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RESEARCH ARTICLE

Upgrading of Syrian petroleum coke by pre-oxidation

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Abstract

Solvent extraction offers a simple but generally ineffective approach to the desulphurization of high-sulphur petroleum coke where the organic sulphur compounds present may be selectively dissolved. Pre-oxidation of petroleum coke at a moderate temperature (600 K) renders the coke more amenable to the solvent extraction treatment. The desulphurization efficiency was greatly improved when pre-oxidized coke samples were extracted using different solvents. A maximum desulphurization of 76% was achieved.

Keywords

Petroleum coke · pre-oxidation · solvent extraction · desulphurization.

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Introduction

High quality low sulphur petroleum coke can be a valuable by-product of the coking process in petroleum refineries, for which there is a continuously increasing demand in many industries such as aluminum and steel industries and in the production of carbonaceous construction materials for high temperature applications [1]. In most refineries, however, where heavy high sulphur crudes are increasingly being processed the produced coke can have high sulphur content and desulphurization of the coke becomes an important and necessary step for its upgrading [2]. Based on statistics, the percentage of sulphur in petroleum coke has increased by about 20% in twenty years (between 1997 and 2007), a trend that is expected to continue in the future.

Tab. 1. Proximate Analysis of Syrian petroleum coke, air-dried basis

0.5	Moisture (wt %)
0.3	Ash (wt %)
84.2	Fixed Carbon (wt %)
15.0	VM (wt %)
7.7	Sulphur (wt %)
1.39	Real density g/cm^3
1.19	Apparent density g/cm^3
0.395	Porosity cm^3/g
35.1 $\times 10^3$	Gross Calorific Value kJ/kg
0.04	BET Surface area m^2/g

Tab. 2. Ultimate Analysis of Syrian petroleum coke, Dry, ash-free basis

Carbon	84.4
Hydrogen	5.1
Nitrogen	1.2
Oxygen	1.5
Sulphur	7.8
C/H (wt.)	16.5

Of the many desulphurization processes available, solvent extraction offers the simplest approach to desulphurization where the organic sulphur compounds present may be selectively dissolved. When coal was treated by solvent extraction about 80% of the organic sulphur was removed. It was suggested that successive sequential extraction of coal might significantly improve the desulphurization efficiency of solvent extraction [3]. However, results obtained when extractions with coke using a large variety of solvents were made clearly indicate that solvent extraction as such is not an effective method of coke desulphurization. While extractions made with different single solvents led to some sulphur removal, in no case was more than 20% sulphur removed [4], but when two solvents, ferric chloride and benzene, were used consecutively in the treatment of Egyptian petroleum coke, more than 35% sulphur removal was obtained [5]. On the other hand, treatment of high-sulphur Syrian petroleum coke, produced by the delayed coking unit at the Homs Oil Refinery, by solvent extraction using different solvents such as benzene and sodium carbonate, proved to be very ineffective, with a maximum sulphur removal not exceeding 3% [6].

The ineffectiveness of solvent extraction as a desulphurization technique is directly related to the nature of sulphur compounds in coke. While free or elemental sulphur, which could be removed by solvent extraction, may be found occasionally in petroleum coke [7, 8], most of the sulphur in coke exists as organic sulphur bound to the carbon matrix of the coke [7, 9]. Effective desulphurization of petroleum coke involves the rupture of the thiophenes, which make up most of the sulphur present in the coke. The selectivity of solvent extraction can therefore be enhanced only if the coke macromolecule could be cleaved. Although the effectiveness of depolymerisation techniques has not been fully investigated, tentative results obtained by different workers indicate that depolymerisation does in fact lead to improved selectivity of the solvent extraction process. When some depolymerisation took place as a result of increasing the extraction temperature the effectiveness of desulphurization by solvent extraction was significantly improved [10].

Coke depolymerisation can be effected by different methods including mild hydrogenation, microwave heating [11], prepyrolysis and pre-oxidation. While some sulphur compounds may undergo thermal decomposition at temperatures below 750 K, such as many mercaptans, which decompose at about 600 K and some sulphides which decompose at 530–670 K [7], most organic sulphur compounds which make up much of the organic sulphur in coke do not decompose at such low temperatures. On the other hand, experimental evidence indicates that coke preoxidation may improve the efficiency of thermal desulphurization processes. When air was injected during the thermal treatment of coke in combination with effluent gas recirculation, very good desulphurization results were achieved due to the partial combustion of coke [12, 13]. Pre-oxidizing the coke at moderate temperatures may also render it more amenable to other desulphurization processes such as chemical treatment with methane [14] and hydrodesulphurization [15, 16]. Up to 75% of the sulphur present in the oil sands coke was removed when the coke was pre-oxidized at 550 K for eight hours followed by hydrodesulphurization with hydrogen at 920 K for eight hours [15]. It has been suggested that the physical basis for this may be based on the chemistry of such thiophenic compounds in coke that are most resistant to conversion by hydrodesulphurization but are most readily amenable to oxidation and extractive desulphurization.

This beneficial effect of pre-oxidation may equally apply to desulphurization by solvent extraction. Zannikos et al. report that a combination of oxidation with solvent extraction is capable of removing up to 90% of the sulphur compounds in petroleum fractions at acceptable yields [17]. Funakoshi and Aida used a simple solvent extraction process to remove sulphur from various hydrocarbon fuels (ranging from gasoline to straight-run bottoms). Using acetone, dimethylformamide or other solvents, more than 90% sulphur removal could be achieved through six to eight stages of extractions with a solvent to oil ratio of 1. When an oxidation step was applied before the extraction, a higher degree of sulphur removal was obtained [18]. In similar conditions, the sulphur compounds in vacuum gas oil were removed successfully by pre-oxidation and extraction by Shiraishi and Hirai [19].

The beneficial effect of pre-oxidation is probably due to the oxidation of the sulphur bonded into the coke matrix, which would be expected to weaken the C-S bonds without at the same time destroying the hydrocarbon matrix. Partial oxidation of the hydrocarbon matrix would, however, be expected and this favours the removal of sulphur, but the key to a desulphurization process based on oxidation would be the minimization of the oxidation of the remainder of the hydrocarbon matrix, which is not always easy [7]. Sulphur removal is probably related to the resulting weight loss of the coke and its improved porosity.

The oxidation potential of organic sulphur compounds would lie roughly in the same region as amines and alcohols. These compounds are vastly more susceptible to oxidation than ethers and benzene derivatives [7]. Organic thiols may be oxidized to disulphides, which may in turn be oxidized to give finally sulphonic acids.

$R_1S_xR_2 \quad \rightarrow R_1SO_3H + R_2SO_3H$

Thus, at every former sulphur position, which has been oxidized and hydrolyzed, an alcohol functional group would remain.

The polarity difference between the sulphur compounds and hydrocarbons found in coke may also be increased as a result of pre-oxidation. Such an approach may be based on the polarity difference between the thiophenic compounds and the hydrocarbons. Because thiophenic compounds comprise many different compounds, they represent a range of solvent polarities, in some cases quite similar to some of the hydrocarbons found in coke. The critical polarity difference between individual hydrocarbon and thiophenic compounds is therefore variable, and in some cases may be insufficient to allow a functional separation by solvent extraction. Polarity difference can, however, be increased by oxidizing the thiophenic sulphur to the corresponding more polar mono- and dioxides, the alkylated aryl thiophene sulphoxide or sulphone. This in turn facilitates the separation and makes possible the extraction of sulphur after a preliminary step of oxidation [20].

It is the aim of the present work to study the effect of coke pre-oxidation on the efficiency of sulphur removal by solvent extraction, thus rendering this simple but otherwise ineffective method of coke desulphurization more attractive and efficient.

Coke pre-oxidation

Multiple coke samples were obtained from the delayed coking unit at the Homs Oil Refinery, where the crude oil processed is mostly a blend of two crude oil varieties, with the blending ratio varying at different times. The heavy residue materials are coked at the delayed coking unit at a temperature of 760 K and a pressure in the range 1.4-1.6 bars.

Multiple coke samples were carefully blended in order to obtain representative samples. The coke samples were crushed, dried and then pulverized to pass a 250-μm sieve. Proximate and ultimate analysis tests were carried out on the samples using standard ASTM test methods (Tables 1-2). The coke samples were then placed in an electric furnace and heated at a controlled rate for 15 minutes at a moderate temperature (600 K). Coke pre-oxidation at lower temperatures is to be preferred because of its expected effects on maximizing the rate of desulphurization and reducing coke consumption at the same time as will be explained below. The optimum temperature for pre-oxidation was found to be in the range 570–620 K [16, 23, 24, 26]. Pre-oxidizing the coke at a lower temperature (550 K) did not have a beneficial effect [15], while the reaction was found to be too slow at 630 K [16].

There is evidence to indicate that using steam as an oxidizing agent would significantly increase sulphur removal. Also, the addition of water during the pre-oxidation treatment may accelerate oxidation especially at lower temperatures, probably by accelerating the liberation of oxidized carbon from the coke surface, thus increasing the surface area of the coke. However, using a mixture of air and steam seems to inhibit desulphurization [15, 22]. Mochida et. al. [23] using ground coke found this role to be small, but when lump coke was used, varying the amount of water slightly changed the desulphurization level significantly [25]. In the present work, the coke samples were heated in air and no steam was used.

During pre-oxidation, water that enters the coke during the hydraulic coke cut is removed at about 400–500 K. The volatile matter, for the most part, distils off also during pre-oxidation exposing thereby the pores and typical lamellar structure of the treated coke. A certain concentration of CO due to the partial combustion of coke and volatiles soon developed.

In agreement with work published by earlier workers [21]-[25], coke pre-oxidation in the low temperature range used lead to some sulphur removal (7%). In comparison, when coal was heated to 450°C in air a maximum of 20% of the organic sulphur was removed [7]. The amount of sulphur removal is related to the weight loss regardless of temperature, but the rate of sulphur reduction is greater at lower temperatures (Table 3), a fact that indicates, according to some, a more selective SO_2 formation at lower temperatures. This preferential oxidation of sulphur as compared with carbon, which takes place at lower temperatures, allows more effective desulphurization with a lower consumption of coke. Lower temperature pre-oxidation promotes higher levels of hydrodesulphurization as well.

Tab. 3. Pre-oxidation of coke.

Temp., K	Time, min.	Desulph., %	Wt. Loss, %	Ref.
720	15	19	27	23
720	45	5	4	25
670	35	23	24	23
620	65	5	4	24
620	125	25	21	23

As to be expected, pre-oxidation would be accompanied by an increase in oxygen and nitrogen and a decrease in carbon content. The coke tends to oxidize or "cure" by adsorbing oxygen at temperatures below 473 K. Addition of oxygen in general tends to promote cross-linking between the graphitoid structures in coke irreversibly decreasing its anisotropy [27]. The presence of oxygen atoms may also strengthen the coke structure sufficiently to make the coke less susceptible to sintering [15]. Carbon-nitrogen complexes are not likely to be formed at this low temperature range [27].

The coke porosity increased on oxidation due to the creation of micro and macroporosity. The increased microporosity may represent the creation of shrinkage cracks as well as pores formed due the escape of volatile matter and other weight loss. As a result of such increase in the coke porosity, its apparent density (DA) measured by Hg pycnometer decreased. The real or true density (DR_{10-20}) of the coke, measured by He pycnometer, also changed significantly on oxidation. It was found to increase from 1.39 g/cm^3 to 1.52. This increase is slightly greater than the corresponding increase found on thermally treating the coke to a similar temperature range [28].

Some increase in the surface area on pre-oxidation is to be expected, particularly at low temperatures ($<$ 700 K) (Table 4). This may be due to the opening up of micropores in the coke matrix or the spreading apart of planes of largely polycyclic carbon causing the exposure of a larger surface area [15, 23]. Pre-oxidation induces also many large cracks in almost all grain cokes at temperatures less than 700 K [23]. When lump coke was pre-oxidized, a large number of small cracks were induced in the coke surface, but these were removed on polishing which indicates that they were very shallow in comparison with grain size [24]. In the present work, even though there is no single experimental method that is a standard method or an approved method to be used for the determination of surface area, the BET method based on the adsorption of nitrogen at 77 K was chosen because it is the preferred method that is normally assumed and quoted. The BET surface area for the treated Syrian coke was found to have increased from an average of 0.04 to 52 m^2/g.

Tab. 4. Variation of surface area with pre-oxidation temperature [16]

Temp. K	Surface area (m^2/g)
Initial value	7.0
610	163
640	339
670	199
730	83
860	10

Weight loss can indeed be substantial if pre-oxidation is prolonged. Mason reported 38% weight loss after pre-oxidation at 640 K for 1020 minutes [11]. The residence time used in the present work, 15 minutes, insured a much smaller weight loss, which was on average about 25%. The calorific value was also reduced but only by about 14%. Table 5 gives a summary of the effects of pre-oxidation on the treated coke.

Tab. 5. Effects of pre-oxidation on the treated coke.

Treated coke	Initial values	
7.2	7.7	Sulphur (wt %)
1.52	1.39	Real density g/cm^3
52	0.04	Surface area m^2/g
0.442	0.395	Porosity cm^3/g
25	-	Weight loss (wt %)
$30.2\ 10^3$	$35.1\ 10^3$	Gross Calorific Value kJ/kg

Solvent extraction

As materials of similar chemical structure are more likely to be mutually soluble in one another, aromatic and similar organic compounds might be used as solvents for the extractive desulphurization of petroleum coke where the sulphur is mostly organic and thiophenes make up most of the sulphur present in the coke. Experience with coal indicates that weak organic acids such as phenols and nitrobenzene are more effective than other organic solvents [7]. These could be used to dissolve sulphides and disulphides and possibly some thiophenes as well.

Extractions with coke using a large variety of solvents were made by different workers. Table 6 gives a summary of the results obtained. Extractions using petroleum ether [29], dioxane [29] or hydrochloric acid [29,30] lead to no sulphur removal. As can be seen from Table 6 the most efficient solvents used were o-chlorophenol and pyridine with a maximum desulphurization of 20% and 19% respectively.

Tab. 6. Desulphurization of petroleum coke by solvent extraction

Solvent	Reaction time (hr)	Max. Desulph. (%)	Ref.
o-chlorophenol	120	20	10
Pyridine	4	19	30
	48	9	15
	120	0.4	29
Aqua regia (1)	2	14	30
	120	–	29
Phenol	2	14	30
Furfural	4	14	30
	48	5	15
Chlorex (2)	4	13	30
Naphthalene	2	13	30
p-cresol	–	8.8	15
Xylene	48	9	15
	120	-	29
Benzene	48	7	15
	6	2	30
	–	2	21
	120	2	29
	8	1	31
Nitrobenzene	–	7.4	15
Ethanolamine	6(3)	6	30
	120	0.2	29
	2	–	30
Toluene	48	5	15
	6	2	30
	120	–	29
Acetone	–	2	21
CCl_4	6	1	30
	120	–	29
CS_2	6	S increase	30
		1	21
	120	–	29

1 Heating just below the boiling point.

2 B, B, dichloroethylether.

3 At room temperature.

Ortho-chlorophenol or 2-chlorophenol C_6H_5ClO is a liquid at room temperature with a boiling point of 449 K. It is an unpleasant water-soluble combustible liquid that is strong irritant to tissue and toxic by skin absorption, inhalation or ingestion and strong irritant to tissue.

Phillips and Chao [10] used o-chlorophenol as the extraction solvent. Their results show that the smaller the particle size of coke, the greater the amount of sulphur removed. At 430 K the optimum reaction time was found to be two hours. Longer time will not further reduce the sulphur content by any significant amount, for all the soluble sulphur would have been removed by the end of the second hour.

Pyridine is a heterocyclic organic compound C_5H_5N. It is a colourless, flammable liquid soluble in water with a boiling point of 388 K. It is a widely used polar but aprotic solvent and it has been used in the refining industry for the treatment of lubricating oils. Sabott [30] tried to use it for refluxing coke for a period of four hours. The extracted coke was filtered and washed ten times with ether. The pyridine coke mixture formed a slime which was difficult to filter and wash.

In order to investigate the effects of pre-oxidation on the efficiency of desulphurization by solvent extraction, extractions with oxidized samples of coke were made in a Soxhlet extractor for two hours using o-chlorophenol and pyridine as solvents. In the choice of the solvents and reaction time, use was made of the results summarized in Table 6.

Results of the extractive desulphurization tests are given in Table 7, where the desulphurization efficiency is seen to have greatly improved as a result of the pre-oxidation treatment. The maximum desulphurization obtained was 76%. The fact that pre-oxidation favours the removal of sulphur is most probably related to the resulting weight loss of the coke and its improved porosity. Treating the coke for longer periods of time would probably improve the desulphurization efficiency even further, but any advantage that is gained thereby would be offset to a certain extent by the resulting greater weight loss of the coke and its reduced calorific value.

Tab. 7. Maximum desulphurization by solvent extraction of pre-oxidized Syrian petroleum coke samples.

Solvent	Maximum desulphurization %	
	Green coke	Pre-oxidized coke
o-chlorophenol	20	76
pyridine	19	69

Conclusion

The results obtained show clearly that pre-oxidation of coke at moderate temperatures for a short period of time renders the coke more amenable to treatment by solvent extraction. Extracting pre-oxidized coke samples improved significantly the desulphurization efficiency and a maximum desulphurization of 76% was achieved using o-chlorophenol as solvent. Complete elimination of the thiophenic and other sulphur compounds however was not achieved due in all probability to incomplete oxidation or to ineffective extraction where the choice of the solvent plays a very important role.

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