Hydrodesulfurization of Petroleum Coke

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Abstract

Properties of petroleum coke affect strongly the quality of anodes used in aluminum industry. A certain level of sulfur in anodes is necessary to reduce the reactivities; however, high levels of sulfur cause environmental problems. The demand for anode-quality coke with acceptable sulfur content is increasing faster than the available supply. Thus, the industry is searching for ways to reduce the sulfur content of cokes containing high levels of sulfur. There are different ways of desulfurizing green petroleum cokes such as solvent extraction, thermal desulfurization, and hydrodesulfurization. Solvent extraction can contaminate the coke. Thermal approach requires higher calcination temperatures leading to greater energy consumption and increases coke porosity. Hydrodesulfurization seems to be a viable option and was investigated in this study. The effect of water injection temperature and duration, water flow rate, and coke particle size on the hydrodesulfurization of green petroleum coke was studied. In addition, a number of calcination and thermal desulfurization experiments were carried out with the same green petroleum coke. Sulfur removal and weight loss results obtained in these experiments were compared. It was found that more sulfur can be removed at lower temperatures using hydrodesulfurization compared to thermal desulfurization. Hydrodesulfurized coke displayed a structure similar to the one calcined normally.

Keywords: Hydrodesulfurization, thermal desulfurization, petroleum coke, calcination, sulfur.

1. Introduction

The primary aluminum is produced using the Hall-Héroult process in which large amounts of carbon anodes are consumed. Anode quality is important due to its impact on cell operation, carbon and energy consumption, and environment. Properties of coke, one of the principal raw materials in anode production, influence significantly the anode quality. The rising demand for aluminum resulted in higher demand for green petroleum coke [1] while the availability of the good quality coke has been decreasing during recent years because of the significant increase in sour crude oil usage in refining industry due to economic reasons [2]. Sour crude oil leads to the production of high sulfur green coke, and aluminum industry uses such cokes by blending with low sulfur cokes [3]. Some amount of sulfur is needed in calcined coke to reduce anode reactivity [4]. However, using calcined coke with a sulfur content higher than necessary in carbon anodes would have a number of adverse effects on environment. The use of high-sulfur anode in electrolysis leads to an increase in emissions such as H_2S, COS, CS_2, and SO_2 [5]. High sulfur content in anodes may also cause sulfur removal during anode baking if the baking is continued above a certain temperature. This increases anode porosity and specific electrical resistivity and decreases anode baked density, leading to shortened anode life, increased energy

and carbon consumption, and higher environmental emissions during electrolysis. Sulfur in anodes also results in a significant loss of current efficiency in the electrolysis cell [6-7].

According to the literature, the nature of sulfur in green petroleum coke is mostly organic, and thiophenes appear to be the most common forms of sulfur present in these cokes [8-10]. There are several methods for removing sulfur from petroleum coke. Solvent extraction uses chemical solvents [11]. This method is not suitable for the treatment of petroleum coke used in anode manufacturing since it contaminates the coke. 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 [12]. However, it was shown recently that the thermal desulfurization in a vertical shaft calciner at slow heating rates produces a coke that can possibly be used in blends at levels of 50% or lower [13]. 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 at industrial scale. In hydrodesulfurization, green petroleum coke is heated under a hydrogen or steam atmosphere, forming H_2S with sulfur present in coke [14-15]. More efficient contact between hydrogen and coke can improve the sulfur removal [16]. In this study, water vapor was directly injected onto the hot coke during calcination where coke comes in contact with water gas ($CO+H_2O$), volatiles, and H_2S (sulfur containing gas) [17].

This study was undertaken to investigate the simultaneous calcination and hydrodesulfurization of high-sulfur containing green coke and to determine if anode-grade coke could be produced. The effects of various experimental conditions (water injection temperature, water flow rate, etc.) on sulfur removal have been studied. The results are compared with those obtained from the calcination and thermal desulfurization experiments. The calcination and thermal desulfurization experiments were carried out at high heating rates, typically found in rotary kilns (40°C/min). The hydrodesulfurization experiments were carried out at low heating rates (slightly below 1°C/min (50°C/h)) representing the heating rates in a vertical shaft calciner since it can be realized only in such systems due to the need for good contact between gas and particles.

2. Methodology

2.1. Material used

A number of different green sponge cokes were used in this study. The available properties of the green petroleum coke used for the hydrodesulfurization experiments are given in Table 1. A number of calcination and thermal desulfurization experiments were also carried out with the same coke to compare the results.

Table 1. Physical and chemical properties of green petroleum coke.

Elements (wt%)		**Impurities (ppm)**		**Proximate analysis**	
Carbon	88.17	Ni	122	**(dry basis)**	
Sulfur	6.87	Fe	319	Volatile content (%)	12.8
Hydrogen	3.87	V	362	Ash content (%)	0.13
Nitrogen	0.97	Si	419	Fixed carbon (%)*	87.07
		Ca	19	Moisture content (%)	0.47
		Na	142		
		P	1	Real density (g/cm^3)	1.39

*by difference

2.2. Sample Analysis and Characterization

2.2.1. X-Ray Photoelectron Spectroscopy (XPS)

Different green, calcined, hydrodesulfurized, and thermally-desulfurized coke samples were studied with an 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 × 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 area was evaluated 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.

2.2.2. X-ray Diffraction (XRD) Analysis

X-ray diffraction (XRD) measurements were conducted on the coke samples after calcination and 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° over the 2θ range from 3° to 70°. 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.

2.2.3. Density and Porosity Analyses

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

2.3. Hydrodesulfurization

Two experimental set-ups were used for hydrodesulfurization experiments. The first one was a packed-bed coupled with gas chromatography (GC). These tests were carried out in order to detect if H_2 and H_2S were forming and thus hydrodesulfurization was taking place. In the second set-up, one layer of coke particles rather than a bed of particles were subjected to hydrodesulfurization. The aim was to eliminate the bed effects in order to study only the hydrodesulfurization.

2.3.1. Experimental Set-up: Packed-Bed Coupled with Gas Chromatography (GC)

The experiments were carried out under N_2 gas in an electrically-heated Pyradia (ALC 182412) furnace. The coke (95 g, -2 mm +1 mm particle size) was placed in an alumina crucible. The

crucible is placed in a rectangular steel box which was covered in order to avoid the air infiltration. A schematic diagram of this set-up is given in Figure 1.
This system was coupled with two different GCs. One GC (Varian 3800), equipped with a TCD (thermal conductivity detector), was used to determine the presence of H_2 and CH_4 in the outlet gas. The second GC (Agilent 7890B), equipped with a PFPD (pulsed flame photometric detector), was used to detect the presence of sulfur compounds. During the normal calcination tests, the data were collected between 400-1080°C. During the hydrodesulfurization tests, water was injected to the system continuously at 4 ml/min flow rate between 618-1000°C, and data were collected simultaneously during the water injection period.

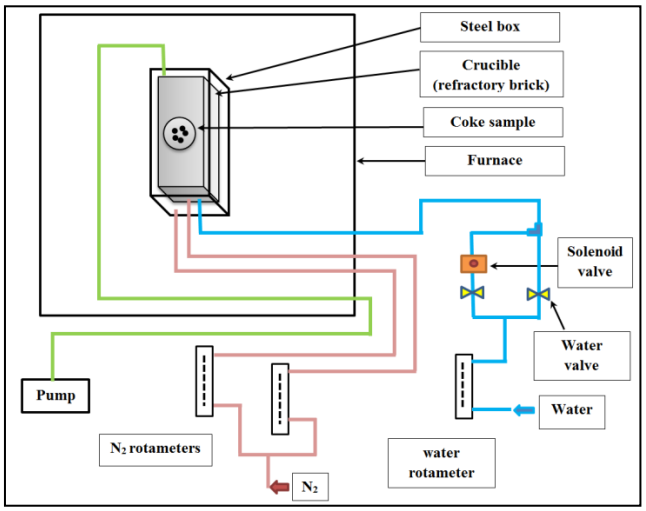
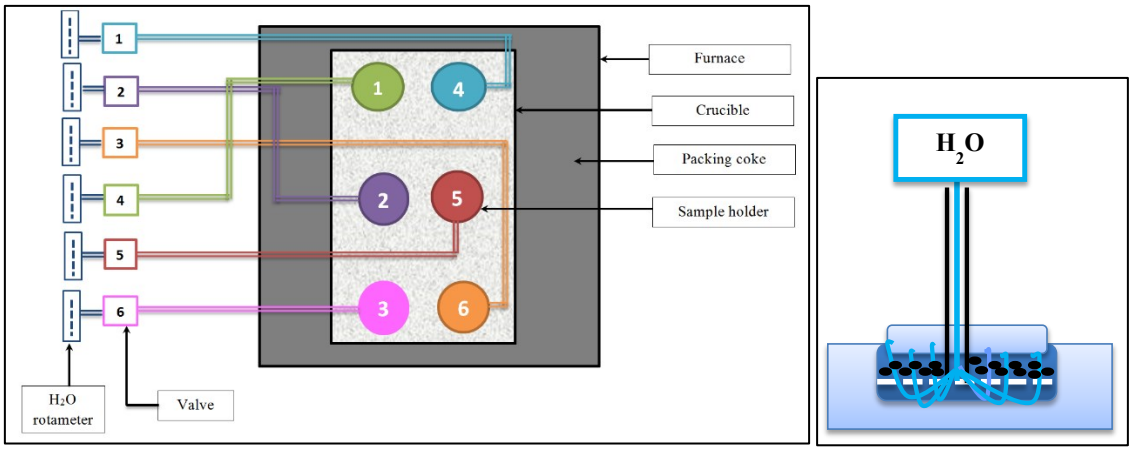


Figure 1. Packed-bed experimental set-up for hydrodesulfurization.

2.3.2. Experimental Set-Up: One Layer of Particles

After the set of experiments with the previous 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. A crucible containing six separate sample holders was fabricated (Figure 2a). Each sample holder had a diffuser plate for a uniform steam distribution, a separate water connection, and 10 g of coke sample. Water flow rate was adjusted precisely (Omega FL-1443-G and FL-1444-G). This arrangement (Figure 2b) made the application of different conditions to different samples possible during the same test.

The crucible was installed in an electrically-heated Pyradia furnace controlled by a PID (Omega CN 7800) and a maximum temperature controller (Omega CN 740). The experiments were conducted under N_2 atmosphere flowing at 4 L/min outside of the crucible. 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. 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. 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, other coke samples with fine and coarse particles were also used. The influence of water injection temperature (650, 750, 850, and 950°C), water flow rate (1, 4, 8 ml/min), and injection duration (6, 37, 60, and 100 min) as well as coke particle size (fine and coarse) on the desulfurization was examined.



(a) (b)

Figure 2. Experimental set-up for one-particle-layer hydrodesulfurization: (a) Schematic representation of the experimental system including the crucible with six sample holders and water connections; (b) Vertical cross-section of one sample holder.

2.4. Calcination and Thermal Desulfurization Set-Up

Calcination and thermal desulfurization experiments were carried out using a thermogravimetric analyzer under N_2 atmosphere. A schematic diagram of the experimental system is shown in Figure 3. The experiments were done with perforated graphite crucibles which can hold 20 to 30 g of particles. The crucible was suspended with a wire (Kanthal-A1 or tantalum) from a balance (Mettler Toledo XS205) to measure the weight loss every 30 seconds. The sample was heated via an induction furnace (Taylor Winfield 5 kW) controlled by a temperature controller (Micristar) with an infrared sensor (OMEGA OS1200).Calcination and thermal desulfurization of green coke samples were carried out up to different temperatures (1080°C, 1200ºC, 1300ºC, 1400ºC) at a heating rate of 40°C/min. Then, the sample was kept at this temperature for 15 min (soaking time) with the objective of using conditions similar to those of a rotary industrial calciner.

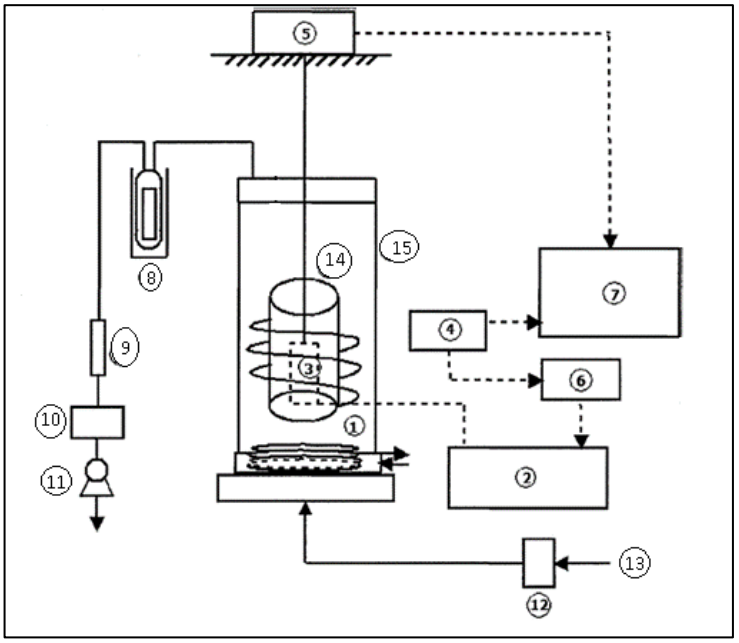


Figure 3. Experimental system for calcination and thermal desulfurization.

3. Results

3.1. Determination of Sulfur Type Present in Green Coke

An XPS analysis was carried out to determine the type of sulfur present in green coke. The analysis of the XPS spectra before convolution showed that the atomic composition of green coke was 91.66% carbon, 6.02% oxygen and 2.32% sulfur (5.84 wt%). This coke didn't contain any nitrogen. SEM/EDX analysis also showed similar sulfur content [17]. The deconvolution of S2p peak was carried out using the procedure reported in the literature [18-20]. Every S2p peak in the spectra appears in pairs which are S 2p3/2 and S 2p1/2 (indicating 3/2 and 1/2 electron spinning). 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 [18]. It was found from the deconvolution of S2p spectra that sulfur is present in the coke sample only in the form of thiophenes (S 2p3/2 at 163.5 eV, S 2p1/2 at 164.7 eV, ratio of the areas ($S2p_{3/2}$/$S\ 2p_{1/2}$): 66.07/33.93=1.95). The deconvoluted S2p spectra is shown Figure 4. This result matches with the existing literature about the dominance of thiophene as sulfur component in green petroleum cokes [8-10].

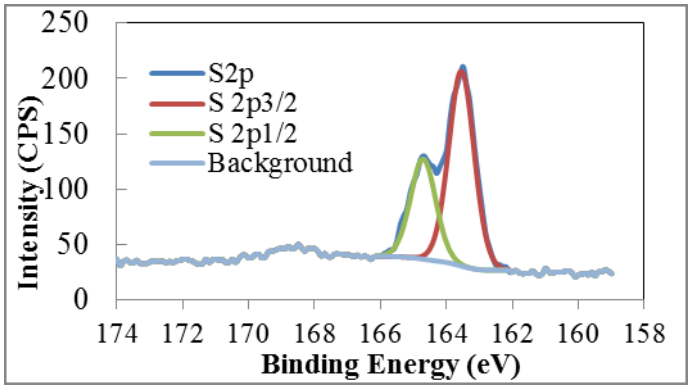


Figure 4. Deconvoluted S2p spectra of green petroleum coke from XPS analysis.

3.2. Gas Chromatography (GC) Analysis of Hydrodesulfurization and Calcination

Figures 5 and 6 show the sulfur and hydrogen peaks obtained, respectively from GC analysis during normal calcination and hydrodesulfurization. There was not much difference in peak areas of methane. The analysis is qualitative. Since the peak areas for hydrogen and methane are proportional to their concentrations, they were used to compare the release of these gases qualitatively at different temperatures. For sulfur compounds, all the species were converted to SO_2 in GC and then measured. 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 these compounds. The presence of sulfur compounds clearly increased after water injection. The increase in H_2 peak can be attributed to the water-gas reaction. The percent hydrodesulfurization is directly related to the favorability of this reaction which depends on temperature [21]. 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).

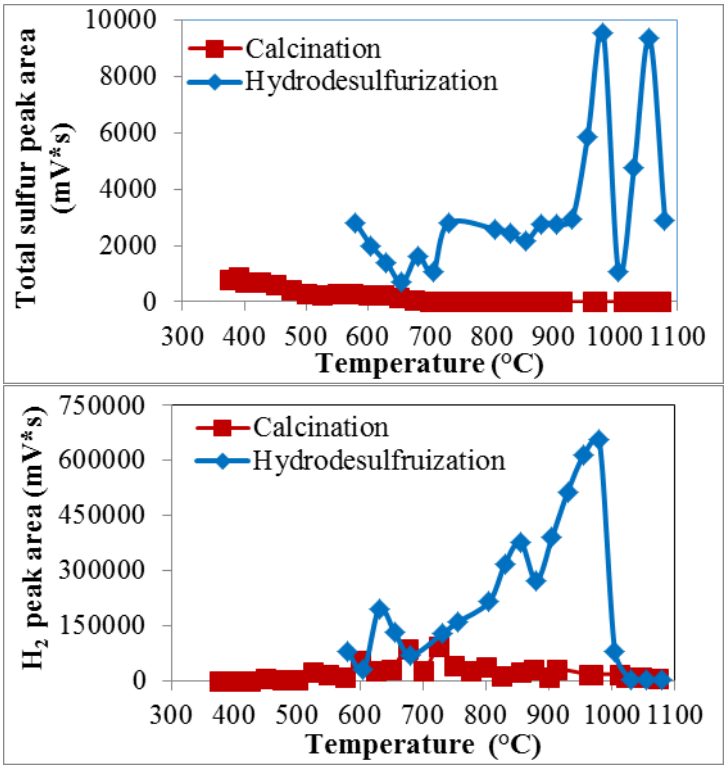


Figure 5. Comparison of (a) S and (b) **H_2 peaks during hydrodesulfurization and calcination as a function of temperature.**

3.3. Hydrodesulfurization

3.3.1. Effect of Injection Duration at Different Injection Temperatures

Figure 6 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 and for injection durations of 37 min, 60 min, and 100 min with a flow rate of 1 ml/min. The amount of water required to remove the sulfur from coke was calculated from the water gas shift reaction and H_2 required for the reaction between sulfur and hydrogen assuming 100% conversion. It was found that the amount of water needed was less 1 g for 10 g of coke sample. 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 most of the experiments except in those for testing the effect of flow rate.

From this figure, it can be seen that 650ºC and 850°C are the suitable injection temperatures for the hydrodesulfurization of coke for 37 min duration (red solid line). 12.89% of the total sulfur was removed from coke at 650°C whereas at 850ºC the percent removal of sulfur was 14.29%. The weight loss of coke increased with increasing injection temperature at this duration (red dashed line). It was 7.6 % at 650°C and 21.87% at 850°C, but it increased dramatically at 950°C to 52.49%. Part of the weight loss is due to volatile release. The total volatile content of the coke was 12.3%. Therefore, the total weight loss is the sum of volatile released and coke consumed to produce H_2. The 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, and coke loss is high.

When the water injection duration was 60 min instead of 37 min, the sulfur removal was obtained at 650°C and 850°C were 22.87% and 22.60%, respectively. Weight loss at the same temperatures were 26.07% and 24.37%, respectively (blue dashed line), which were higher

compared to the previous case. On the other hand, sulfur removal was also higher compared to the experiment with the injection duration of 37 min. 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. When the duration of water injection was increased to 100 min, sulfur removed at 850°C was 19.31% (green solid line). The weight loss of coke was 40.45% for the same injection temperature which is quite high (green dashed line).

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 [21]. 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 such as the sintering of coke particles [21], agglomeration of particles [22], formation of complex sulfides by the reaction of H_2S with coke [21-23]. Also, the fixation of inorganic impurities present in petroleum coke to high-molecular-weight ring structures containing sulfur bridges makes coke less susceptible to hydrodesulfurization [21, 24].

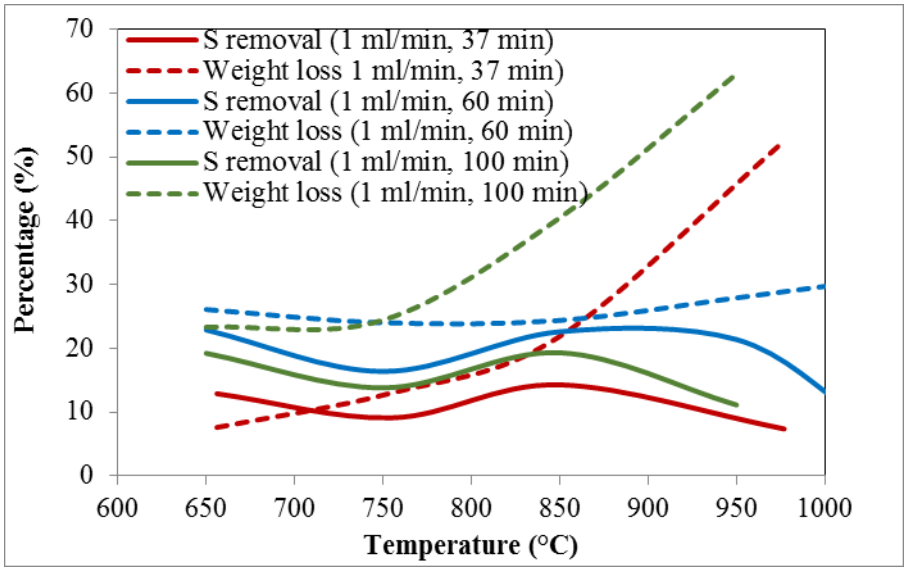


Figure 6. Percent sulfur removal and weight loss for the hydrodesulfurization experiments with a water flow rate of 1 ml/min, particle size of -2 mm +1 mm at different water injection temperatures and injection times.

3.3.2 Effect of Water Flow Rate

The effect of water flow rate was studied at 850°C water injection temperature and 37 min injection duration. As it can be seen from Figure 7, the results showed that the hydrodesulfurization decreases with increasing water flow rate and was highest (14.29%) at the flow rate of 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 by the higher quantity of steam.

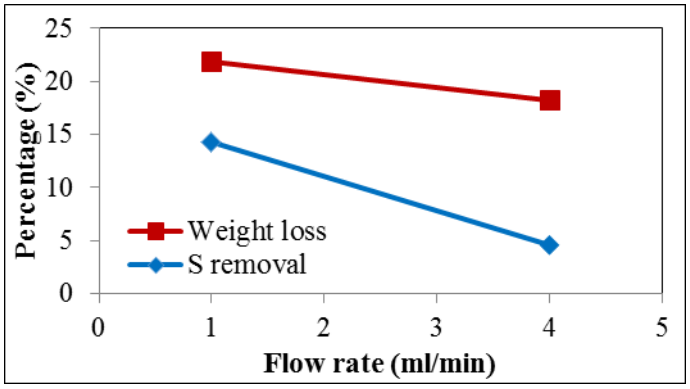


Figure 7. Effect of water flow rate on desulfurization of coke with -2 mm +1 mm particle size, 850°C injection temperature and 37 min injection duration.

3.3.3. Effect of Particle Size

Fine particles (-100 µm +75 µm) of green coke were desulfurized, and the results were compared with those of -2 mm +1 mm particles. During these experiments, 10 g sample, 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 8.

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. As can be seen from the figure, increasing the injection duration increased the sulfur removal for larger particles while its effect is less significant for smaller particles. This may be due to increasing external surface area and decreasing internal mass transfer resistance (shorter diffusional path) as the particle size decreases [21].

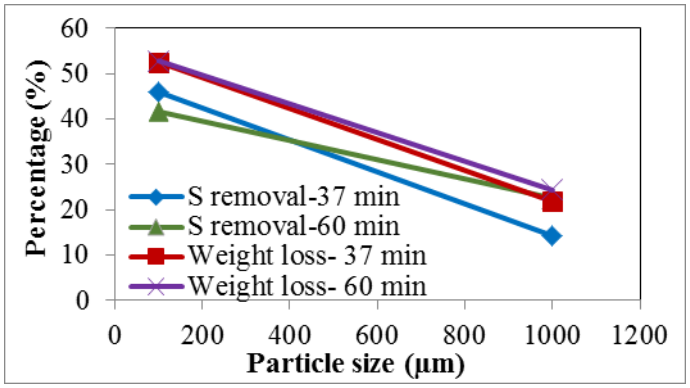


Figure 8. Effect of particle size on hydrodesulfurization for 850°C injection temperature and 1 ml/min water flow rate at different durations.

Another set of experiments were carried out with coarse particles to study the effect of coke particle size (granulometry used in anode preparation) on hydrodesulfurization. The conditions were similar to that used for fine particles. 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. Figure 9 shows the sulfur removal and weight loss results after the hydrodesulfurization with the above mentioned granulometry. 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 9 also shows that the experimental results are in agreement with expected trend. The fluctuations observed in weight loss may be attributed to the non-homogeneity of the coke.

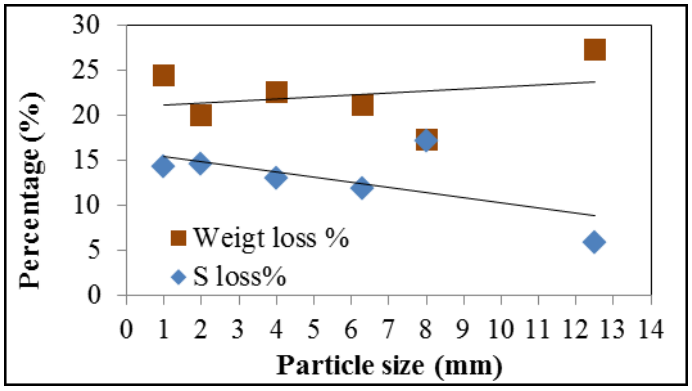


Figure 9. Percent sulfur removal and weight loss as a function of particle size (coarse particles) of coke hydrodesulfurized using 850°C injection temperature, 1 m/min of water flow rate and 37 min injection duration with a 10 g sample.

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 aim was to improve the particle-steam contact. The sulfur removal and weight loss results of these experiments with respect to different particle sizes are given in Figure 10.

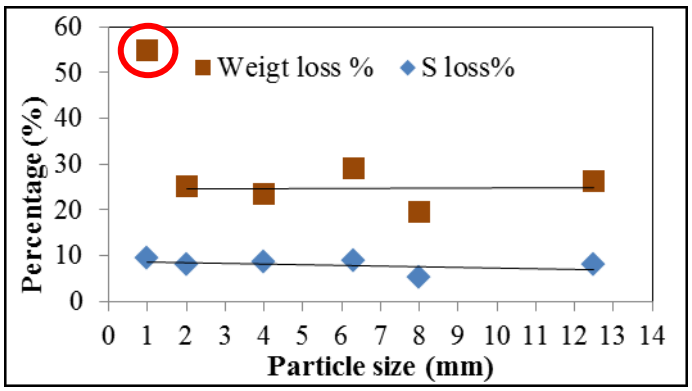


Figure 10. Sulfur removal and weight loss vs coke particle size hydrodesulfurized using 850°C injection temperature, 1 m/min of water flow rate and 37 min injection duration with one layer of sample.

When the coke quantity used for the hydrodesulfurization was reduced, the percentage of sulfur loss slightly reduced with increasing particle size. However, in this case, percent sulfur removal was lower compared to that of the previous case. 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 (indicated by a red circle in Figure 10), 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.

Particle-gas contact is important. At industrial scale, the configuration would be similar to the packed bed used for the results shown in Figure 9. However, the particles would have a wide size distribution, ranging from a few microns to a few centimeters. Thus, one would expect some combination of the sulfur removal rates given in Figure 9. Nevertheless, tests need to be done in a pilot vertical shaft calciner to see the extent of sulfur removal under the conditions similar to those in industry.

3.4. Calcination and Thermal Desulfurization

Calcination and thermal desulfurization of the same green coke at different temperatures was carried out. Weight loss and sulfur removal percentages of coke with respect to maximum temperature are given in Figure 11.

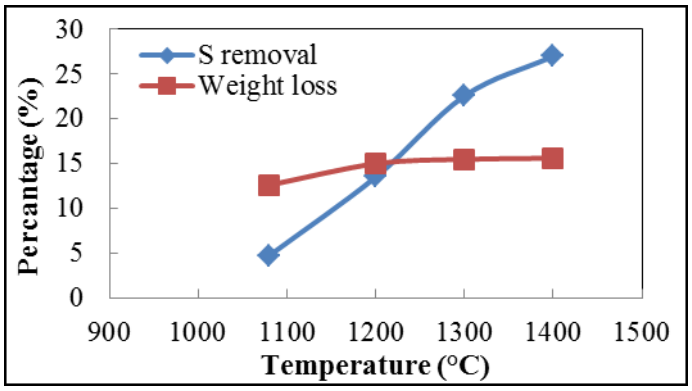


Figure 11. Weight loss and sulfur removal results of green coke with calcination at 1080, 1200ºC and thermal desulfurization at 1300 and 1400ºC.

The samples which were treated up to 1200°C, 1300°C and 1400°C lost similar amount of weight (around 15%). The weight loss obtained at 1080°C was 12.6% The sulfur removal increased with increasing temperature (4.72%, 13.51%, 22.56%, and 27.01% at 1080°C, 1200°C, 1300°C, and 1400°C, respectively). Thermal desulfurization increased the sulfur removal significantly.

3.5. Comparison of Hydrodesulfurization and Normal Calcination

Due to the limitation of the furnace used for hydrodesulfurization, it was difficult to heat the coke samples above 1080ºC. Thus, the efficiency of hydrodesulfurization and desulfurization under normal calcination conditions can only be compared for the samples heated up to 1080ºC. However, a coke calcined to 1200ºC was also included in the comparison.

As a result of several hydrodesulfurization tests under different conditions, the best sulfur removal percentages obtained with -2 mm +1 mm coke 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 calcination up to 1080ºC (4.72% sulfur removal), it is clear that hydrodesulfurization is a more efficient method for sulfur removal than thermal desulfurization. To remove the same amount of sulfur with thermal desulfurization, the calcination should be carried out up to 1300ºC (Figure 11). This means a considerable energy saving. Although there is some carbon loss, which is around 10%, in addition to volatile release during hydrodesulfurization, this carbon loss can possibly be reduced by further modification of the experimental conditions.

It is also important to compare the structure of coke desulfurized with both methods in order to determine their effect on coke porosity. 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 and the abbreviations used are shown in Table 2.

Table 2. Hydrodesulfurized (HDS) and calcined (CC) cokes and the abbreviations used for the comparison of two methods

Calcined coke*			Hydrodesulfurized coke**			
Abbreviation	**T (ºC)**	**SL (%)**	**Abbreviation**	**T (ºC)**	**Duration (min)**	**SL (%)**
CC-1080	1080	4.72	HDS-37	1080	37	14.29
CC-1200	1200	13.51	HDS-60	1080	60	22.60

*Calcination tests were carried out under conditions similar to those in a rotary kiln

**Calcination tests were carried out under conditions similar to those in a shaft calciner; water flow rate: 1 ml/min, water injection temperature: 850ºC, SL: Sulfur loss

3.5.1. Density and Porosity

Table 3 shows the porosity as well as the apparent and real densities of green, calcined, and hydrodesulfurized cokes. Even though slightly higher for HDS-37, the porosities in general were found to be similar showing that hydrodesulfurization did not create significantly more porosity compared to calcination. The real densities of calcined coke samples (CC-1080 and CC-1200) decrease with increasing temperature. The trend is the opposite of what is normally observed. This is quite likely due to the non-homogeneity of the coke.

Table 3. Comparison of properties of coke before and after calcination and hydrodesulfurization.

	Green coke	**CC-1080**	**CC-1200**	**HDS-37**	**HDS-60**
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

3.5.2. Crystal Length (XRD)

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 its quality [25]. In order to be able to use a calcined coke as anode raw material, it has to have a certain degree of crystallinity. Table 4 presents the crystalline length (Lc) of the coke samples. The cokes desulfurized with both methods up to 1080ºC (CC-1080 and HDS-60) had similar Lc values. It can be seen that increasing the calcination temperature (CC-1080 and CC-1200) increased Lc as expected. Even though small, the injection duration of hydrodesulfurization (HDS-37 and HDS-60) seems to have some effect. Further testing is needed to determine whether this difference is due to injection duration or non-homogeneity of the samples. The crystallinity of hydrodesulfurized coke at 1200ºC remains to be seen.

Table 4. Crystal length of calcined/hydrodesulfurized coke samples.

Coke	Lc, Å
CC-1080	26.00
CC-1200	35.05
HDS-37	28.78
HDS-60	26.86

3.5.3. Sulfur Content and Type (XPS)

An XPS analysis was carried out. The atomic percentages of different elements in all cokes are given in Table 5. The sulfur contents of HDS-37 and HDS-60 samples are lower than those of green coke, CC-1080, and CC-1200. Although CC-1200 has a higher sulfur content than those of hydrodesulfurized samples, it has a lower sulfur content compared to that of CC-1080. The results show that thermal desulfurization requires much higher temperatures to remove the same amount of sulfur as the hydrodesulfurization. The type of sulfur present is determined from deconvolution of S2p peaks using the same method explained in Section 3.1. It was found that the sulfur was present in all samples as thiopene as shown in Table 6. EDX results also confirmed these findings [17].

Table 5. Percentage of sulfur in coke samples.

	S (atomic %)	S (wt %)
Green coke	2.32	6.87
CC-1080	1.83	5.42
CC-1200	1.51	4.47
HDS-37	0.40	1.18
HDS-60	0.37	1.10

Table 6. Type of sulfur present in green and calcined/hydrodesulfurized coke samples.

	Thiophene %	For thiophene $S\ 2p_{3/2}$/ $S\ 2p_{1/2}$
Green coke	100	66.07/33.93=1.95
CC-1080	100	64.60/35.40=1.82
CC-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

3.5.4 Coke structure (SEM)

The coke structure is important. The aim is to desulfurize coke without creating excessive 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 green and calcined cokes was analyzed with SEM-EDX to study the coke structure. Figure 12 presents the structure for CC-1080 and HDS-60 at different magnifications. SEM images of all samples show certain crack and pore formation. Larger pores were observed in calcined samples. When porosity analysis results are combined with SEM analysis images, it can be stated that hydrodesulfurization carried out under the conditions studied (HDS-37 and HDS-60) did not create a more porous cokes compared to those calcined normally (CC-1080, CC-1200).

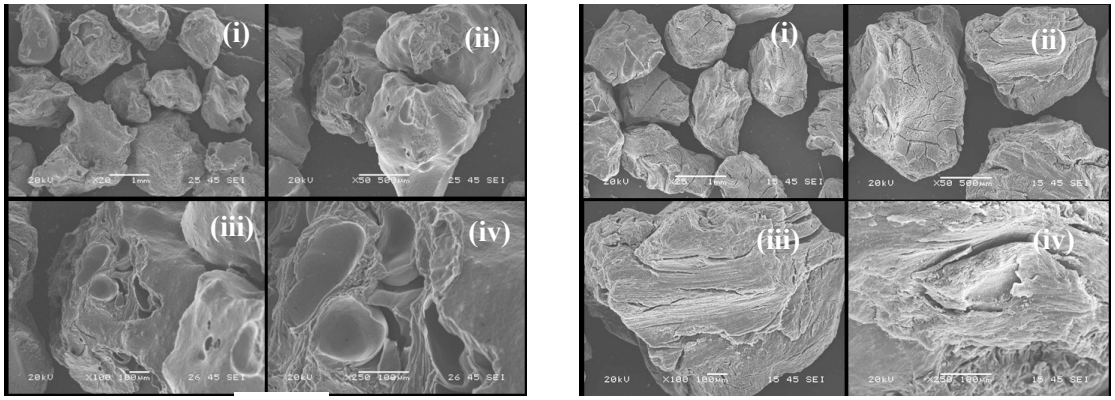


Figure 12. SEM micrographs of (a) CC-1080 and (b) HDS-60 at magnifications of (i) x20 (ii) x50 (iii) x100 (iv) x250.

4. Conclusions

In this project, an experimental study on the calcination, hydrodesulfurization, and thermal desulfurization of green petroleum coke was undertaken. Effects of different parameters on coke hydrodesulfurization such as water injection temperature and duration, water flow rate, and coke particle size were studied. Maximum sulfur removal was obtained when the water was injected to the coke sample at 850°C for 60 min. Since hydrogen required for the hydrodesulfurization is obtained through water shift reaction, part of the coke was consumed. Under the conditions given above, the coke loss (difference between the total weight loss and the weight loss due to volatiles) was acceptable (about 10%). Sulfur removal increased with increasing injection duration from 37 min to 60. However, further increase in injection duration reduced the percent sulfur removal at all water injection temperatures.

Sulfur is removed at lower temperatures by hydrodesulfurization compared to thermal desulfurization. To remove the same amount of sulfur, thermal desulfurization requires much higher temperatures, hence higher energy consumption, especially in a rotary calcination kiln. It should also be noted that hydrodesulfurization will increase the energy consumption in a vertical shaft calciner as well since water has to be vaporized before injection into the calciner or the cooling due to water injection in liquid form has to be compensated in the calciner itself. Further analysis is needed to compare the additional energy requirements for the two processes.

It would also be interesting to compare the hydrodesulfurized coke with the one calcined and thermally desulfurized in a shaft furnace since the work by Edwards [13] found that such cokes give better results than those calcined in a rotary kiln. Particle-gas contact is important for hydrodesulfurization, and thus tests need to be done in a vertical shaft calciner to determine the extent of sulfur removal under the conditions which are normally used in industry.

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