Desulfurization of Syrian Petroleum Coke by Chemical Treatment

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Abstract: *We studied the effect of some acidic chemicals (hydrochloric acid, sulfuric acid, nitric acid) and alkalis (sodium hydroxide, potassium hydroxide, sodium carbonate and potassium carbonate) on the desulfurization rate of Syrian petroleum coke, in order to determine the best treatment method to reduce the sulfur content in it.We carried out the chemical treatment of the petroleum coke produced by the Homs Refinery. Where we used acids in their concentrated form to perform the treatment, while we used different concentrations of alkaline solutions during the treatment. The curing was performed at normal temperature and different curing times (30, 60, 90, 120) min.The study showed that the best removal of sulfur from the Syrian petroleum coke by the chemical treatment method was done when using concentrated nitric acid where the sulfur content decreased by 48.80% at a processing time of 120 min.XRD patterns was studied to investigate the structure change by chemical treatment.*

Keywords: Syrian petroleum coke, Chemical treatment, sulfur content, XRD.

1- Introduction

Petroleum coke or petcoke for short can be produced from virgin crude residues by precipitation reactions of high molecular weight compounds, asphaltenes, and resins or from highly aromatic tar or decanted oil stokes by condensation and polymerization of aromatic compounds. Delayed petcoke is produced by a semi continuous process which can be carried through in one of the following ways: ultimate, once through, or intermediate coking [1]. Delayed petcoke has a much more uniform crystallinity than other types of petroleum coke since the delayed coking process allows the time needed for the coke crystals to orient themselves upon one another

The sulfur content of the petcoke strongly depends on the nature of the coking feedstock (crude oil) and its sulfur content. The sulfur content of the feedstocks seems to increase with increasing the concentration of asphaltenes and Conradson carbon content. For instance, higher sulfur contents were found in “sponge” coke (produced from high-resin asphaltene feedstocks) than in “honeycomb” coke (produced from low-resin asphaltene feedstocks) or “needle” coke (produced from highly-aromatic feedstocks) [2].

The sulfur content in petcoke varies widely (from less than 0.5% in gilsonite to more than 10%) mainly depending on the sulfur content of feedstock [3].

Most of the sulfur in petcoke exists as organic sulfur bound to the carbon matrix of the coke. Some sulfur could also exist as sulfates and as pyritic sulfur but these do not in general make up more than 0.02% of the total sulfur in coke In at least one case, however, pyritic sulfur was reported to be as high as 0.4%. Free sulfur may occasionally be present [2].

For high sulfur petroleum coke a desulfurization process is often necessary before it is used as fuel, otherwise it may result in serious environmental problems [4].

Syrian petroleum coke is produced by the delayed coking unit at the Homs oil refinery. The coke produced by this unit is characterized by a high sulfur content, which tend to reduce its commercial value [5].

There are at least four basic types of delayer petroleum coke: (needle coke, honeycomb coke, sponge coke and shot coke) [6].

Different types of delayed coke are due to the nature of feedstock and the difference in operating which gives different microstructure to each type [7].

Advanced oxidation processes (AOPs) involve two stages of oxidation:
1) the formation of strong oxidants (e.g., hydroxyl radicals).
2) the reaction of these oxidants with organic contaminants in water**.** However, the term advanced oxidation processes refer specifically to processes in which oxidation of organic contaminants occurs primarily through reactions with hydroxyl radicals [8].

It is well known that activated carbons can be prepared from a variety of raw materials. The most frequently used precursors are hard coal, brown coal, wood, coconut shells and some polymers[9].

Activation refers to the processes and procedures taken to obtain high microporous materials from low porosity materials. That is, the aim of the activation process is to enhance the size of the pores and expand their diameters, in addition to forming new pores. The structure of the pores and their distribution are largely determined by the nature of the raw material used and the date of carbonization. Activation in its first stage leads to the stripping of the irregular charcoal particles and the expansion of the aromatic plaques by the action of the activation factor, which leads to the development of the micro-porous structure. At a later stage of activation, the important effect is to expand existing pores or to form large pores as a result of burning (shattering) the walls between adjacent pores. This increases the meso-porosity while decreasing the size of the micro pores.

Numerous studies have been conducted on petroleum coke to reduce the percentage of sulfur in it in order to benefit from it in various industries. The effect of heat treatment of petroleum coke at elevated temperatures up to 1600°C and different times of up to three hours was studied[10].

On the other hand, one of the advanced oxidation processes (AOPs) has been used, which has gained increasing attention in the recent period, as research technology in this field is considered effective and feasible in treating environmental pollutants [11].

2. Experimental

2.1. Coke Samples

Samples of Syrian petroleum coke were taken from the coke heaps stored nearby the Homs Oil refinery according to ASTM D-346 specification, the sample was of moderate to high sulfur content. Proximate analysis and ultimate analysis of the Syrian petroleum coke is shown in Tables 1, 2.

For the sulfur determination the high temperature tube furnace combustion method (ASTM D-4239) was used in which the sulfur is determined by burning a weighed sample in a tube furnace at a minimum operating temperature of 1350°C in a stream of oxygen. During combustion, all sulfur contained in the sample is oxidized to gaseous oxides of sulfur (sulfur dioxide, SO_2, and sulfur trioxide, SO_3). Sulfur trioxide is then absorbed into a solution of hydrogen peroxide (H_2O_2) where they dissolve forming dilute solutions of sulfuric acid (H_2SO_4).

Table. 1. Proximate analysis of Syrian petroleum coke

Properties	
Moisture %	0.28
Ash, wt%	0.80
VM, wt%	11.97
Sulfur, wt%	8.4
Fixed Carbon wt%	86.95
Real Density (g/cm^3)	1.39
Caloric value (K Cal/Kg)	8372

Table. 2. Ultimate analysis of Syrian petroleum coke

Carbon	84.2
Hydrogen	4.5
Nitrogen	1.1
Oxygen	1.8
Sulfur	8.4
C / H (wt)	18.71

2.2. Conditions of Acid treatment

Usually acids are widely used in the petrochemical industry in esterification, ether, hydrogenation, alkylation of aromatics and amines, and hydrocarbon cracking reactions [12].

In this research, we used nitrogen acid, hydrochloric acid and sulfuric acid in their concentrated form in treating Syrian petroleum coke.

Petroleum coke treatment with acids was carried out according to the conditions shown in Table (3), where it was performed in a glass reactor consisting of a double-hole 250ml glass tank, in which we poured 100ml of acid according to the studied concentration and added to it later 5g of charcoal with stirring the previous mixture by a magnetic mixer during a period Experiment, then we filtered on a Buchner funnel, then washed the sediment coke with distilled water several times and well, then dried the treated charcoal in a drying oven at a temperature of 105°C until the weight was stable.

Table. 3. conditions of acid treatment

Sample weight (g)	5
Pressure (atm)	Ordinary
Treatment time (min)	30, 60, 90, 120
Treatment temperatures (ºC)	Ordinary

2.3. Conditions of Alkaline treatment

we used potassium hydroxide, sodium hydroxide, sodium carbonate and potassium carbonate according to the conditions applied in the acid treatment shown in Table (3) with the use of different concentrations of the alkaline solutions used as in Table (4).

Table. 4. Concentrations of solutions used in alkaline treatment

	Concentration (Mol/lit)			
KOH	2	1	0.5	0.1
NaOH	2	1	0.5	0.1
Na_2CO_3	4	3	2	1
K_2CO_3	4	3	2	1

2.4. Determination of sulfur content

The sulfur content was determined according to the standard specification (ASTM D-4239) (called the thermal method shown in Figure (1)). This method depends on burning the sample of petroleum coke in a tube furnace by passing a stream of oxygen gas to help the combustion, and then passing the resulting gas onto the hydrogen peroxide with concentration 1% for oxidation of SO_2 to SO_3 and finally obtaining sulfuric acid, whose concentration is determined later by titrating it with NaOH N = 0.05 using a Phenolphthalein as indicator.

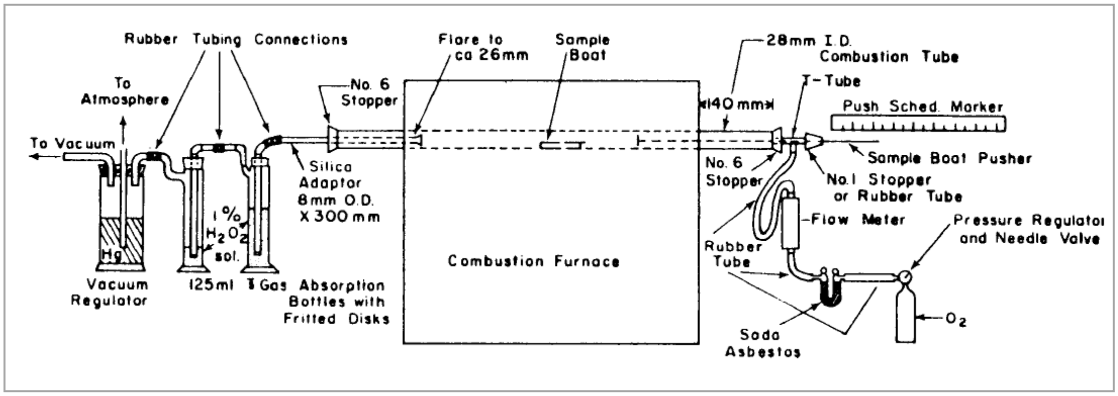

Figure 1. Sulfur content determination diagram

3. Results and discussion

3. 1. Sulfur content by acid treatment

The acid treatment of the petroleum coke was carried out according to the conditions specified in Table (3), then a washing process was carried out with distilled water for the sample of the treated petcoke to remove the traces of acids and the results of the reaction of the acid with the petcoke from the coke pores. Table (5) shows the sulfur content in the samples after treatment with acids.

Table. 5. Sulfur content in petcoke after acid treatment

Treatment time (min)	Sulfur Content (%)		
	HCl	HNO_3	H_2SO_4
0	8.4	8.4	8.4
30	8.2	5.4	7
60	8.2	5	6.6
90	8.2	4.4	6.2
120	8.2	4.1	6

Figure (2) also shows the low sulfur content as a result of acid treatment.

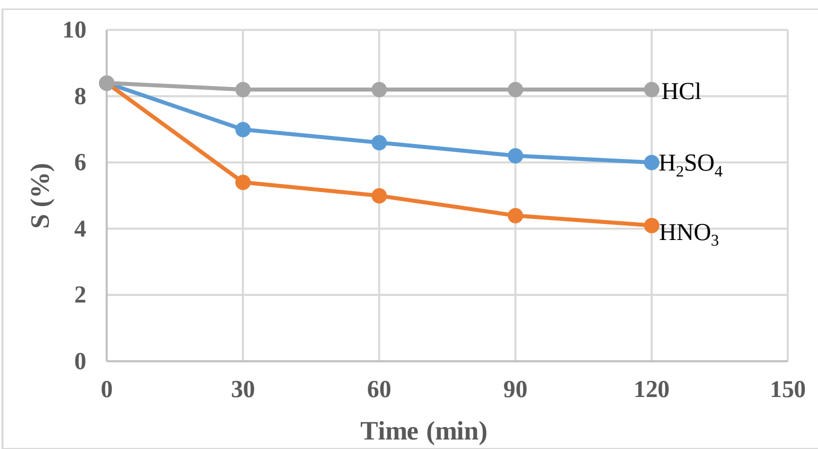

Figure 2. Sulfur content by acid treatment

We note that the treatment with hydrochloric acid has no significant effect on the change of sulfur content in petroleum coke, while we find that treating coke with nitric acid and sulfuric acid significantly reduces the percentage of sulfur due to the oxidation of the inherent sulfur, which exists mainly as a type of organic sulfur, Including thiophene, benzothiophene, and dibenzo-thiophene[13], which can be easily oxidized.

3. 1. Sulfur content by alkaline treatment

The alkaline treatment of the petroleum coke was carried out according to the conditions specified in Table No. (3) and the concentrations of the alkaline solutions used as in Table No. (4). Then a washing process was carried out with distilled water for the sample treated petcoke to remove traces of the alkaline solutions.

Table No. (6) shows the sulfur content in samples of petroleum coke treated with alkaline solutions.

Table. 6. Sulfur content in petcoke after alkaline treatment

Treatment time (min)	Sulfur content (%)			
	K_2CO_3	Na_2CO_3	KOH	NaOH
0	8.4	8.4	8.4	8.4
30	8.2	8.2	7	7.4
60	8.2	8.2	6.8	7.1
90	8.2	8.2	6.7	6.9
120	8.2	8.2	6.7	6.9

Figure No. (3) shows the low sulfur content as a result of alkaline treatment.

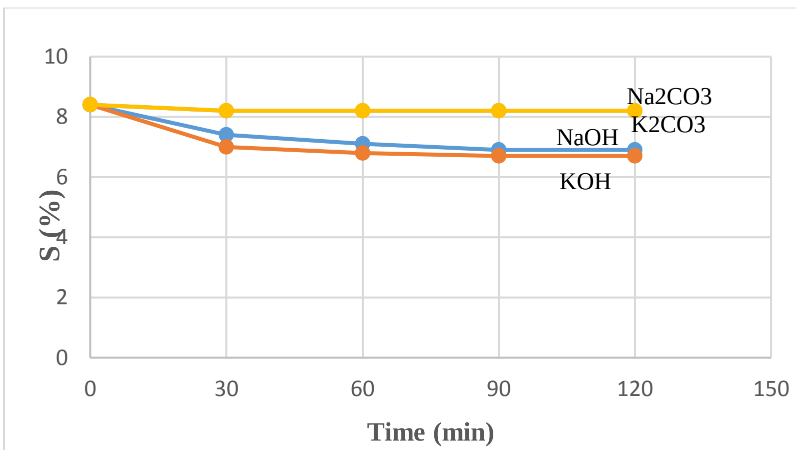

Figure 3. Sulfur content by alkaline treatment

We note from the figure that the values of sulfur removal from petroleum coke using both sodium carbonate and potassium carbonate are identical, but when using sodium and potassium hydroxides, we notice a greater decrease in the value of desulfurization, noting that potassium hydroxide is better than sodium hydroxide with a slight difference between them in desulfurization.

The following reactions occurred as a result of the hydroxide treatment:

$$\text{Coke-S} + 2KOH \rightarrow K_2S + \text{Coke-O} + H_2O$$

$$K_2S + 2H_2O \rightarrow 2KOH + H_2S$$

Where sodium and potassium hydroxide are considered strong bases that attack the C-S bond to form as a result potassium or sodium sulfide[14].

But there is a problem facing the use of the alkaline treatment method, especially the sodium and potassium hydroxides, which is the difficulty of separating the alkali from petroleum coke.

3.3. X-ray diffraction analysis

XRD measurements were made with a Rigaku MiniFlexII bench-top system fitted with an ultra-sensitive D/tex Ultra Si slit detector capable of detecting nanoparticles down to about 1.2 nm in diameter**.** The 2θ range was (10°-70°).

The XRD analysis was carried out on powder samples to investigate the structural changes with the treatment with acid (nitric acid) and alkaline (potassium hydroxide). The typical XRD patterns of crude petcoke, acid and alkaline treated petroleum coke are shown in Figures (4, 5, 6).

It can be clearly seen that there is no significant difference in diffraction peaks in each spectrum.

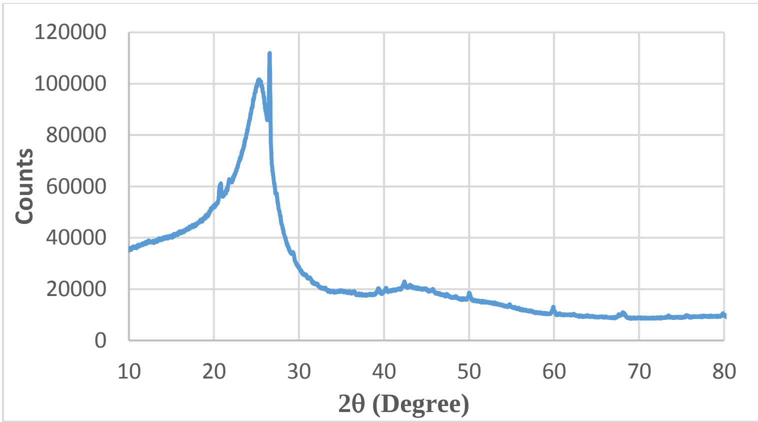

Figure 4. XRD pattern of crude petroleum coke.

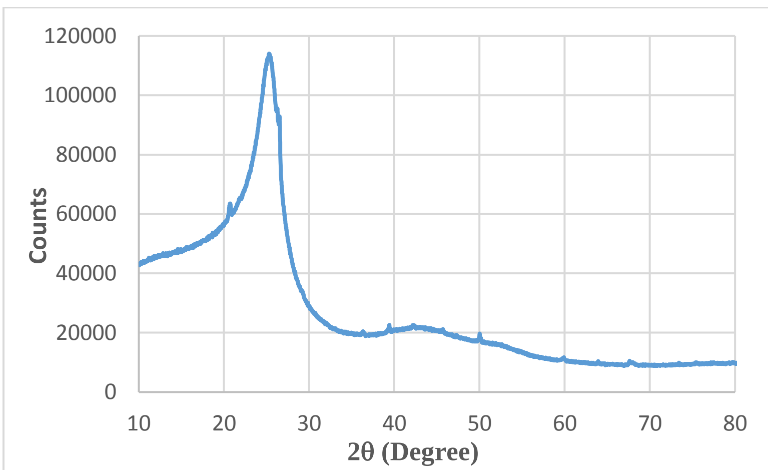

Figure 5. XRD pattern of acid (HNO_3) treated petroleum coke.

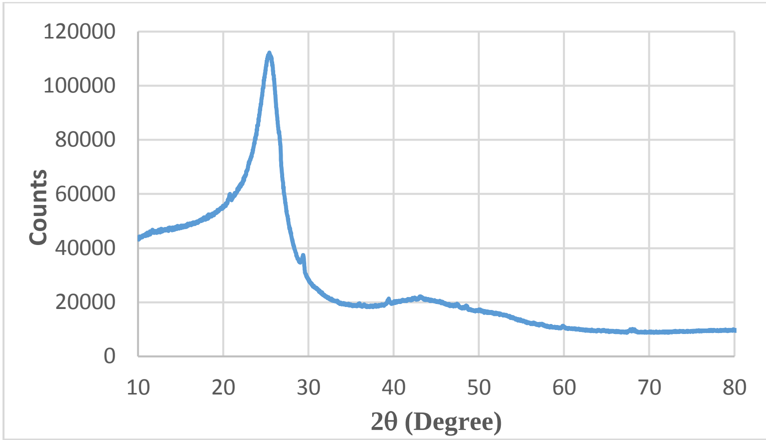

Figure 6. XRD pattern of alkaline (KOH) treated petroleum coke.

4. Conclusion

Petroleum coke has low cost of production and it can be used widely in different industries like anode production, activated carbon, Nano technology, and as solid fuel in different industries (like cement industry) that it has high caloric value, petroleum cokes deserve some attention especially Syrian petroleum coke which has a high sulfur content (8.4%) compared to other origins of petroleum coke.

The study showed that it is possible to perform an acid treatment for Syrian petroleum coke with the aim of reducing the percentage of sulfur in it, by using strong oxidizing acids such as nitric and sulfuric acid, while hydrochloric acid did not reduce the sulfur content.

The best desulfurization by the acid treatment is when nitric acid is used as an oxidant at a two-hour treatment time, where the sulfur content is reduced to 4.1%, with a decrease of 48.80%.

When using alkali metal hydroxides, the percentage of sulfur in petroleum coke decreased, but the removal results were not significant compared to the acid treatment method.

XRD pattern shows that there is no significant change in structure while acid and alkaline treatment to petroleum coke.

Although much research and experiments have been carried out on removing sulfur from petroleum coke, there is still no industrially used process for removing sulfur. Rather, it is experimental research experiments. The reason for this is that the sulfur removal process from petroleum coke is subject to various factors such as the structure of coke, its porosity, the nature of coking feedstock, in addition to the nature of the C-S bond.

5. Acknowledgment

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