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THE EFFECT OF INCREASED RESIDENCE TIME ON THE THERMAL DESULPHURIZATION OF SYRIAN PETROLEUM COKE

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Abstract

High sulphur Syrian delayed petroleum coke was thermally treated at high temperatures in order to reduce its sulphur content. It was found that the high temperature required for effective desulphurization can be reduced by increasing the residence time at the maximum heating temperature, avoiding thereby the adverse effects associated with thermal treatment at high temperatures, particularly in the case of the high sulphur Syrian coke. A maximum desulphurization of 90% was possible at a temperature of 1700 K and a residence time of 180 minutes.

Keywords: petroleum coke, thermal desulphurization, residence time.

1. Introduction

Delayed petroleum coke, or petcoke for short, is coke produced by the delayed coking process. This is a semi-continuous batch process carried out in two coke drums.

The sulphur content of petcoke varies widely from less than 0.5% to more than 10% [1]. It depends strongly on the sulphur content and the nature of the coking feedstock. It is also affected by the coking process variables.

Most of the sulphur in petcoke exist as organic sulphur bound to the carbon matrix of the coke [2]. Some sulphur could also exist as sulphates and pyritic sulphur [3], but these do not in general make up more than 0.02% of the total sulphur in coke [4]. In at least one case, however, pyritic sulphur was reported to be as high as 0.04% [5]. Free sulphur may occasionally be present [3].

Organic sulphur may exist in the coke in many forms [4]:

- 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 to be found on the coke surface or in coke pores bound by capillary condensation, adsorption or chemisorption [4].

The desulphurization of petcoke involves in general the desorption of the inorganic sulphur present in the coke pores or on the coke surface, and the partition and removal of the organic sulphur attached to the aromatic carbon skeleton. For the removal of the sulphur in the first category a purely thermal treatment at temperatures less than 1100 K is generally sufficient, but a more severe treatment and/or the use of chemicals is, however, necessary for the removal of the sulphur attached to the carbon skeleton, particularly in the case of the thiophenic sulphur which is much more stable than the other organic sulphur compounds and are therefore much more difficult to remove. The thiophenes not only do they make up most of the sulphur present in the original coke, but other less stable compounds may be transformed into the more refractory thiophenes during the desulphurization process.

Much experimental work has been done on the desulphurization of petcoke and several techniques have so far been proposed including solvent extraction, chemical treatment, hydrodesulphurization and thermal desulphurization [6, 7]. Thermal desulphurization is 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. This process was felt to be 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 with Syrian petcoke.

The maximum temperature to which the coke is subjected determines to a large extent the amount of sulphur removal. Most organic sulphur compounds do not undergo thermal decomposition below 750 K, even though some compounds decompose at lower temperatures such as many mercaptans which decompose at about 600 K and some sulphides which decompose at 530–670 K [8]. However, such compounds, as was pointed out earlier, do not in general make up much of the organic sulphur in coke. The efficiency of desulphurization, however, is dependent not only on the maximum temperature to which the coke is subjected, but is affected also by other factors including the rate of heating, gas atmosphere and in particular the residence time at the maximum temperature.

2. Desulphurization of Syrian Petcoke

Syrian petroleum coke is a coke produced by the delayed coking unit at the Homs Oil Refinery. This unit was designed and built during the late sixties of the 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. To make this coke a commercially viable commodity it is imperative that the sulphur be reduced or eliminated altogether.

Some work has been done on Syrian petcoke, where several desulphurization techniques were employed. Solvent extraction, using different solvents such as benzene and sodium carbonate, proved to be very ineffective, with a maximum sulphur removal not exceeding 3% [7]. For effective desulphurization, thermal treatment was found to be essential. For a purely thermal treatment, high temperatures (1900K) were required. The use of hydrogen or LPG, however, could reduce the required temperature to 1600 or 1800K respectively. Heat treatment to a temperature in the range of 1100–1600 K was not found to be effective.

3. The Adverse Effects of High Maximum Temperatures

The high temperatures required for effective desulphurization could have some detrimental effects on the treated petcoke. For cokes of high sulphur content, such as Syrian petcoke, a significant change in the coke structure takes place as a result of sulphur removal.

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 [9].

As coke is heated its porosity increases due to the creation of micro and macroporosity as the sulphur is vaporized and leaves the solid coke matrix [10]. This increase is, therefore, dependent on the total sulphur content of the coke. When the sulphur content is low, little porosity change is observed and the sulphur can be removed without any change in the coke structure, merely by making use of pre-existent pores. The more sulphur to be removed, the greater is the reorganization of the coke structure [11]. Increasing the porosity of petcoke is disadvantageous for electrode making.

Increasing the coke porosity leads to the decrease of its apparent density. The apparent density (DA) is the density of 10–20 Tyler sample (corresponding to 0.83–1.65 mm) measured by Hg pycnometer either at 1.1 bars (DA_1) or at 600–1000 bars (DA_2). The true or real density is also observed to decrease at temperatures between 1700 and 2400 K. 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 [4, 12].

As the coke is heated its reactivity decreases up to the desulphurization temperature, but the total effect of further heating is the increase of the reactivity. The reactivity of the coke investigated by BARRILLON was doubled as the coke was heated from 1400 to 1800 K [11].

Higher temperatures cause the resistivity of petcoke to increase until a maximum (180 Ohm/m^2/m) is reached around 2300 K.

4. The Effects of Residence Time

Residence time at the maximum heating temperature can affect desulphurization. However, most desulphurization seems to occur within the first 30 minutes of the thermal treatment up to a temperature of 1600 K. According to AKHMETOV and SYUNYAEV [13], the highest rate of desulphurization is within the first five minutes, but this does not seem to apply in all cases as can be shown by the results of BRANDT and KAPNER, for example, where more desulphurization took place during the last ten minutes of the initial 30 minute period of the thermal treatment [10]. Increasing the residence time beyond 30 minutes does not seem to affect significantly the degree of sulphur removal for most cokes at temperatures less than 1600 K. Similarly, at temperatures above 1800 K increasing the residence time does not seem to have any effect on desulphurization [3, 10, 14, 15, 16, 17]. On the other hand, the effect of increasing the residence time in the temperature range of 1600–1800 K is likely to be much more pronounced.

5. Experimental Work

The above considerations lead to the conclusion that it would be preferable to treat the Syrian high sulphur coke at temperatures less than the optimum for maximum desulphurization in order to reduce the undesirable detrimental effects of extra high temperatures on petcoke quality. The negative effects of reducing the maximum thermal treatment temperature on desulphurization would then be offset by increasing the residence time. In the present work, the residence time was increased from 30 to 180 minutes. The Syrian petcoke was thermally treated in an 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 centre of the heating zone and is lead to the temperature control unit.

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. *Table 1* gives the results of the proximate and ultimate analyses carried out on the treated petcoke. *Table 2* is a summary of the treatment conditions used.

A moderate rate of heating (3.5 °C/min.) was used throughout. It is evident to indicate that a higher rate of heating would reduce the coke yield by increasing the weight loss [17]. No other data is available on the effects of the rate of heating on sulphur removal.

It is not clear whether the elimination of sulphur is affected in any way by the inert gas used during the thermal treatment [18]. Most workers used either nitrogen or argon. Carbon-nitrogen complexes are not likely to be formed when petcoke is heated in a nitrogen atmosphere [2]. Nitrogen, however, has been reported to exhibit considerable reaction towards carbon and graphite above 1700 K [19]. As the use of argon may inhibit desulphurization at lower temperatures, nitrogen was deemed preferable in the present study.

Thermal treatment under atmospheric pressure gave better desulphurization results. Thermal desulphurization under vacuum does not seem to be beneficial to

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

Proximate Analysis, Air-dried basis	
Ash	0.5
Moisture	0.3
Fixed carbon	87.2
Volatile Matter	12.0
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

the desulphurization efficiency. The phenomena observed during the course of the treatment include a significant amount of weight loss along with the removal of sulphur [9].

Decreasing the mean diameter of coke particles may improve the desulphurization efficiency [2, 13, 20], but there is no consensus on this point. Kalinowski who investigated the effect of grain size reported an optimum size for maximum desulphurization, but other workers obtained results that did not follow a recognizable pattern [3]. Briquetting does not improve the desulphurization efficiency according to HUSSEIN et al. [2]. It is important also to keep in mind that anodes cannot be made without a coarse fraction, and cokes that have to be pulverized, in order to improve their desulphurization efficiency, 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 [10].

It is reported by many workers that grinding a coke sample to smaller particle size causes structural defects or crystalline distortion of the coke sample [21]. KMETKO observed by scanning electron microscopy that the grinding of coke destroyed the lamellar structure of the coke as well as the microcrystalline orientation [21]. Other workers reported that grinding a coke sample decreases its anisotropy. Even natural graphite can loose some of its anisotropy by overgrinding. While some of the loss of anisotropy may be regained upon heat treatment, it is never fully recovered. Some workers claim that the isotropy rapidly increases when the coke is ground to less than 0.85 mm. Others report that the minimum particle size needed to retain the macrostructures of major interest is in the range of 0.8–1.6 mm [19]. The Coke Size range used in the present work was in the range of 0.85–1.60 mm.

6. Results and Conclusions

Different Syrian petcoke samples were thermally treated. Typical results for a representative sample are given in *Tables 3* and *4*. *Table 5* gives a summary of the average and maximum rates of desulphurization at different temperature ranges as obtained using different petcoke samples.

Table 3. Effects of residence time on rate of desulphurization

Temperature K	S wt %	
	30 Min.	180 Min.
300	7.7	7.7
1100	7.2	7.1
1300	5.5	5.0
1400	4.5	4.2
1500	4.1	3.5
1600	3.6	2.6
1700	2.8	0.8

The effect of increasing the residence time is apparent from a consideration of the results shown in *Table 3*. Increasing the residence time from 30 to 180 minutes did significantly improve the desulphurization efficiency, particularly in the temperature range 1600–1800 K. More sulphur was removed at 1600 K and 180 min (66%) than was removed at 1700 K and 30 min (53%).

The results obtained indicate clearly that the process of desulphurization may be conveniently divided into at least four stages (*Table 4*):

Table 4. Typical results for a representative coke sample

Temperature K	Wt loss %	CV $\times 10^3$ kJ/kg	S wt %	S reduction %
300	–	34.9	7.7	–
500	0.6	35.0	7.3	5
775	5.2	34.4	7.3	5
875	7.9	32.8	7.2	6
975	7.4	32.5	7.1	8
1075	9.5	32.1	7.1	8
1175	10.8	31.5	6.0	22
1450	12.9	31.2	3.8	51
1550	16.1	31.1	3.1	60
1650	19.1	31.0	1.3	83
1700	19.4	30.9	0.8	90

Table 5. Average and maximum rates of desulphurization

Temperature range (K)	Average degree of desulphurization (%)	Maximum degree of desulphurization (%)	Average rate of desulphurization per 100 K (%)
300–1075	7	9	1
1075–1175	18	22	18
1175–1450	23	29	8
1450–1550	13	17	13
1550–1650	22	29	22
1650–1700	7	7	14

1. *An initial stage* (300–1075 K) in which little desulphurization (less than 9%) takes place. The average rate of desulphurization for a temperature increase of 100 K was about 1% only. A weight loss of about 9.5% was observed at the end of this stage, with a corresponding decrease in the calorific value, as a result of the evaporation of the moisture and volatile matter in the coke. During this stage the following phenomena are expected to occur:
    - At about 400–500 K, water that enters the coke during the hydraulic coke cut is removed [15]. This is accompanied by a slight increase in the calorific value (*Table 4*).
    - At about 800 K the evaporation of the volatile matter adsorbed on the coke surface or in the pores is indicated, with the desorption of sulphur bound also on the surface or in the pores. Simultaneously cracking of the side chains of aromatic hydrocarbons including some sulphur

hydrocarbons takes place and sulphur in the form of H_2S and RSH is separated. The greater part of the separated sulphur gases results, however, from the desorption of chemisorbed sulphur in coke pores or on the coke surface. This is indicated, according to VRBANOVIC [14], by the fact that increasing the residence time from 30 to 180 minutes was not found to influence desulphurization at temperatures less than 1100 K.

- As a consequence of volatile matter release, 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 800–1100 K temperature range [22].
- Experimental work indicates that no reaction occurs during this stage between metal contaminants and sulphur gases since no variation in the degree of desulphurization of different cokes, with different amounts of metals, was observed [15].
- The maximum amount of sulphur removed at this stage is about 9%, which can be taken as a rough indication of the amount of non-thiophenic sulphur in coke.

2. *A second stage* (1075–1175) in which desulphurization is dramatically increased, with an average rate of 18%. Most of the sulphur removed during this stage is derived from the decomposition of the thermally-stable sulphur compounds bound in side chains.
3. The rate of desulphurization slows down in *the third stage* (1175–1450), dropping to about 8% only. It is evident to indicate that the process of sulphur separation stops at about 1300 K [15], as the desorbed sulphur may enter into reactions with quinone (or chinone $C_6H_4O_2$) and phenol groups. These reactions usually result in the formation of sulphur hydrocarbon complexes that are thermally refractory and very difficult to separate from the coke structure [15]. Desulphurization is also significantly decreased by the metal-hydrocarbon compounds which react with the dissociated sulphur to form refractory sulphur [15].
4. *The final stage* is reached when the coke is heated to temperatures above 1450 K. The average rate of desulphurization was found to vary during this stage between 13 and 22%. At temperature $\geq$ 1500 K desulphurization may be inhibited by the formation of thermally-stable metal sulphides [23]. A marked increase in the degree of desulphurization is to be expected at temperatures above 1600 K, as the energy available is sufficiently high for the decomposition of sulphur-hydrocarbon compounds of stabilities up to those of thiophene structure [15]. The highest rate of desulphurization was observed in the temperature range 1550–1650 K where it reached an average value of 22%. Complete elimination of sulphur is not likely, however, even at the high temperature of 1700 K [14, 16].

The observed weight loss at the conclusion of the thermal treatment was about 19.4%. This amount corresponds to the moisture and volatile matter content of the coke as well as to the amount of sulphur removed. The overall decrease in the gross calorific value was 4×10^3 kJ/kg or about 11%. In at least one case there was a slight anomalous increase observed in the calorific value in the temperature range 1450–1650 K, which could not be explained.

In conclusion, it is evident that effective desulphurization of petroleum coke can be achieved by means of thermal treatment to a temperature of 1700 K by increasing the residence time to 180 minutes, while avoiding at the same time the adverse effects associated with thermal treatment at the higher temperatures deemed necessary for effective desulphurization.

Nomenclature

CV	Gross calorific value
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.
VM	Volatile matter

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