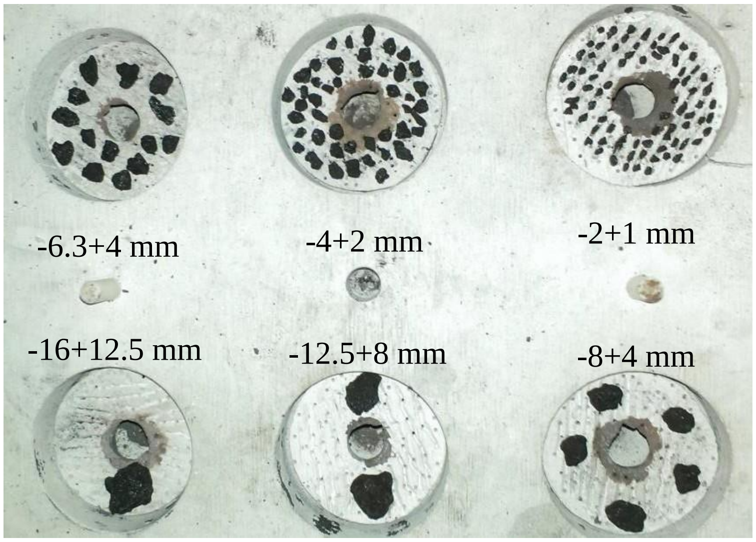


Figure 3.15 Single layer of coke particles in samples holders with different particle size

Table 3.8 Experimental conditions for the hydrodesulfurization of coke with the 3rd set-up using different particle sizes and green coke D

Water injection temperature (ºC)	**Water injection duration (min)**	**Water flow rate (ml/min)**	**Particle size (mm)**
850-870	37	1	-16+12.5
	37	1	-12.5+8
	37	1	-8+6.3
	37	1	-6.3+4
	37	1	-4+2
	37	1	-2+1

CHAPTER 4

EXPERIMENTAL RESULTS AND DISCUSSION

4.1. Introduction

In this chapter, the characterization of green coke D as well as the results of the thermal and hydrodesulfurization of this coke under different conditions have been presented. Thermal desulfurization of green coke D samples were carried out up to different calcination temperatures (1080°C, 1200ºC, 1300ºC, 1400ºC). The effect of maximum calcination temperature on percent sulfur removal and the weight loss from coke was investigated. Several series of runs were carried out during which green coke D was hydrodesulfurized with water under different conditions using different experimental set-ups at atmospheric pressure. The effects of different parameters such as water injection temperature, duration, and flow rate as well as particle size were studied. The results of the hydrodesulfurization of green coke are presented in three separate parts according to the experimental set-up used for each set of experiments. In order to calculate percent sulfur removal, the sulfur contents of all treated samples as well as the green coke sample were analysed. The sulfur removal (%) was calculated using Equation 4.1.

$$S\,removal\,(\%) = \frac{initial\ S\ (wt\%)\ in\ coke - final\ S\ (wt\%)\ in\ coke}{initial\ S\ (wt\%)\ in\ coke}\ x100 \qquad (4.1)$$

The percentage weight loss of coke was also calculated after each experiment in order to determine how much coke is lost after each desulfurization experiment. The weight loss (%) of coke was calculated using Equation 4.2.

$$Weight\ loss\ (\%) = \frac{initial\ weight\ of\ coke\ (wi) - final\ weight\ of\ coke\ (wf)}{initial\ weight\ of\ coke\ (wi)} \times 100 \qquad (4.2)$$

In addition to sulfur removal and weight loss results of thermal and hydrodesulfurization experiments, other coke properties such as crystalline length (Lc), density, and porosity were compared before and after the treatment. Surface characterization of the cokes with SEM/EDX and XPS are explained in the following parts.

4.2. Green Coke Characterization

The characterization of green coke D was done using FT-IR, XPS, and SEM-EDX in order to investigate the surface functional groups and the morphology of green coke D. Results of these analyses are presented in this section.

4.2.1. FT-IR Analysis Results

The surface functional groups of the green petroleum coke D were identified with FT-IR. Figure 4.1 shows the FT-IR spectra of the green petroleum coke D. The assignment of the bands was done based on the FT-IR data for green petroleum coke available in the literature (see Table 4.1). The spectra were determined by testing four samples of green coke D and averaging their spectra.

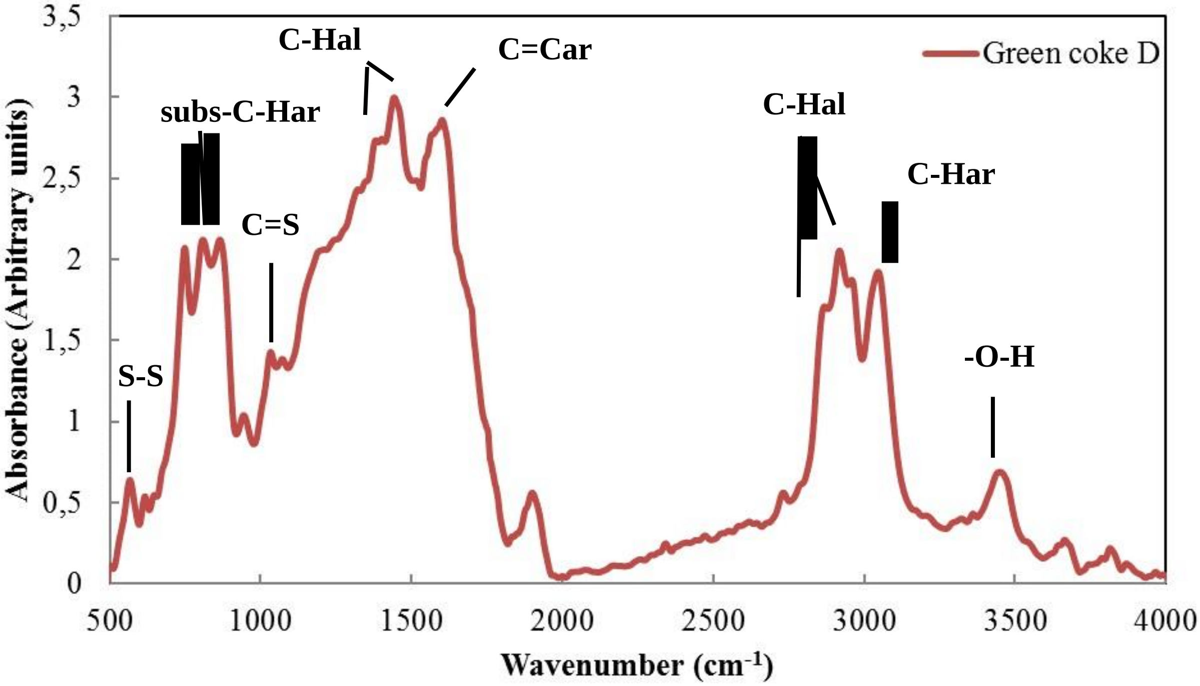


Figure 4.1 FT-IR analysis of green petroleum coke D by DRIFT method at room temperature

The FT-IR spectra of green petroleum coke D sample display an absorbance band near 3047 cm^{-1} due to aromatic C-H stretching vibrations. A pattern of absorption bands between 900 and 700 cm^{-1} which arose from the out-of-plane vibration of aromatic C-H bonds and bands corresponding to aromatic C=C bond near 1600 cm^{-1} were observed for green coke D particles. On the aliphatic side, the spectra consist of a pattern of absorption bands corresponding to alkyl functional groups (unsaturated and saturated C-H stretching vibrations corresponding to the region between 2700 and 2965 cm^{-1}) and those corresponding to C=C stretching vibration for aromatics or C-H bending vibrations of methylene (1445 cm^{-1}) and methyl groups (1375 cm^{-1}). It was also mentioned in the literature that, basically, the functionalities are related to the existing carbonyl groups (shoulder at 1670 cm^{-1}) corresponding to C=O vibration modes, -O-H stretching vibrations made of hydroxyl, phenolic functionalities or moisture (3453 cm^{-1}), and C-O groups (ether, carboxylic acid, ester, alcohol) (1300-1100 cm^{-1}). C=S stretching vibrations display an absorbance band near 1033 cm^{-1} as well as S-S stretching bonds between 550-700 cm^{-1} which can be attributed to the high sulfur content of the green coke D. The list of functional groups that were found on coke structure is given in Table 4.1.

Table 4.1 List of functional groups in green petroleum coke from the FT-IR analysis

Wavenumber (cm^{-1})	Functional group
550-700	S-S stretching vibrations [109, 110]
745	Aromatic C-H out of plane vibration frequencies [111-113]
804	Aromatic C-H out of plane vibration frequencies [111-113]
855	Aromatic C-H out of plane vibration frequencies [111-113]
1033	C=S (thiocarbonyl) stretching vibration [109, 110]
1375	C=C stretching vibration for aromatics or C-H bending vibrations of methyl groups [112-114]
1445	C=C stretching vibration for aromatics or C-H bending vibrations of methylene groups[112-114]
1601	Aromatic C=C bond stretching vibrations [112-115]
2730	Aliphatic C-H stretching vibrations for sp hybridization of C [111, 113, 114, 116]
2865	Aliphatic C-H stretching vibrations for sp^2 hybridization of C [111, 113, 114, 116]
2915	Aliphatic C-H stretching vibrations for sp^3 hybridization of C [111, 113, 114, 116]
2962	Aliphatic C-H stretching vibrations for sp^3 hybridization of C [111, 113, 114, 116]
3047	Aromatic C-H stretching vibrations [110, 111, 113, 114]
3453	-O-H stretching vibration made of hydroxyl functional groups [116]

4.2.2. XPS Analysis

FT-IR analysis was used to identify the chemical functionality of petroleum coke D surface. During the XPS analysis, the information obtained from the FT-IR analysis was used to carry out the de-convolution of C1s and S2p peaks. Figure 4.2 shows the XPS spectra for green petroleum coke D. Atomic percentages of different elements for green petroleum coke D are presented in Table 4.2 for the survey spectra.

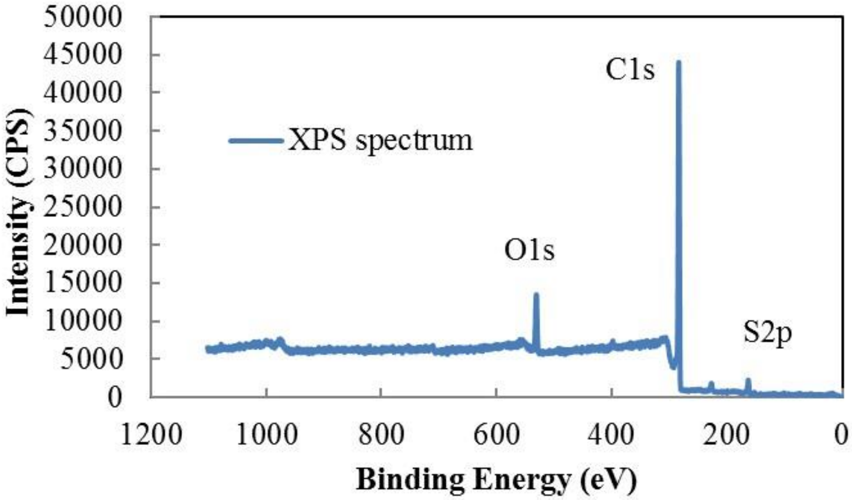


Figure 4.2 General spectra from XPS analysis for green petroleum coke D

Table 4.2 Atomic percentages of different elements in green petroleum coke D

Coke type	**C (atomic %)**	**O (atomic %)**	**N (atomic %)**	**S (atomic %)**
Green coke D	91.67	6.02	0.00	2.32

In general, XPS spectra of green petroleum coke D, the most prominent peak at 284.3 eV is designated as C1s. Other notable peaks include the O1s peak at 531.10 eV and S2p peak at 163.50 eV. Even though there is a small peak at around 400 eV for Nitrogen, the area of that peak was less than 0.005%. In Table 4.2 percentage of nitrogen appears to be zero due to the rounding of the number. The area of these peaks can be used to determine the chemical nature of these elements. The deconvolution of C1s and S2p peaks of green coke D were done according to available literature [111, 112, 115, 117-122]. The deconvolution of the C1s and S2p peaks was done based on the peak positions shown in Table 4.3.

Table 4.3 Peak positions used in CasaXPS for deconvolution

C1s		S2p		
Species	Peak, eV	Species	S2p3/2 peak, eV	S2p1/2 peak, eV
C=C	284.3	Sulfide	161.5	162.7
C-C	285.1	Thiol	162	163.2
C-OH/C-S/ C-O-C	286	Sulfate	169	170.2
C=O	287	Thiophene	163.5	164.7
COO	288.6	Oxidized S	166	167.2

The de-convoluted C1s and S2p spectra of green coke D are presented in Figure 4.3 and Figure 4.4. The functional group content ratios of C and S from deconvoluted spectra of C1s and S2p are given in Table 4.4.

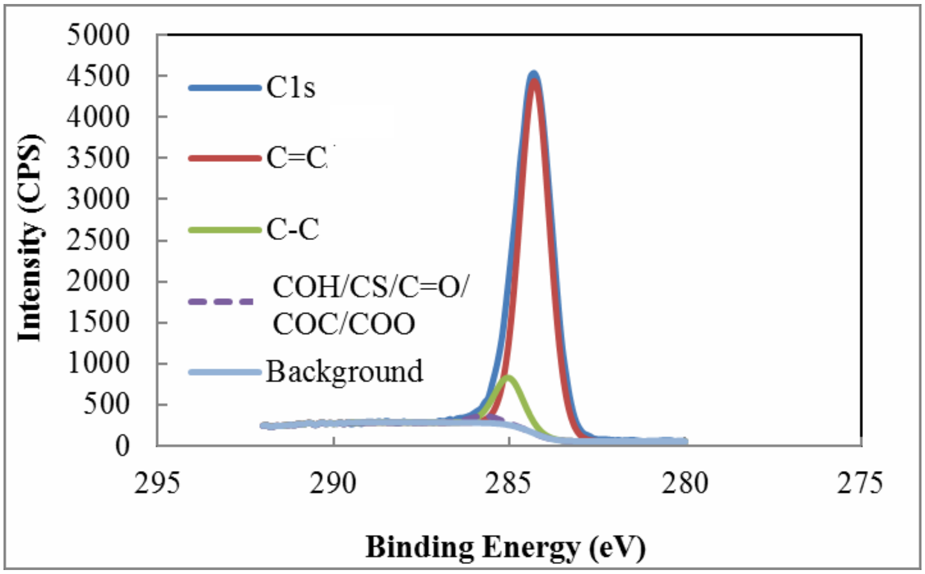


Figure 4.3 Deconvoluted C1s spectra of green petroleum coke D from XPS analysis

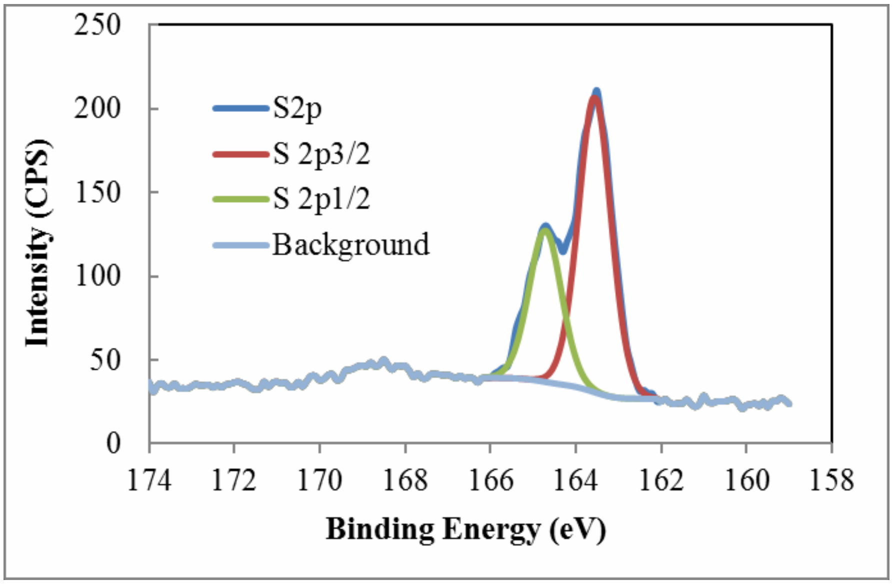


Figure 4.4 Deconvoluted S2p spectra of green petroleum coke D from XPS analysis

Table 4.4 Atomic percentages of different components in green petroleum coke D

	Carbon components			**Sulfur components**	
	C=C %	C-C %	C-OH/C-S/C=O /C-O-C/COO %	Thiophene %	For thiophene $S2p_{3/2}$/S $2p_{1/2}$
Green coke D	86.81	11.33	1.86	100	66.07/33.93=1.95

It is evident from the XPS results that green coke D sample contains large quantities of C=C and C-C bonds and trace amounts of oxygen and sulfur compounds. According to atomic percentages from XPS analyses shown in Table 4.2, it was found that green coke D sample did not contain any nitrogen. The sulfur content of green coke D was high as it was found previously with the combustion sulfur analysis as well as SEM-EDX analyses of the same coke.

Inspection of C1s high resolution peak of green coke D in Figure 4.3 reveals three peaks located at around 284.3, 285.1, 286-288.6 eV that form the asymmetrical C1s peak. The dominant peak at 284.3 eV is associated with C=C bonds. 285.1 eV which is the second dominant bond in C1s spectra can be attributed to the aliphatic carbon in C-C bond. The peak at higher energy position (286-288.6 eV) is associated with the C-OH/ C-S/C-O-C/C=O/COO bonds. In this case C-OH/C-S/C-O-C/C=O/COO species were combined to have an overall idea.

Every S2p peak in the spectra appears in pairs which are S 2p3/2 and S 2p1/2 doublets. Therefore, the S2p spectrum should be studied through peak-differentiation-imitating analysis. Every form of sulfur should have two peaks in the S2p spectrum which are S 2p3/2 and S 2p1/2. In addition, the two peaks should follow an approximate 2:1 relative area separated by 1.18 eV to 1.2 eV with equal full width at half maximum (fwhm) level [111, 120, 122, 123]. When the deconvolution of S2p spectra of green petroleum coke D was carried out accordingly, it was found that sulfur existed in the green petroleum coke sample only in the form of thiophenes (S 2p3/2 at 163.5 eV and S 2p1/2 at 164.7 eV) as shown in Figure 4.4 and Table 4.4. This result matches with the existing literature about the dominance of thiophene as sulfur component in green petroleum cokes. According to the previous studies, XANES (X-ray absorption near-edge structure) spectroscopy should be used to have more detailed sulfur functionality analysis [45].

4.2.3. SEM-EDX Analysis

Scanning electron microscopy (SEM) is an important tool to visualize the surface texture of coke particles at nano-scale. SEM makes it easy to visualize the structural and morphological details of coke particles. EDX was used to determine the sulfur content of certain regions for a number of different samples. Figure 4.5 shows the SEM images of green petroleum coke D at different magnification values.

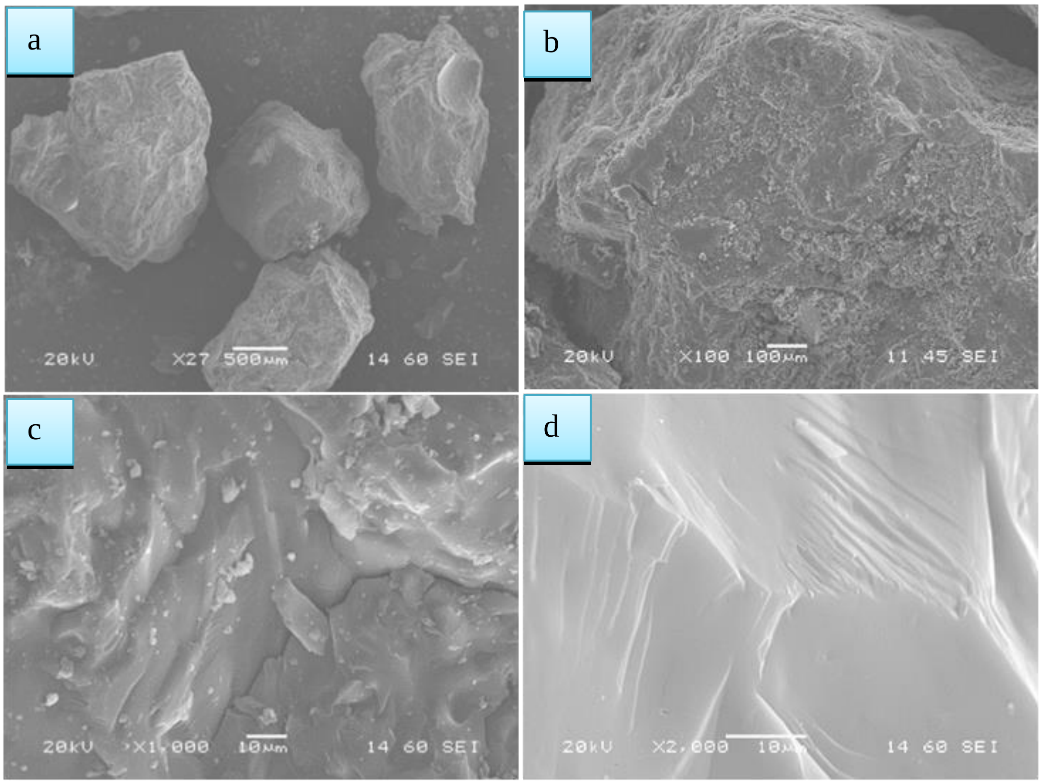
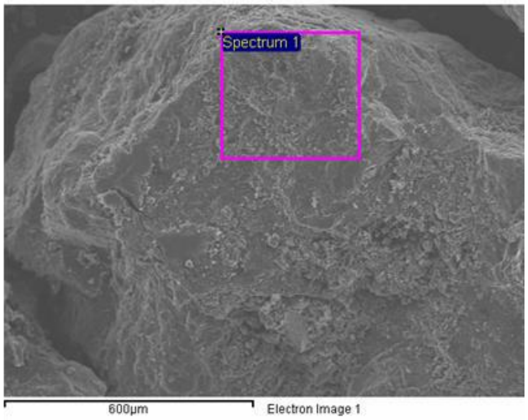
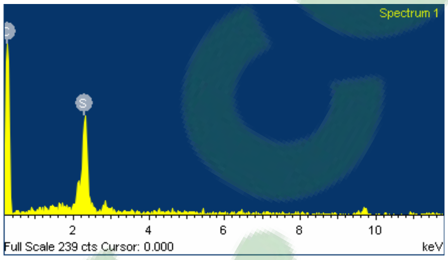


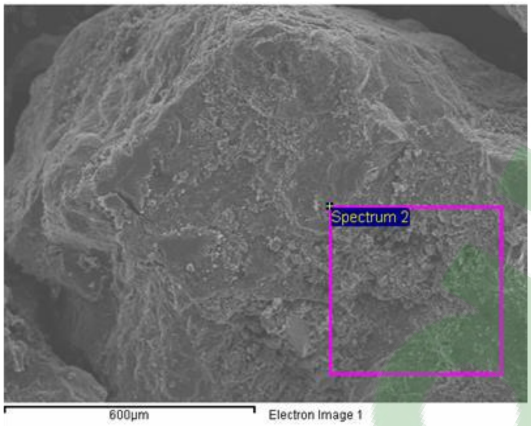
Figure 4.5 SEM images of green petroleum coke D at magnifications of (a) x27 (b) x100 (c) x1000 (d) x2000

EDX analysis was done for two different green coke D particles on different parts of the surfaces. The SEM pictures and EDX patterns with elemental analysis results are shown in Figure 4.6 and Figure 4.7. C Kα peak in EDX should ideally correspond to the C1s peak in XPS. However, due to the non-homogeneity of coke, the results of EDX and XPS did not match at all the points of the particle. EDX helps to know the distribution of sulfur at different points on the coke surface.

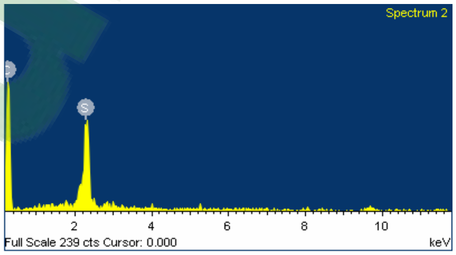


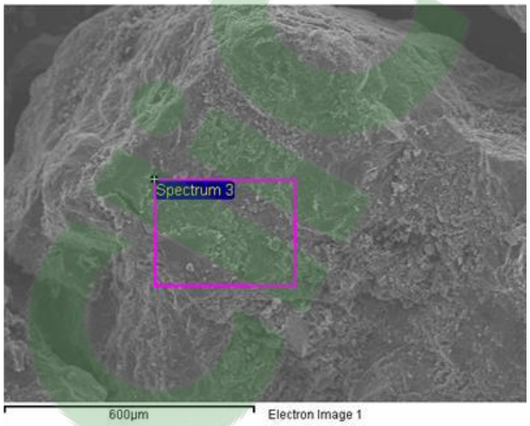
Element	Weight %	Atomic %
C	92.55	97.07
S	7.45	2.93
Totals	100.00	





Element	Weight %	Atomic %
C	91.66	96.70
S	8.34	3.30
Totals	100.00	





Element	Weight %	Atomic %
C	92.04	96.86
S	7.96	3.14
Totals	100.00	

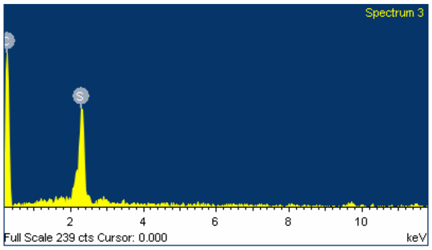
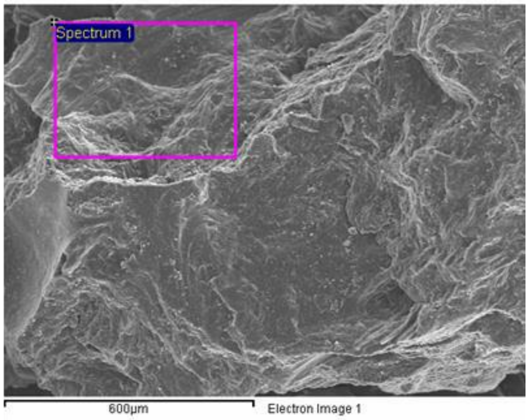
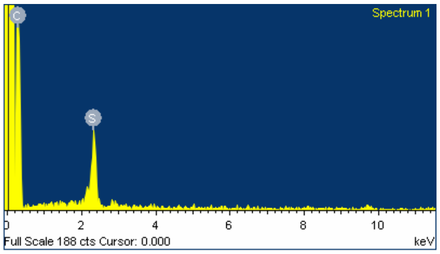
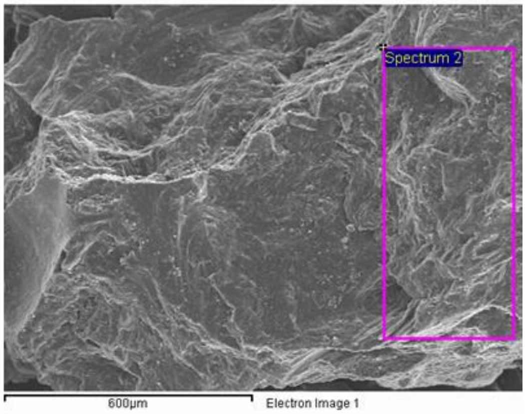


Figure 4.6 SEM-EDX images and EDX patterns of different regions on -2 mm +1 mm green coke D particle 1

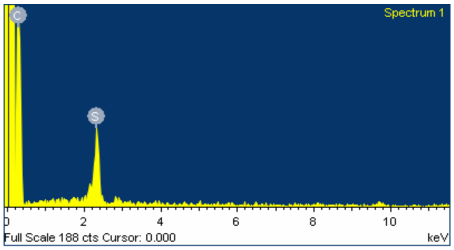


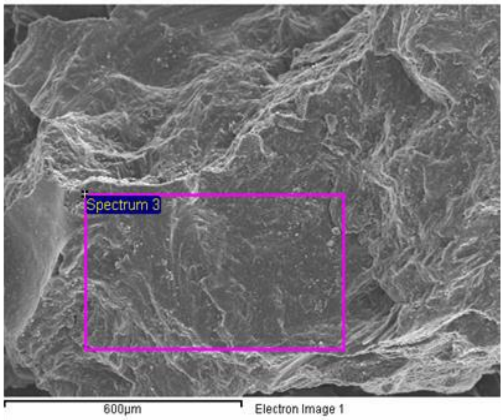
Element	Weight %	Atomic %
C	94.27	97.77
S	5.73	2.23
Totals	100.00	





Element	Weight %	Atomic %
C	92.28	96.96
S	7.72	3.04
Totals	100.00	





Element	Weight %	Atomic %
C	92.58	97.09
S	7.42	2.91
Totals	100.00	

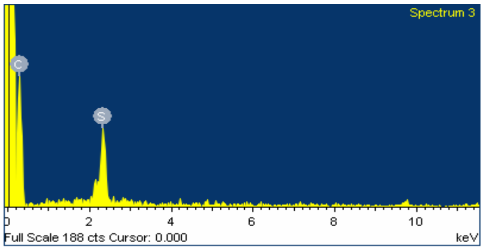


Figure 4.7 SEM-EDX images and EDX patterns of different regions on -2 mm +1 mm green coke D particle 2

4.3. Thermal Desulfurization

Thermal desulfurization of green coke D under the same heating rate and residence time up to different maximum temperatures was carried out. Weight loss of the samples were calculated by measuring the initial and final weight of the sample. The sulfur removal percentage was calculated based on the initial and final sulfur content of sample measured according to ASTM D5016. Weight loss and sulfur removal percentages of the green coke D with respect to maximum temperature of the thermal desulfurization experiments are given in Figure 4.8.

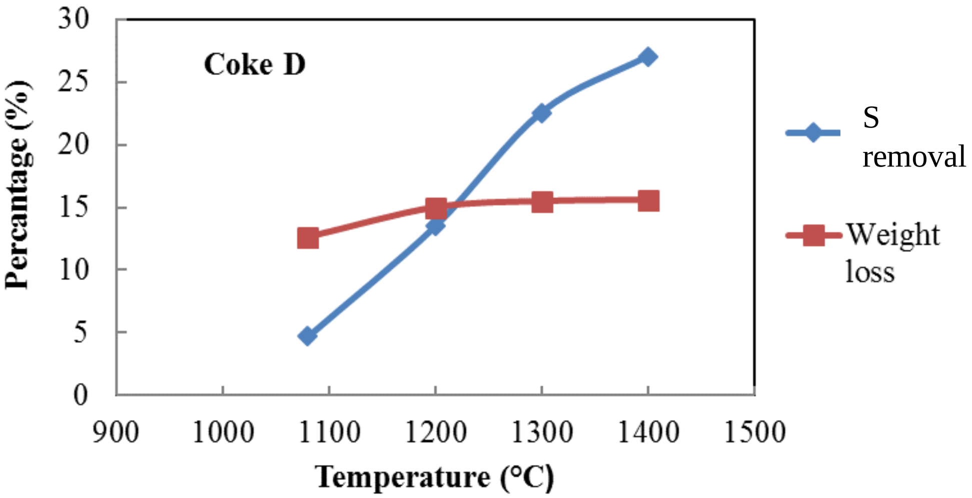


Figure 4.8 Weight loss and sulfur removal results of green coke D with thermal desulfurization at 1080, 1200, 1300, and1400°C

The samples which were treated up to 1200°C, 1300°C and 1400°C showed very similar weight loss rates of around 15%. Thermal desulfurization at 1080°C gave a lower weight loss value of 12.6% which is approximately equal to the volatile content of coke D (see Table 3.1). The sulfur removal rates were found to be proportional to the maximum temperature. Increasing the maximum temperature led to more sulfur removal:

4.72%, 13.51%, 22.56%, and 27.01% at 1080°C, 1200°C, 1300°C, and 1400°C, respectively.

4.4. Hydrodesulfurization

The results of the hydrodesulfurization of green coke D at different experimental set-ups will be presented in this section.

4.4.1. Sulfur Removal and Weight Loss Results of Experiments Conducted with the First Set-up

The results of the hydrodesulfurization experiments which are performed with the 1st system are given in a numbered sequence of HDS-1, HDS-2, HDS-3, etc. Four separate hydrodesulfurization tests were carried out with the 1st experimental set-up for which the details as well as the experimental conditions were explained in detail in Chapter 3. Water injection duration, flow rate as well as coke particle size were kept constant while the effect of water injection temperature was investigated in these experiments. The percent sulfur removal found in four tests and the percent sulfur removal vs. water injection temperature data are given in Table 4.5 and Figure 4.9, respectively.

Table 4.5 Percent sulfur removal of hydrodesulfurization tests conducted with the 1st experimental set-up (temperature of water injection varied keeping all other conditions constant)

	HDS-1	**HDS-2**	**HDS-3**	**HDS-4**
Temperature of water injection, °C	600-650	700-750	808-858	900-950
Sulfur removal (%)	0	3.12	0	0

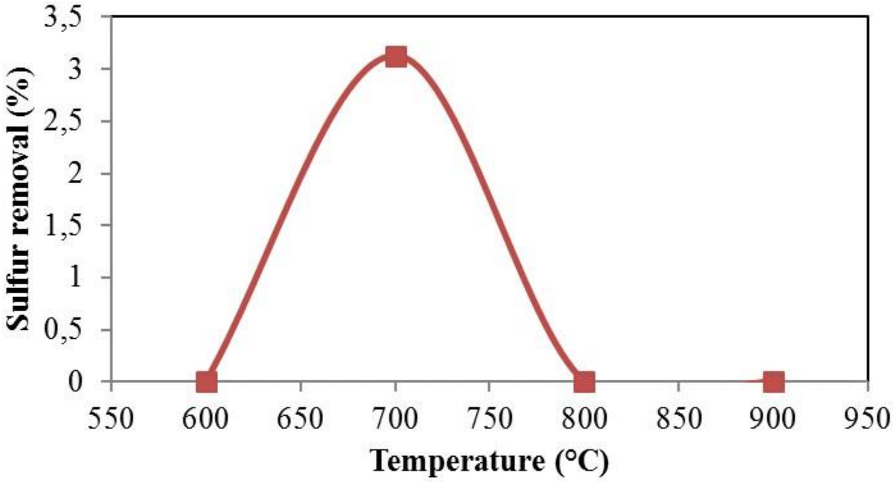


Figure 4.9 Sulfur removal vs. water injection temperature for tests done using the 1st experimental set-up

As can be seen from Table 4.5 and Figure 4.9, 700°C water injection temperature gave more desulfurization than those at 600°C, 800°C, and 900°C. It is possible that, in this set-up, there was oxygen infiltration. Presence of oxygen may have influenced the removal of sulfur. In this experiment, the PID controller of the furnace worked based on the furnace temperature, not based on the sample temperature. It is possible that the sample temperature was much lower than that of the furnace. Under the same experimental conditions, water injection in the range of 700-750ºC showed maximum loss of sulfur. In this set-up, steam could not diffuse much into the coke bed and react with the particles. This might be the reason of low sulfur removal. The coke particles also agglomerated when they came in contact with steam. Thus, the contact was highly limited. Another possibility is the back-reaction of H_2S with coke to form stable sulfur compounds. This needs to be studied further.

4.4.2. Sulfur Removal and Weight Loss Results of Experiments Conducted with the Second Set-up

Based on the observations from the first set of experiments, the 1st experimental set-up was modified, and other experiments were carried out. The results of the tests performed with the 2nd set-up are given in this section. In this case, the PID controller of the furnace was connected to the furnace temperature. This might have resulted in a lower sample temperature compared to the furnace temperature.

All the tests which were done using the 2nd set-up had the same heating rate and maximum temperature. The same water flow rate, injection duration, and coke particle size were used except for the two continuous injection runs which had a longer duration of water injection. Also, various other scenarios have been tried in these tests such as injecting water during the cooling step (HDS-7 and HDS-8) after calcination is completed, continuous water flow during calcination (HDS-10 and HDS-11), application of suction at the gas exit (HDS-5, HDS-6, HDS-7,HDS-8, HDS-10, and HDS-11), no suction (HDS-12), discontinuous injection of water (pulse) (HDS-9), and their combinations (HDS-6, HDS-8, and HDS-11). Except for HDS-10 and HDS-11, efforts were made to inject water in the range of 700-750ºC. It was not possible to control the temperature precisely as the injected water influenced the sample temperature. When the water was injected between 700ºC and 750ºC, the temperature of the sample decreased to 650ºC due to energy required to heat and evaporate the water. The percent sulfur removal and weight loss results of these tests are presented in Table 4.6 and Figure 4.10.

Table 4.6 Hydrodesulfurization experiments carried out with the 2nd set-up

HDS	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
Suction	+	+	+	+	-	+	+	-
Pulse	-	+	-	+	+	-	+	-
Temperature of sample during water injection, °C	700-750	700-750	750-647	750-650	700-750	400-1080	500-1080	700-750
S removal (%)	6.83	0	0	0	0	0	17.73	2.76
Weight loss (%)	16.32	15.79	13.16	13.68	13.16	50	77.89	28.42

+: Yes -: No

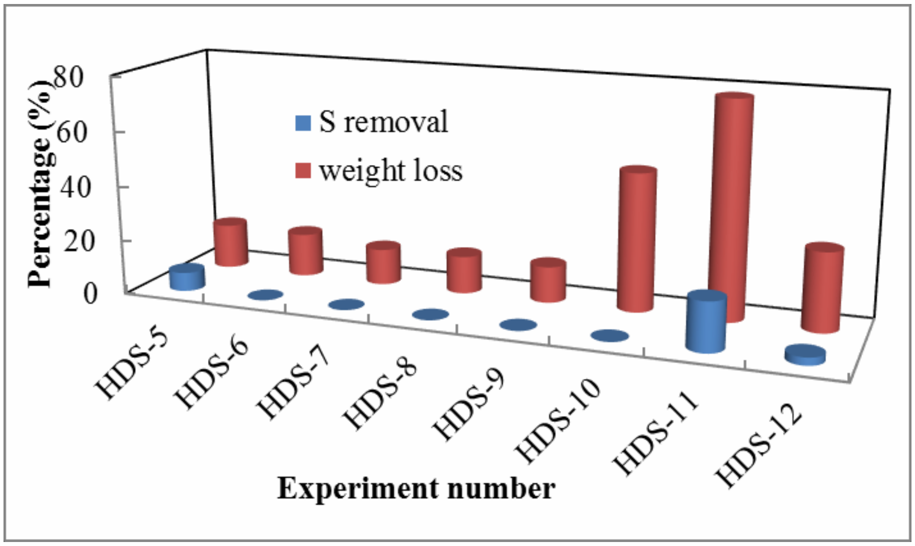


Figure 4.10 Sulfur removal and weight loss results of hydrodesulfurization experiments with the 2nd set-up

No significant sulfur removal was observed from the second set of experiments except the one with continuous water injection as well as pulse and suction. However, major quantity of coke was lost during this experiment which is not desirable. The weight loss was very high due to two possible reasons: a) oxygen infiltration, and b) large quantity of water injection. The large quantity of water could have reacted with coke and produced water gas. In the other experiments, the weight loss and percent sulfur reduction were comparatively low. It is possible that the contact of coke with water was limited. When suction was applied, it is possible that the pump sucked out a large amount of steam which could not react with the coke. Another reason could be that the produced H_2S reacted again with the coke. It is difficult to identify a specific reason to explain the experimental observations. The reason for low desulfurization levels obtained from these experiments might also be due to the 150-200°C temperature difference between the furnace and sample temperatures as a consequence of the low thermal conductivity of the crucible material. To remedy the problem of low sample temperature, a thermocouple was placed inside the sample, and the furnace was controlled with respect to sample temperature in order to get the desired temperatures. Also to ensure good contact between steam and coke, the 3rd set-up was designed and a single layer of coke was used during the experiments. The results obtained with the 3rd set-up are presented in Section 4.4.3.

Gas Chromatography (GC) Analysis of Hydrodesulfurization and Thermal Desulfurization

After the experiments with the 2nd experimental set-up, the system was controlled with respect to sample temperature and connected to two different gas chromatographs for which the details were given in Chapter 3. GC equipped with TCD (thermal conductivity detector) was used to determine H_2 and CH_4 peaks during thermal and hydrodesulfurization. GC equipped with PFPD (pulsed flame photometric detector) was used to detect sulfur peaks coming from sulfur compounds which formed during thermal and hydrodesulfurization. One thermal desulfurization test and one hydrodesulfurization test were carried out, and S, H_2, and CH_4 peaks were determined with two GCs in a temperature range where the data were collected for each experiment. For the thermal test, the data were collected during the heating process between 400°C and 1080°C. For the hydrodesulfurization test, water was injected to the system continuously at 4 ml/min flow rate for 8 h 15 min between 618°C and 1000°C, and data were collected between 580°C and 1080°C. The GC data of these two separate runs are given in Figure 4.11, Figure 4.12, and Figure 4.13.

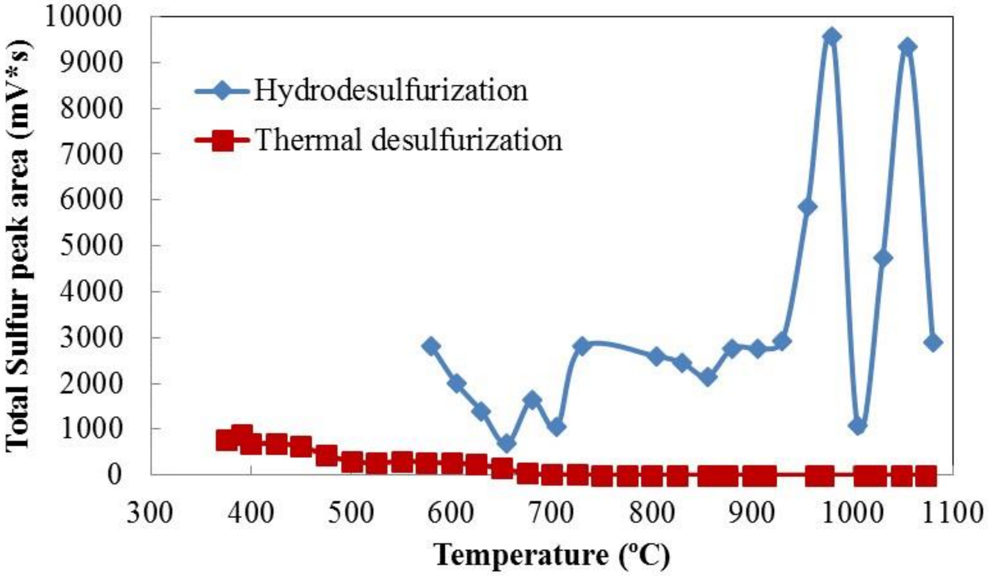


Figure 4.11 Comparison of sulfur peaks during hydrodesulfurization and thermal desulfurization as a function of sample temperature

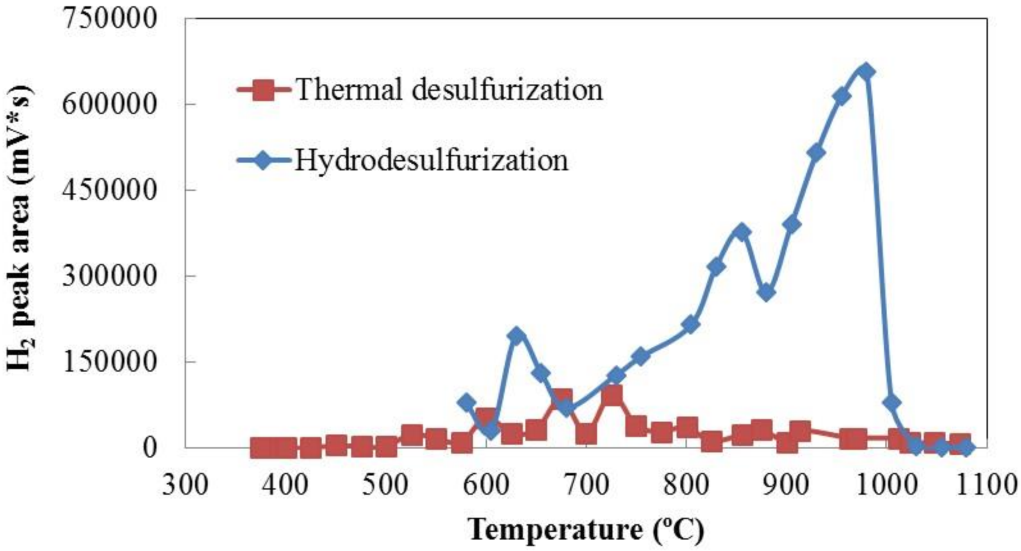


Figure 4.12 Comparison of H_2 peaks during hydrodesulfurization and thermal desulfurization as a function of sample temperature

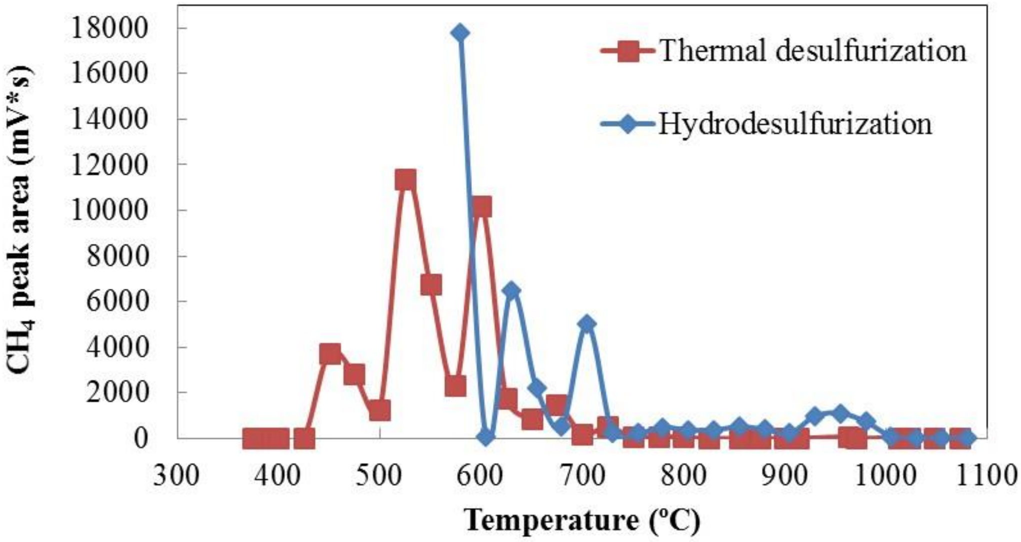


Figure 4.13 Comparison of CH_4 peaks during hydrodesulfurization and thermal desulfurization as a function of sample temperature

The peak areas were not calibrated against known concentrations of different gases. As the peak areas for hydrogen and methane are proportional to their concentrations, they were used to compare the quantity of gases released at different temperatures during thermal and hydrodesulfurization. For sulfur compounds, all the species are converted to SO_2 inside the combustion chamber of the GC and measured using an infra-red detector. Thus, the calibration for different sulfur compounds were not done since the total area of the peaks gives an estimate of the SO_2 equivalent of different compounds. Figure 4.11 and Figure 4.12 show much higher sulfur and hydrogen peak areas during hydrodesulfurization compared to thermal desulfurization. The presence of sulfur compounds clearly increased at the temperatures when water was injected to the system. The increase in H_2 peak can be attributed to the water-gas reaction, which is the reaction between coke and water that produces H_2. The percent hydrodesulfurization is directly related to the favorability of this reaction which depends on temperature [66]. The water injection temperatures for the following hydrodesulfurization runs were chosen according to the temperatures at which the sulfur peak area was most prominent (650-980°C). There was not much difference in peak areas of methane during thermal and hydro-desulfurization treatments (Figure 4.13).

4.4.3. Sulfur Removal and Weight Loss Results of Experiments Conducted with the Third Set-up

Based on the observations from the experiments with the 1st and 2nd set-ups, the 3rd set-up was developed for the 3rd set of hydrodesulfurization experiments. The details of this set-up are given in Chapter 3.

The hydrodesulfurization experiments with the 3rd set-up were carried out at different water injection temperatures in the range of 650-1020°C. The impact of water injection temperature, water flow rate, and injection duration as well as particle size of coke on desulfurization was investigated. The water injection durations of 37 min, 60 min, and 100 min were chosen according to certain studies published on the hydrodesulfurization of petroleum coke. Due to the unsatisfactory sulfur removal results which were obtained with the 1st and 2nd set-ups at high water flow rates, a low water flow rate of 1 ml/min was chosen for this set of experiments.

If it is assumed that a 10 g of coke sample containing 7% sulfur is hydrodesulfurized to 3% sulfur, then the weight of sulfur to be removed is (0.7-0.3) g or 0.4 g. 32 g of sulfur can react with 2 g of H_2 to produce 18 g of H_2S assuming 100% conversion. Thus, for 100% conversion, 0.4 g of sulfur requires (2/32)×0.4 g or 0.025 g of H_2 to produce H_2S. This H_2 comes from water upon reaction with coke (Equation 2.4). 18 g of water can produce 2 g of H_2 for 100% conversion. Thus, (18/2)×0.025 g or 0.225 g of water can supply the required hydrogen. As the conversions for the two reactions (H_2O to H_2, and S to H_2S) are never 100%, higher quantity of water is necessary. Since the conversions of these reactions were not known and the minimum flow available with the rotameters was 1 ml/min, this flow rate was used as the minimum flow rate for the experiments. Figure 4.14 shows the percent sulfur removal from coke and the weight loss of coke during the hydrodesulfurization experiments at water injection temperatures of 650, 750, 850, and 950°C for an injection duration of 37 min with a flow rate of 1 ml/min.

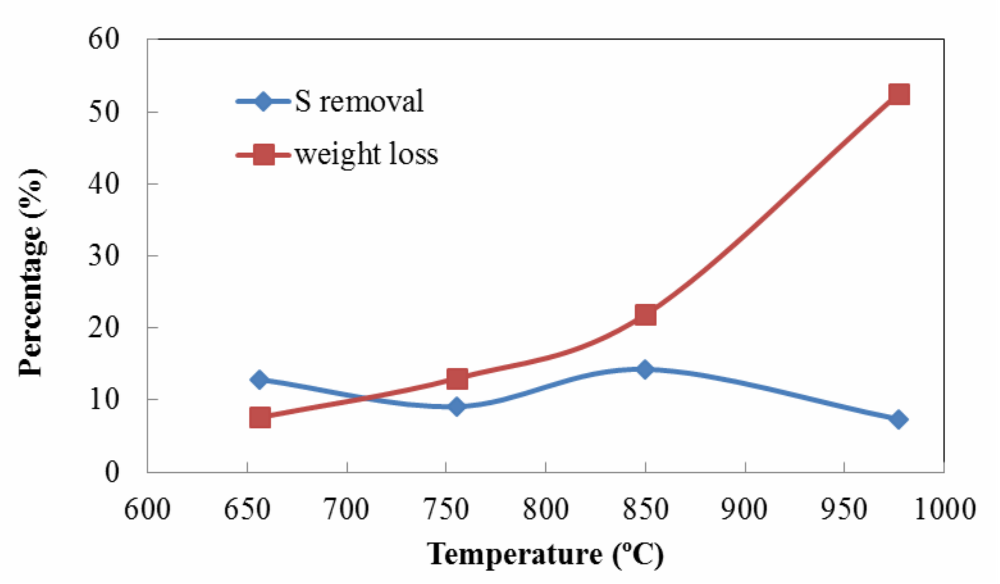


Figure 4.14 Percent sulfur removal and weight loss for the hydrodesulfurization experiments with a water flow rate of 1 ml/min, injection duration of 37 min, and particle size of -2 mm +1 mm at different water injection temperatures

From this figure it may be concluded that 650ºC and 850°C are the suitable injection temperatures for the hydrodesulfurization of coke D under the conditions of 1 ml/min water flow and 37 min duration. 14.29% of the total sulfur was removed from coke in the experiment at 850°C whereas at 650ºC, the percent removal of sulfur was 12.89. Under the same conditions, 750°C and 950°C gave lower sulfur removal of 9.10% and 7.36%, respectively. The weight loss of coke increased with increasing injection temperature. It was 21.87% at 850°C, but it increased dramatically at 950°C to 52.49%, which means half of the coke was lost at this temperature. These results show that when water was injected above 850ºC, rate of formation of H_2 is high and rate of formation of H_2S is low. In all the cases, percent sulfur removal was higher compared to those of the 1st and 2nd set-ups. This clearly shows that the contact of steam with coke played a significant role. Also, the sample temperature was controlled properly by eliminating the difference between the furnace control temperature and the sample temperature. These significantly improved the removal of sulfur.

When the water injection duration was 60 min instead of 37 min, the suitable water injection temperature for the hydrodesulfurization of coke D was found as 650°C and 850°C as shown in Figure 4.15. 22.87% and 22.60% of sulfur removal was obtained at 650°C and 850°C water injection temperatures, respectively. Weight loss values for the experiments using injection temperatures of 650°C and 850°C were 26.07% and 24.37%, respectively, which were higher compared to the previous case (Figure 4.14). The weight loss of coke increased due to the reaction of steam with coke to produce hydrogen. On the other hand, sulfur removal was also higher compared to the experiment with injection duration of 37 min. This shows that a portion of the hydrogen reacted with sulfur compounds. Weight loss from coke shows a stable trend with temperature under these conditions. In this case, the weight loss also seems to increase and the sulfur removal seems to decrease if the water injection temperature is higher than 850ºC, similar to the previous case.

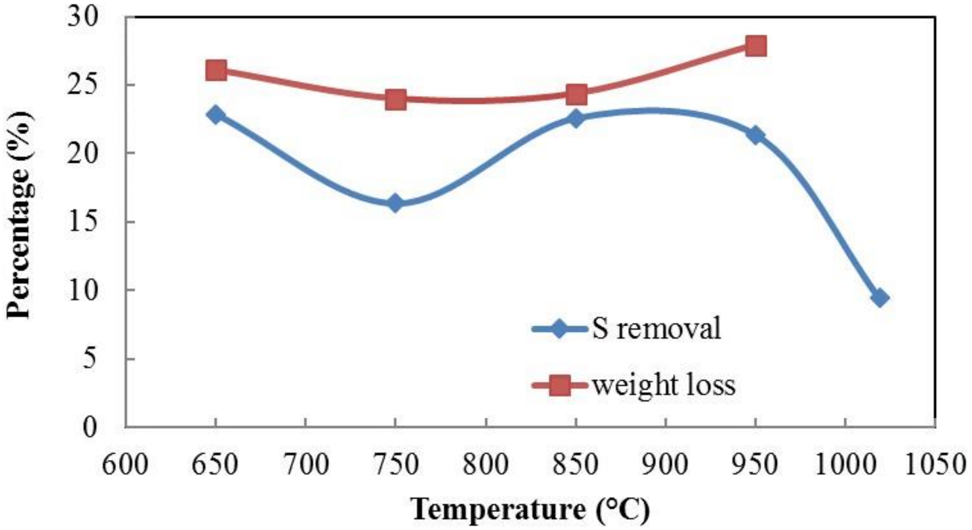


Figure 4.15 Percent sulfur removal and weight loss for the hydrodesulfurization experiments with water flow of 1 ml/min, injection duration of 60 min, and coke particle size of -2 mm +1 mm at different water injection temperatures

As shown in Figure 4.16, when the duration of water injection was increased to 100 min, the highest rate of desulfurization was obtained at 850°C as 19.31%. The weight loss of coke was 40.45% for the same injection temperature which is quite high. Desulfurization at 650°C injection temperature was also found high as 19.22%. The weight loss at this injection temperature was 23.32%. In this case, sulfur removal decreased and weight loss increased above 850ºC as well.

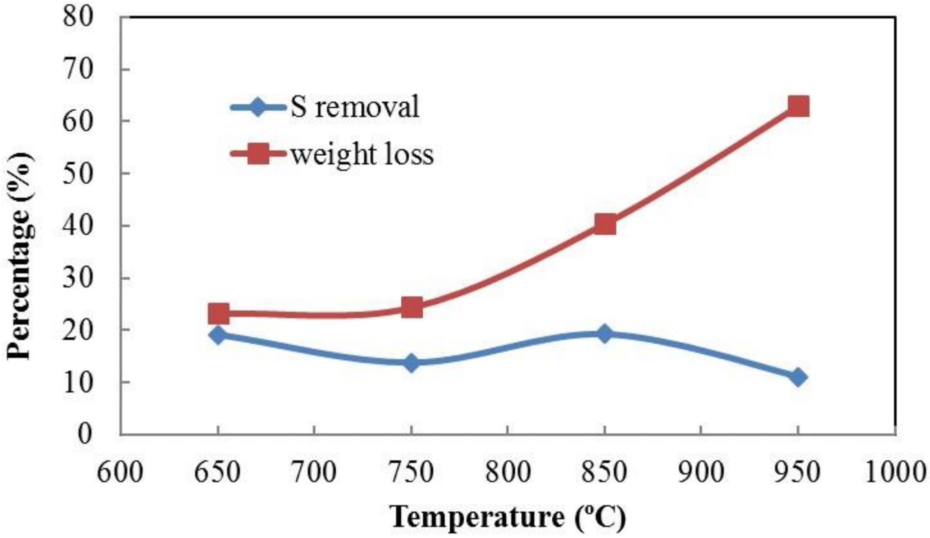


Figure 4.16 Percent sulfur removal and weight loss for the hydrodesulfurization experiments with water flow of 1 ml/min, injection duration of 100 min, and coke particle size of -2 mm +1 mm at different water injection temperatures

Figure 4.14, Figure 4.15, and Figure 4.16 suggest that in addition to the loss of volatile matter, some coke is lost at the water injection temperatures of 650°C and above due to the gasification of carbon by water [64, 66]. The maximum percentage of carbon gasified by water is approximately 28.15% (40.45% total weight loss-12.3% weight loss due to volatile matter of coke) for the injection of water at 850°C over a 100 min period. At the conditions which gave the highest sulfur removal (850°C, 1 ml/min, 60 min), approximately 11.97% (24.27% total weight loss-12.3% weight loss due to volatile matter of coke) carbon appears to be gasified by hydrogen. It may be inferred from the above figures that the additional gasification of carbon by water above the injection temperature of 850ºC does not have a beneficial effect on the hydrodesulfurization of high sulfur petroleum coke [66]. The effect of water injection duration on desulfurization and total weight loss of coke for different water injection temperatures of 650°C, 750°C, 850°C, and 950°C are presented in Figure 4.17 and Figure 4.18, respectively. The values of sulfur removal and weight loss percentages are given separately in Table 4.7 and Table 4.8, respectively. Figure 4.17 shows that percentage of sulfur removal is high at water injection temperatures of 650ºC and 850ºC. It may be noted that injection at a specific temperature does not mean that the temperature of the sample was maintained at that temperature during the water injection. It means that water injection was started at that temperature. However, during the injection process, the sample temperature decreased due to heat consumed for heating and evaporating the water and then started increasing again. Thus, the ideal temperature to start the water injection for removal of sulfur from the coke sample is around 650ºC and 850ºC.

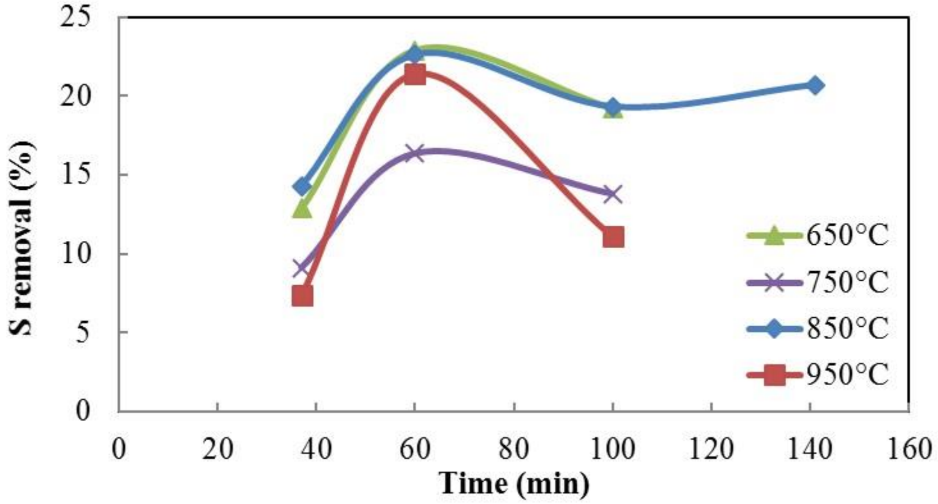


Figure 4.17 Variation of sulfur removal from coke D with -2 mm +1 mm particle size with respect to water injection duration for 650°C, 750°C, 850°C and 950°C of water injection temperatures and 1 ml/min water flow

Table 4.7 Sulfur removal percentages of cokes for several hydrodesulfurization tests carried out under different conditions using 1 ml/min water flow rate, -2 mm +1 mm coke particle size

	Sulfur removal (%)			
T (°C) \ t (min)	**37**	**60**	**100**	**141**
650	12.88	22.87	19.21	-
750	9.10	16.37	13.80	-
850	14.28	22.60	19.30	20.69
950	7.36	21.38	11.11	-

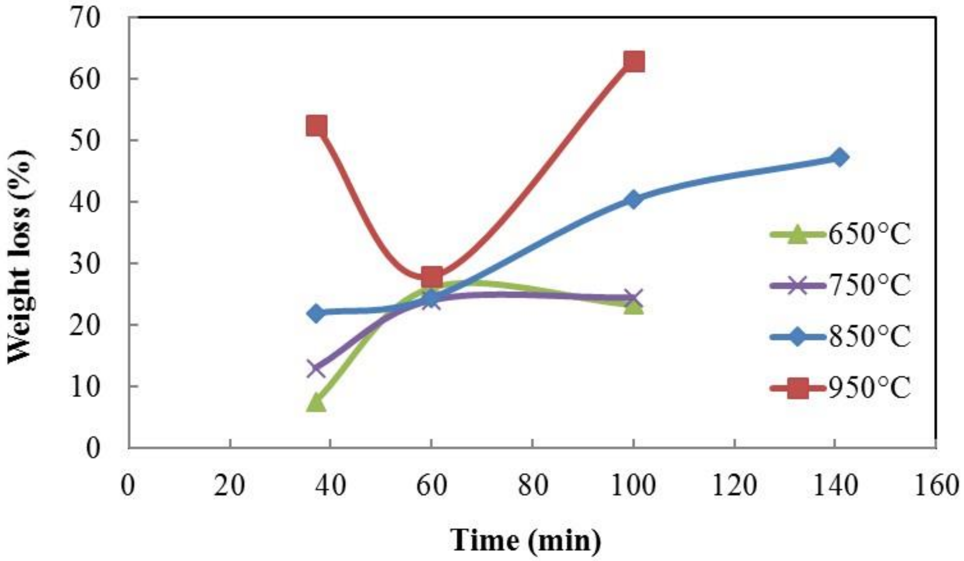


Figure 4.18 Variation of weight loss from coke D with -2 mm +1 mm particle size with respect to water injection duration for 650°C, 750°C, 850°C and 950°C water injection temperatures and 1 ml/min water flow

Table 4.8 Weight loss percentages of cokes for several hydrodesulfurization tests carried out under different conditions using 1 ml/min water flow rate, -2 mm +1 mm particle size

Weight loss (%)				
t (min) **T (°C)**	**37**	**60**	**100**	**141**
650	7.6	26.07	23.32	-
750	13	24.00	24.42	-
850	21.87	24.37	40.45	47.26
950	52.49	27.9	62.98	-

Water was injected at four different temperatures in the experiments, water injection durations were varied at these temperatures (650°C, 750°C, 850°C, and 950°C). Injection durations were chosen as 37, 60, 100, and 140 min based on the previous works on the hydrodesulfurization of petroleum coke in the literature. A water flow rate of 1 ml/min was used for these runs. It may be concluded from Figure 4.17 that in all the temperatures, percent desulfurization increases with increasing water injection duration up to a certain point and then starts decreasing. 60 min of water injection duration was found to be the most favorable for all water injection temperatures that were tried during the current hydrodesulfurization study. The longest water injection duration was 100 min except for the case of 850°C. During the hydrodesulfurization experiment using this injection temperature, longer water injection duration of 140 min was also tried. Although desulfurization increased at this value, weight loss of coke also increased from 24.37% at 60 min to 47.26% at 140 min. The highest sulfur removal values were obtained after 60 min of water injection at 650°C and 850°C as 22.87% and 22.60%, respectively.

It can be seen from Figure 4.18 that the weight loss from coke at 650°C and 750°C increases with increasing injection duration from 37 min to 60 min after which it remains almost constant. The weight loss at 850°C continuously increases with the injection duration while at 950°C the trend is completely different than the others. It decreases to a certain minimum and starts increasing with further increase of injection duration. The trend at 950ºC needs to be studied in detail. In this study, the total weight loss was measured. Thermogravimetric analysis should be done in order to determine the weight loss of coke with respect to time during the hydrodesulfurization experiments that were carried out under different conditions.

The effect of water flow rate at 850°C water injection temperature and 37 min injection duration were also studied in this project and is given in Figure 4.19.

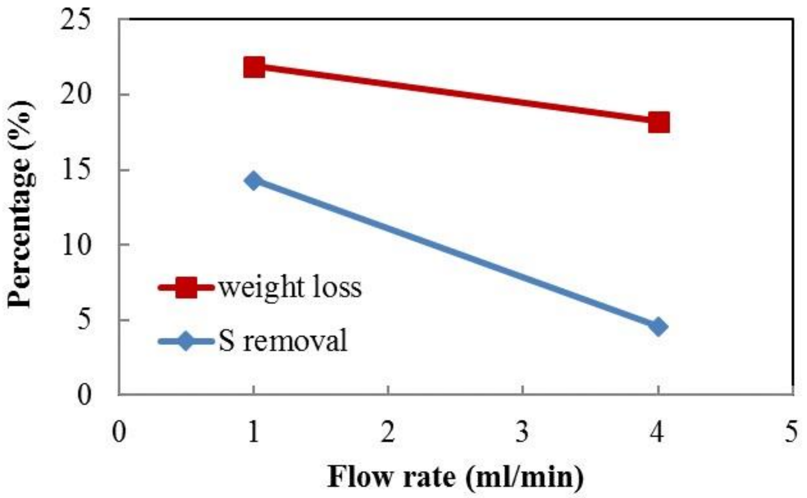


Figure 4.19 Effect of water flow rate on desulfurization of coke D with -2 mm +1 mm particle size, 850°C injection temperature and 37 min injection duration

Figure 4.19 shows that the hydrodesulfurization decreases with increasing water flow rate and was highest (14.29%) when the injection duration was 37 min and the flow rate was 1 ml/min, which was the minimum flow rate used during the experiments. At

4 ml/min flow rate, sulfur removal decreased to 4.58%. This might be due to several reasons. When higher quantity of water is injected to the system during the same time period, it might have reduced the coke temperature, making the hydrodesulfurization reaction less favorable. Another reason can be the dilution of hydrogen that was produced from the reaction of coke and steam by the higher quantity of steam. This reduces the reaction rate of hydrodesulfurization which results in lower sulfur removal.

Fine particles (-100 µm +75 µm) of green coke D were desulfurized, and the results were compared with those of -2 mm +1 mm particles. During these experiments, 1 ml/min water flow rate, 850°C injection temperature as well as 37 and 60 min of injection durations were used. The results are presented in Figure 4.20 and Table 4.9.

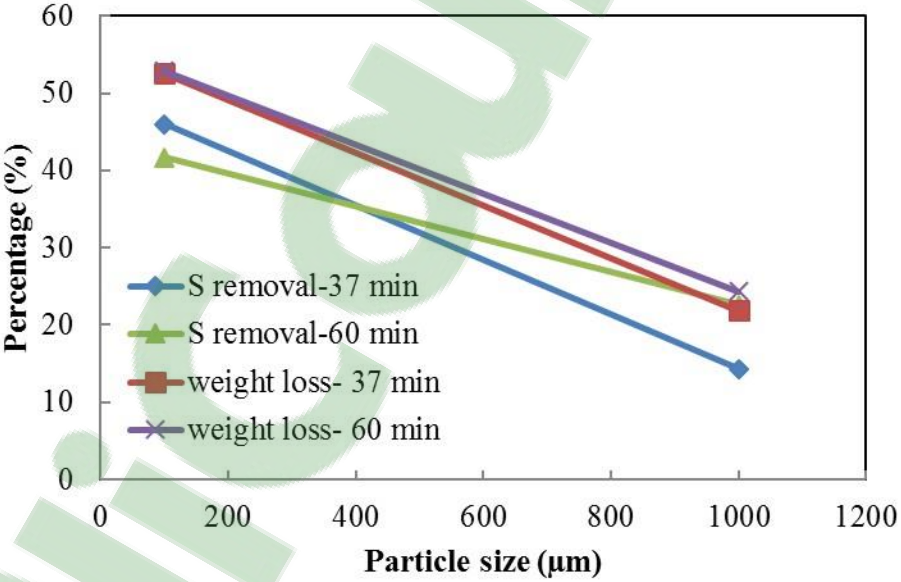


Figure 4.20 Effect of varying particle size on hydrodesulfurization for 850°C injection temperature and 1 ml/min water flow rate

Table 4.9 Effect of varying particle size on hydrodesulfurization for 850°C injection temperature and 1 ml/min water flow rate

Water injection duration (min)	37		60	
Particle size (mm)	-0.1 +0.075	-2 +1	-0.1 +0.075	-2 +1
S removal (%)	45.97	14.28	41.67	22.60
Weight loss (%)	52.57	21.87	52.87	24.37

Figure 4.20 and Table 4.9 show that decreasing particle size has a beneficial effect on the desulfurization of coke D. The percent sulfur removal increased from 22.60% to 41.67% during the experiment with water injection duration of 60 min whereas sulfur removal increased from 14.28% to 45.97% when 37 min injection duration was used. It was mentioned that this may be due to either an increase in external surface area and accessible internal surface area or a decrease in the resistance of the pore diffusional path [66].

Also, a number of hydrodesulfurization tests were done with green coke D to see the effect of injecting high amount of water (higher water flow rate) in a shorter time compared to those of the previous experiments. Figure 4.21 and Table 4.10 shows the variation of the percent desulfurization of coke D using 8 ml/min water flow rate injected over a 6-min period at different water injection temperatures.

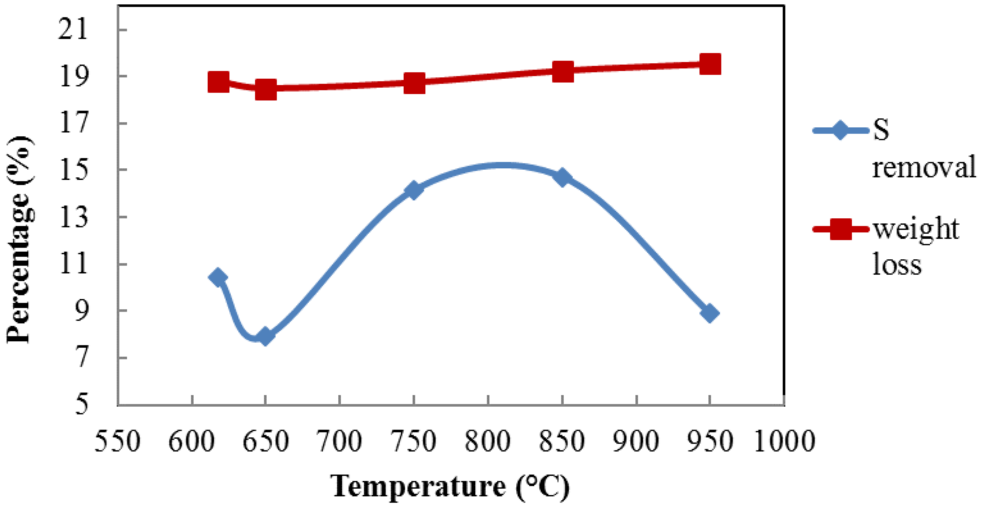


Figure 4.21 Variation of sulfur removal from coke D with -2 mm +1 mm particle size with respect to water injection temperature using 8 ml/min water flow rate and 6 min injection duration

Table 4.10 Sulfur removal and weight loss values of hydrodesulfurized coke D with -2 mm +1 mm particle size at varying injection temperatures using 8 ml/min water flow rate and 6 min injection duration

T (°C)	**618**	**650**	**750**	**850**	**950**
S removal (%)	10.42	7.92	14.17	14.72	8.89
Weight loss (%)	18.79	18.49	18.74	19.25	19.54

The highest rate of sulfur removal was obtained at 850°C injection temperature and was found as 14.72% under these conditions. The weight loss from coke wasn’t as high and was almost constant at 19% within the temperature range studied. The major reaction leading to the weight loss was conversion of steam to hydrogen by carbon. As the quantity of the steam was same, the weight loss was nearly the same. The amount of sulfur did not influence the weight loss significantly as the quantity of sulfur in coke was low.

The hydrodesulfurization results for the particle size of -2 mm +1 mm presented up to here are summarized in Figure 4.22 as a function of temperature. The weight loss results of all experiments are given in Figure 4.23.

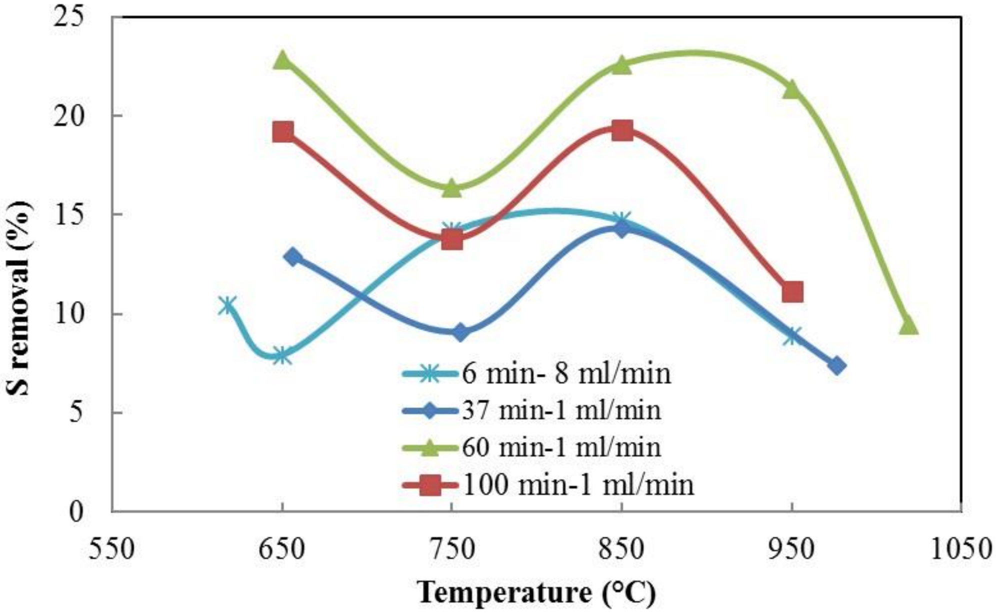


Figure 4.22 The effect of temperature on the extent of desulfurization obtained at different reaction times and flow rates (coke particle size -2 mm +1 mm)

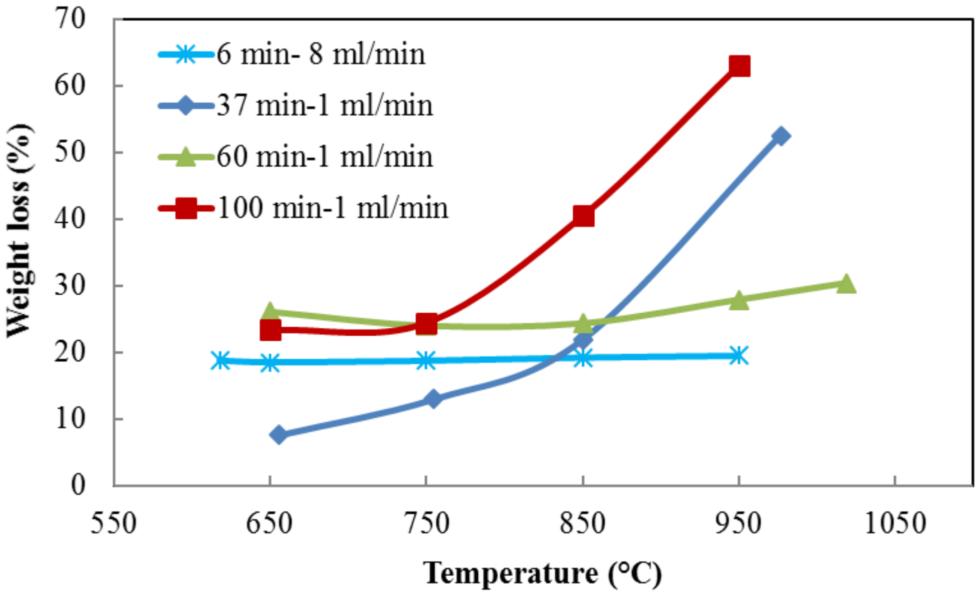


Figure 4.23 The effect of temperature on the coke weight loss obtained at different reaction times and flow rates (coke particle size -2 mm +1 mm)

The maximum sulfur removal was obtained when the water was injected to the sample at 650°C and 850°C for 60 min followed by injection at 650°C and 850°C for 100 min, and the percent sulfur removal was found as 22.87%, 22.60%, 19.22%, and 19.31%, respectively. Weight loss percentages under these conditions are 26.07%, 24.34%, 23.32%, and 40.45%, respectively. It can be concluded from these results that 60 min of water injection at 650°C and 850°C temperatures are the most suitable conditions for the hydrodesulfurization of coke D among all the conditions that were tested. The weight loss from coke under these conditions was around 25% with the exception of the last experiment. The percent sulfur removal as a function of temperature for different water-coke contact times seems to follow similar trend; however, additional experiments should be done to investigate the effect of temperature and duration in a narrower temperature range. The fact that sulfur removal shows a peak at certain temperatures and starts decreasing with further increase in temperature might have different reasons according to the literature. The sintering of coke particles above a certain temperature, depending on the origin of petroleum coke, was reported to decrease the surface area and the amount of hydrodesulfurization [66]. The agglomeration of the particles reduces the surface area of the coke inducing a decrease in the rate of diffusion for both hydrogen going in and H_2S coming out of the coke particles [65]. Another explanation for the decrease in desulfurization level above a certain temperature is that hydrogen sulfide reacts with coke which forms complex sulfides of carbon along with the volatile carbon sulfide [64, 66, 100]. It was stated that at temperatures of 500-700°C, the primary sulfur compounds disintegrate, and react with coke forming more stable sulfur-organic complexes and inorganic sulfur compounds. The decomposition and removal of these compounds take place at much higher temperatures [79]. The fixation of inorganic impurities present in petroleum coke to high-molecular-weight ring structures containing sulfur bridges and thus forming more complex compounds, and making coke less susceptible to hydrodesulfurization was also mentioned in the literature [26, 66]. All these possible reasons are directly related to the origin of coke, its sulfur and ash contents as well as the operating conditions of refining and coking. The rates of possible reactions between water; carbon, hydrogen, sulfur, and hydrogen sulfide are some of the parameters that affect the desulfurization of coke.

Another set of experiments were carried out to study the effect of coke granulometry on hydrodesulfurization. During these experiments, 850°C water injection temperature, 37 min water injection duration, and 1 ml/min water flow rate were used. The particle sizes used were -16 mm +12.5 mm, -12.5 mm +8 mm, -8 mm +6.3 mm, -6.3 mm +4 mm, -4 mm +2 mm, -2 mm +1 mm. One experiment was done with a standard sample of 10 g while in the second experiment the sample amount was reduced to have a single layer of particles. The effect of this change on hydrodesulfurization was also investigated. Figure 4.24 and Table 4.11 show the sulfur removal and weight loss results after the hydrodesulfurization of 10 g coke sample with the above mentioned granulometry.

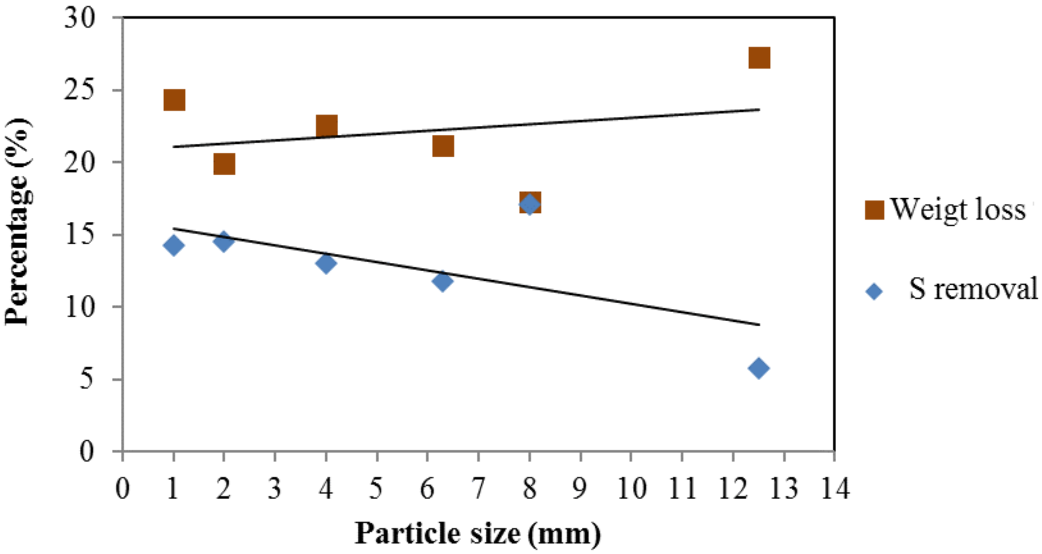


Figure 4.24 Percent sulfur removal and weight loss vs different particle sizes of coke D hydrodesulfurized using 850°C injection temperature, 1 m/min of water flow rate and 37 min injection duration with a 10 g sample

Table 4.11 Percent sulfur removal and weight loss values of coke D with different particle sizes hydrodesulfurized using 850°C injection temperature, 1 m/min of water flow rate and 37 min injection duration with a 10 g sample

Particle size (mm)	**-16 +12.5**	**-12.5 +8**	**-8 +6.3**	**-6.3 +4**	**-4 +2**	**-2 +1**
S removal (%)	5.82	17.13	11.77	13.02	14.54	14.29
Weight loss (%)	27.31	17.25	21.14	22.55	19.92	24.37

One would expect a decrease in desulfurization with increasing particle size since the surface area decreases when the particle size is larger and the diffusion path is longer. Figure 4.24 also shows that the experimental results are in agreement with expected trend. The fluctuations observed in experimental results might be attributed due to the non-homogeneity of the coke as well as experimental error. Based on the results of this experiment, another experiment was done with a lower quantity of coke sample using different particle sizes under the same conditions. The sulfur removal and weight loss results of these experiments with respect to different particle sizes are given in Figure 4.26 and Table 4.12. It was thought that steam could not come in contact with the surface of the coke sample touching other coke particles or the diffuser plate although agglomeration can also be a cause. Hence, slots were made close to the holes in the diffuser plate. The coke particles were placed on the slots, which eliminated particle-particle contact and minimized significantly the contact of particles with the diffuser plate. The only contact of particles with the sample holder was at the two edges of the slots (Figure 4.25).

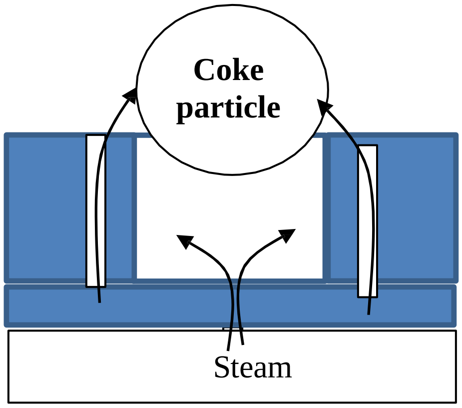


Figure 4.25 Position of coke particles in the slots

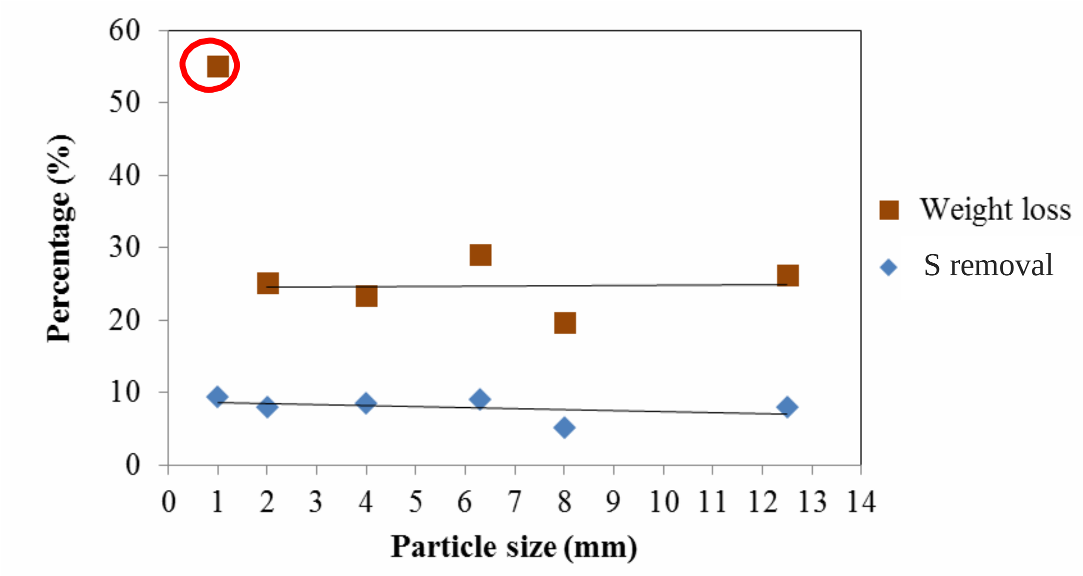


Figure 4.26 Sulfur removal and weight loss vs coke D particle size hydrodesulfurized using 850°C injection temperature, 1 m/min of water flow rate and 37 min injection duration with one layer of sample

Table 4.12 Sulfur removal and weight loss values of coke D for different particle sizes hydrodesulfurized using 850°C injection temperature, 1 m/min of water flow rate and 37 min injection duration with one layer of sample

Particle size (mm)	**-16 +12.5**	**-12.5 +8**	**-8 +6.3**	**-6.3 +4**	**-4 +2**	**-2 +1**
S removal (%)	8.07	5.16	9.01	8.58	7.99	9.45
Weight loss (%)	26.19	19.69	29.13	23.44	25.2	55.77

When the coke quantity used for the hydrodesulfurization was reduced, the percentage of sulfur loss again reduced with increasing particle size. However, in this case, percent sulfur removal was lower compared to that of the previous case. In addition, the fluctuation in data was also less. The low sulfur removal percent might be partially attributed to the non-homogeneity of coke. Also, the water flow rate and duration of injection used was the same as those used in the previous case, but the amount of coke was significantly less. It is possible that the produced hydrogen was diluted by steam resulting in less sulfur removal. Except for the percent weight loss for -2 mm +1 mm particle (highlighted by a red circle in Figure 4.26), there was a slight increase in weight loss with increasing particle size showing that the trend is similar to that of the previous case. However, in this case, the change in weight loss with respect to particle size was small. The high percent weight loss observed for -2 mm +1 mm particles can be due to non-homogeneity of coke particles or particle loss while handling the small particles. As the amount of sample was small, a small error in weight measurement can significantly affect the result. The weight loss observed for -2 mm +1 mm particles was higher compared to the previous experiment. The reason might be due to relative increase in the quantity of water due to the decrease in coke quantity for the same water flow rate.

4.5. Comparison of Thermal Desulfurization and Hydrodesulfurization

Due to the limitation of the furnace used for hydrodesulfurization, it was difficult to heat the coke samples above 1100ºC. Thus, the efficiency of thermal and hydro-desulfurization can only be compared for the samples heated up to 1100ºC. At high temperature, the gradient between the furnace and sample temperatures became small and sometimes it was difficult even to reach 1100ºC in this furnace. Therefore, 1080ºC was chosen as the maximum calcination temperature for comparison purposes. As a result of several hydrodesulfurization tests under different conditions, one of the highest sulfur removal percentages obtained with coke D of -2 mm +1 mm particle size was 22.60% using 850ºC water injection temperature, 60 min water injection duration, and 1 ml/min water flow rate. When this result is compared with the one obtained from the thermal desulfurization up to 1080ºC (4.72% sulfur removal), hydrodesulfurization seems to be a more efficient method for sulfur removal than thermal desulfurization. Although there is some carbon loss, which is around 10%, in addition to volatile release during hydrodesulfurization, this carbon loss can be reduced by further modification of the experimental conditions. However, it should be noted that the hydrodesulfurization requires a good contact between gas and coke, which is not the case for thermal desulfurization. Changes in coke structure were analyzed before and after hydro and thermal desulfurization in order to investigate their effect on coke porosity and are presented in this section. Apparent density and real density of cokes were measured by water pycnometer and He pycnometer, respectively. Then, the porosities of cokes were calculated using these densities. Coke structure and morphology before and after the treatments were characterized with SEM-EDX, XPS, and XRD in order to determine the structural changes in cokes as well as the sulfur functional groups present on the coke surface. The cokes compared are as follows: green petroleum coke D, coke D thermally desulfurized up to 1080ºC (4.72% S loss) and 1200ºC (13.51% S loss), coke D hydrodesulfurized up to 1080ºC using 850ºC injection temperature, 37 min injection duration, 1 ml/min water flow rate (14.29% S loss) and coke D hydrodesulfurized up to 1080°C using 850°C injection temperature, 60 min injection duration, 1 ml/min water flow rate (22.60% S loss).

4.5.1. Coke Properties

Table 4.13 shows the porosity as well as the apparent and real densities of green, thermally and hydrodesulfurized cokes. The coke hydrodesulfurized using 850ºC injection temperature, 37 min injection duration, 1 ml/min water flow is identified as

HDS-37 while coke hydrodesulfurized using 850°C injection temperature, 60 min injection duration, 1 ml/min water is identified as HDS-60. Thermally desulfurized cokes are assigned the identifications of TDS-1080 and TDS-1200 according to their maximum calcination temperatures. Porosity of coke samples was calculated using Equation (3.1).

Table 4.13 Comparison of density and porosity values of coke D before and after thermal and hydrodesulfurization

	Petroleum coke D				
	Green	TDS-1080 (T_{max}=1080°C)	TDS-1200 (T_{max}=1200°C)	HDS-37 (T_{max}=1080°C)	HDS-60 (T_{max}=1080°C)
Apparent density (g/cm^3)	1.29	1.76	1.73	1.81	1.79
Real density (g/cm^3)	1.39	1.96	1.91	2.11	2.04
Porosity (%)	7.08	10.17	9.20	14.21	11.98

According to density and porosity results, it can be concluded that hydrodesulfurization treatments that the green coke D was subjected to at two different conditions increased the porosity to some extent, but the increase was not to the extent to disqualify the coke as raw material for carbon anodes. The coke after HDS-60 treatment had a porosity of 11.98% which is lower than that of HDS-37 which was 14.21%. HDS-60 coke had also a higher sulfur removal (22.60%) than that of HDS-37 (14.28%). Also the real densities of hydrodesulfurized cokes were found higher than those of thermodesulfurized cokes. Specifically, the real density of HDS-37 coke seems too high considering the maximum temperature it was heated to (1080°C). However, this value was obtained after only one measurement. Due to the non-homogeneity of coke, more measurements should be done to obtain a precise real density value. On the other hand, the real density values of thermally desulfurized cokes up to 1080°C and 1200°C are lower than the real density of industrial standard calcined coke which is around 2.08-2.13 g/cc [124]. The results can be compared on a relative basis. This might be due to the insufficient calcination and graphitization of these cokes. Thus, hydrodesulfurization might have some influence on the real density of the coke. The hydrogen produced during the process might have created a reducing atmosphere which helped in the carbonization of coke samples. Also, the variations in porosity may be attributed to the non-homogeneity of the coke particles.

4.5.2. XRD Analysis

The degree of crystalline alignment of cokes was determined with X-ray Diffraction (XRD) analysis. Crystallinity of petroleum coke is, in general, a measure of quality indicating the suitability for end use and a function of the heat treatment [125]. In order to be able to use a calcined coke as anode raw material, it has to have a certain degree of crystallinity. For calcined cokes, the average stacking height of graphene layers, Lc, is a good indication of their graphitizability upon heat treatment [125]. The XRD patterns of coke D samples were recorded over the range of angles from 3° to 70°. Figures 4.27, 4.28, and 4.29 show the XRD patterns of HDS-37, HDS-60, TDS-1080, and TDS-1200.

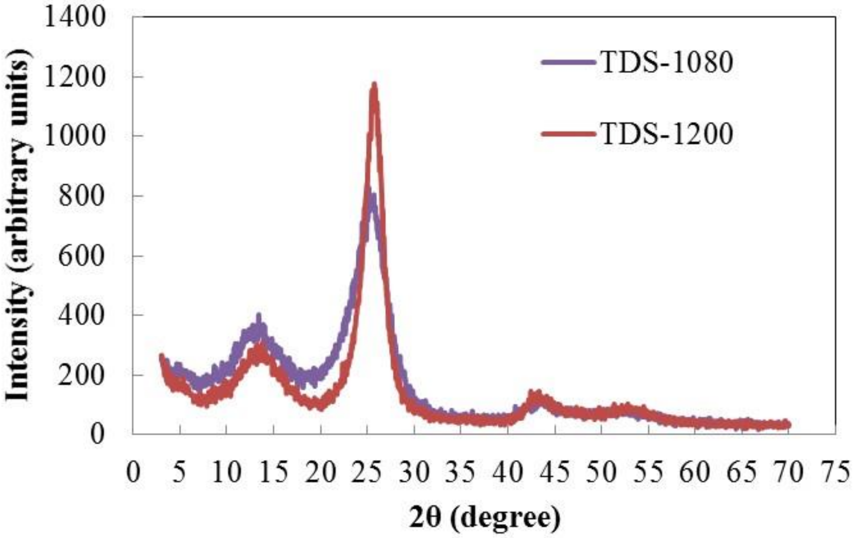


Figure 4.27 XRD patterns of thermally desulfurized cokes at 1080°C and 1200°C

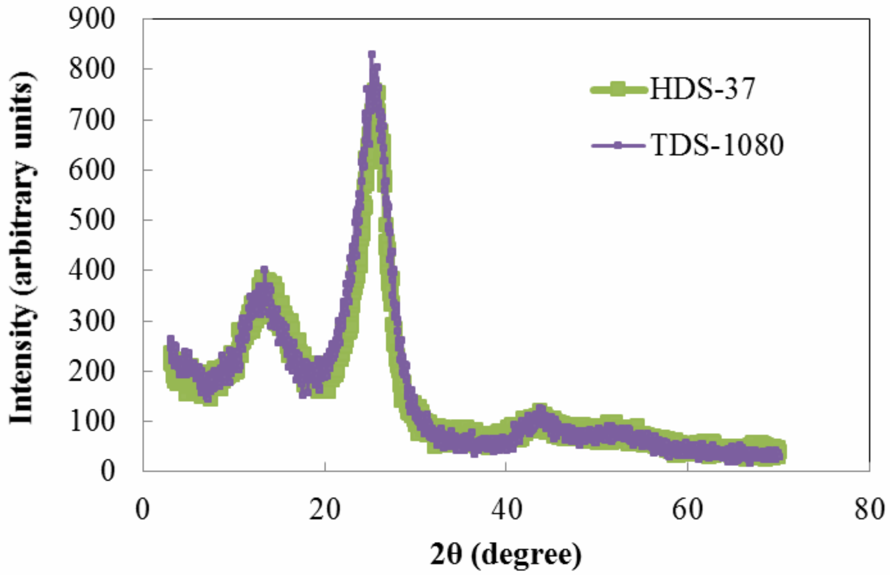


Figure 4.28 XRD patterns of cokes after hydrodesulfurization and thermal desulfurization

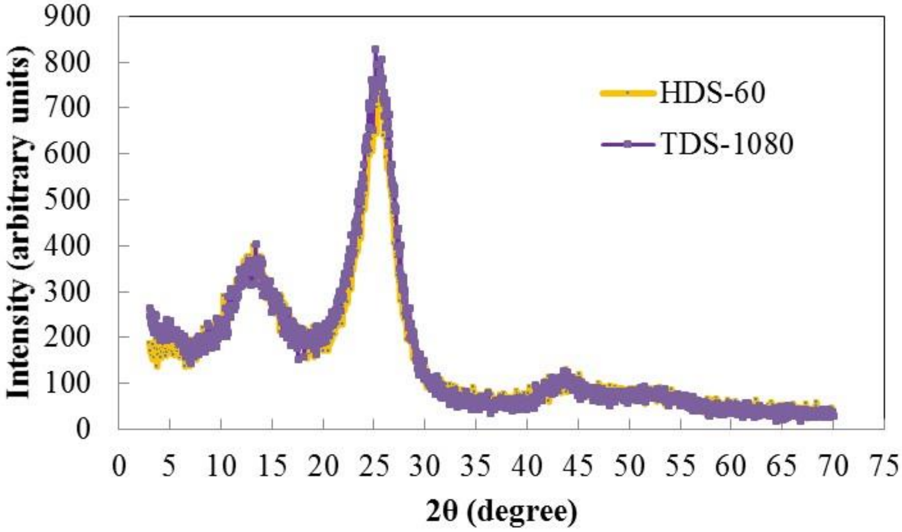


Figure 4.29 XRD patterns of cokes after hydrodesulfurization and thermal desulfurization

The Lc values of the coke samples were calculated using Figures 4.27, 4.28, and 4.29 by the Scherrer formula. Table 4.14 lists the Lc values of the coke samples.

Table 4.14 Lc values of different treated coke samples

Sample	Lc, Å
TDS-1080	26.00
TDS-1200	35.05
HDS-37	28.78
HDS-60	26.86

The coke samples subjected to XRD analysis produced three peaks at Bragg angle 2θ position of around 12º, 26.5º, and 44º corresponding to 001, 002, 121 planes of graphite crystals, respectively [126]. The extent of graphitisation was calculated based on the Bragg angle 2θ position of around 26.5°. The graphitisation degree of coke was maximum when it was calcined to 1200°C (Lc 35.05 Å). The Lc was lower when calcination was done up to 1080°C (Lc 26.00 Å). This shows that increase in calcination temperature increases the Lc value (Table 4.14). Also, the Lc values of hydrodesulfurized cokes were slightly higher than that of TDS-1080. This shows that hydrodesulfurization may have somewhat increased the Lc of the coke samples. As the maximum temperature of both hydrodesulfurization experiments was the same as that of TDS-1080, the increase in Lc during the hydrodesulfurization process might be attributed to chemical reactions. It is possible that, during the hydrodesulfurization process, the hydrogen produced by the water-gas reaction may have created a reducing atmosphere which helped graphitization. The Lc of the sample HDS-37 (Lc 28.78 Å) was higher compared to that of HDS-60 (Lc 26.86 Å).

4.5.3. Surface Functionality with XPS Analysis

XPS analysis was done to determine the differences between the surface functionalities of TDS-1080, TDS-1200, HDS-37, and HDS-60 coke samples. Figures 4.30, 4.31, 4.32, and 4.33 show the XPS survey spectra of these four samples. The XPS survey spectra of green coke D is given in Figure 4.2. The atomic percentages of different elements in all cokes were calculated using CasaXPS software and are given in Table 4.15.

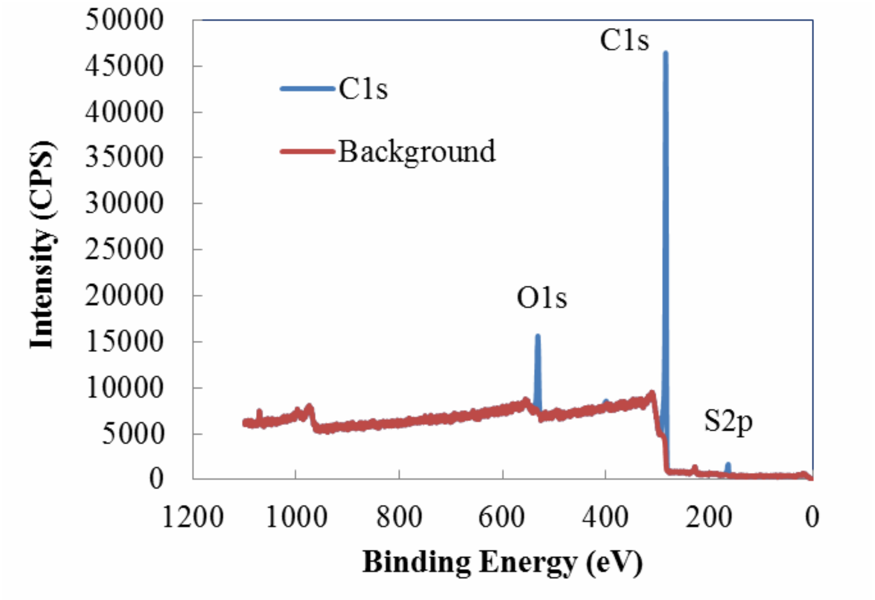


Figure 4.30 General spectra of TDS-1080 coke sample from XPS analysis

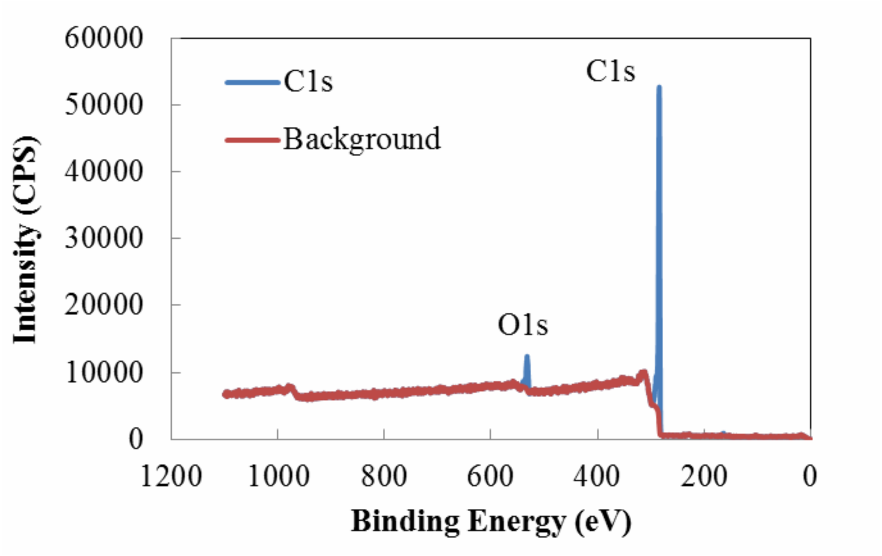


Figure 4.31 General spectra of HDS-37 coke sample from XPS analysis

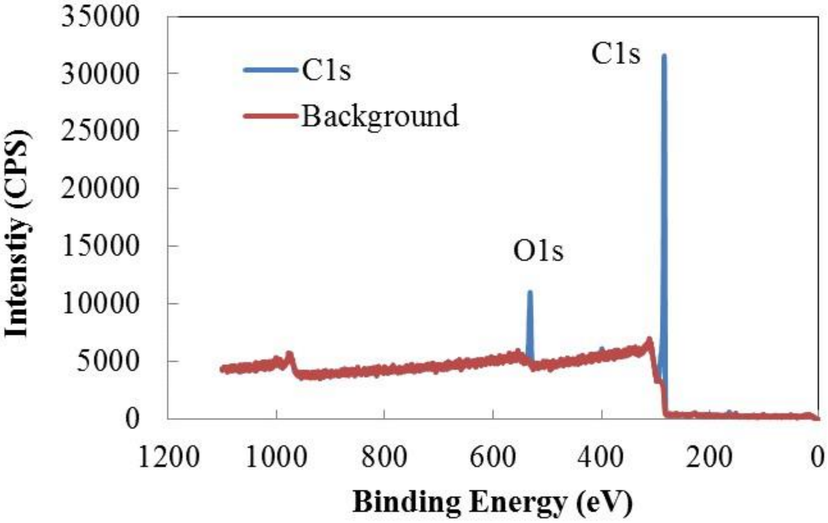


Figure 4.32 General spectra of HDS-60 coke sample from XPS analysis

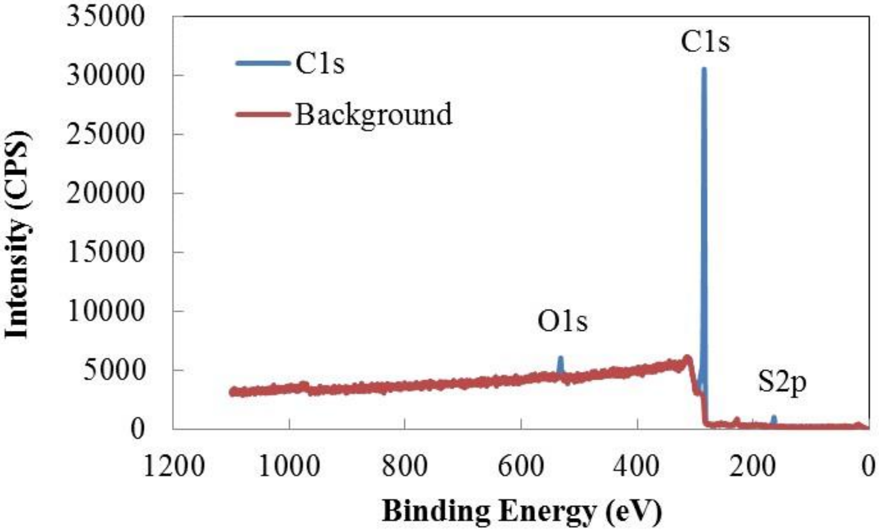


Figure 4.33 General spectra of TDS-1200 coke sample from XPS analysis

Table 4.15 Atomic percentages of the different components of green, TDS-1080, TDS-1200, HDS-37, and HDS-60 coke samples

Coke type	**C (at %)**	**O (at %)**	**N (at %)**	**S (at %)**
Green coke D	91.67	6.02	0.00	2.32
TDS-1080	90.55	7.46	0.16	1.83
TDS-1200	96.47	2.01	0.00	1.51
HDS-37	95.03	4.57	0.00	0.40
HDS-60	92.25	7.12	0.25	0.37

In general, the XPS spectra of all coke samples show the most prominent peak at 284.3 eV which is designated as C1s. Other notable peaks include the O1s peak at around 531.90 eV and S2p peak at 163.10-164.70 eV depending on different samples. The relative positions of these peaks were used to determine the chemical nature of these elements. The variation in percentage of carbon (Table 4.15) can explain the results obtained by XRD measurements. The percentages of C of the green coke and TDS-1080 are close (91.67 and 90.55 respectively). The slight variation in C content can be attributed to the non-homogeneity of the coke surface. TDS-1200 has the highest C content (96.47) and the highest Lc value (35.05 Å). HDS-37 and HDS-60 have C content higher than that of TDS-1080, and the same trend was observed for Lc. HDS-37 has higher C content (95.03) compared to that for HDS-60 (92.25). The Lc of the two hydrodesulfurized samples followed the same trend. Lc of HDS-37 (28.78 Å) was higher compared to that of HDS-60 (26.86 Å).

The deconvoluted C1s spectra of all the coke samples are presented in Figures 4.34, 4.35, 4.36, and 4.37. The percentage distribution of the different functional groups obtained from the deconvoluted spectrum of C1s is given in Table 4.16.

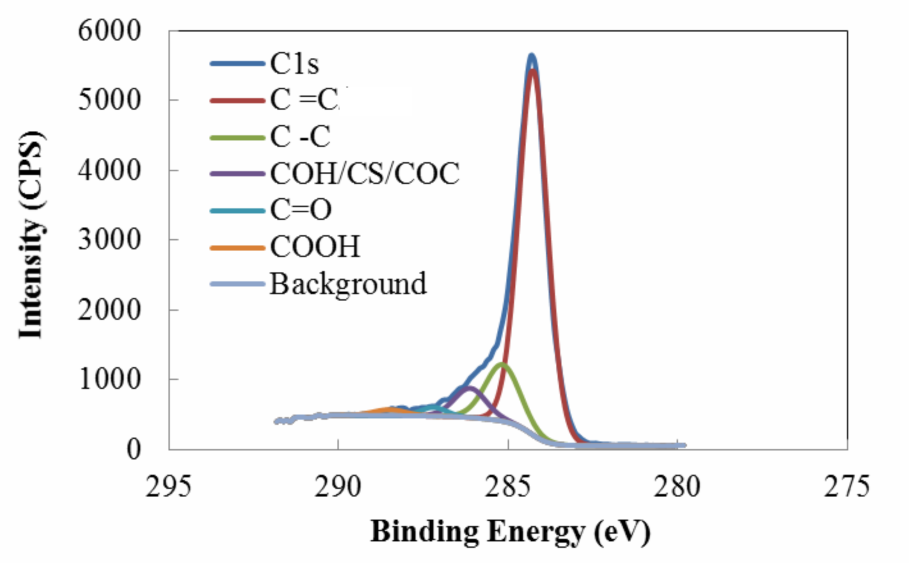


Figure 4.34 Deconvoluted C1s peak of TDS-1080 coke D sample

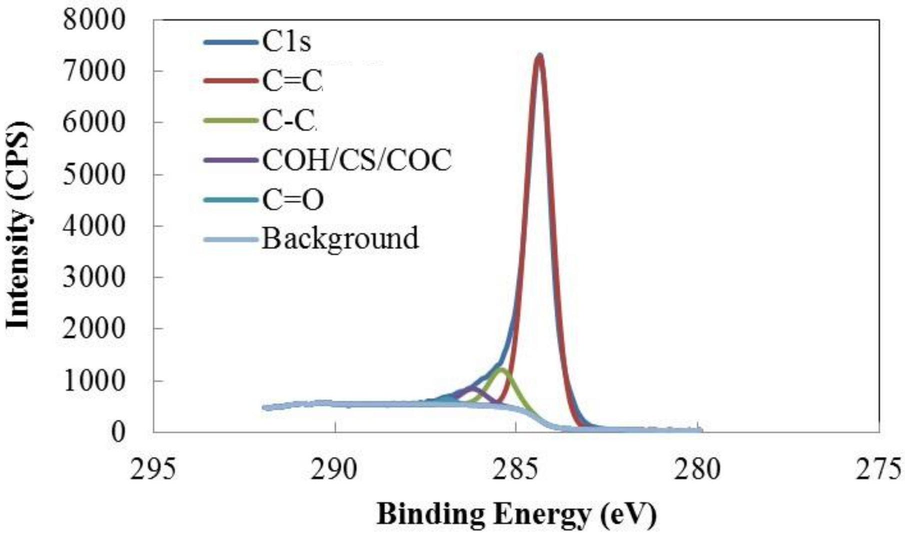


Figure 4.35 Deconvoluted C1s peak of HDS-37 coke D sample

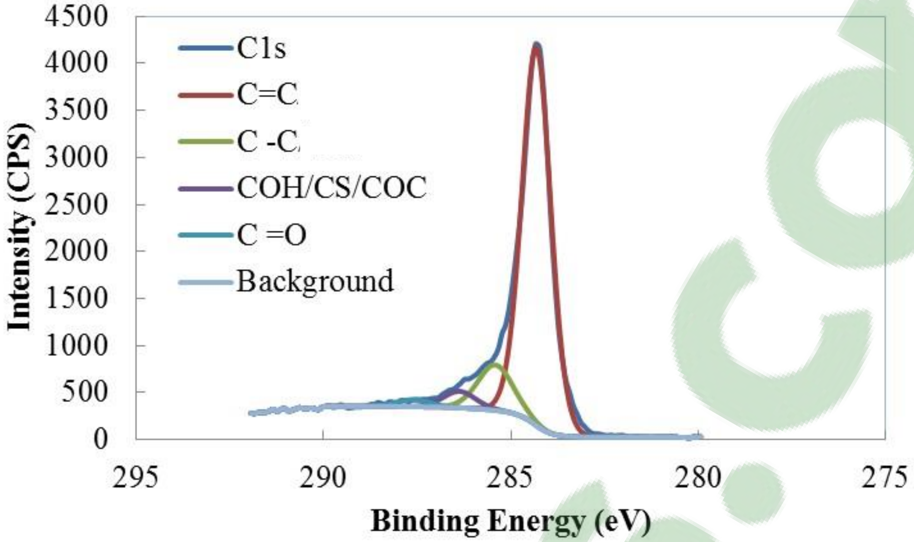


Figure 4.36 Deconvoluted C1s peak of HDS-60 coke D sample

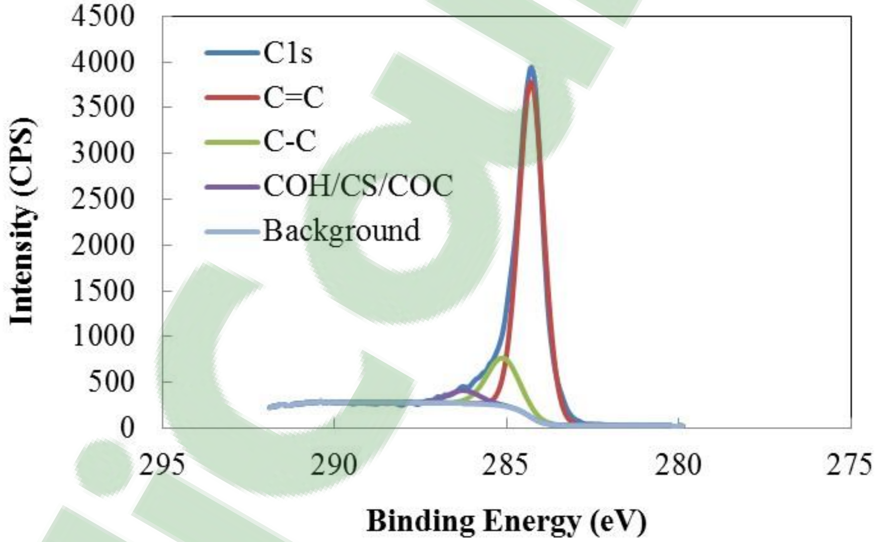


Figure 4.37 Deconvoluted C1s peak of TDS-1200 coke D sample

Table 4.16 Atomic percentages of the different carbon components of green, TDS-1080, TDS-1200, HDS-37 and HDS-60 coke samples

	Carbon components				
	C=C **%**	**C-C** **%**	**COH/CS/COC** **%**	**C=O** **%**	**COOH** **%**
Green coke D	86.64	11.31	1.85	-	-
TDS-1080	76.16	14.15	6.74	1.61	1.34
TDS-1200	80.94	15.03	4.03	-	-
HDS-37	86.38	8.92	3.93	0.76	-
HDS-60	82.23	12.06	3.98	1.72	-

The deconvolution of C1s and S2p peaks of green coke D were done according to the available literature [111, 112, 115, 117-122] based on Table 4.3. It is evident from the XPS results that all samples contain greater quantities of C=C and C-C bonds and trace amount of oxygen and sulfur compounds. According to atomic percentages of different elements in coke samples which are shown in Table 4.15, it was found that all the samples had no or very low nitrogen content. The sulfur content on the surface of HDS-37 and HDS-60 samples is quite low compared to green coke D, TDS-1080, and TDS-1200 coke samples. Although TDS-1200 coke has higher sulfur content than hydrodesulfurized samples, it has lower sulfur content compared to TDS-1080 coke sample. These findings confirm the sulfur removal results that were obtained previously with the combustion sulfur analysis method. It shows that in the case of thermal desulfurization, sulfur is removed more at higher temperature. However, hydrodesulfurization can remove more sulfur compared to that of thermal desulfurization. The oxygen atomic percentages were high for TDS-1080 and HDS-60 coke samples. This might be due to the lower graphitization degree of these samples. Their graphitic carbon content (C-C, C=C) which can be seen in Table 4.16 is slightly lower than the others. It might also be that oxygen in coke might reorganize during the desulfurization process. There is a possibility of reaction of water with organic molecules in coke resulting in an increase in oxygen content. The inspection of C1s high resolution peaks of four cokes in Figures 4.34, 4.35, 4.36, and 4.37 reveals five peaks located at around 284.3, 285.1, 286, 287, and 288.6 eV with variation ±0.5 eV form the C1s peak. The dominant peak at 284.3 eV is associated with C=C aromatic structures. 285.1 eV which is the second dominant bond in all C1s spectra can be attributed to the aliphatic carbons (C-C). The peaks at higher energy positions are associated with the C-O/C-S/C-O-C (286 eV), C=O (287 eV) and COO (288.6 eV) bonds, respectively. It was observed from C1s spectra of all samples that only TDS-1080 coke sample contains COO (carboxyl) functional groups. C=O functional group exist in TDS-1080, HDS-37, and HDS-60 samples among which HDS-60 has the highest value. All treated samples contain higher C-OH/C-S/C-O-C functional groups than green coke D which can be seen from Table 4.16.

The specific rule for the deconvolution of S2p peak is already mentioned in Section 4.2.2 where the XPS analysis of green petroleum coke D is presented. The deconvolution of S2p peak of four samples was also done according to this rule. It was found that sulfur existed in the treated coke sample in the form of thiophenes (S 2p3/2 at 163.5 eV and S 2p1/2 at 164.7 eV) as shown in Figures 4.38, 4.39, 4.40, 4.41 and Table 4.17. High resolution S2p spectra of all cokes also reveal that the type of S that exists in coke structure stays the same as thiophenes after both thermal and hydrodesulfurization. Based on these results, it can be concluded that thermal or hydrodesulfurization treatment did not change the type of sulfur present on the coke surface while the hydrodesulfurization resulted in more sulfur removal. It may also be noted that if there are other species of sulfur present in coke, their quantity is lower than the detection limit of the XPS equipment. To have a precise idea about the types of S that exist in the coke structure, a method which enables more detailed sulfur functionality analysis such as XANES (X-ray absorption near-edge structure) should be used.

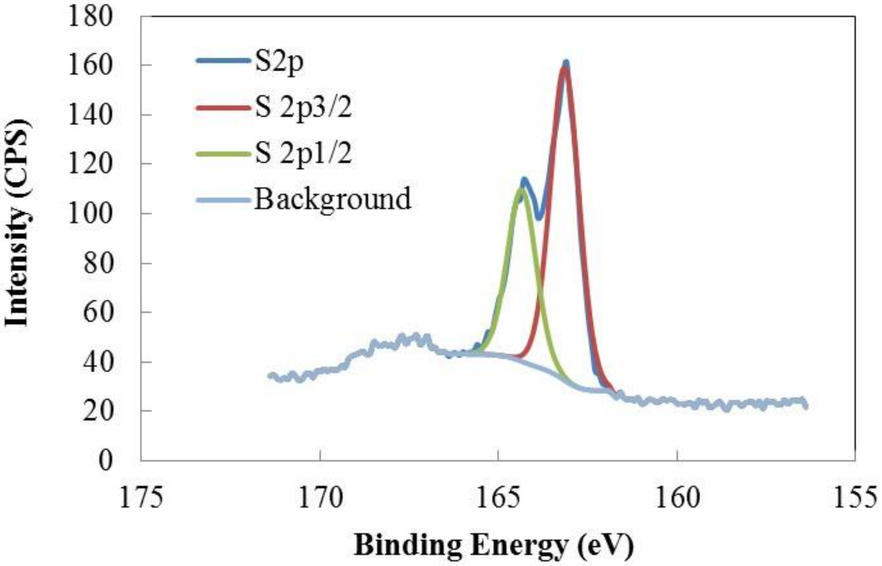


Figure 4.38 Deconvoluted S2p peak of TDS-1080 coke D sample

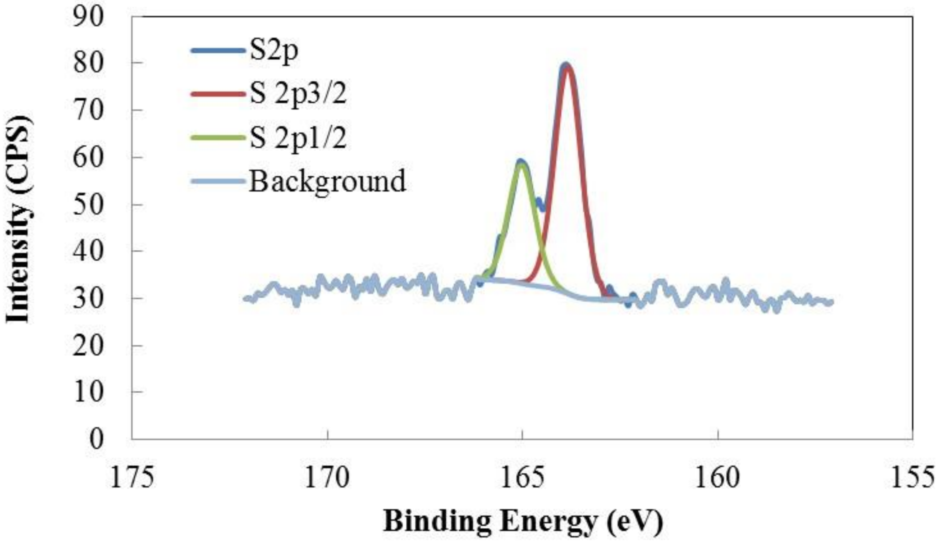


Figure 4.39 Deconvoluted S2p peak of HDS-37 coke D sample

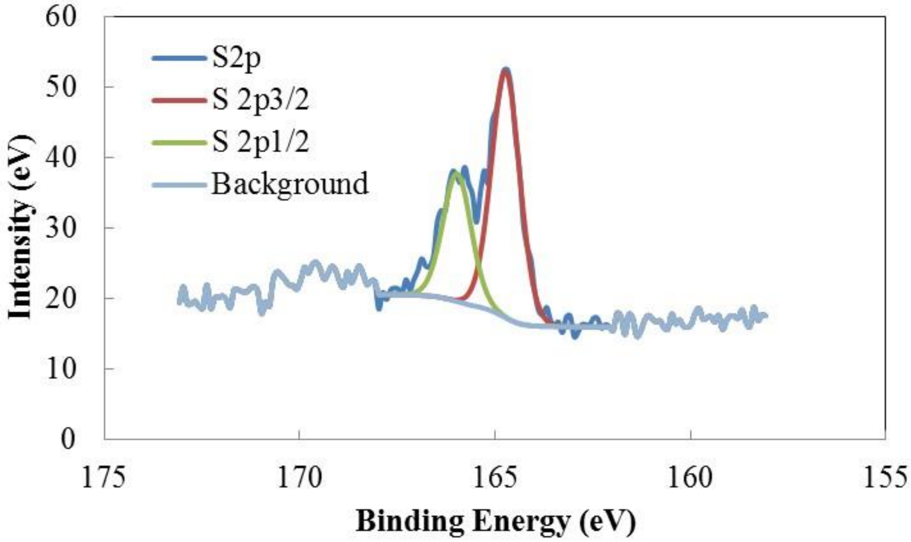


Figure 4.40 Deconvoluted S2p peak of HDS-60 coke D sample

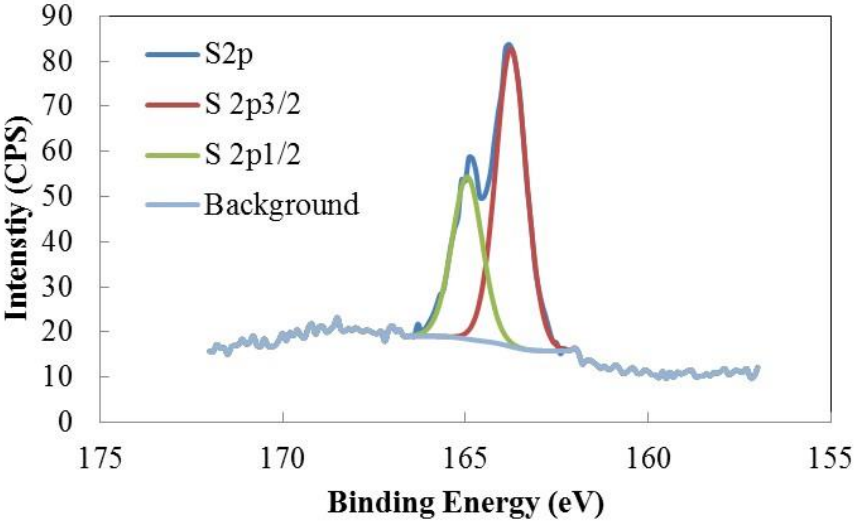


Figure 4.41 Deconvoluted S2p peak of TDS-1200 coke D sample

Table 4.17 Different sulfur components of green, TDS-1080, TDS-1200, HDS-37 and HDS-60 coke samples

	Sulfur components	
	Thiophene %	**For thiophene S $2p_{3/2}$/ S $2p_{1/2}$**
Green coke D	100	66.07/33.93=1.95
TDS-1080	100	64.60/35.40=1.82
TDS-1200	100	64.63/35.37=1.83
HDS-37	100	65.88/34.12=1.93
HDS-60	100	65.72/34.28=1.92

4.5.4. Surface Morphology with SEM

The coke structure is an important parameter which determines the suitability of the utilization of hydrodesulfurized cokes in anode manufacture. The objective is to desulfurize coke without creating high porosity. Porous cokes result in anodes with low density, high resistivity and reactivity. Consequently, it increases the GES emissions and carbon consumption. The surface morphology of treated and untreated cokes was analyzed with SEM-EDX to study the coke structure. This part will be presented in two sections.

Comparison of Green, Hydro and Thermally Desulfurized Coke D

In this section, surface morphology analyses of different treated coke samples (TDS-1080, HDS-37, HDS-60, and TDS-1200 are presented using SEM images in Figures 4.42, 4.43, 4.44 and 4.45, respectively. SEM pictures of green coke were given in Figure 4.5.

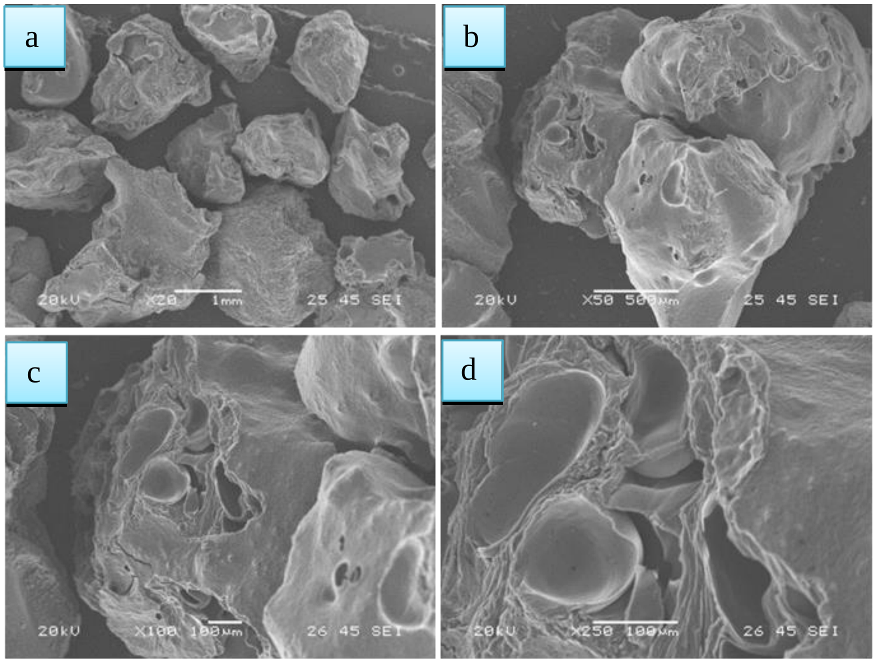


Figure 4.42 SEM images of TDS-1080 sample at magnifications of (a) x20 (b) x50 (c) x100 (d) x250

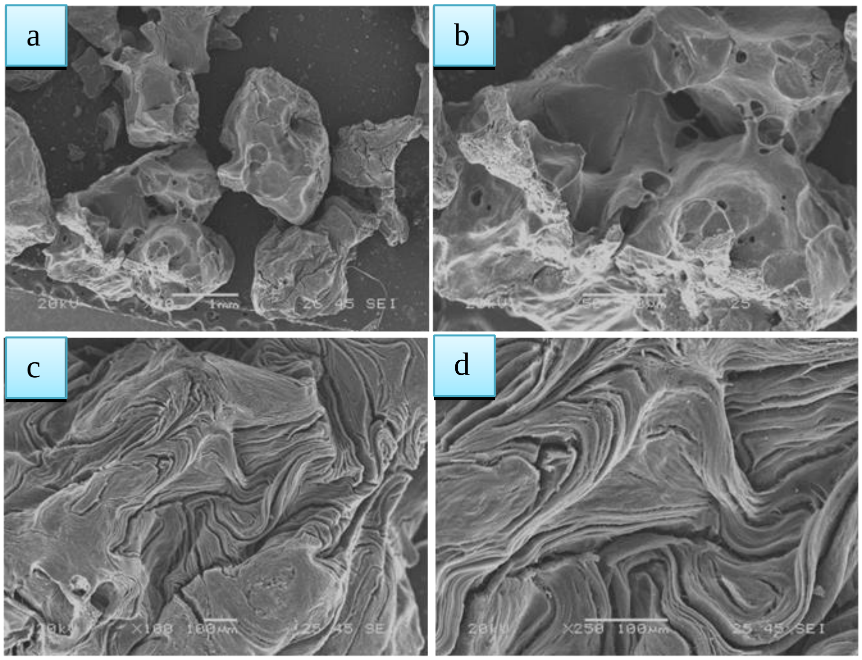


Figure 4.43 SEM images of HDS-37 sample at magnifications of (a) x20 (b) x50 (c) x100 (d) x250

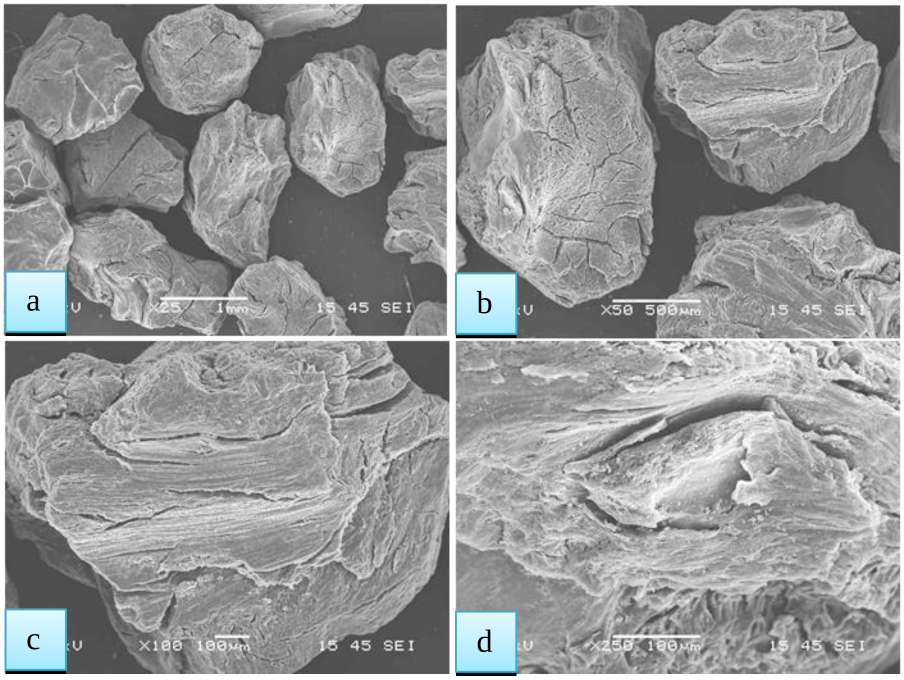


Figure 4.44 SEM images of HDS-60 sample at magnifications of (a) x20 (b) x50 (c) x100 (d) x250

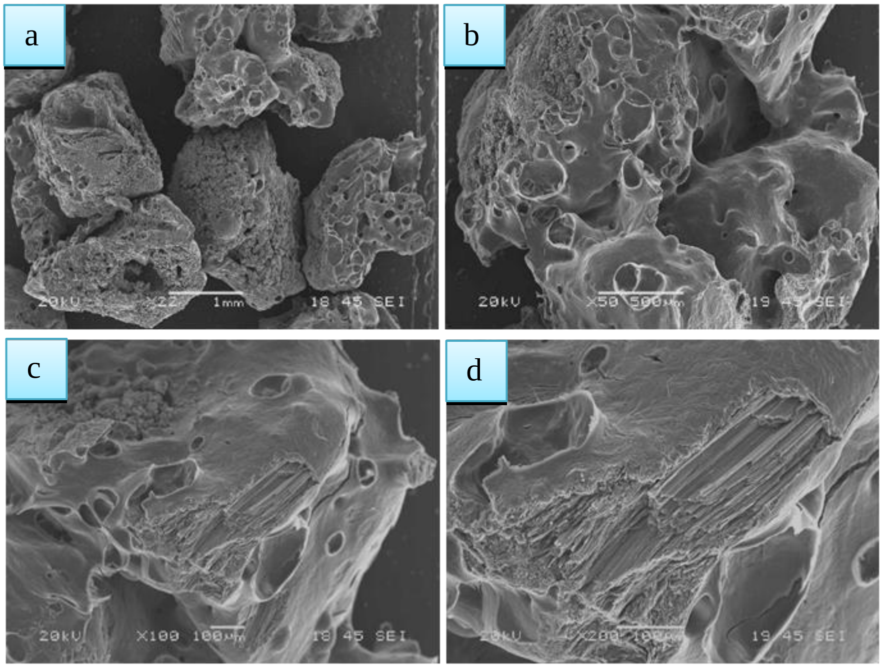


Figure 4.45 SEM images of TDS-1200 sample at magnifications of (a) x20 (b) x50 (c) x100 (d) x250

SEM images of all samples show certain crack and pore formation. It appears that hydrodesulfurization caused some changes in texture. Large pores were not observed in the case of hydrodesulfurized samples. When porosity analysis results are combined with SEM analysis images, it can be stated that hydrodesulfurization carried out under the conditions for samples HDS-37 and HDS-60 did not create a more porous coke compared to those of thermal desulfurization (TDS-1080, TDS-1200).

Comparison of the coke structure of green coke with hydrodesulfurized coke for large particles (-16 mm +12.5 mm) as well as their EDX analysis for sulfur are given in the following section.

Comparison of Green and Hydrodesulfurized Coke D with Bigger Particle Size

In this section, specific regions of the surface of two coke D particles which have -16 mm +12.5 mm particle size was analyzed with SEM-EDX before and after hydrodesulfurization using 850ºC injection temperature, 37 min injection duration, and 1 ml/min water flow rate. EDX was used to determine the sulfur content of the specific regions before and after the treatment. Figure 4.46 shows pictures at x30 and x100 magnifications for the same area of 1st coke D particle before and after hydrodesulfurization. Figure 4.47 shows SEM-EDX images of the same area with elemental analysis.

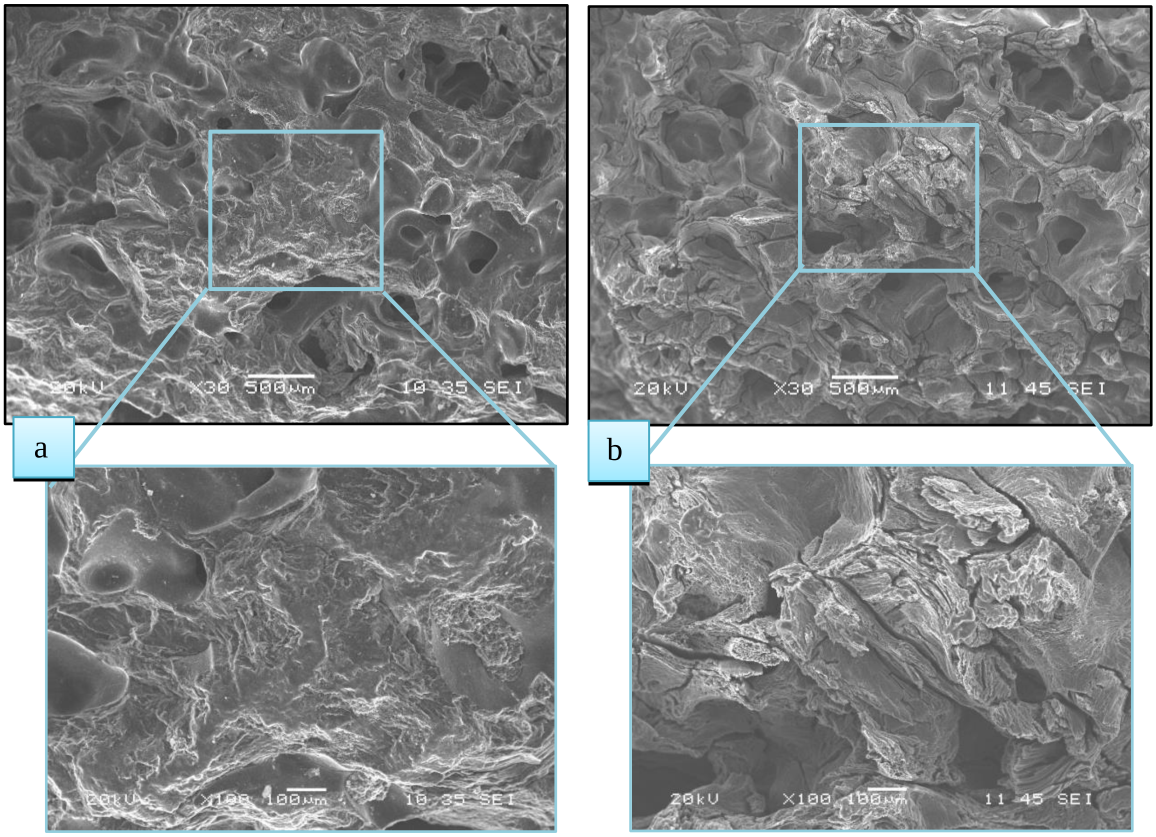
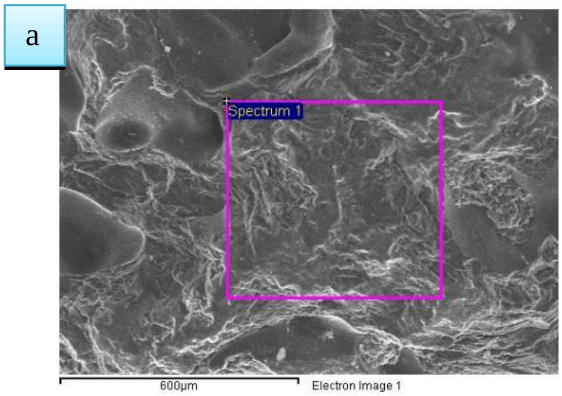
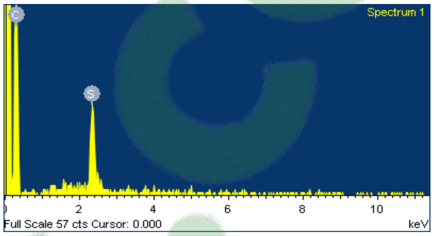
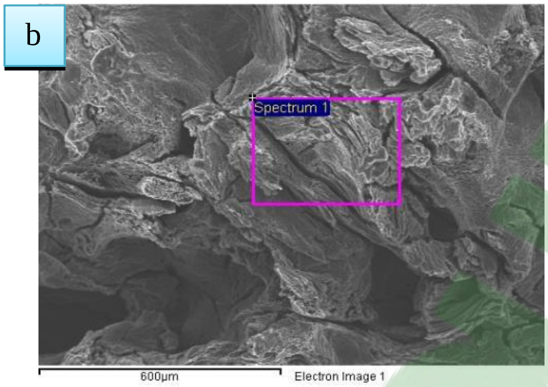


Figure 4.46 SEM images of 1st particle a) green coke D b) hydrodesulfurized coke D, -16 mm +12.5 mm particle size x30 and x100 magnifications

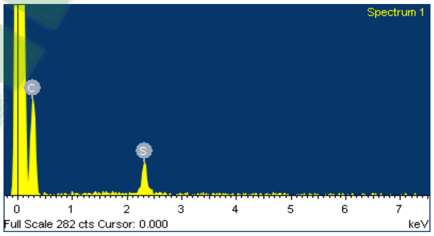


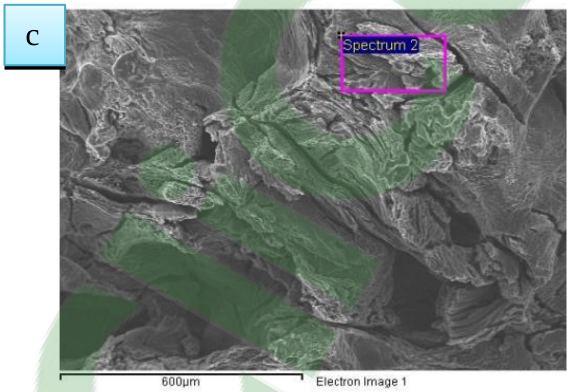
Element	Weight %	Atomic %
C	93.74	97.56
S	6.26	2.44
Totals	100.00	





Element	Weight %	Atomic %
C	94.19	97.74
S	5.81	2.26
Totals	100.00	





Element	Weight %	Atomic %
C	94.35	97.81
S	5.65	2.19
Totals	100.00	

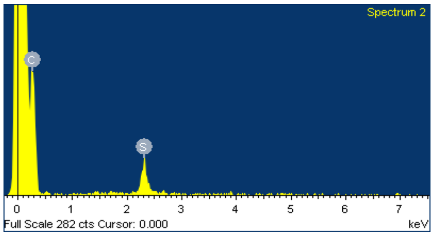


Figure 4.47 SEM-EDX images, EDX patterns and elemental analysis of 1st particle a) green coke D b) hydrodesulfurized coke D-spectrum 1, c) hydrodesulfurized coke D-spectrum 2, -16 mm +12.5 mm particle size

Certain crack and pore formation can be seen from the SEM images of 1st particle after hydrodesulfurization. According to sulfur content analysis with the combustion method, the sulfur removal from this coke was 5.82%. The elemental analyses of b and c regions of the 1st particle of hydrodesulfurized coke D with SEM-EDX, which is given in Figure 4.44, shows 7.19% and 9.74% sulfur removal, respectively. The difference between sulfur removal values obtained from sulfur analysis with the combustion method and the elemental analysis method might be due to the characteristics of each technique as well as the non-homogeneous nature of the coke. EDX measures only the sulfur existing on the surface of the material whereas the combustion method burns a certain quantity of coke sample. The difference between the values obtained with the elemental analysis on different areas of the same sample can be attributed to the non-homogeneous structure of the coke as well as the level of contact of that area with water during the experiment.

Figure 4.48 shows the surface morphology of a different specific area on the 1st particle of hydrodesulfurized coke D using 850ºC injection temperature, 37 min injection duration, and 1 ml/min water flow rate at x100 and x500 magnifications. The elemental analysis by EDX was done on these two different areas on green and hydrodesulfurized coke D as shown in Figure 4.49 and Figure 4.50.

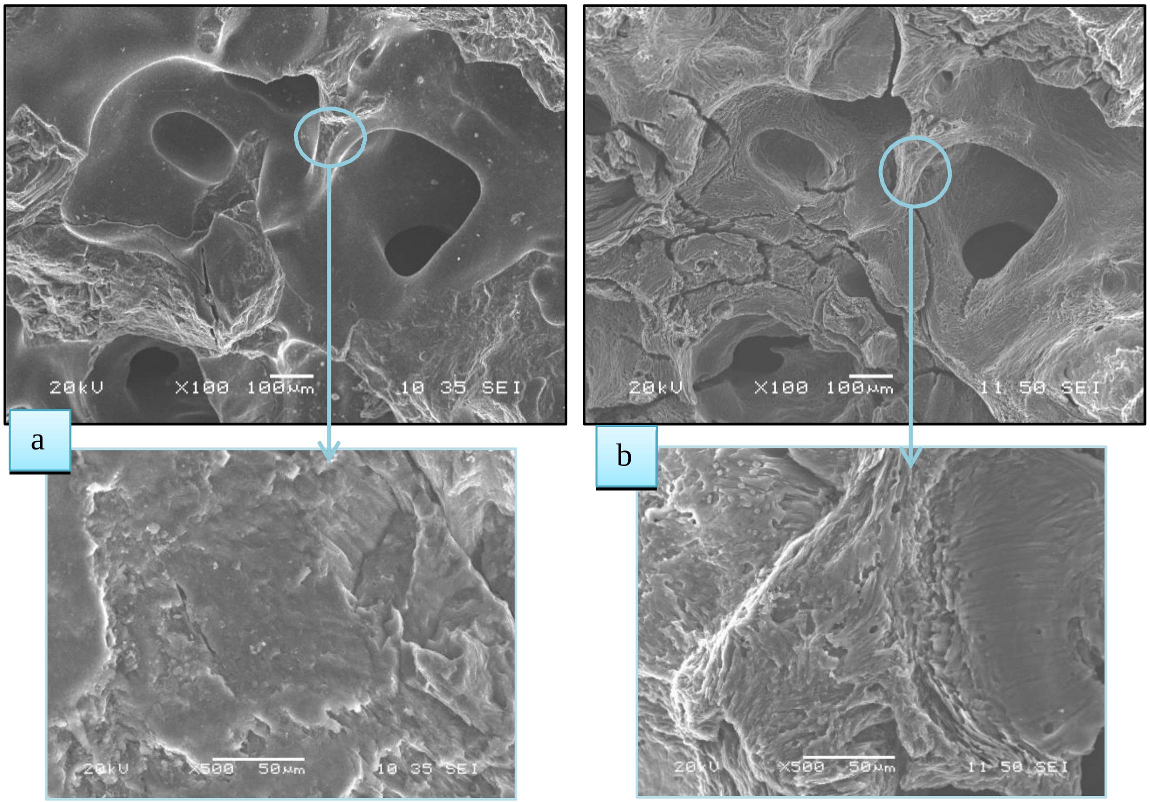
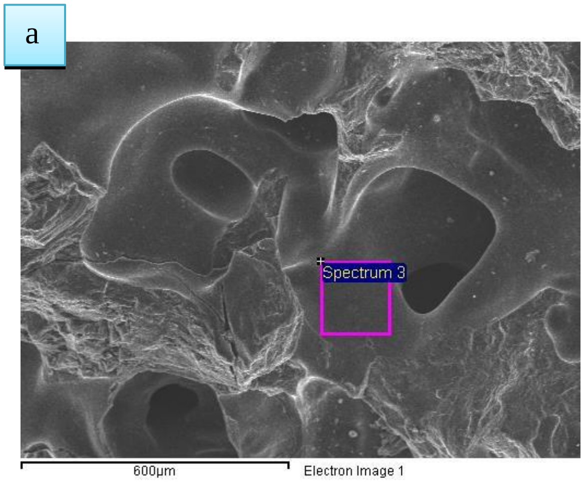
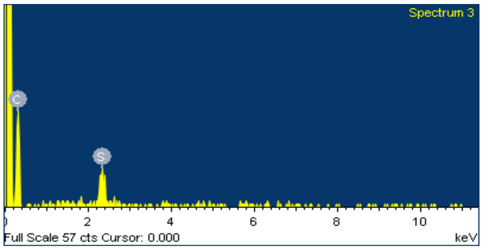
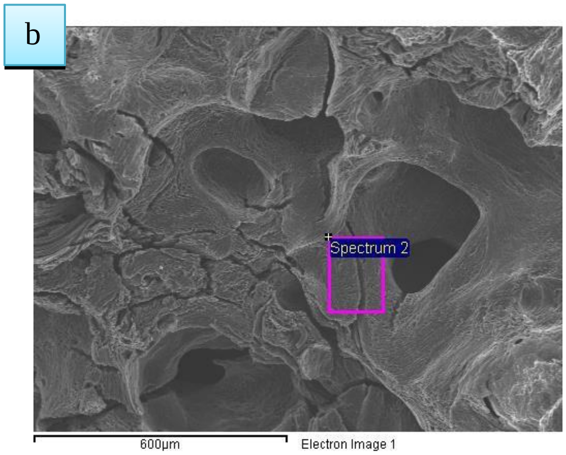


Figure 4.48 SEM images of the 1st particle a) green coke D b) hydrodesulfurized coke D, -16 mm +12.5 mm particle size, x30 and x500 magnifications



Element	Weight %	Atomic %
C	94.24	97.76
S	5.76	2.24
Totals	100.00	





Element	Weight %	Atomic %
C	93.63	97.51
S	6.37	2.49
Totals	100.00	

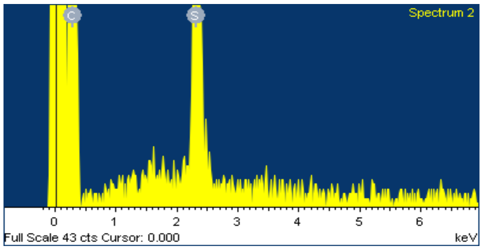
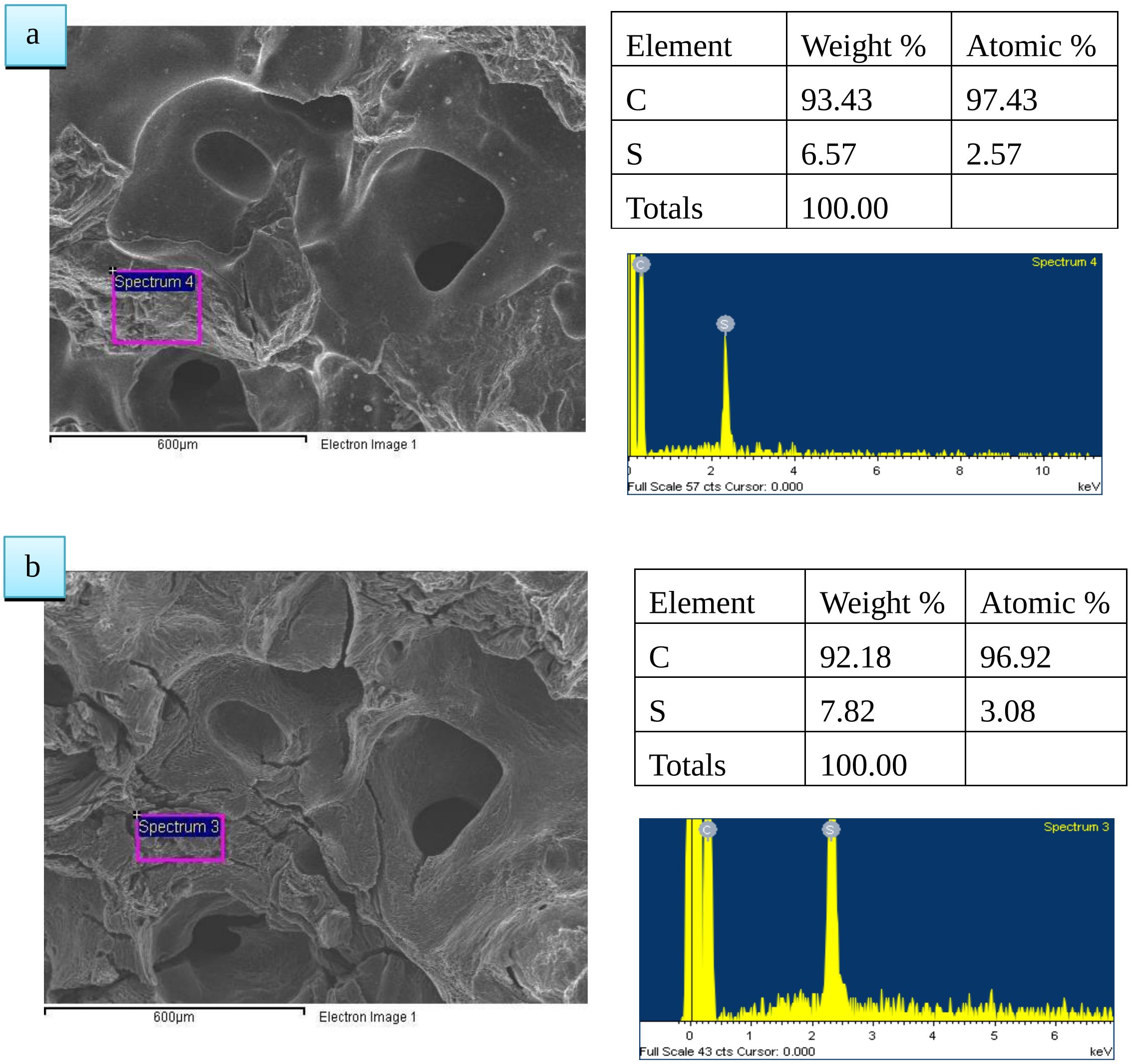


Figure 4.49 SEM-EDX images, EDX patterns and elemental analysis of the 1st particle a) green coke D b) hydrodesulfurized coke D, -16 mm +12.5 mm particle size



Element	Weight %	Atomic %
C	93.43	97.43
S	6.57	2.57
Totals	100.00	

Element	Weight %	Atomic %
C	92.18	96.92
S	7.82	3.08
Totals	100.00	

Figure 4.50 SEM-EDX images, EDX patterns and elemental analysis of the 1st particle a) green coke D b) hydrodesulfurized coke D, -16 mm +12.5 mm particle size

The elemental analysis on the same area of the 1st particle of coke D before and after hydrodesulfurization which is given by Figure 4.49 shows an increase in sulfur content from 5.76% to 7.37% after hydrodesulfurization. The same result can be observed from a different area on the same particle as shown in Figure 4.49. This result can be attributed to different reasons, one of which is the reaction of hydrogen sulfide with coke which forms complex sulfides of carbon along with the volatile carbon sulfide as mentioned in many previous works [64, 66, 100].

Figure 4.51 shows the SEM pictures of the 2nd particle of green and hydrodsulfurized coke D at 850°C water injection temperature, 37 min water injection duration and 1 ml/min water flow rate at x30, x100 and x500 magnifications. Crack formation after hydrodesulfurization can be clearly observed from images. Figure 4.52 show the SEM-EDX images, EDX patterns, and elemental analyses of different parts of the surface of the 2nd particle before and after hydrodesulfurization.

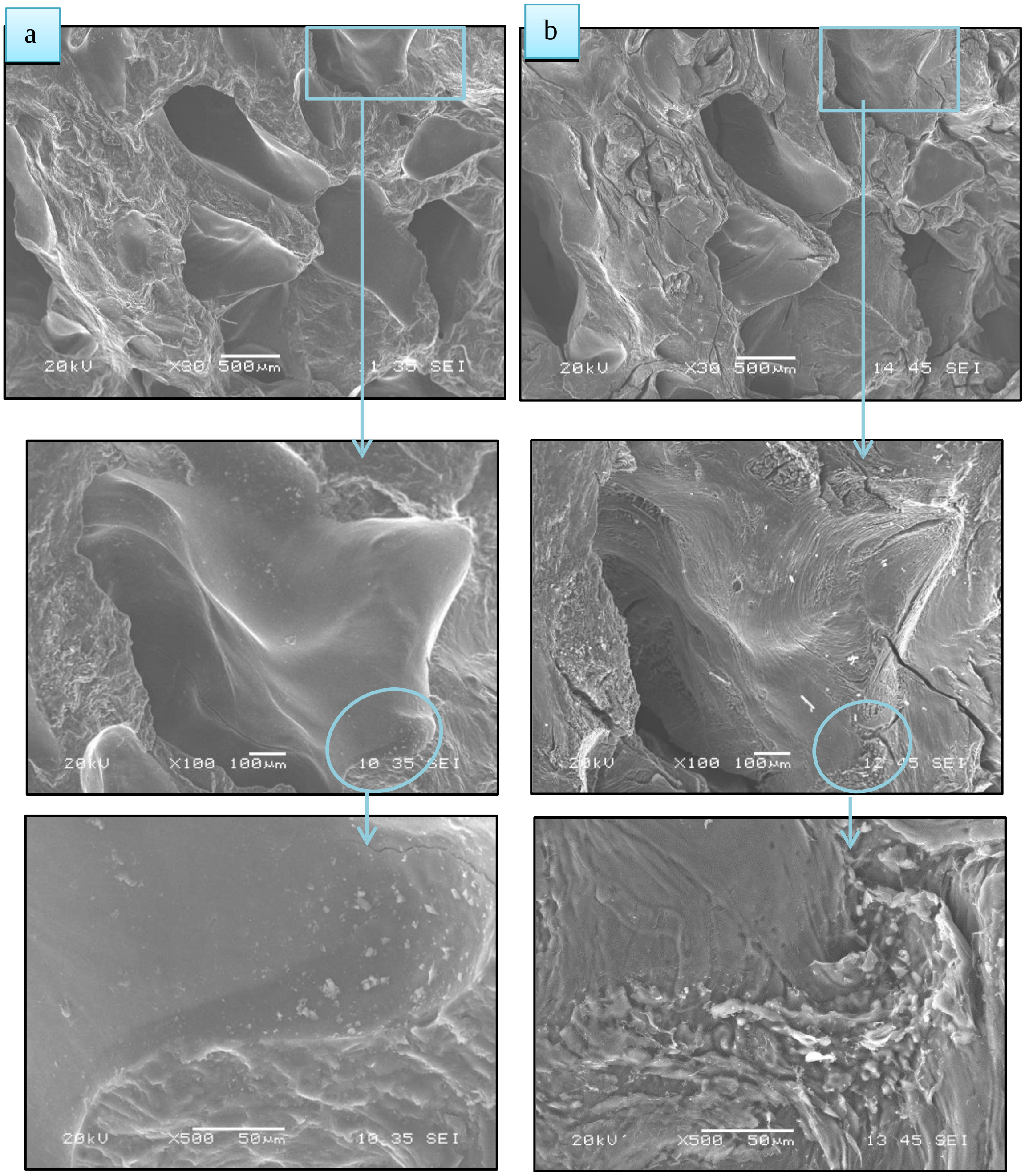
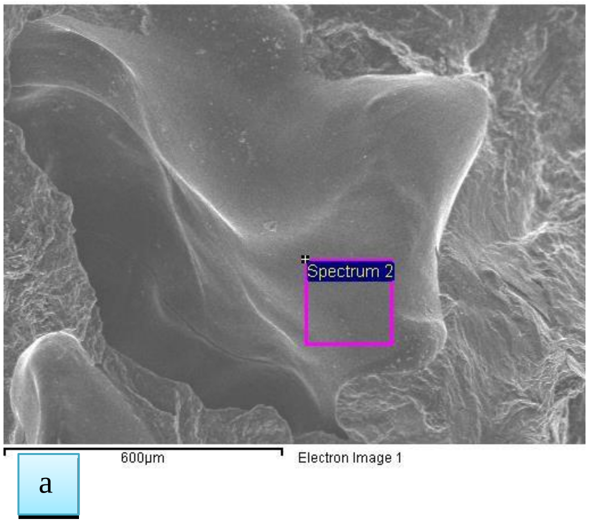
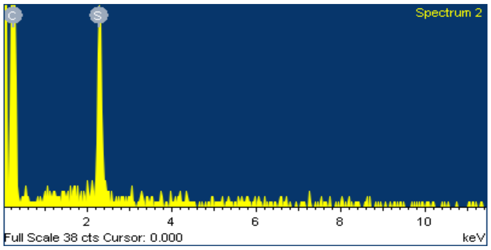
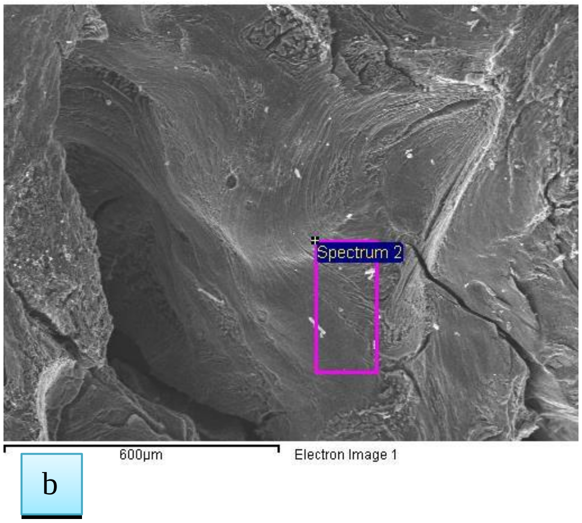


Figure 4.51 SEM images of the 2nd particle a) green coke D b) hydrodesulfurized coke D, -16 mm +12.5 mm particle size x30, x100, x500 magnifications



Element	Weight %	Atomic %
C	93.37	97.41
S	6.63	2.59
Totals	100.00	





Element	Weight %	Atomic %
C	95.80	98.38
S	4.20	1.62
Totals	100.00	

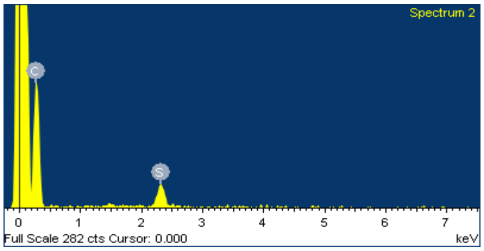
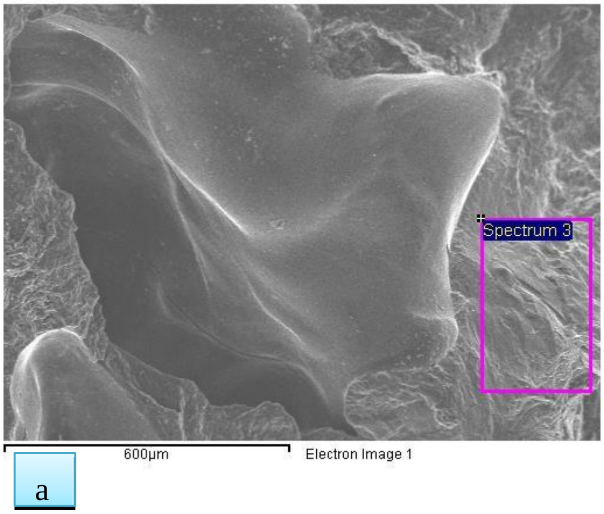
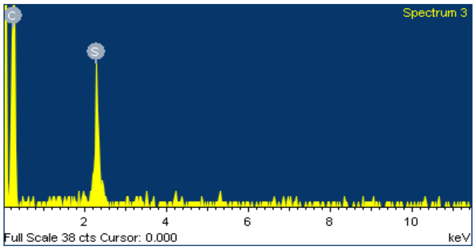


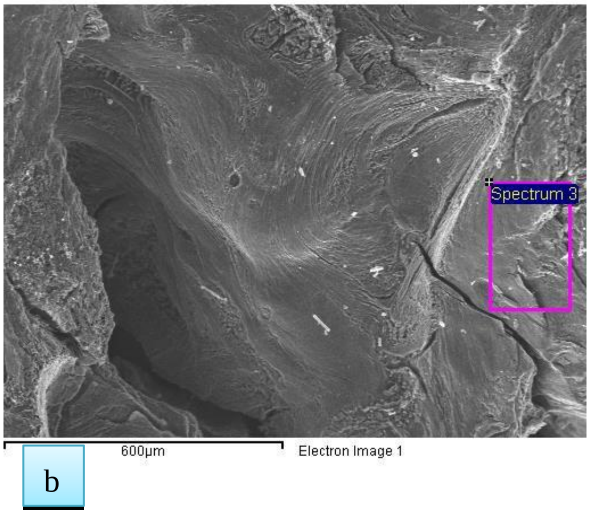
Figure 4.52 SEM-EDX images, EDX patterns and elemental analysis of the 2nd particle a) green coke D b) hydrodesulfurized coke D, -16 mm +12.5 mm particle size

As it can be seen from Figure 4.52, the hydrodesulfurization resulted in 36.65% sulfur removal on the coke surface according to the elemental analysis results. The sulfur content on the surface of the 2nd particle has decreased to 4.20% from 6.63%. 36.65% sulfur removal which is higher than the sulfur removal found by the combustion method (5.82%) again demonstrates the effect of non-homogeneity of the petroleum coke on sulfur analysis. Figure 4.53 also shows another part of the surface of the 2nd coke particle where sulfur content decreased from 7.44% to 4.43% after hydrodesulfurization which means 40.46% sulfur removal.



Element	Weight %	Atomic %
C	92.56	97.08
S	7.44	2.92
Totals	100.00	





Element	Weight %	Atomic %
C	95.57	98.29
S	4.43	1.71
Totals	100.00	

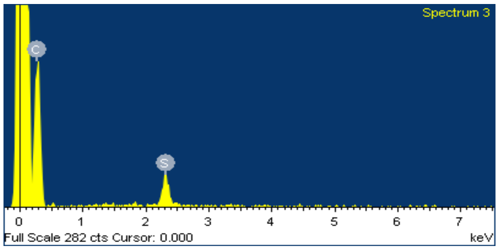


Figure 4.53 SEM-EDX images, EDX patterns and elemental analysis of the 2nd particle a) green coke D b) hydrodesulfurized coke D, -16 mm +12.5 mm particle size

Figure 4.54 shows another surface of the 2nd coke particle which was chosen from x30 magnification SEM image and zoomed to x100 to visualize the effect of hydrodesulfurization on the coke surface as well as sulfur content which was measured via elemental analysis.

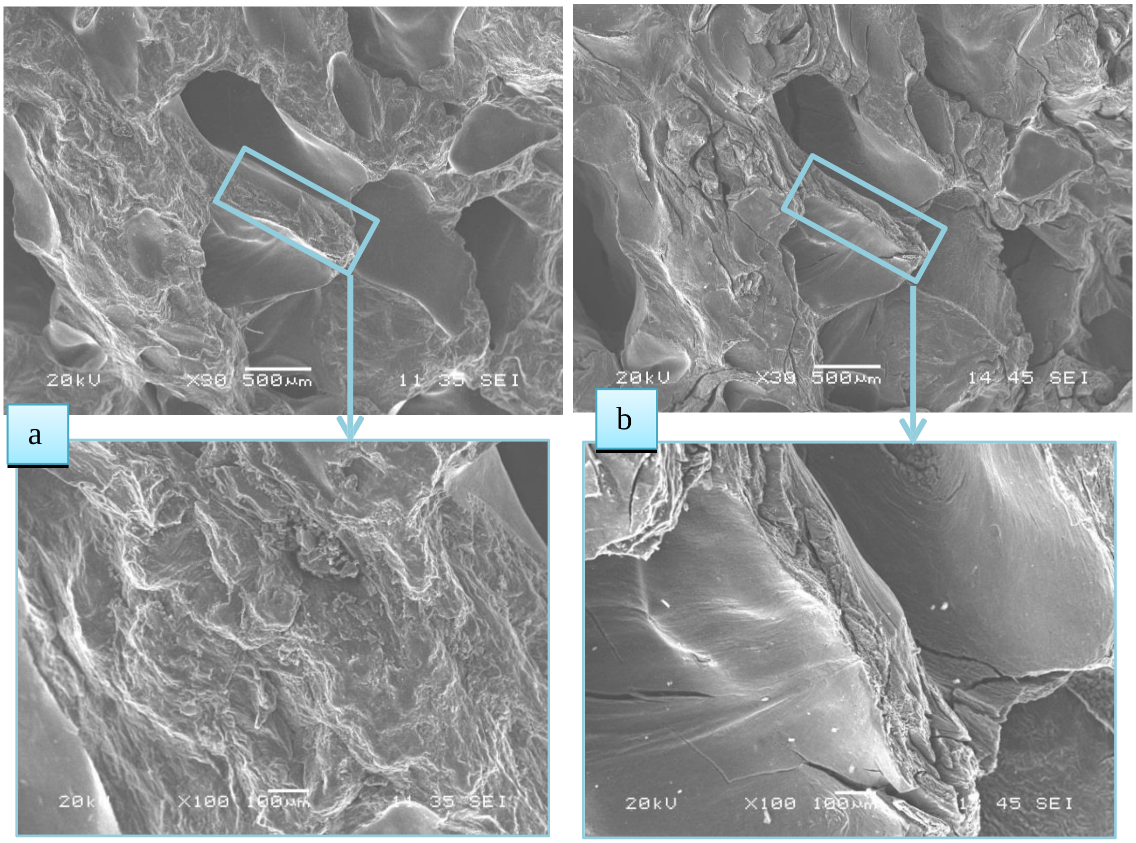
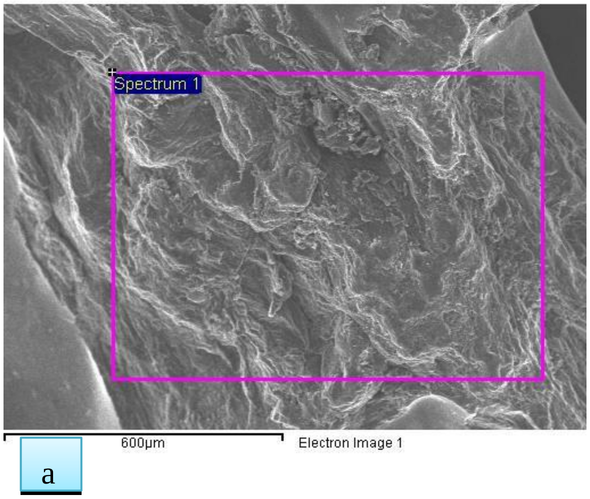
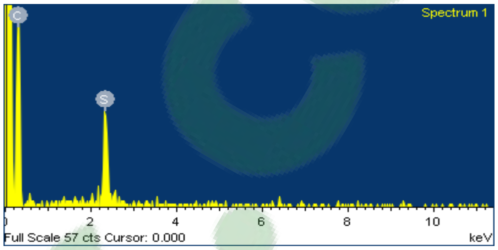


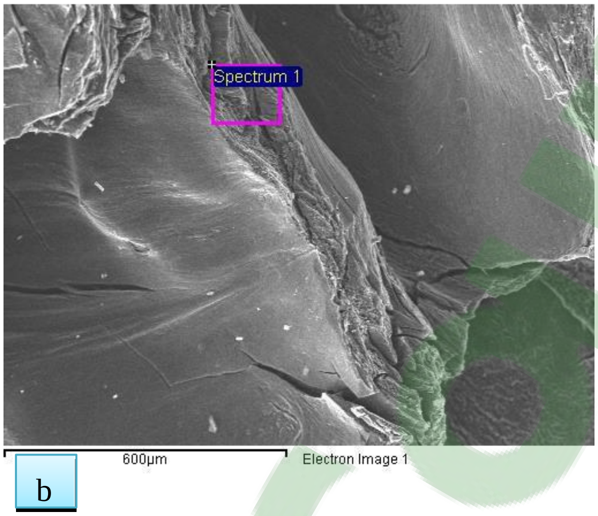
Figure 4.54 SEM images of the 2nd particle a) green coke D b) hydrodesulfurized coke D, -16 mm +12.5 mm particle size x30 and x100 magnifications

The shrinkage that has occurred on the coke surface during hydrodesulfurization can be clearly seen with SEM images that were taken on the same area of the 2nd coke D particle before and after hydrodesulfurization. The shrinkage in the coke structure during calcination of coke is a well-documented phenomenon by many previous studies in the literature. In addition to shrinkage, certain crack formation was also observed on this part of the 2nd coke D particle. Figure 4.55 and Figure 4.56 show SEM-EDX images, EDX patterns and elemental analysis of the 2nd coke D particle before and after hydrodesulfurization.



Element	Weight %	Atomic %
C	92.70	97.14
S	7.30	2.86
Totals	100.00	





Element	Weight %	Atomic %
C	94.69	97.94
S	5.31	2.06
Totals	100.00	

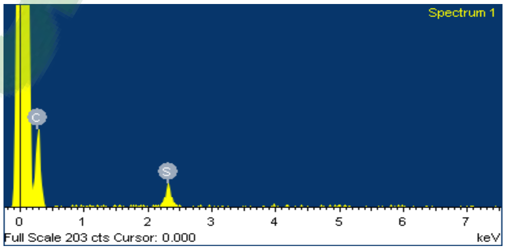
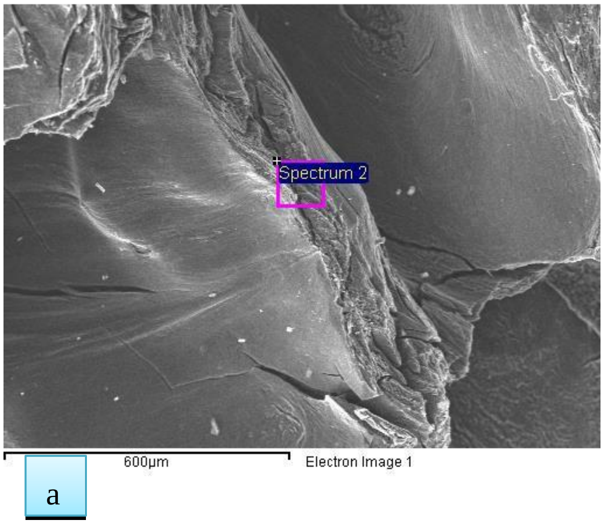
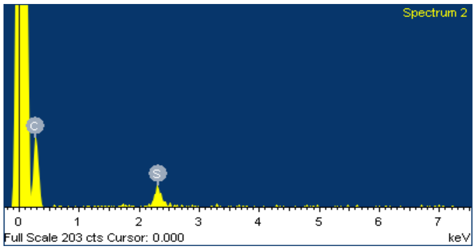
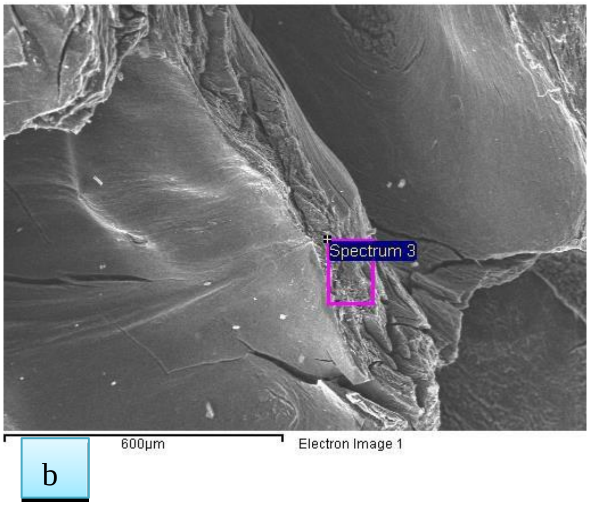


Figure 4.55 SEM-EDX images, EDX patterns and elemental analysis of the 2nd coke D particle a) green coke D b) hydrodesulfurized coke D (area 1), -16 mm +12.5 mm particle size



Element	Weight %	Atomic %
C	94.79	97.98
S	5.21	2.02
Totals	100.00	





Element	Weight %	Atomic %
C	94.91	98.03
S	5.09	1.97
Totals	100.00	

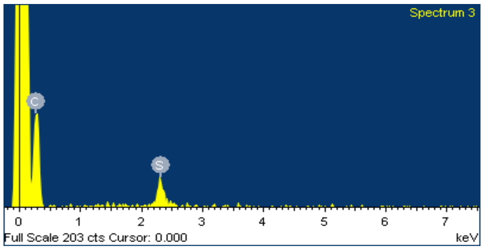


Figure 4.56 SEM-EDX images, EDX patterns and elemental analysis of the 2nd particle a) hydrodesulfurized coke D (area 2) b) hydrodesulfurized coke D (area 3), -16 mm +12.5 mm particle size

The elemental analysis of green coke D surface is given in Figure 4.55 (a); Figure 4.55 (b), Figure 4.56 (a) and (b) show the elemental analysis results of three different small areas located on the hydrodesulfurized coke sample. While sulfur content was 7.30% on the surface of green coke D, it decreased to 5.31%, 5.21%, and 5.09% on different parts of the same surface of coke D after hydrodesulfurization. 27.26%, 28.63%, and 30.27% of sulfur removal was obtained in these areas, respectively.

4.6. Conclusions

In this chapter, the characterization of raw material, the results of different tests of thermal and hydrodesulfurization as well as the characterization results of desulfurized cokes are presented. Different experimental set-ups were used for hydrodesulfurization experiments. After developing the suitable experimental set-up, several hydrodesulfurization experiments were carried out with high-sulfur green petroleum coke under different conditions by changing different parameters. Maximum sulfur removal of 22% was obtained with hydrodesulfurization. After thermal and hydrodesulfurization tests, two thermodesulfurized, two hydrodesulfurized coke samples were compared with green coke D as well as with each other. The comparison of certain characteristics of these cokes such as density, porosity, surface morphology, and surface functionality showed that hydrodesulfurized coke which gave 22% sulfur removal shows a similar structure to its counterpart that was thermally desulfurized to the same maximum temperature. This result seems promising in terms of the utilization of hydrodesulfurized coke in carbon anode production.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

In this project, an experimental study on both green petroleum coke hydrodesulfurization as well as thermal desulfurization was undertaken. Several hydrodesulfurization experiments were carried out with high sulfur green petroleum coke under different conditions by changing different parameters. Water injection temperature, water flow rate, water injection duration, and particle size are the parameters studied. This study has indicated that all of the parameters affect desulfurization to varying degrees. The effect of water injection temperature on the hydrodesulfurization of coke was investigated using four different injection temperatures (650°C, 750°C, 850°C, and 950°C), which were determined based on a GC analysis at three different water injection times (37, 60, and 100 min). Maximum sulfur removal was obtained when the water was injected to the sample at 650°C and 850°C for 60 min and at 650°C and 850°C for 100 min: 22.87%, 22.60%, 19.22%, and 19.31%, respectively. Weight loss percentages under these conditions were 26.07%, 24.34%, 23.32%, and 40.45%, respectively. The sulfur removal trend was similar at all three injection times used. The removal was high when 650°C injection temperature was used and decreased when water injection temperature was increased to 750°C. For 850°C injection temperature, sulfur removal increased similar to the one observed for the case with 650°C injection temperature. It decreased again with further increase in temperature to 950°C. The effect of water injection time on sulfur removal at each injection temperature showed a similar tendency where sulfur removal increased when injection duration increased from 37 min to 60 min in four different water injection temperatures (650°C, 750°C, 850°C, 950°C). Further increase in water injection duration to 100 min reduced the percent sulfur removal in all water injection temperatures. At 850°C, a longer duration for water injection (140 min) showed a slight increase in sulfur removal. However, the maximum sulfur removal was achieved in 60 min at all water injection temperatures. It can be concluded based on these results that in order to understand the reason for the desulfurization behavior of petroleum coke as a function of water injection duration and temperature (it reaches a maximum and starts decreasing when these parameters are increased), the reaction kinetics of hydrodesulfurization of coke should be studied both during heating and water injection steps.

It was also observed during this experimental study that the water flow rate is inversely proportional to the desulfurization rate. Particle size effect on the hydrodesulfurization of green coke is found to be significant when fine coke particles are used. When coke particle size was reduced 20 times (from -2 mm to -100 μm), the desulfurization percentage was doubled using the injection temperature of 850°C, water flow rate of 1 ml/min, and injection durations of 37 and 60 min. Weight loss values have also remarkably increased with the use of fine particles. The hydrodesulfurization tests were done with different coke particle sizes using the injection temperature of 850°C, water flow rate of 1 ml/min, and injection durations of 37 min (HDS-37) and 60 min

(HDS-60). The results showed 8 to 17% sulfur removal. Nevertheless, this series of experiments showed the importance of gas and coke contact.

The green coke structure was compared with hydrodesulfurized coke and thermally desulfurized coke structure. Among different hydrodesulfurized coke samples, two of them have been chosen for comparison with the thermally desulfurized coke samples. These were the samples hydrodesulfurized at the injection temperature of 850°C, water flow rate of 1 ml/min, and injection duration of 60 min and 37 min which gave 22.60% and 14.28% sulfur removal, respectively. Two coke samples which were thermally desulfurized up to 1080°C (TDS-1080) and 1200ºC (TDS-1200), respectively, were chosen for comparison with hydrodesulfurized cokes. Sulfur removal percentages of thermally desulfurized cokes were 4.72% and 13.51%, respectively, for these samples. XRD analysis results showed that TDS-1200 sample has the highest graphitization degree. The degree of crystallinity of hydrodesulfurized cokes was slightly higher than that of TDS-1080, but all of them were lower than that of TDS-1200. Among hydrodesulfurized samples, the Lc of the sample HDS-37 was slightly higher compared to the Lc of HDS-60. XPS analysis of five samples showed that all cokes have different C functional groups to varying extents. The sulfur content on the surface of HDS-37 and HDS-60 was quite lower than that of green coke and thermally desulfurized cokes. These results confirm the sulfur removal values obtained with the sulfur combustion analysis method. The C content results obtained from XPS are also consistent with the Lc results. TDS-1200 has the highest C content and the highest Lc value while HDS-37 and HDS-60 have C contents higher than that of TDS-1080 and the same trend was observed for Lc. Among the hydrodesulfurized cokes, HDS-37 has higher C content and Lc compared to those of HDS-60. According to the high resolution S2p spectra analysis, sulfur exists in all samples in the form of thiophenes. The visual analysis of samples with SEM shows the formation of cracks and pores to the similar extent for all samples that were compared. Porosity analysis was done to clarify the change in the surface after hydrodesulfurization and thermal desulfurization. It was found that hydrodesulfurization did not create additional internal porosity that can deteriorate and disqualify the coke for anode manufacturing. The real densities of two hydrodesulfurized coke samples (HDS-37 and HDS-60) were closer to the real density of a conventionally-calcined coke used in anodes than the coke samples thermally desulfurized in this study.

Based on sulfur content results of all samples, it may be concluded that considerable amount of sulfur has been removed from high sulfur coke at different water injection temperatures and durations with hydrodesulfurization without losing too much coke due to gasification. Thermal desulfurization that was carried out to the same maximum temperature resulted in lower sulfur removal in coke, which demonstrates the effectiveness of the hydrodesulfurization method compared to the thermal desulfurization. In terms of coke structure, hydrodesulfurized cokes show promising results without creating any additional porosity and with proper real density and crystallinity. It can be stated that sulfur in coke can be removed at lower temperatures with hydrodesulfurization compared to thermal desulfurization; and this will reduce the energy consumption while maintaing the coke structure intact. This can make the utilization of hydrodesulfurization method possible to produce anode-grade calcined coke for carbon anode production.

The results of this experimental study can help coke industry reduce the sulfur content of high sulfur petroleum coke. Hydrodesulfurization can be incorporated into a conventional calcination process without any need for high temperatures which cause higher energy consumption and the detoriation of coke structure. However, for the industrial application of the results of this work, further study needs to be carried out to find the most favorable conditions for sulfur removal, reduction of the weight loss, and to increase the coke-gas contact during combined hydrodesulfurization and calcination.

5.2. Recommendations

In this project, the research was carried out to investigate hydrodesulfurization method and characterize the hydrodesulfurized coke structure to see its suitability as a carbon anode raw material. In the light of the results obtained in this work, further studies could be undertaken on the influence of hydrodesulfurization conditions such as water injection temperature, duration, and flow rate on desulfurization percentage. Especially, water flow rate and water injection duration could be investigated over a greater range. Water injection temperature could also be investigated further using smaller ranges. The weight loss of coke due to gasification during hydrodesulfurization is one of the most important points that needs further attention.

In this study, hydrodesulfurization was carried out up to 1080ºC maximum temperature. Further work on the hydrodesulfurization of high sulfur coke could be done up to 1200ºC-1250ºC, typical calcination temperatures used in industry. The coke structure after hydrodesulfurization up to 1200ºC can also be examined in terms of density, porosity, crystalline length, mechanical properties, electrical and thermal conductivities. These properties are essential for a calcined coke to be considered as a potential anode raw material.

Following the work done in this project, further studies could be undertaken on the thermogravimetric analysis of the hydrodesulfurization of petroleum coke under most favorable conditions. The evolution of sulfur and other compounds as well as reaction rates can be determined in order to understand the fundamental reactions taking place during this process.

In addition to the above points, different high-sulfur petroleum cokes with different structures (shot or sponge, isotropic or anisotropic) which have different origins and sulfur contents (high, medium or low sulfur) could be used to see the effect of green coke type on the hydrodesulfurization rate.

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APPENDIX A

EXPERIMENTAL RESULTS AND DISCUSSION: THERMAL DESULFURIZATION AND CHARACTERIZATION OF GREEN COKE A, B, C

A.1. Introduction

In this appendix, the results for the thermal desulfurization of different green petroleum coke samples (coke A, coke B, and coke C) up to different calcination temperatures (1200ºC, 1300ºC, 1400ºC) and their characterization are presented. The effect of maximum calcination temperature on percentage sulfur removal and weight loss from coke were investigated. In order to calculate percent desulfurization, sulfur analysis was carried out for all treated samples as well as green coke samples. The weight loss percentage was also calculated after each experiment.

The characterization of three different green petroleum cokes (coke A, coke B, and coke C) was also done prior to thermal desulfurization. The coke surface structure was investigated with scanning electron microscope (SEM) before and after different treatments. The green cokes surface functionality was investigated by FT-IR and XPS. The green coke characterization along with the sulfur removal and weight loss results of thermal desulfurization experiments are presented and discussed in the following sections.

A.2. Green Coke Characterization

The characterization of three different green cokes was done with FT-IR, XPS and SEM in order to investigate the surface functional groups and the morphology of cokes. Results of these analyses are presented in this section.

A.2.1. FT-IR Analysis Results

The surface functional groups of the green petroleum coke samples were identified with FT-IR. Figure A1 shows the FT-IR spectra of the three green petroleum cokes. The assignment of the bands was done based on FT-IR data for green petroleum coke available in the literature and was given in Table 4.1. Before the detailed analysis, each sample was tested four times and each of the spectra was obtained by averaging four spectra (Figure A.1).

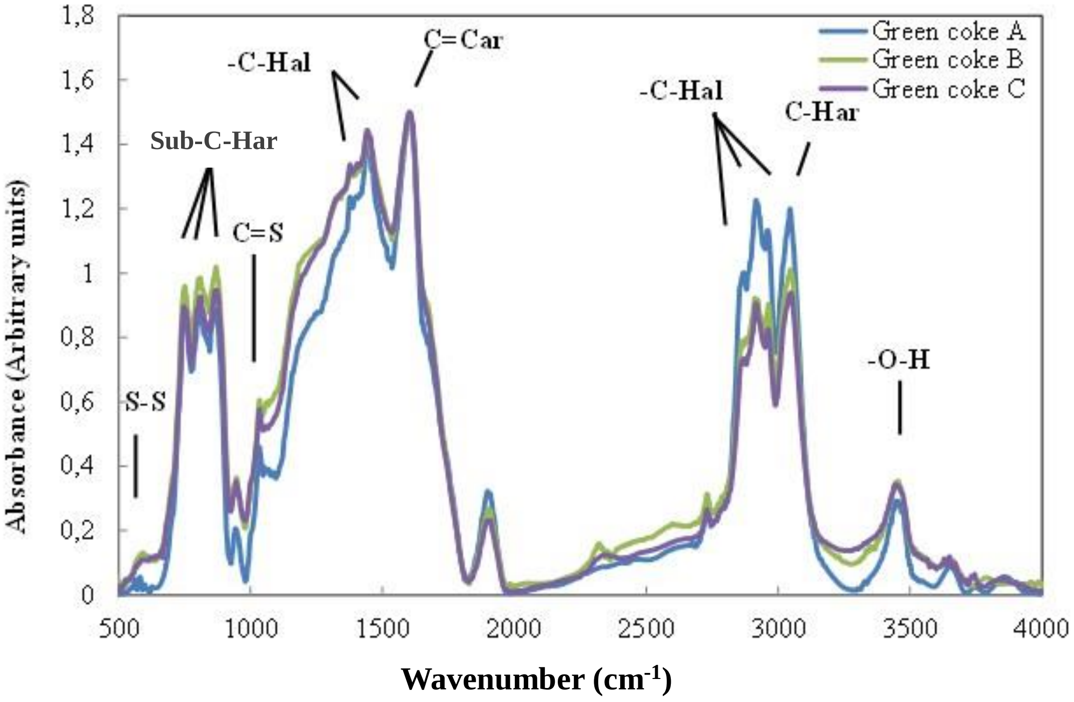

Figure A.1 FT-IR analysis of green petroleum cokes by DRIFT method at room temperature

The FT-IR spectra of three different green petroleum coke samples are quite similar. The FT-IR spectra typically display an absorbance band near 3047 cm^{-1} due to aromatic C-H stretching vibrations for all the green cokes. A pattern of absorption bands between 900 and 700 cm^{-1} which arose from the out-of-plane vibration of aromatic C-H bonds and bands corresponding to aromatic C=C bond near 1600 cm^{-1} were observed for all three coke particles. On the aliphatic side, the spectra consist of a pattern of absorption bands to alkyl functional groups (unsaturated and saturated C-H stretching vibrations corresponding to the region between 2700 and 2965 cm^{-1}) and those corresponding to C=C stretching vibration for aromatics or C-H bending vibrations of methylene (1445 cm^{-1}) and methyl groups (1375 cm^{-1}). It was also mentioned in the literature that, basically, the functionalities are related to the existing carbonyl groups (shoulder at 1670 cm^{-1} corresponding to C=O vibration modes), -O-H stretching vibrations made of hydroxyl, phenolic functionalities or moisture (3453 cm^{-1}), and aryl O groups (1300-1100 cm^{-1}). C=S stretching vibrations display an absorbance band near 1033 cm^{-1} as well as S-S stretching bonds between 550-700 cm^{-1}, which can be attributed to the high sulfur content of all petroleum cokes. In general, the FT-IR spectra of three cokes are similar with regard to functionality. The differences might be quantitative rather than qualitative [113].

A.2.2. XPS Analysis Results

Atomic percentages of different components of green petroleum coke A, B and C, which were obtained from the general XPS spectra, are presented in Table A.1 for the survey spectra and in Table A.2 for de-convoluted C1s spectrum. The de-convoluted C1s high resolution spectra of three cokes are presented in Figure A.2, Figure A.3, and Figure A.4.

Table A.1 Atomic percentages of the different components of the three different green petroleum cokes

Coke type	**C (%)**	**O (%)**	**N (%)**	**S (%)**
Green coke A	91.08	6.96	0.00	1.96
Green coke B	95.50	2.52	0.00	1.98
Green coke C	93.71	4.47	0.01	1.81

Table A.2 Atomic percentages of carbon components of the three different green petroleum cokes

	Carbon components				
	C=C	**C-C**	**C-OH /C-S/ COC**	**C=O**	**COO**
Green coke A	78.82	10.43	6.26	3.05	1.43
Green coke B	85.99	9.48	2.11	0.88	1.54
Green coke C	84.56	7.91	4.44	1.56	1.53

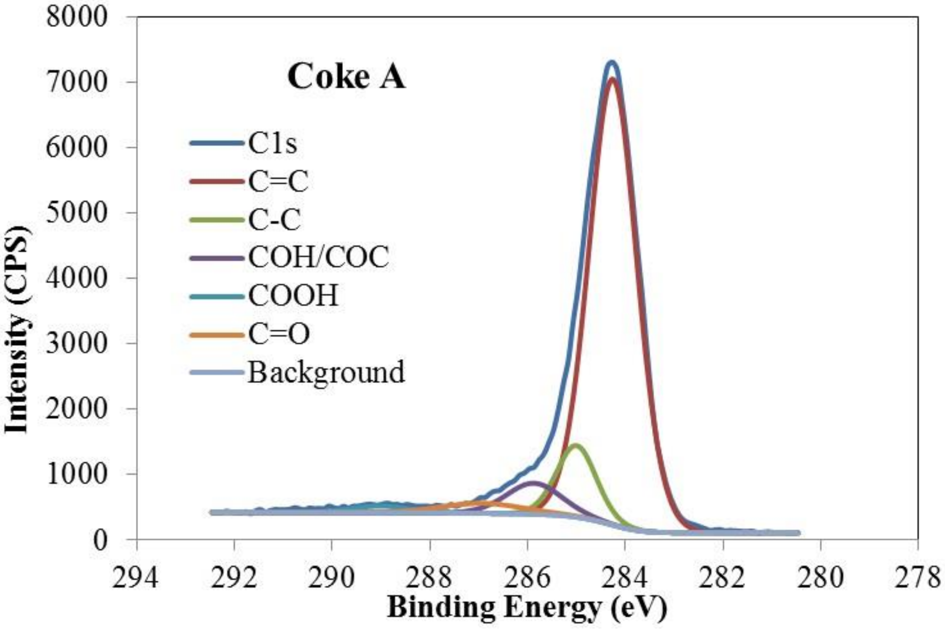

Figure A.2 Deconvoluted C1s peak of green coke A

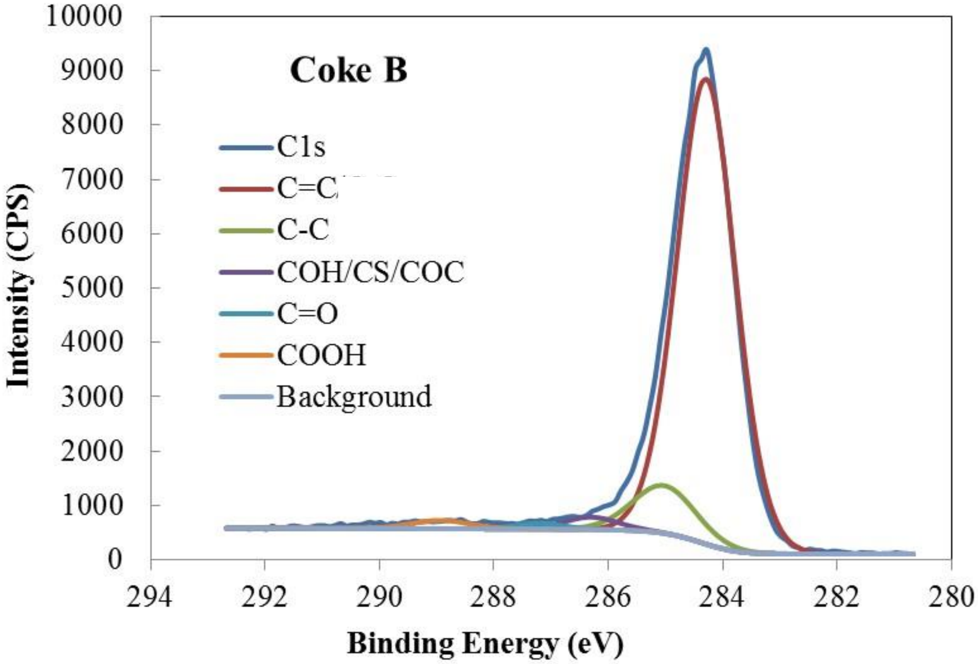

Figure A.3 Deconvoluted C1s peak of green coke B

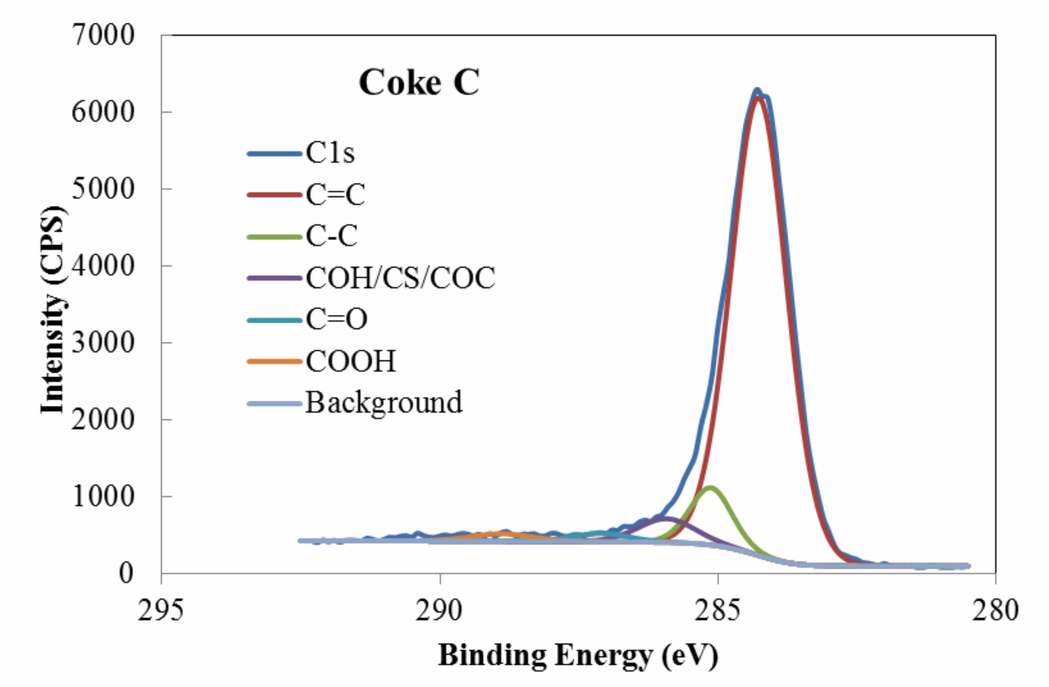

Figure A.4 Deconvoluted C1s peak of green coke C

The deconvolution of C1s peaks of three cokes were done according to available literature [112, 117-120, 123]. It is evident from the XPS results that all the green coke samples have similar functional groups and contains greater quantities of C=C and C-C bonds and trace amount of oxygen and sulfur compounds. According to atomic percentages from XPS analyses, which are shown in Table A.1, it was found that none of the three green coke samples contains nitrogen. Also, it can be seen from Table A.2 that coke A has the highest oxygen percentages whereas coke B has the lowest. The sulfur content of all cokes is high as it was found previously with the combustion sulfur analysis as well as SEM-EDX analyses of the same cokes. Green coke C has slightly lower sulfur content compared to Coke A and B which was also detected with other sulfur analysis methods.

Inspection of C1s high resolution peaks of three green cokes in Figure A.2, Figure A.3, and Figure A.4 reveals five peaks located at around 284.3, 285.1, 286, 287 and 288.6 eV that form the asymmetrical C1s peak. The dominant peak at 284.3 eV is associated with C=C bonds of aromatic structures. 285.1 eV, which is the second dominant bond in all C1s spectra, can be attributed to the aliphatic carbon (C-C). The peaks at higher energy positions are associated with the C-OH/C-S/C-O-C, C=O and COOH bonds, respectively.

A.2.3. SEM Analysis Results

Figure A.5, A.6, and A.7 shows the SEM images of three different green petroleum cokes at different magnification values.

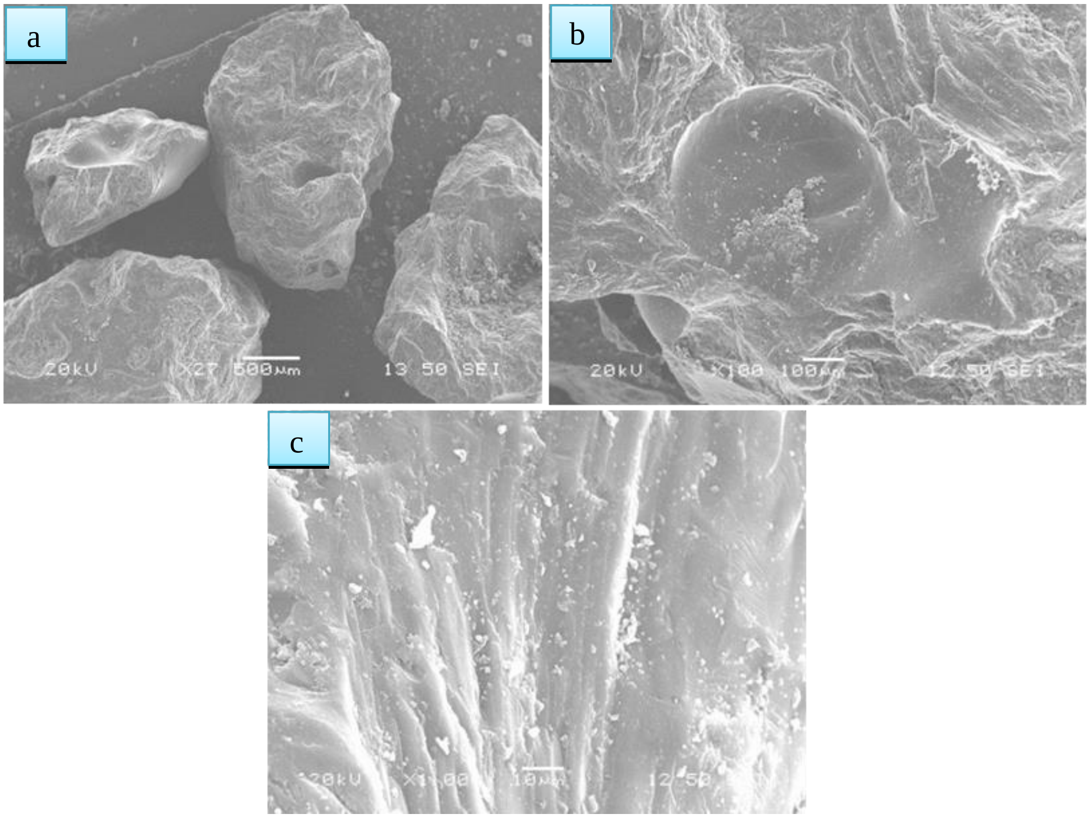

Figure A.5 SEM images of green coke A at different magnifications (a) x 27 (b) x 100 (c) x 1000

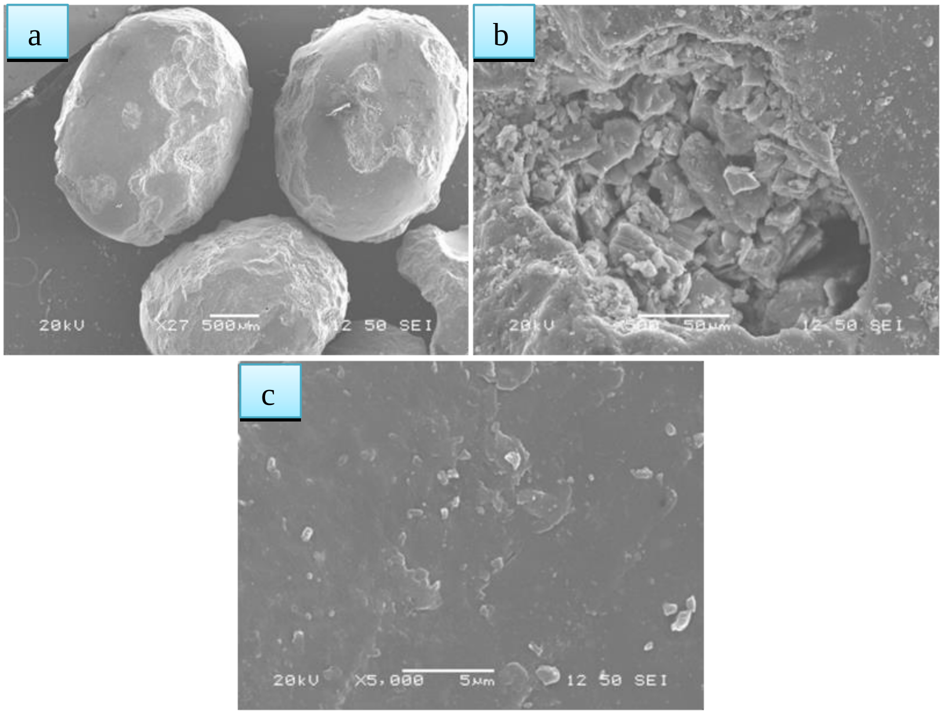

Figure A.6 SEM images of green coke B at different magnifications (a) x 27 (b) x 500 (c) x 5000

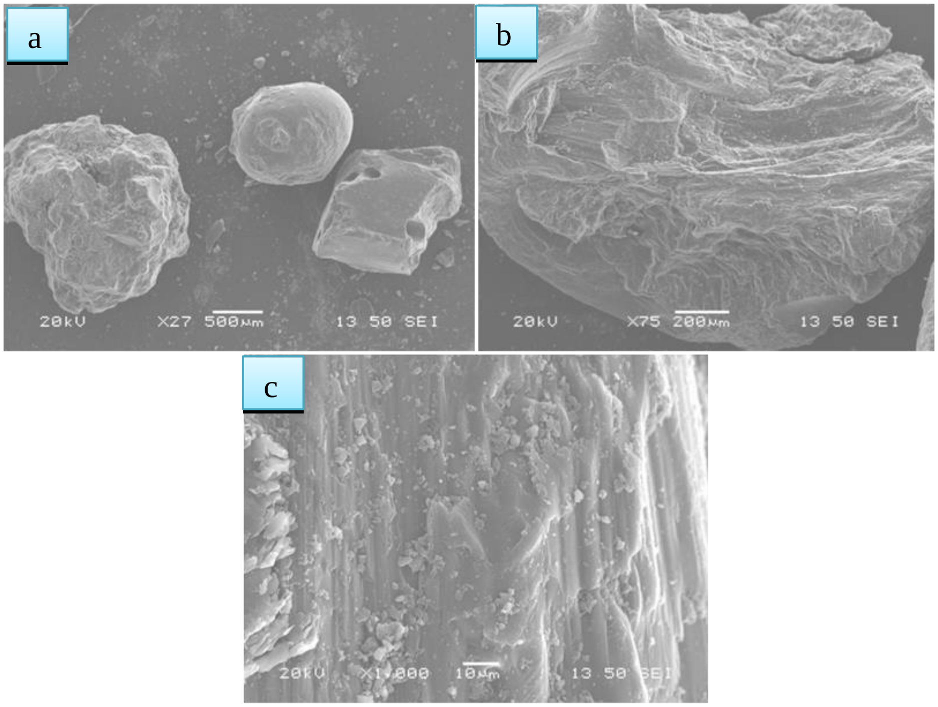

Figure A.7 SEM images of green coke C at different magnifications (a) x 27 (b) x 75 (c) x 1000

Green coke A and C are sponge cokes and have anisotropic structure, which means their properties are directionally dependant. Their directional structure can be seen from SEM images. Green coke B is not a shot coke, but it has an isotropic structure where properties are identical in all directions. SEM images of green coke B shows its isotropic structure.

A.3. Thermal Desulfurization

In the context of petroleum coke thermal desulfurization, various experiments were conducted with three different kinds of petroleum cokes (Cokes A, B and C) at different maximum temperatures (1200, 1300 and 1400°C) using the experimental system explained in Chapter 3, Section 3.3. The sulfur removal (%) was calculated with Equation 4.1: The weight loss (%) from coke was calculated with Equation 4.2.

The sulfur removal and weight loss percentages from cokes after thermal desulfurization experiments at different maximum temperatures are given in Table A.3 and Table A.4, respectively.

Table A.3 Sulfur removal (%) results of the four petroleum cokes after thermal desulfurization

T_{max} of Thermal Desulfurization (°C)	**S removal (wt %)**		
	Coke A	**Coke B**	**Coke C**
1200	9.08	13.14	27.29
1300	8.14	21.94	25.66
1400	55.40	20.43	48.88

Table A.4 Weight loss (%) results of the four petroleum cokes after thermal desulfurization

T_{max} of Thermal Desulfurization.,ºC	**Weight loss (%)**		
	Coke A	**Coke B**	**Coke C**
1200	12.74	23.37	14.89
1300	14.50	25.09	17.86
1400	15.85	29.26	16.91

The tabulated sulfur removal and weight loss results of thermal desulfurization of each coke are plotted with respect to temperature and are presented in the following part. The sulfur removal and weight loss results of thermal desulfurization of green coke A up to different maximum temperatures are given in Figure A.8.

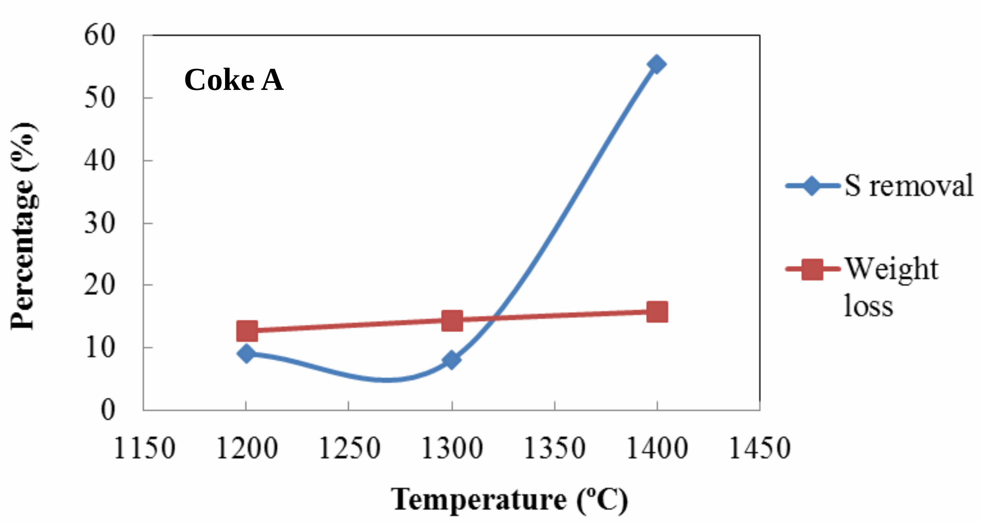

Figure A.8 Percentage weight loss and sulfur removal for coke A during thermal desulfurization at 1200-1300-1400ºC

Despite its high sulfur content, green coke A gave 9.08% and 8.14% of sulfur removal after its thermal desulfurization up to 1200°C and 1300°C. These values are quite low compared to the sulfur removal percentages after thermal desulfurization of green coke B and C. This might be due to either non-homogeneous nature of the coke or its properties which are related to its origin, sulfur and ash content as well as operating conditions of refining and coking. When maximum temperature increased to 1400°C, desulfurization increased significantly to 55.40%, as expected (significant increase in sulfur removal that occurs at elevated temperatures). This phenomenon was reported in detail by many studies. The weight loss percentages were found to be in the expected range and changed slightly from 12.74% to 15.85% when maximum temperature was increased from 1200ºC to 1400ºC, respectively.

Figure A.9 shows sulfur removal and weight loss percentages of coke B after the thermal desulfurization experiments up to 1200ºC, 1300ºC, and 1400ºC maximum temperatures.

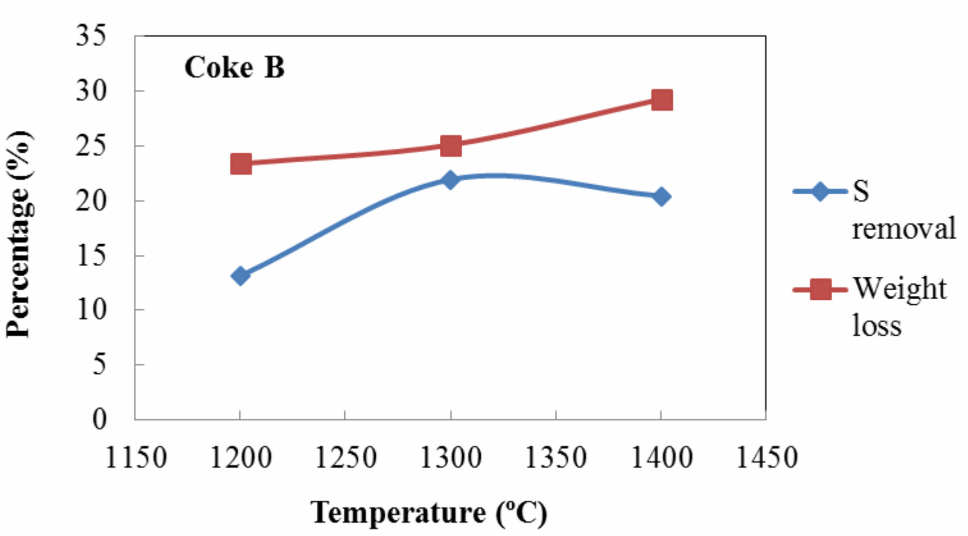

Figure A.9 Percentage weight loss and sulfur removal results of coke B during thermal desulfurization at 1200-1300-1400ºC

13.14%, 21.94% and 20.43% of sulfur removals were obtained after the thermal desulfurization of coke B up to 1200ºC, 1300ºC, and 1400ºC. The sulfur removal of coke B at 1200ºC and 1300ºC was higher than the ones for coke A. However, the significant sulfur evolution which occurs at 1400ºC wasn't observed for this coke. This might be due to many reasons such as the isotropic structure of coke B, the nonhomogenity of coke, and its properties.

Although the volatile content of green coke B is much less than the volatile content of other cokes, the weight loss values after the thermal desulfurization of coke B at different maximum temperatures seems to have higher values than all other cokes. Since green coke B has an isotropic structure which is different than the two other cokes, the high weight loss values were attributed to its structure.

The sulfur removal and weight loss percentages after thermal desulfurization of green coke C are presented in Figure A.10. High sulfur removal percetanges of 27.29% and 25.66% were obtained after the desulfurization of green coke C at 1200ºC and 1300ºC, respectively. The weight loss values at these temperatures were 14.89% and 17.86%, respectively. When thermal desulfurization was carried out at 1400ºC maximum temperature, sulfur removal increased to 48.88%. 16.91% of weight loss was found at this temperature.

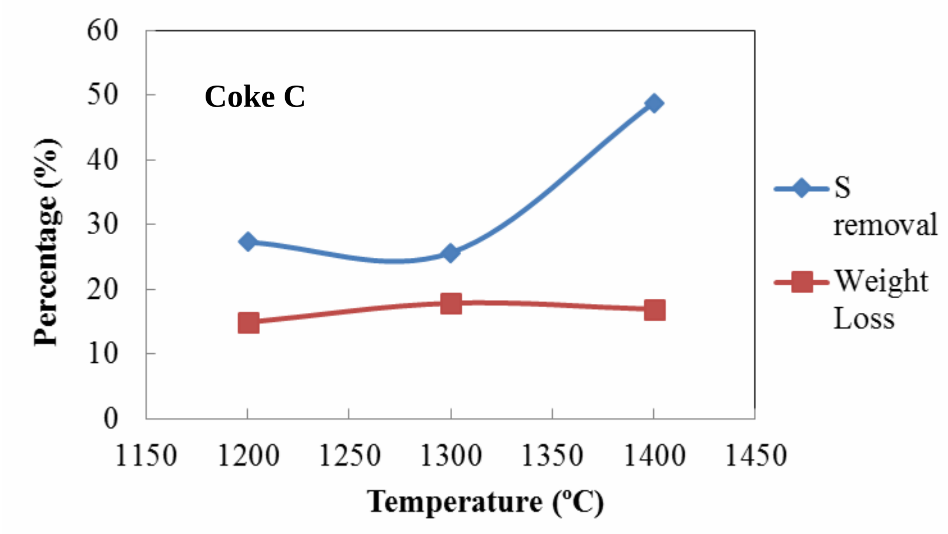

Figure A.10 Percentage weight loss and sulfur removal results of coke C during thermal desulfurization at 1200-1300-1400ºC

A.3.1. SEM Analysis of Cokes after Thermal Desulfurization

Figures A.11 and A.12 show SEM images of coke A after its thermal desulfurization at 1200°C and 1400°C, respectively. Figure A.13 and Figure A.14 show the SEM pictures of coke B after its thermal desulfurization at 1200°C and 1400°C, respectively. Figure A.14 and Figure A.15 show the SEM pictures of coke C after its thermal desulfurization at 1200°C and 1400°C, respectively. Apparently, all calcined coke surfaces contain pores and cracks. On calcined cokes, there are very small pores although there are also larger pores in addition to some interconnected pores. The presence of very small pores is not desirable, since it prevents the penetration of pitch into the coke particles and reduces the wetting of coke by pitch. This results in low anode quality. In addition to pores and cracks, puffing effect can be seen on the cokes which were calcined at 1400°C. Cokes seem to have popcorn like structure after calcination at 1400°C, which makes them unsuitable for carbon anode manufacture. However, due to the non-homogeneity of coke, SEM images may not represent the actual pore distribution in the bulk of the coke sample. In order to determine the changes on the coke structure precisely, porosity and density analysis of the calcined coke samples should be carried out.

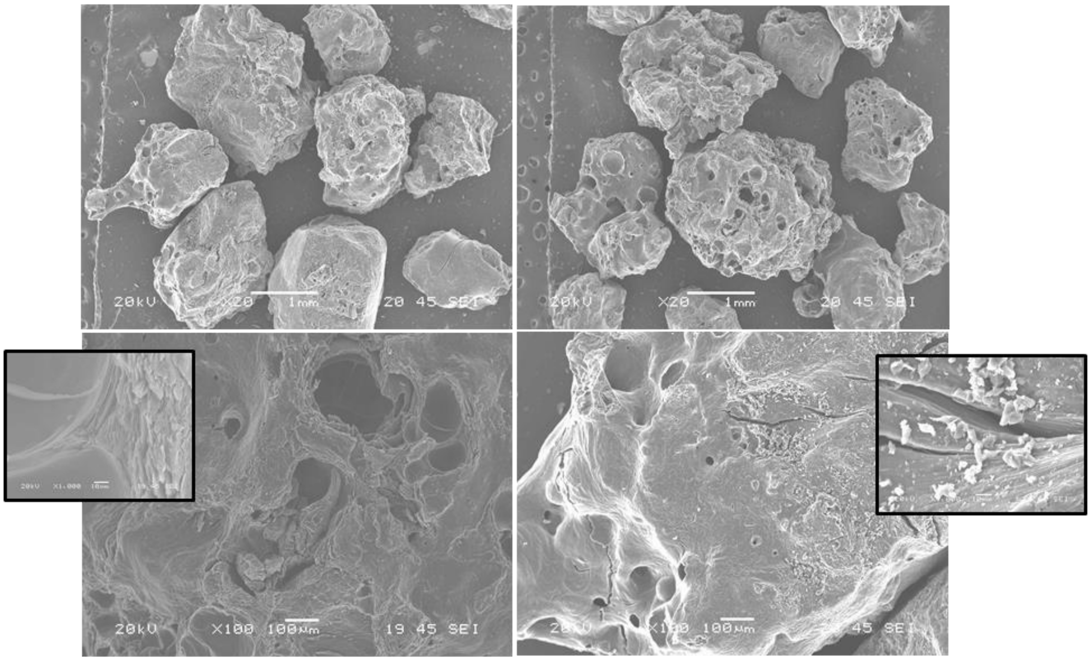

Figure A.11 SEM images of coke A after thermal desulfurization up to 1200ºC (x20 x100 x1000 magnifications)

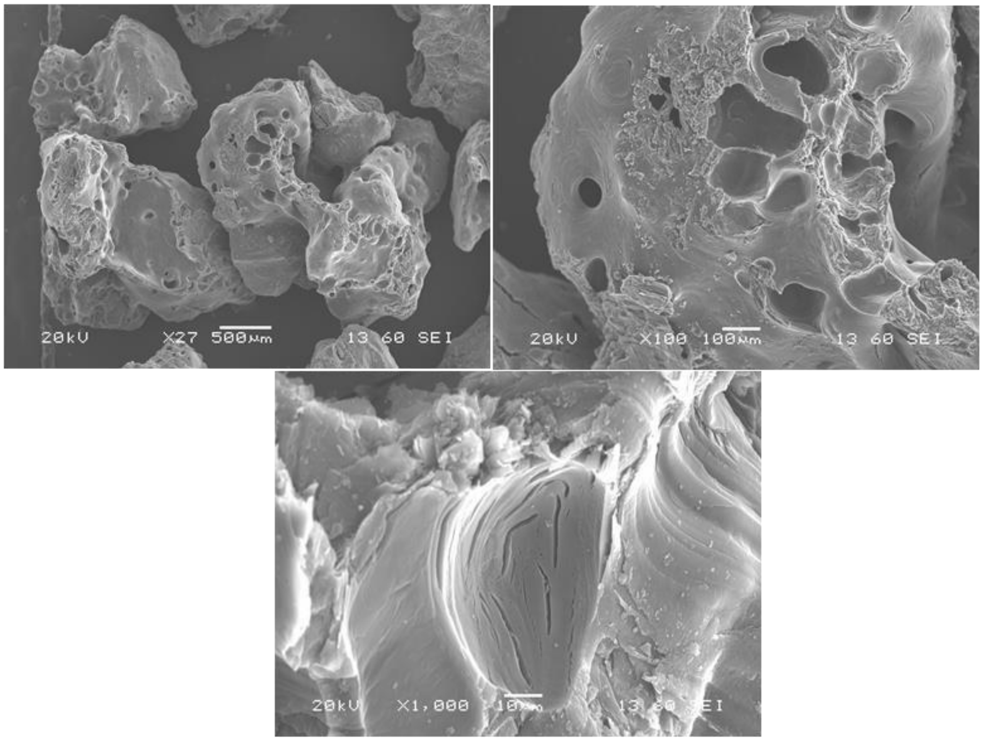

Figure A.12 SEM images of coke A after thermal desulfurization up to 1400ºC (x20 x100 x1000 magnifications)

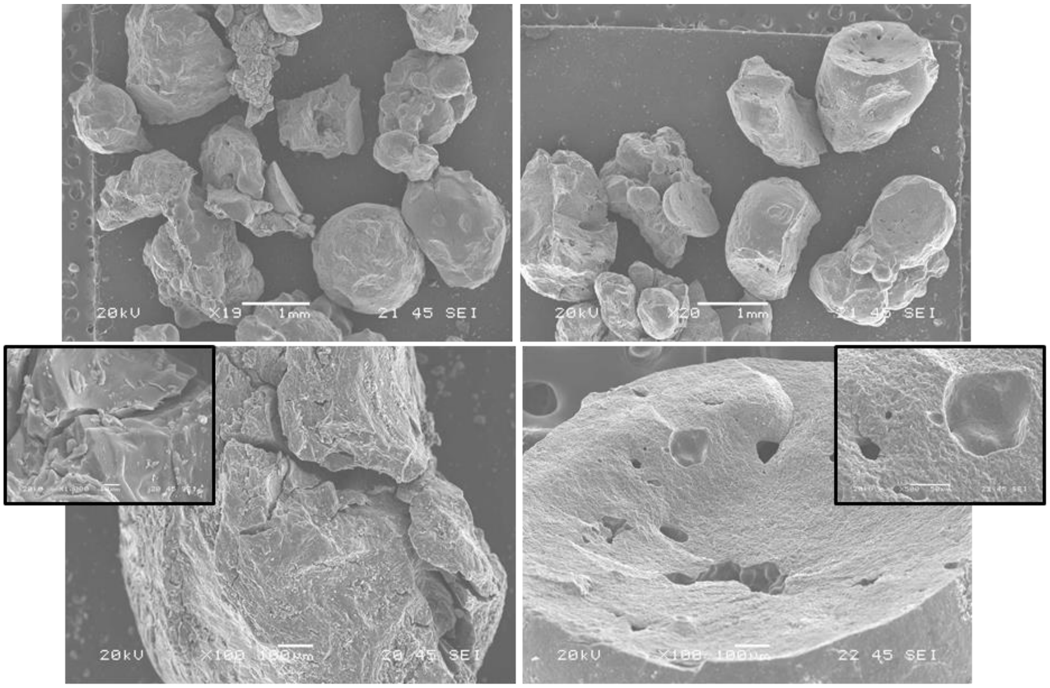

Figure A.13 SEM images of coke B after thermal desulfurization up to 1200ºC (x20 x100 x1000 magnifications)

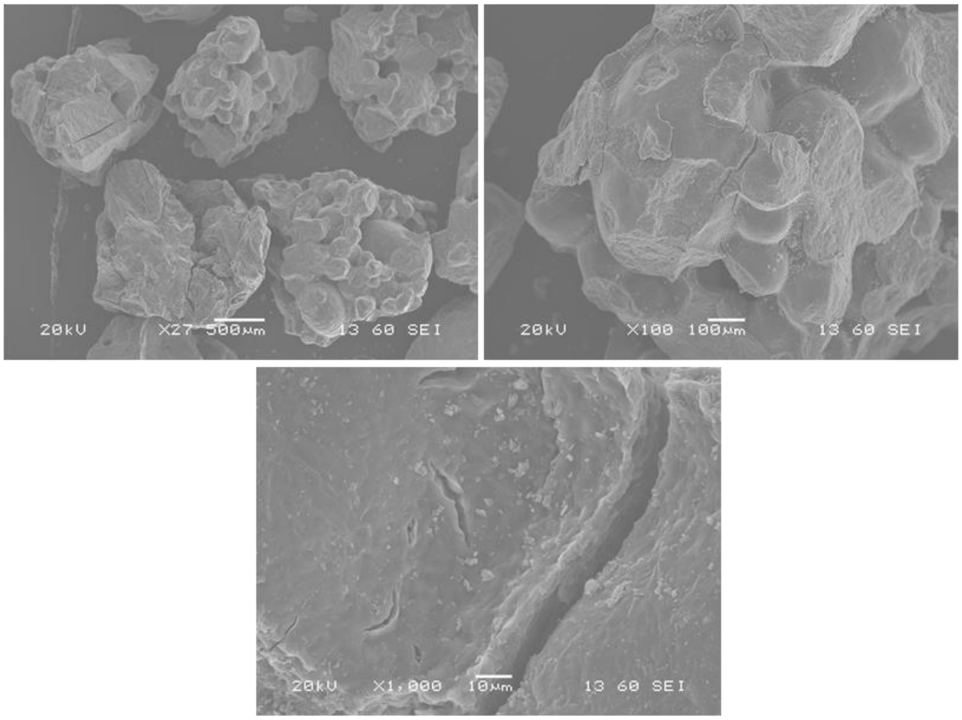

Figure A.14 SEM images of coke B after thermal desulfurization up to 1400ºC (x20 x100 x1000 magnifications)

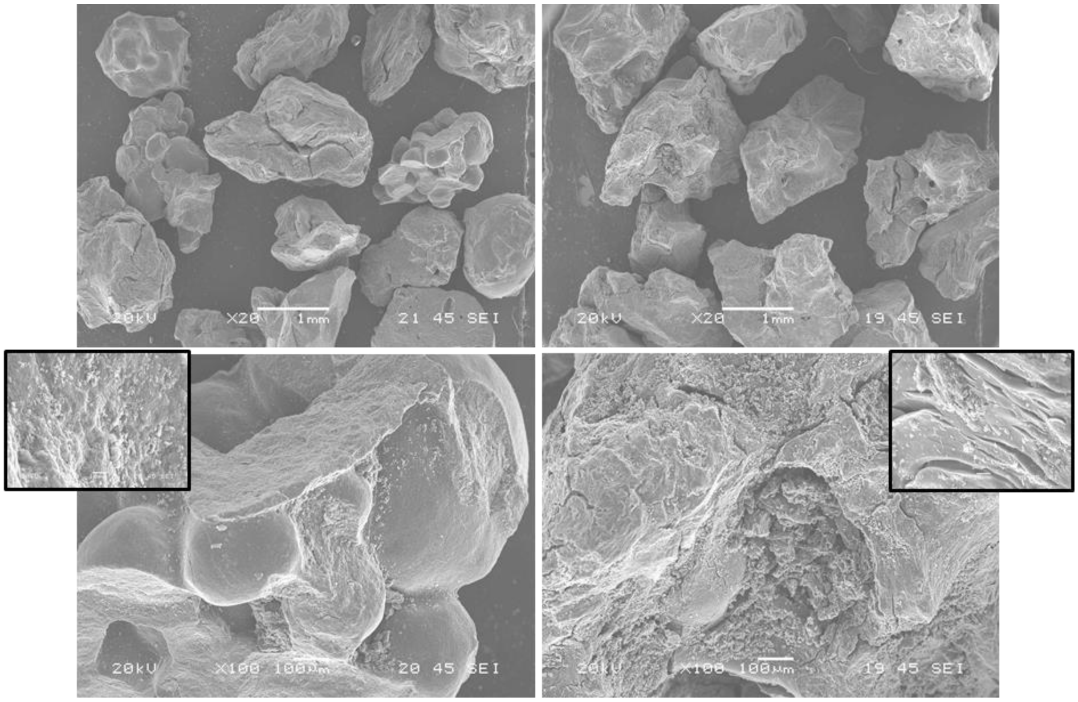

Figure A.15 SEM images of coke C after thermal desulfurization up to 1200ºC (x20 x100 x1000 magnifications)

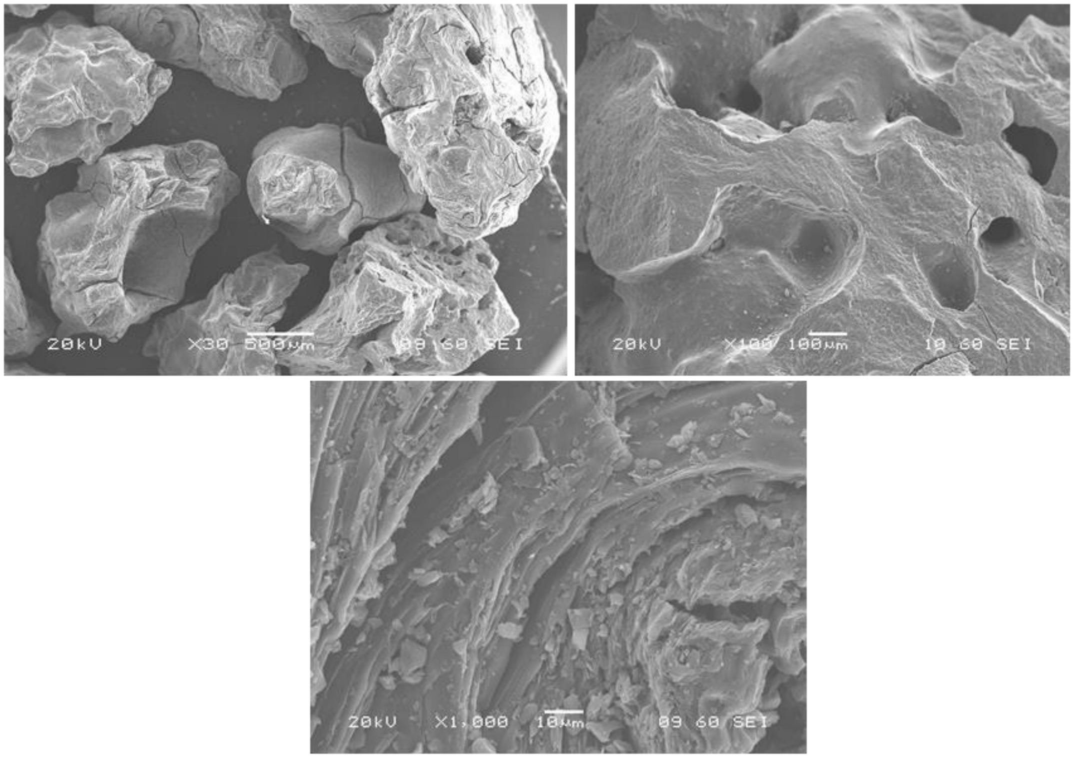

Figure A.16 SEM images of coke C after thermal desulfurization up to 1400ºC (x20 x100 x1000 magnifications)

A.4. Summary and Conclusions

In this section, commercially available different high sulfur green petroleum cokes were desulfurized with thermal desulfurization method and the resulting cokes were characterized. The effect of maximum calcination temperature on sulfur removal from different cokes was studied. It was shown that all of the cokes have similar aromatic and aliphatic functional groups at different quantities. Thermal desulfurization of green coke A, B, and C induced different amounts of sulfur removal for each coke. For coke A, sulfur removal at 1200ºC and 1300ºC was similar and their values were 9.08% and 8.14%, respectively. Calcination of coke A at 1400ºC showed a dramatic increase in sulfur removal which was also the case for coke C. Both cokes showed around 50% of sulfur removal at this temperature. Coke C gave much higher sulfur removal at 1200ºC and 1300ºC than coke A. The percent thermal desulfurization for coke B was 13.14%, 21.94% and

20.43% at 1200ºC, 1300ºC, and 1400ºC, respectively. High temperature calcination did not create high sulfur removal for coke B which might be due to its either isotropic structure or origin. For all cokes, thermal desulfurization up to different maximum temperatures resulted in considerable volatile release. For coke A and C, it was in the range of 12-16% while coke B showed higher weight loss values at all temperatures which were between 23-30%. The SEM investigations of the coke structures before and after thermal desulfurization at 1200ºC and 1400ºC revealed that this treatment creates a considerable amount of pores and cracks on the coke surface. Some coke particles seemed to have popcorn like structure after calcination at 1400ºC according to SEM analysis. However, the extent of the structural change of coke cannot be quantified with SEM analysis which gives only a visual idea. Further analyses should be done to investigate the structure change of coke.