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EFFECT OF THE REMOVAL OF SULPHUR AND VOLATILE MATTER ON THE TRUE DENSITY OF PETROLEUM COKE

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Abstract

The true density of petroleum coke is a factor of its structure and properties. As the removal of volatile matter and sulphur from the coke is accompanied by significant changes in its structure and microporosity, changes in its density are to be expected. In this paper, the effects of the removal of volatile matter and sulphur on the true density of petroleum coke were investigated. The density was found to increase significantly with the evaporation of the volatile matter as a result of the thermal treatment of the coke at a temperature of 1200 K. Removal of part of the sulphur in the coke led also to a significant increase in the value of its true density. Temperatures greater than 1600 K were necessary for effective sulphur removal.

Keywords: true density, petroleum coke, volatile matter.

1. Introduction

Density is an important property of petroleum coke. It is related to the coking severity and the type and usage of the coke produced. It is also, and more particularly, related to the coke structure. Petroleum coke is normally characterized by its proximate analysis including the measurement of its volatile matter and sulphur contents. These are of particular importance as indicators of the coke structure and quality. As the removal of sulphur and volatile matter from the coke affects greatly its structure and microporosity, its density is likely to be affected also.

2. Experimental Work

In this paper, the effects of the removal of sulphur and volatile matter on density are investigated. Average samples of green delayed Syrian petroleum coke were crushed and dried. Proximate and ultimate analysis tests were carried out on the samples using standard ASTM test methods (*Table 1*). The coke samples were thermally treated in an electrical tube furnace heated by a SiC element fully covering the working tube. The outside diameter of the working tube was 59 mm, and the heated length was 250 mm. A PtRh-Pt thermocouple was placed in the centre of the heating zone and was connected to the temperature control unit. The thermal treatment was carried out in an inert atmosphere of nitrogen at atmospheric pressure. The coke samples were divided into two groups. The first group of samples was heated to a temperature of 1200 K in order to investigate the effect of the removal of volatile matter on the true density of the coke. The second group of samples was heated to a higher temperature (1700 K) deemed necessary for effective removal of sulphur. A summary of the conditions of the thermal treatment is given in *Table 2*.

Table 1. Proximate and ultimate analyses of Syrian delayed petroleum coke

Proximate Analysis, Air-Dried Basis:
Ash = 0.45
Moisture = 0.28
Fixed carbon = 87.30
Volatile Matter = 11.97
Sulphur = 7.7
Gross Calorific Value = 34.9×10^3 kJ/kg
Real density = 1.39 g/cm^3
Ultimate Analysis, Dry, Ash-Free Basis:
C = 85.3
H = 4.6
N = 1.0
S = 7.8
O = 1.3
C/H (wt.) = 18.5

Table 2. Conditions of Thermal Treatment:

Average weight of treated sample: 10 g
Coke Size range: 0.85–1.60 mm
Rate of heating: 3.5 °C/min.
Gas atmosphere: N_2
Pressure: Atmospheric
Rate of nitrogen flow = 0.5 l/min/g
Residence time at the maximum temperature = 180 min

3. Results

Results of the increase of the true density of petroleum coke with increased treatment temperature are given in *Table 3*.

Table 3. Increase of coke density (g/cm^3) with temperature

Temperature K	DR_{10-20}
300	1.39
500	1.42
775	1.44
875	1.48
975	1.57
1075	1.76
1175	1.80
1450	1.92
1550	1.82
1650	1.92
1700	2.04

Thermal treatment of the coke samples to a temperature of 1200 K led to the removal of the volatile matter adsorbed on the coke surface or in the pores. Although some volatile matter may be removed at temperatures less than 800 K, the rapid evaporation of the volatile matter does not normally take place except at temperatures greater than about 800 K [1]. As a consequence, there is a sharp increase in dimensional shrinkage as well as in the ordering and growth of the polycrystalline structures of petroleum coke [2]. With the removal of volatile matter, a continuous increase in the true density of the coke was observed. The density increase was greater for cokes of higher volatile matter content (*Table 4*). In the temperature range investigated for the first group of runs, the amount of sulphur removed is minimal and is not likely to have a significant effect on density increase. The maximum amount of sulphur removal at a temperature of 1200 K was 30% (*Table 5*).

In the temperature range 800–1200 K, the real density was observed to increase regularly with temperature at a given residence time to such an extent that it may be used to characterize the thermal treating temperature [3]. Variation of DR with temperature up to 1300 K was correlated for delayed coke as follows:

$$\mathrm{DR} = 1.4 + 0.00112(T - 753), \qquad (1)$$

where T is the heating temperature in degrees Kelvin. The density increase is adequately described in the temperature range 800–1200 K by this equation, which can be used to compute the true density with an acceptable level of accuracy. As it

Table 4. Effect of volatile matter on density increase in the temperature range 300–1175 K:

Coke Sample	VM	Density Increase (g/cm^3)
1	9.9	0.35
2	12.0	0.41
3	12.5	0.41
4	14.7	0.47
5	15.0	0.47

Table 5. Effect of rate of sulphur removal on density change in the temperature range 1200–1700 K:

Coke sample	1200–1450 K		1450–1550 K		1550–1650 K		1650–1700 K	
	S reduction %	Density change (g/cm^3)	S reduction %	Density change (g/cm^3)	S reduction %	Density change (g/cm^3)	S reduction %	Density change (g/cm^3)
1	30	0.14	1	– 0.14	29	0.15	4	0.00
2	29	0.12	9	– 0.10	23	0.10	7	0.12
3*	26	0.08	11	– 0.10	19	0.05	11	0.02
4	20	0.05	11	– 0.02	23	0.11	7	0.10
5	14	0.02	19	0.00	14	0.02	4	0.00

* coke fines.

can be seen in *Table 6*, the difference between the calculated and measured density is ≤ 0.1 (or less than 7%).

Above 1600 K, density changes are influenced by the sulphur content of the coke. For cokes of high sulphur content, a significant change in the coke structure takes place as a result of sulphur removal leading to an increase in its microporosity, and the apparent density decreases. For cokes of low sulphur content, DA could increase continuously as the heating temperature is raised between 900 and 3300 K. On the other hand, when graphitization starts or before, DA could decrease [4, 5, 6].

It is generally known that the removal of sulphur is connected with the creation of an organized phase detectable by x-ray methods. The reduction of sulphur content increases the amount of this phase to a maximum of 10–20 % of the total mass. The mean interplanar distance along the 001 axis is close to that of graphite ($\sim$ 3.36 Å), while the tridimensional organization remains poorly developed [7].

The highest rate of sulphur removal was observed in the temperature range 1550–1650 K [1]. The dependence of density change on the rate of sulphur removal

Table 6. Measured and calculated density (g/cm^3) at different temperatures:

Temperature K	DR_{10-20}	Calculated	Difference
300	1.39	–	–
500	1.42	–	–
775	1.44	1.4	0.0
875	1.48	1.5	0.0
975	1.57	1.6	0.0
1075	1.76	1.8	0.0
1175	1.80	1.9	0.1
1450	1.92	1.9	0.0
1550	1.82	1.9	0.1
1650	1.92	2.0	0.1
1700	2.04	2.0	0.0

is clearly indicated by the results shown in *Table*5. The only exception to this rule is in the case of coke fine samples. This could be an indication of certain differences between coke fines and other types of coke in the manner and form of sulphur presence in the coke structure.

The results obtained indicate clearly that the density increase as a result of sulphur removal is less in general than the density increase due to the removal of VM. The density increase in temperature range 1200–1700 K may be described by the following equation:

$$\mathrm{DR} = 1.7 + 0.0004(T - 1000), \qquad (2)$$

where T is the heating temperature in degrees Kelvin. A reasonable degree of correlation was indicated between the computed and measured values, where the maximum difference observed was 0.1 (or about 5%) (*Table*6). Series of tests were run on different Syrian petcoke samples to check the accuracy of this correlation. The results are given in *Table 7*.

4. Conclusions

It can be concluded from the above considerations that the removal of VM and sulphur leads to density increase. The release of the volatile matter in the coke, which takes place at about 800 K, with consequent structural changes, has a significant effect on density increase. Although the removal of sulphur contributes effectively to density increase, its effect in this respect is not, in general, as significant as that of volatile matter removal. With increasing degree of desulphurization at higher temperatures, sulphur removal would have a greater effect on density increase.

Table 7. Measured and calculated density (g/cm^3) for different coke samples:

Temp. K	Coke sample					Average	Calculated	Difference
	1	2	3	4	5			
1175	1.9	1.9	1.8	1.8	1.8	1.8	1.8	0.0
1450	1.9	1.9	1.9	1.9	1.9	1.9	1.9	0.0
1550	1.9	1.8	1.8	1.8	1.8	1.8	1.9	0.1
1650	1.9	1.9	1.9	2.0	1.9	1.9	2.0	0.1
1700	1.9	1.9	1.9	2.1	2.0	2.0	2.0	0.0

5. Nomenclature

DA	Apparent density
DA_1	Apparent density measured at 1.1 bars.
DA_2	Apparent density measured at 600–1000 bars.
DR	Real density
DR_{10-20}	Real density of 10–20 Tyler sample measured by He pycnometer.

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