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Thermal Treatment of Syrian Sponge Coke

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Abstract. Samples of Syrian sponge coke were thermally treated at high temperatures and increased residence time. A coke of higher quality was thereby obtained, with reduced sulphur content and higher real density. The observed weight loss was minimal, and the decrease in the calorific value was of the order expected for other types of petroleum coke.

Keywords: Petroleum coke, Sponge coke, Thermal treatment, Desulphurization.

Introduction

There are at least four basic types of delayed petroleum coke, namely, needle coke, honeycomb coke, sponge coke and shot coke. Different types of delayed coke have different microstructures due to differences in operating variables and the nature of feedstock. Significant differences are also to be observed in the properties of the different types of delayed coke, particularly ash and volatile matter contents.

With the increasing value and importance of delayed coke, many studies have been undertaken for the purpose of investigating different processes for upgrading the coke such as activating the coke, reducing its sulphur content and/or increasing its real density.

All such studies, however, have one factor in common, and that is taking average samples of the coke without regarding the different types that make up the coke as produced. In view of the significant differences that exist between different coke types, in structure and properties, specific studies for particular types of petcoke are merited for better and more economical utilization of the coke.

Sponge Coke

Sponge coke is a coherent, dull black porous delayed petroleum coke in which the individual spheres are not apparent and the coke has a continuum of structure. Sponge coke may also refer to an intermediate type of coke between this and shot coke.

In physical appearance, sponge coke is very porous. It has small pores surrounded by relatively thin [1] or thick [2] walls to the extent that there is no interconnection between the pores. The name sponge coke is used because the lumps of coke are porous and at times resemble sponge-like material

Sponge coke is produced from virgin crude residues which have a large number of cross-linkages with less than 6 carbon atoms. It is produced by precipitation reactions of the high molecular weight compounds, asphaltenes and resins. At the same time, the naphthenic and aliphatic chains are destroyed as is evidenced by the C/H ratio of 8-10 in the feed rising to 20-24 in the coke.

Sponge coke is a disordered highly cross-linked amorphous, or isotropic, coke with high concentrations of impurities. This type of coke is difficult to graphitize. The optical structure is smaller than that of needle coke; it is of coarse-grained mosaic (5 - 10 µm dia.) with some flow anisotropy (10 – 50 µm). However, more ordered inclusions of carbon exist within sponge coke, possibly arising from incomplete mixing (lack of homogeneity) of the blend which constitutes the feedstock [3].

Magnification of the surface fractures show the sponge coke with structures characterizing both the shot and needle cokes, namely the whirled, or non-linear structure in the isotropic shot coke and the aligned structure of anisotropic needle coke [4].

The electrical conductivity of sponge coke is low, but its structure ensures the required electrical conductance for anode usage [5]. It is generally of lower hardness than shot coke. The Hardgrove Grindability Index of good green sponge coke is typically less than 70 and its strength is also adequate. When calcined, it gives an isotropic structure. Typically, it contains between 1 and 6% sulphur (Table 1).

The coefficient of thermal expansion is used sometimes to determine a quantitative value describing coke structure. The coke is calcined, ground to a flour, mixed with coal tar pitch, extruded to orientate particles into 13 mm rods, baked to 850ºC and graphitized to 2900ºC, and then the difference in expansion at 0ºC and 50ºC is measured for coefficient of thermal expansion determination. For green sponge coke, the coefficient of thermal expansion is probably greater than that of needle coke [6]. Typical values for sponge cokes are in the range 8 to 18 (cm/cm/ºC $\times 10^{-7}$) as compared to zero to 4 for needle cokes [6].

It is a regular-grade coke with adequate strength for use in carbon anodes for aluminum production where electrical conductivity is essential but mechanical stressing is less than with the arc electrodes. It may also be used for the manufacture of electrographites, provided that strict property specifications are met [3, 5, 6].

Table 1. Analysis of green uncalcined sponge cokes [3]

Property	Coke from Port Arthur Refinery (USA)	Coke from Lake Charles Calcining Plant (USA)
Moisture	0.18	0.50
Volatile matter	12.32	8.24
Fixed carbon	87.21	91.16
Ash	0.29	0.10
Carbon	87.97	88.53
Hydrogen	3.85	3.96
Sulphur	3.85	5.19
Nitrogen	1.74	1.07
Oxygen	1.60	1.93
Silicon	< 0.010	< 0.1
Vanadium	0.118	0.033
Nickel	0.045	0.013
Iron	< 0.010	0.024
Density in Hg (g/cm^3)	1.320	1.292
Density in Helium (g / cm^3)		1.345
Total pore volume (cm^3)		0.031

Experimental Work

Thermal treatment of petcoke is the most promising process for the desulphurization of petcoke, and can be the only one possible when other techniques prove to be difficult or inefficient as was found in at least one case with Syrian petcoke [7]. By thermal treatment is meant the process whereby a fixed static bed of petcoke is heated under atmospheric pressure in an inert atmosphere to a specified temperature and then kept at that temperature for a specified period of time.

For the present work samples of Syrian sponge coke were taken from the coke heaps stored to the west of the Homs Oil refinery. The coke samples were classified and divided into porous coke and continuous sponge coke with inclusions of high relative structural order.

The coke samples were first crushed so that 95% of the coke passed through a 4-mm sieve. The samples were then weighed and spread on a drying floor to a depth of 8 mm and left to dry until the loss in weight of the total samples was not more than 0.1% per hour. After the determination of the moisture content (As-received basis), the coke samples were pulverised to pass a 250-µm sieve. Proximate and ultimate analysis tests were carried out on the samples using standard ASTM test methods. The gross calorific value was measured using the adiabatic bomb calorimeter (ASTM D 2025), in which a weighed sample is burnt completely in oxygen under controlled conditions. The calorific value is computed from temperature observations made before, during and after combustion, making proper allowances for heat contribution by acid formation and other corrections.

For the sulphur determination, the bomb washing method (ASTM D-3177) was used in which the sulphur is precipitated as $BaSO_4$ and the precipitate is filtered, ashed and weighed.

The real or true density ($DR_{10–20}$) is the density of 10-20 Tyler (0.83–1.65 mm) sample measured by He pycnometer. Tables 2 and 3 give the results of the proximate and ultimate analysis for the coke samples used in the study.

Table 2. Proximate analyses of Syrian sponge coke, air-dried basis

Property	Porous sponge coke	Continuous sponge coke
Ash (wt. %)	0.2	0.3
Moisture (wt. %)	0.3	0.5
Fixed carbon (wt. %)	87.0	84.2
Volatile matter (wt. %)	12.5	15.0
Sulphur (wt. %)	7.7	7.7
Gross calorific value (kJ/kg)	34.8×10^3	35.1×10^3
Real density (g/cm^3)	1.40	1.39

Table 3. Ultimate analyses of Syrian sponge coke, dry, ash-free basis

	Porous sponge coke	Continuous sponge coke
Carbon	84.9	84.4
Hydrogen	4.6	5.1
Nitrogen	1.1	1.2
Oxygen	1.7	1.5
Sulphur	7.7	7.8
C/H (wt.)	18.5	16.5

The coke samples were thermally treated in an inert atmosphere of nitrogen at atmospheric pressure. The treatment was carried out in an electrical tube furnace heated by a SiC element fully covering the working tube. The outside diameter of the working tube is 59 mm, and the heated length is 250 mm. A PtRh-Pt thermocouple is placed in the center of the heating zone and is lead to the temperature control unit. The conditions used in the treatment were such that were expected to lead to a maximum rate of desulphurization at moderately high temperatures [8]. Table 4 is a summary of the treatment conditions used. A summary of the results of the thermal treatment is shown in Table 5 and Figs. 1-4.

Table 4. Conditions of thermal treatment

Average weight of treated sample: 10 g
Coke Size range: 0.85 – 1.60 mm
Rate of heating: 3.5 ºC/min.
Gas atmosphere: N_2
Pressure: Atmospheric (748 mm Hg)
Rate of nitrogen flow = 0.5 l/min/g
Residence time at the thermal treatment temperature = 180 min

Table 5. Results of the thermal treatment

Temperature K	Porous sponge coke				Continuous sponge coke			
	Wt loss %	CV $\times 10^3$ kJ/kg	S wt %	DR_{10-20}	Wt loss %	CV $\times 10^3$ kJ/kg	S wt %	DR_{10-20}
300	-	34.8	7.7	1.40	-	35.1	7.7	1.39
500	0.6	35.1	7.5	1.40	1.0	35.1	7.5	1.41
775	3.2	34.7	7.5	1.45	4.8	34.9	7.5	1.48
875	3.7	34.3	7.7	1.34	4.1	34.9	7.5	1.32
975	8.1	33.3	7.2	1.49	9.2	32.4	7.0	1.52
1075	9.1	32.4	7.3	1.78	10.9	32.4	7.4	1.80
1175	10.1	31.9	5.6	1.81	12.4	31.4	5.3	1.82
1450	9.8	31.1	4.1	1.84	14.5	31.2	4.2	1.88
1550	15.5	32.0	3.2	1.95	17.0	32.2	2.8	1.90
1650	17.7	30.6	1.5	1.86	19.1	32.4	1.5	1.82
1700	18.1	32.1	0.9	1.99	20.2	31.2	1.0	1.95

Sulphur Removal

Table 6 shows the results of sulphur removal for both types of sponge coke at the different temperature ranges of thermal treatment as identified previously [8]. A similar trend is observed with other types of Syrian coke [8]. The maximum degree of desulphurization was 88% for porous coke and 87% for continuous coke.

Table 6. Average rates of desulphurization for sponge and other types of Syrian petroleum coke

Temperature range (K)	Average degree of desulphurization (%)		
	Porous sponge	Continuous	Other types
300 – 1075	5	4	7
1075 – 1175	22	27	18
1175 – 1450	19	14	23
1450 – 1550	12	18	13
1550 – 1650	22	17	22
1650 - 1700	8	7	7

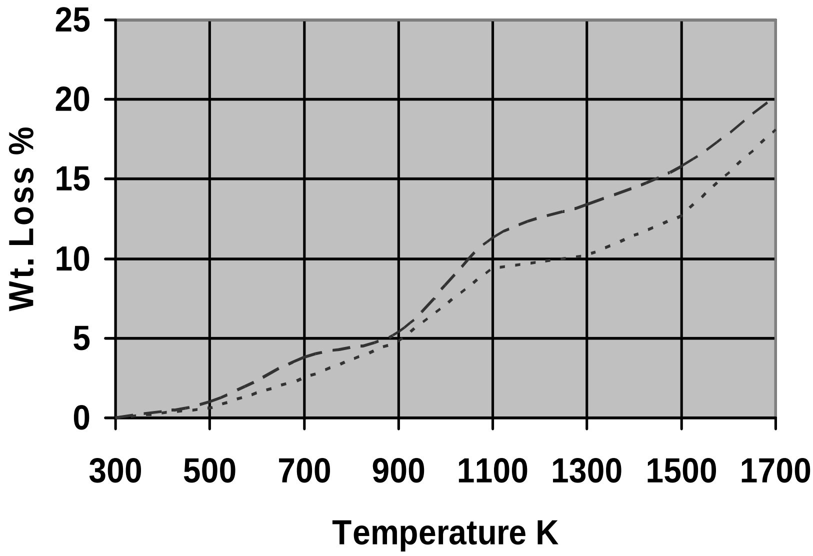

Fig. 1. Wt. loss (% on thermal treatment of coke.
Porous – – – – Continuous ------

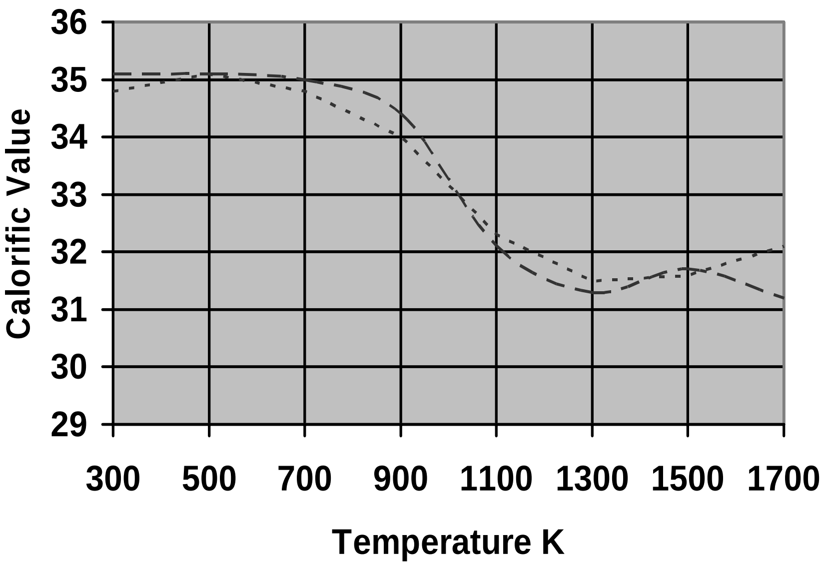

Fig. 2. Calorific value change (x 10^3 kJ/kg) on thermal treatment of coke.
Porous – – – – Continuous ------

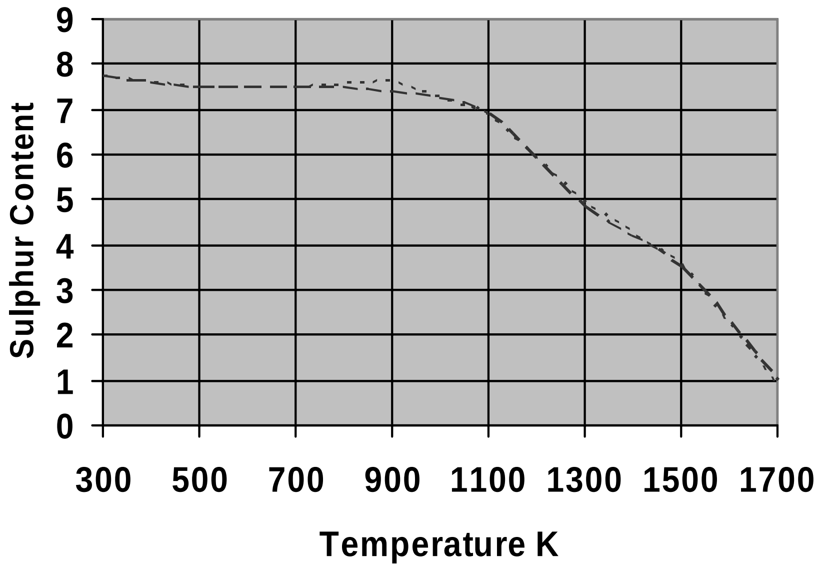

Fig. 3. Sulphur content change (%) on thermal treatment of coke.
Porous – – – – Continuous ------

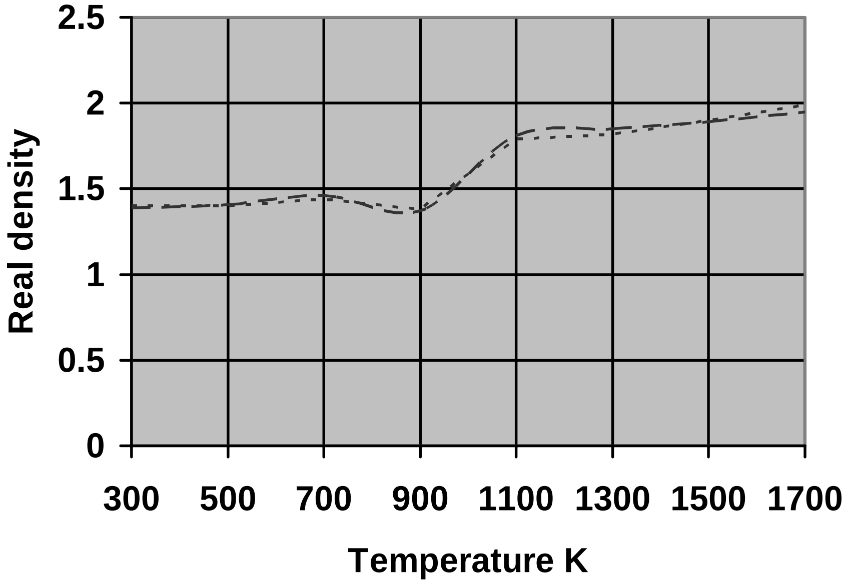

Fig. 4. Real density change (g/cu. cm) on thermal treatment of coke.
Porous – – – – Continuous ------

Density Increase

The true density of petcoke is expected to increase continuously with increasing treatment temperature. The rate of this increase is different, however, at different temperature ranges. Three stages of density change were recognized [9]:

1. An initial stage (300–800 K), with minimal density increase due probably to the removal of moisture and some volatile matter in the coke. The density increase observed was 0.05 g/cm^3 in the case of porous sponge coke and 0.09 g/cm^3 in the case of continuous sponge coke.
2. A second stage (800–1200 K) characterized by rapid increase in density related to the evaporation of the volatile matter adsorbed on the coke surface or in the pores. For porous sponge coke, with 12.5 VM (wt.%), the density increased during this stage by 0.36 g/cm^3. The corresponding density increase for continuous sponge coke, with 15.0 % VM, was 0.34 g/cm^3. These values are less than expected considering the relatively high volatile matter content of the coke. This points to influences other than VM on density change.
3. A final stage (1200–1700 K), where the density increase may be related to the rate of sulphur removal. The density increased by 0.18 g/cm^3 for porous sponge coke and 0.13 g/cm^3 for continuous sponge coke.

Calorific Value

The calorific value decreases, in general, with increasing temperature of the thermal treatment. However, there were observed two exceptions to this rule, where the calorific value increased rather than decreased.

A slight increase in the calorific value was observed towards the end of the first initial stage of thermal treatment (300-500 K). This is the overall effect of the evaporation and removal of moisture and volatile matter which take place during this stage, where the removal of moisture, as an inert material, has an opposite effect on the calorific value to that of removing the volatile matter. Whereas the removal of moisture is accompanied by an increase of the calorific value, the removal of the volatile matter tends to lower this value. The overall effect of the thermal treatment is therefore a factor of both volatile matter and moisture content. Since the moisture and volatile matter content of sponge coke are both higher, in general, than for other types of coke, the effect of the removal of volatile matter on the calorific value is expected to counterbalance the effect of the removal of moisture, with the result that the increase in the calorific value is less pronounced for sponge coke.

The calorific value was also observed to increase slightly in the temperature range 1450-1550 K and/or in the range 1650–1700 K. This must be related no doubt to the decreased sulphur content, as the heat of combustion of sulphur (9420 kJ/kg) is considerably less than that of carbon (33820 kJ/kg). A similar result was also obtained with other types of coke [8].

Weight Loss

The observed weight loss at the conclusion of the thermal treatment varied between 18% for porous coke and 20% for continuous coke (Table 5). The amount of weight loss corresponds generally to the moisture and volatile matter content of the coke as well as to the amount of sulphur removed. The observed weight loss was greater in the case of continuous coke due to the higher content of moisture and volatiles (Table 2). This is in agreement with the generally observed weight loss for other types of coke which is normally of the order of 20% or so.

Conclusions

Effective desulphurization of sponge coke was achieved by means of thermal treatment to a temperature of 1700 K and increased residence time (180 minutes). The treated coke has a low sulphur content (0.9-1%) and a high real density (2.0 g/cm^3). The adverse effects normally associated with thermal treatment of high sulphur cokes at temperatures above 1700 k, as indicated by many workers, are thereby minimized. Such effects include changes in the coke structure as a result of sulphur removal, porosity increase (which is disadvantageous for electrode making), reduction of both apparent and real densities and resistivity increase [1, 10-13].

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ا عا ة ا رارية للكوك الإسفنجي السوري

حسان ا اج إبراهيم

قسم الهندسة الكيميائية ، جامعة البعث ،

صندوق البريد ٢٤٦٨ ، حمص، سورية

(قدِّم في ٢٠٠٥/٠٥/١٧م، وقبل للنشر في ٢٠٠٦/٠٣/٢١م)

ملخص البحث. أجريت في هذه الدراسة معالجة حرارية لعينات من الكوك الإسفنجي السوري في درجات مرتفعة من الحرارة وزمن بقاء طويل ، وأمكن بذلك الحصول على كوك أجود وأفضل في خصائصه ، فقلت نسبة الكبريت فيه وارتفعت كثافته الحقيقية ، أما الفاقد في الوزن فكان قليلاً ، كما كان النقص المشاهد في القيمة الحرارية متفقاً في مقداره مع القيم المتوقعة من دراسة أنواع الكوك النفطي الأخرى.