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Evaluation of the Physical-Chemical Properties in Petroleum Coke

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Abstract

In this paper, commercial petroleum cokes were analyzed, before and after heat treatment in order to evaluate the physical-chemical properties. The content of moisture, volatile matter, sulphur, ash and metals (Fe Ni, Cr) was determined. The results showed that temperature increasing led to the removal of volatile matter and sulphur content; higher separation of sulphur was observed for coke obtained from atmospheric residue and from decanted oil. The ash content indicates the presence of inorganic admixtures in coke. Metal concentrations increased through calcining, due to the weight loss from removal of the volatile matter; the coke samples revealed the higher content of nickel (151 to 279 ppm) which is the most represented metal component in the coking feedstock. Physical-chemical parameters indicate that the analyzed cokes can be used in anode –grade production.

Key words: Anode materials; Petroleum coke; Moisture; Sulphur; Volatile matter; Metals

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INTRODUCTION

Coke is a gray to black solid carbonaceous residue (90-95% carbon) which is produced from petroleum during thermal processing. The two most important categories are green coke and calcinated coke; green petroleum coke are mostly used as utility fuels and as feedstocks for further upgrading caltinations. The calcinated petroleum coke are used in production of aluminium, anode-grade, graphite electrodes, needle-grade, TiO_2 pigments[1].

A number of factors determine the quality of petroleum coke, such as: density, metal and sulphur content, electrical resistivity. Knowledge of structure parameters also contributes to the characterization and utilization of petroleum coke[2].

The chemical composition of petroleum coke is determined by the composition of the feedstocks used in the coking process, which to their turn depend on the composition of the crude oil and refinery processing from which the feedstock is derived. Cokes produced from feedstocks high in asphaltenes will contain higher concentrations of sulphur and metals than cokes produced from high aromatic feedstocks, because the asphaltenes contain a disproportionate fraction of those heteroatoms[3].

The sulphur content of petroleum coke varies from 0.5% to 10%, depending on its content in oil (cokinf feedstock) and on the coking process variable.

Organic sulphur may exist in the coke in many forms: as thiophenes attached to the aromatic carbon skeleton; as attached to side chains of aromatic or naphthenic molecules; between the aromatic sheets or on the surface of clustered molecules. Inorganic sulphur compounds are mostly found on the coke surface or in coke pores bound by capillary condensation, adsorption or chemisorption.

Separation of sulphur can be achieved in several ways: through calcination at higher temperature, hydrodesuphurization and chemical treatment with different agents[4-6].

Metals, mainly vanadium and nickel, occur as metal chelates or porphyrins in the asphaltene fraction. Some metals are intercalated in the coke structure and are not chemically bonded, so they become part of the ash and particulates.

The aim of the present paper consists in the evaluation of the physical-chemical characteristics of some petroleum cokes, before and after thermal treatment, which was used to observe the alterations which took place over the coke's quality.

1. EXPERIMENTAL

1.1 Samples

The petroleum coke is often used in anode production; this is why the selection of premium matter depends on the chemical composition. For this study, we have used the cokes which were produced by delayed coking process from high aromatic feedstock, characterized by low content of asphaltene and metallic and non-metallic admixtures.

According to the data from literature, the high temperatures may have some negative effects on petroleum cokes quality. As coke is heated, its porosity increases due to the creation of micro and macroporosity as the sulphur and volatile matter are vaporized. Increasing the porosity of petroleum coke is disadvantageous for electrode making[7].

The above considerations led to the conclusion that it would be preferable to treat the coke samples at temperatures of 1300 °C and the residence time was 3 hours. The coke size used in the present study was between 0.8-1.6 mm.

Average samples of green petroleum coke were crushed and dried. Coke A is calcinated coke produced from atmospheric residue, coke B is produced from decanted oil and coke C is calcinated coke produced from pyrolysis residues.

The coke samples were heated at a temperature of 1300 °C in the electric furnace, in order to investigation the effect of calcinated temperature on physical-chemical properties of petroleum cokes.

The physical-chemical parameters were determined before and after heat treatment.

1.2 Determination of Moisture and Volatile Matter Content

Moisture content was determined by heating the coke samples at 110 °C to constant mass and volatile matter content was determined applying the standard ASTM D3175 method[8].

1.3 Determination of Ash Content

The ash content was determined by first drying 5g of coke at 110 °C to constant mass and then ashing it for 1 hour at 500 °C, followed by 2 hours at 750 °C, until constant ash mass was obtained.

1.4 Determination of Metal Content

Metal content (Ni, Fe, Cr) was determined applying the standard ASTM D3686 method using an atomic absorption spectrometry whit flame atomizer[9].

A ZEENIT 700 atomic absorption apparatus equipped with air-acetylene flame was used to determine individual elements. Calibration standards are prepared from stock solutions; the corresponding absorbance response for each standard is plotted versus concentration for calibration. Samples responses are compared directly with the calibration curve

1.5 Determination of Sulfur

The sulfur was determined by wavelength dispersive X-ray Fluorescence Spectrometry, applying the standard Test Method for determination of total sulfur, ASTM D2622[10]. In this method, a weighed portion of a sample of coke is dried at 110 °C (230 °F) and crushed, mixed with stearic acid, and then milled and compressed into a smooth pellet. The pellet is irradiated with an X-ray beam, and the characteristic X-rays of the elements analyzed are excited, separated and the peak intensity of the sulfur Kα line at 0.5373 nm is measured. The background intensity, measured at 0.5190 nm is subtracted from the peak intensity, and the resultant net counting rate is then compared with a previously prepared calibration curve. All measurements were conducted using a VENUS 200 apparatus. For optimum sensitivity to sulphur, the instrument should be equipped with the configuration presented in Table 1.

Table 1
Instrument Configuration

Item	Value
Optical Path	- helium
Excitation conditions	- 30 KW, 50 mA
Detector	- detection of X-rays in the range 0.25-0.55 nm
Analyzing Critstal	- germanium
X-ray Tube	- anode of rhodium, chromium or scandium

Prepare calibration standards by careful mass dilution of the certified di-n-butyl sulphied with a sulphur-free white oil. Using the standard Test Method and serial concentrations of sulphur solutions (1-50 ppm), a standard curve for sulphur concentrations was obtained, with R^2 greater than 0.9991.

1.6 Determination of Mass Loss

Mass loss was determined from the difference in mass of the sample before and after thermal treatment of the samples.

2. RESULTS AND DISCUSSION

Table 2 summarizes analysis results of typical properties of green petroleum cokes and Table 3 the proximate analysis of calcinated cokes.

Table 2
Typical Properties of Green Petroleum Cokes

Proximate, wt % (Dry-basis)	A	B	C
Moisture	0.28	0.21	0.26
Volatile	9.9	12.2	10,7
Ash	0.09	0.06	0,04
Sulphur	1.7	1.57	1.16

Data from Table 2 show that coke A is produced from the feedstock with a higher sulphur content than coke C. Decanted oil and atmospheric residues have higher sulphur and metal content (ash content) in comparison with pyrolysis residue. All samples analyzed are low in moisture, the content ranges between 0.21-0.28 % and volatile matter in range 9.9-12.2%.

For all samples, the increasing of the temperature (1300 °C) led to the removal of volatile matter and sulphur contents, the results are presets in Table 3.

Table 3
Proximate Analysis of Calcinated Petroleum Cokes

Properties	A	B	C
Ash, %	0.13	0.12	0.24
Volatile Matter, %	0.16	0.14	0.20
Sulphur, Wt, %	0.81	0.79	0.86

During heat treatment, metallic and non-metallic constituents are either transformed into other types of compounds or separated, depending on their concentration, metal affinity to sulphur[11].

Volatile matter in calcinated petroleum cokes varies between 0.14-0.20%, the limit of 0.25% maximum is frequently imposed in order to be used as anode material[12]. The volatility differences are not significant between the three types of petroleum cokes.

Higher separation of sulphur (52.3%) was observed for coke A, which is calcinated coke obtained from atmospheric residues. From the initial 1.7% of sulphur in coke A only 0.81% of sulphur remained at the end of treatment at 1300 °C. Similary results were obtained for calcinated coke obtained from decanted oil (coke B).

Some researches showed that before calcination treatment, the sulphur is present in elemental, metallic sulphides and sulphates form. After the heating of petroleum coke, partial separation of sulphur compounds and transformation in the most stable compounds take place[13].

The results obtained indicate that the process of desulphurization may be divided into several steps: in the first step of heat treatment (about 500 °C) the biggest part of the separated sulphur takes place in the form of gases (H_2S and RSH), from desorption of chemisorbed sulphur in coke pores or in the coke surface. This is the inorganic form of sulphur in coke samples. The partial decomposition of organic sulphur also takes place; this is the organic sulphur compounds bound in some chain.

On the other hand, a weight loss at the end of treatment, of about 19.4% for coke C produced by pyrolysis residue was observed. The observed weight loss is a result of the evaporation of moisture and volatile matter absorbed on the coke surface or in the pores.

According to the data from literature, atmospheric residue and decanted oil have less aliphatic compounds than the pyrolysis residue[14]. Aliphatic character is given by the presence of numerous side chains containing of 2-4 atoms, which mutually bond aromatic compounds.

It is stated by many researchers that the stability of sulphur compounds is given by the fact that sulphur atom can have more valence bonds, whose breaking requires more thermal energy than the breaking of single bonds[15].

The ash content indicates the presence of inorganic admixtures in coke. The analyzed sample contains 0.12 – 0.24 % of ash, which is advisable in anode production, should the ash content be kept below 0.3%[12]. A consequence of higher ash content is the formation of higher quantity of slag, which can cause difficulties in utilization. The content of metals Fe, Ni and Cr was determined and the results are presented in Figure 1.

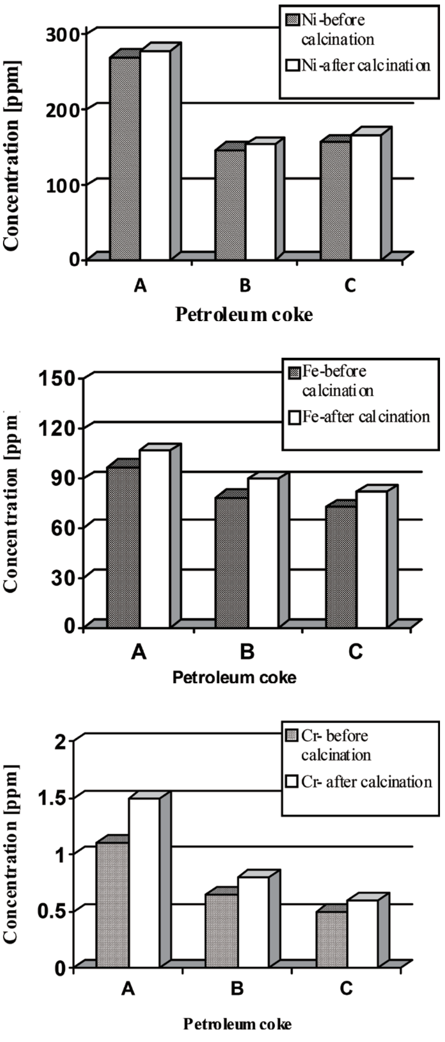

Figure 1
The Fe, Ni and Cr Content in Petroleum Cokes

Metal concentrations are analyzed cokes increased through calcining due to the weight loss from removal of the volatile matter.

The results of investigation showed that coke samples contain the higher content of nickel (151 to 279 ppm in calcinated samples); it can see that is the most represented metal component in the coking feedstock. Data from literature indicated that, before heat treatment, the metals are present as elemental, oxides, sulfides and suphates form; with the increase of temperature, the metal-oxygen bonding decreases and the affinity for carbon and sulphure increases, generating stable compounds[16].

CONCLUSIONS

The physical and chemical properties of some petroleum cokes have been examined. The evaluated coke properties are: moisture, volatile matter, sulphur, ash and metals (Fe, Ni and Cr).

The increasing of the temperature (1300 °C) led to the partial separation of sulphur compounds and transformation in the stable compounds.

The results have shown that coke properties vary and depend on the source of the crude oil and the quality specifications dictated by producing refinery.

The results showed that the analyzed coke has a low ash, metallic and volatile matter contents therefore can be used as carburizer in the foundries or in the production of anodes.

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