خصائص الكوك النفطي السوري المسحوق ومعالجته بالحرارة

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الخلاصة :

تنتج مصفاة النفط في حمص أنواعاً مختلفة من الكوك النفطي السوري منها الكوك الإسفنجي وكوك الدقاقة والكوك المسحوق ، وهي أنواع تختلف في خصائصها وبنيتها ونسبة الكبريت فيها . وقد أجريت هذه الدراسة على النوع المسحوق منها ، حيث تمت معالجته معالجة حرارية في درجات مرتفعة من الحرارة (١٧٠٠ كلفن) وزمن بقاء طويل (١٨٠ ثانية) ، وأمكن بذلك الحصول على كوك أجود وأفضل في خصائصه ، فقلت نسبة الكبريت فيه حتى ٠,٩ ٪ وارتفعت كثافته الحقيقية إلى ١,٩ غ / سم^{3} ، 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 .

الكلمات المفتاحية : الكوك النفطي المسحوق ، المعالجة الحرارية .

Characterization and thermal treatment of Syrian petcoke fines

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INTRODUCTION

Syrian petroleum coke is produced by the delayed coking unit at the Homs Oil Refinery. This unit was designed and built during the late sixties of last century for the purpose of maximizing gasoline and distillate yields using a feedstock of residue materials.

The coke produced by this unit is characterized by a high percentage of fines. This, as well as its high sulphur content, tends to reduce the commercial value of the Syrian coke. There seems to be less demand for coke fines than for other types of coke. While coke fines may be easier to burn as a fuel, their use for other applications is not always to be recommended. It is important also to keep in mind that anodes cannot be made without a coarse fraction, and coke fines require an agglomerating step. This in turn would require a coal tar pitch binder and a baking step. The final product becomes a relatively weak lump with prohibitive cost [1]. Furthermore, the creation of coke dust, associated with the presence of coke fines, is a major cause of environmental problems. It results also in loss of productivity.

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 [2, 3]. 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 coke fines were taken from the coke heaps stored to the west of the Homs Oil refinery. Proximate and ultimate analysis tests were carried out on the samples using standard ASTM test methods. 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. 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.

Tables 1 and 2 give the results of the proximate and ultimate analysis for these samples. The coke fines, as can be seen from these results, are characterized by a higher volatile matter content (14.7 as compared to 12.0 for lump coke), higher oxygen content (3.0 as compared with 1.3 for lump coke) and lower C/H ratio (16.9 as compared to 18.5).

Table 1: Proximate Analyses of Syrian coke fines, Air-dried basis.

Ash (wt. %)	0.7
Moisture (wt. %)	0.3
Fixed carbon (wt. %)	84.3
Volatile Matter (wt. %)	14.7
Sulphur (wt. %)	7.9
Gross Calorific Value (kJ/kg)	34.9×10^3
Real density (g/cm^3)	1.38

Table 2: Ultimate Analyses of Syrian coke fines, Dry, ash-free basis.

Carbon	82.9
Hydrogen	4.9
Nitrogen	1.2
Oxygen	3.0
Sulphur	8.0
C / H (wt.)	16.9

The volatile matter content of coke fines may be related to the effect of grinding. Korai et. al. observed in a study made on the effects of grinding on needle coke that grinding increases the volatile matter content of the coke. It was argued that grinding leads to grain fracture and breakage of the weak C-C bonds of the coke structure releasing thereby the low molecular-weight substances included in the coke particles or combined chemically with the crystallites of these particles. The volatile matter content was found to increase from 14.6 to 15.7 as a result of grinding [4].

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 (Fig. 1). 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 centre of the heating zone and is lead to the temperature control unit. The conditions used in the treatment were such that would be expected to lead to a maximum rate of desulphurization at moderately high temperatures [5]. Table 3 is a summary of the treatment conditions used. A summary of the results of the thermal treatment is shown in Table 4.

Table 3: Conditions of Thermal Treatment

Average weight of treated sample: 10 g
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

Fig. 1

Table 4: Results of the thermal treatment.

Temperature K	Wt loss %	CV $\times 10^3$ kJ/kg	S wt %	DR_{10-20} g/cm^3
300	-	34.9	7.9	1.38
500	0.5	35.1	7.3	1.39
775	7.0	34.5	7.6	1.43
875	7.4	34.0	7.6	1.35
975	8.5	32.8	7.0	1.52
1075	10.9	32.3	7.2	1.87
1175	11.4	31.7	5.9	1.85
1450	15.2	30.9	3.9	1.82
1550	17.1	32.4	3.0	1.83
1650	20.1	32.0	1.5	1.88
1700	21.0	32.1	0.9	1.92

SULPHUR REMOVAL

Table 5 shows the results of sulphur removal for coke fines. A Similar trend is observed with other types of Syrian coke [5]. The maximum rate of desulphurization was 89%. This may be taken as evidence that original grain size has little effect on the rate of desulphurization. However, there is no consensus on this point. Some workers reported a positive correlation between the rate of desulphurization and the mean diameter of coke particles, where decreasing the mean diameter of coke particles was found to improve the desulphurization efficiency [6, 7, 8], and Kalinowski, who investigated the effect of grain size, reported an optimum size for maximum desulphurization. Other workers, on the other hand, obtained results that did not follow a recognizable pattern [3]. According to Hussein et. al. [6], briquetting does not improve the desulphurization efficiency.

Table 5: Average rates of desulphurization for coke fines and other types of Syrian petroleum coke.

Temperature range (K)	Average degree of desulphurization (%)	
	Coke fines	Other types
300 - 1075	9	7
1075 - 1175	16	18
1175 - 1450	25	23
1450 - 1550	11	13
1550 - 1650	19	22
1650 - 1700	7	7

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 coke fines.
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 coke fines, with 14.7 VM (wt.%), the density increased during this stage by 0.42 g/cm^3. This value is rather low considering the relatively high volatile matter content of the coke. This points to influences other than volatile matter 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 0.07 g/cm^3 for coke fines.

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 (300-1200 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 volatile matter content of coke fines is higher, in general, than for other types of coke, the effect of the removal of volatile matter on the calorific value is expected to be greater

also, with the result that the increase in the calorific value is less pronounced for coke fines.

The calorific value was also observed to increase slightly in the temperature range 1450-1550 K and 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 [9].

WEIGHT LOSS

The amount of weight loss at the conclusion of the thermal treatment corresponds generally to the moisture and volatile matter content of the coke as well as to the amount of sulphur removed. For most types of petroleum coke this weight loss is in the order of 20% or so. The observed weight loss for coke fines was about 21% (Table 4). This greater than average value is most probably due to the higher content of moisture and volatiles in coke fines (Table 1).

CONCLUSIONS

Effective desulphurization of coke fines 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%) and a high real density (1.9 g/cm^3). The adverse effects normally associated with thermal treatment at high temperatures were minimal.

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ABSTRACT

Samples of Syrian coke fines 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, coke fines, thermal treatment.