

Analysis and Characterization of High-Volatile Petroleum Coke



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Abstract

A high percentage of Syrian petroleum coke is in the form of high volatile coke, which is a type of delayed petroleum coke with a high percentage of volatile matter content. Analysis and characterisation of this important type of Syrian petcoke were carried out. Compared to other types of Syrian petcoke, high volatile coke is less anisotropic. It is characterised in general by its high volatile matter and low sulphur contents. It has a higher calorific value and a lower real density. Its moisture and ash contents are also higher than other types of Syrian petcoke but its fixed carbon content is lower.

Keywords: VM: Volatile matter content; DA: Apparent Density

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 petcoke produced is considered merely as a by-product of little commercial value. This is mainly because of its high sulphur content and the high percentage of fines produced. It is being sold at present in the home market or exported as green untreated coke. Upgrading the produced petcoke by improving its quality and reducing the sulphur content to an acceptable level has always been a prime target of the Syrian refining industry.

The five main basic types of Syrian petcoke, namely shot coke, clustered shot coke, porous sponge coke, continuous sponge coke and fines, have already been analysed and characterized in a previous work [1]. In several studies, upgrading these different types of petcoke was investigated and a better quality low sulphur petcoke was achieved. Of the several desulphurization techniques investigated, thermal desulphurization [2,3] and upgrading by pre-oxidation were of special relevance and efficacy [4]. Varieties of Syrian petcoke were also activated in order to produce active carbon of high surface area suitable for treatment of polluted water [5,6] and natural gas [7]. Blending coke fines using appropriate binders, such as bitumen and polyacrylic acid, was also used to obtain an improved coke that is similar in structure, appearance and other properties to better-quality coke lumps [8].

A high percentage of the coke produced by the Homs Oil Refinery is, however, in the form of high volatile coke, which is

characterised in general by its high volatile matter and low sulphur contents. It is in general less hard than other types of petroleum coke and less anisotropic, with greater particle strength. The lower anisotropy of high-volatile coke is an indication of the deviation of its structure from needle coke structure, as the structure of petcoke in general and needle coke in particular is commonly described in terms of anisotropy [9]. Despite its significance, no previous analysis or characterization of high volatile coke has ever been undertaken before.

The coke volatile matter is composed of heavy hydrocarbons that are deposited in the coke matrix and fill the pores. The high volatile matter content of green coke gives it a characteristic hydrocarbon smell. The volatile matter content of green coke which has not been calcined is generally high varying between 9 and 21% (wt.), but green premium cokes have volatile matter of less than 5% (wt.) typically. For Syrian petcoke, the volatile matter content varies between a minimum of 9.8% for clustered shot coke to a maximum of 15.0% for continuous sponge coke [1].

Volatile matter content (VM) is mainly a function of the coking drum temperature, the maximizing of which gives a low volatile matter content [10]. Other critical factors that control the volatile matter content include coking drum pressure and recycle ratio. Longer residence time helps to decrease the volatile matter. Insulation of the transfer line and coke drum, especially the upper sections of the coke drum, are critical for obtaining low VM coke [9]. When operating at high temperatures for maximum liquid yield operations, it is possible to produce shot coke which is low in volatiles.

Volatile matter, which marks the high-volatile coke, can be an important indication of coke quality and properties. Green coke volatility levels can be qualitatively related to calcined coke quality [11]. Low-volatile coke is a more concentrated sulphur-bearing coke. Cokes of low volatile matter content are in general easier to remove from the coke drums and easier to grind [10].

Volatile matter content is significantly related to the calorific value [12] and apparent density and inversely related to the real density of the coke [4]. On thermal treatment of coke, its density showed continuous increase with treatment temperature. The major factor in density increase is the release of the volatile matter in the petcoke, which takes place at about 800K, with consequent structural changes (Table 1) [13]. Volatile levels also correlate well with the expected hardness and particle strength of the coke. In general, the lower the green coke volatile level, the harder is the coke and the more anisotropic. As isotropic coke particles are stronger than anisotropic coke particles, the higher the volatile level of the green coke, the higher is the expected strength of the calcined coke particle [11]. Shot coke produced at high temperatures is low in volatiles and very hard, i.e. of low Hardgrove grindability index.

Table 1: Effect of volatile matter on density increase in the temperature range 300-1175K.

Coke Sample	VM	Density Increase (G/Cm ³)
1	9.9	0.35
2	12	0.41
3	12.5	0.41
4	14.7	0.47
5	15	0.47

The greater part of the volatile matter in the green coke distills off during calcinations and pre-oxidation exposing thereby the pores and typical lamellar structure of the treated coke. In thermal desulphurization, the evaporation and removal of the volatile matter is accompanied by an increase in the density of the coke. Thermal treatment of the coke samples to a temperature of 1200K 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 800K, the rapid evaporation of the volatile matter does not normally take place except at temperatures greater than about 800K. 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 in the 800-1100K temperature range [14]. 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 1) [3,15-18].

On pre-oxidation of the coke, partial combustion of the volatiles takes place to some extent. Due the escape and partial combustion of volatile matter, the coke porosity increases on pre-oxidation due to the creation of micro and macroporosity. As a result of such increase in the coke porosity, its apparent density

(DA) measured by Hg pycnometer will decrease [4]. Grinding, on the other hand, increases the volatile matter content of the coke as observed by Korai et al. in a study made on the effects of grinding on needle 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 [19].

Experimental Work

Samples of Syrian high volatile coke were taken from the coke heaps stored to the west of the Homs Oil refinery. The coke samples were first crushed so that 95% of the coke passed through a 4mm sieve. The samples were weighed and spread on a drying floor to a depth of 8mm 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 pulverized to pass a 75 μ m sieve (for the density determination) or a 250 μ m sieve (for the other tests). Proximate and ultimate analyses were carried out on these samples using standard ASTM procedures. For the sulphur determination, the bomb washing method (ASTM D-3177) was used in which the sulphur is precipitated as BaSO₄ and the precipitate is filtered, ashed and weighed. A He pycnometer was used for the true density determination (ASTM 2638) where the volume of the sample is derived by the volume displaced when the sample is introduced into the pycnometer. The precision for this test method is as follows: 0.018g/cm³ (Repeatability) and 0.025g/cm³ (Reproducibility). Table 2 gives the results of the proximate and ultimate analysis. The high volatile coke, as can be seen from these results, is characterised by a higher volatile matter content (17.5 as compared to 12.0 for other types of coke) and lower sulphur content (6.64 as compared with 7.7 for other types of delayed coke). Its moisture and ash contents are also higher than in other types of Syrian petcoke. Its fixed carbon content, on the other hand, is lower. It has a higher calorific value and a lower real density.

Table 2: Proximate Analyses of Syrian High volatile delayed coke.

Property	High Volatile Coke	Other Types of Syrian Coke [4]
Ash (wt. %)	1.09	0.1-0.7
Moisture (wt. %)	0.99	0.2-0.5
Fixed carbon (wt. %)	80.43	84.2-89.7
Volatile Matter (wt. %)	17.49	9.8-15.0
Sulphur (wt. %)	6.64	7.7-8.0
Gross Calorific Value (kJ/kg)	35.9 \times 10 ³	34.3 \times 10 ³ -35.1 \times 10 ³
Real density (g/cm ³)	1.29	1.37-1.40

Conclusion

High-volatile coke is delayed petroleum coke with a high percentage of volatile matter content. It is one of the main types of

Syrian delayed petroleum coke produced by the Coking unit at the Homs Oil Refinery. High-volatile coke is mainly characterised by its higher moisture and ash contents and lower sulphur content. It has in addition a higher calorific value and a lower real density. As previously indicated, the VM of the high-volatile coke can be considerably reduced by calcination.

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