

Sulphur Separation by Heat Treatment of Petroleum Coke

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The impact of heat treatment (temperature, heat-soak time and heating rate) on petroleum coke properties were examined. Investigated coke produced from feedstock with different compositions. The sulphur content, volatile matter, density value and ash content before and after heat treatment to 2 400 °C were analysed.

Results implies partially desulphurization of the coke by performed examinations. Phase analysis of the cokes showed that during the heating, separation and transformation of some inorganic sulphur compounds took place. The sulphides are most stable sulphur compounds identified even after heating coke at 2 400 °C.

Key words: Heat treatment, petroleum coke, sulphur

INTRODUCTION

Petroleum coke is a solid residue of oil refining. According to world indicators, 3.1% of oil on average is refined into petroleum coke.

Depending on its content in oil, i.e. coking feedstock, petroleum coke can contain up to 7% of sulphur.^{4,15,20}

Sulphur content in petroleum coke is a significant indicator of the properties important for its application. It is directly related to sulphur content in the coking feedstock, i.e. oil. Sulphur and its compounds in oil are responsible for difficulties which arise during storage, processing and transportation, which partially pass into obtained products, diminishing their quality. Typical problems refer to catalyst contamination and deactivation, corrosion of units and formation of compounds such as SO₂ and H₂S, which can cause serious consequences for the health of people and protection of the environment.

Characterization and distribution of sulphur compounds in oil and its products is important for successful elimination of sulphur, employing different desulphurization processes. Sulphur is the third ele-

ment (after carbon and hydrogen) in heavy fractions of oil. Since sulphur compounds are parts of complex composition mixtures in the coking feedstock, interactions with other compounds sometimes make identification difficult.

Elemental sulphur, hydrogen sulphide, mercaptanes, sulphides, disulphides, thiophene and its homologues have been found in oil and its fractions. However, sulphur is mostly present in the form of thiophene, sulphide, mercaptan and disulphide. Organic sulphur predominates in petroleum cokes.^{6,16,19,21} Breaking of C-S bonds in organic groups and separation of sulphur can be achieved in several ways: through calcination at higher temperatures, hydrodesulphurization and chemical treatment with different agents and acids.^{2,7,11,14,18}

The paper investigates the impact of heat treatment at high temperatures (up to 2 400 °C) on separation of sulphur and changes in some physical and chemical properties of petroleum coke.

Table 1. The basic characteristics of the coking feedstock

Characteristic	Atmospheric residue	Pyrolysis residue	Decanted oil
Density, kgm ⁻³	940	1 050	1 012
C/H ratio	1.5	1.68	1.4
Carbon, wt. %	84	89	82
Sulphur, wt. %	1.3	0.3	1.1
Aromatics, wt %	38	68	56
Asphaltens, wt. %	0.6	6.1	0.8
Ash, wt. %	0.02	0.018	0.019
Iron, mgkg ⁻¹	28	32	10
Nickel, mgkg ⁻¹	75	32	45
Vanadium, mgkg ⁻¹	7	3	5

Table 2. The basic properties of petroleum coke		
Properties	Sample	
	Coke 1	Coke 2
Density, kgm ⁻³	2 086	2 126
Volatile matter, wt. %	0.16	0.15
Sulphur, wt. %	1.67	0.73
Ash, wt. %	0.134	0.112
Iron, mgkg ⁻¹	120	52
Nickel, mgkg ⁻¹	267	101
Vanadium, mgkg ⁻¹	17	13

EXPERIMENTAL PART

Sulphur content was determined before and after heat treatment (HT) of petroleum coke samples at 1 500, 2 000 and 2 400 °C. The samples were heated at rates of 10 °C/min and 60 °C/min during 2 and 4 hours. For the determination of types of sulphur compounds, phase analysis of the coke ashes was applied before and after heat treatment.

Samples

Coke samples obtained by coking of feedstocks with different compositions were tested.

Coke 1 is a calcined coke produced from light atmospheric residue of a mixture of crude oils of domestic origin (70% from the Moslavina region and 30% from the Slavonija region), and coke 2 is calcined coke produced from a mixture of atmospheric residue (50%), decanted oil (25%) and pyrolysis residue of the same crude oil. Characteristics of the coking feedstock are shown in Table 1, and basic properties of petroleum cokes in Table 2.

Heat treatment of petroleum coke

Coke samples were subjected to heat treatment in inert atmosphere (argon) in a high-temperature "Astro" oven, type 1000-3060 FP, with boron-graphite thermocouple. Temperature, time and rate of heating were programmed by the "Theta" temperature programmer.

Transformation of samples into ash

5 g of coke with $\leq 63 \mu\text{m}$ grain-size particles were first dried at 110 °C to the constant mass. Afterwards they were heated for 1 hour at 500 °C, 2 hours at 750 °C and finally at 950 °C to the constant ash mass.

Determination of mass loss, density and sulphur content

Mass loss was determined from the difference in mass of the sample before and after HT of petroleum coke.

Coke density was determined applying the standard DIN 51 901 method.

The sulphur content in coke samples was determined by the standard DIN 57 724 method.

Determination of the type of inorganic sulphur compounds

Ash samples were crushed in an achat mortar and introduced into the 0.3 mm capillary made of Lindemann glass. The types of inorganic sulphur compounds (phase analysis) were determined applying the X-ray diffraction

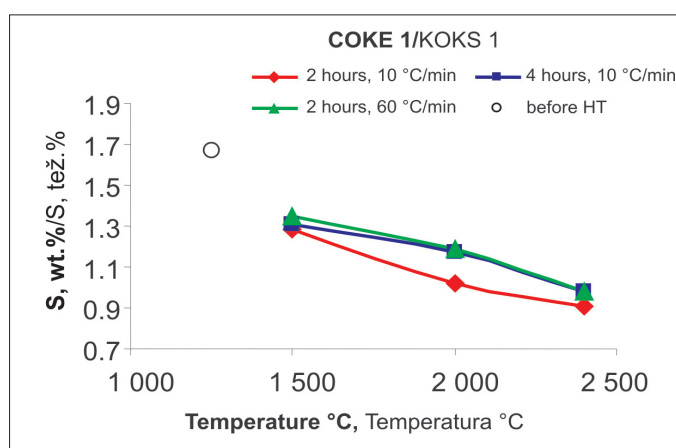


Fig. 1. Change of sulphur content by HT (coke 1)
Sl. 1. Promjena sadržaja sumpora nakon TO koksa 1

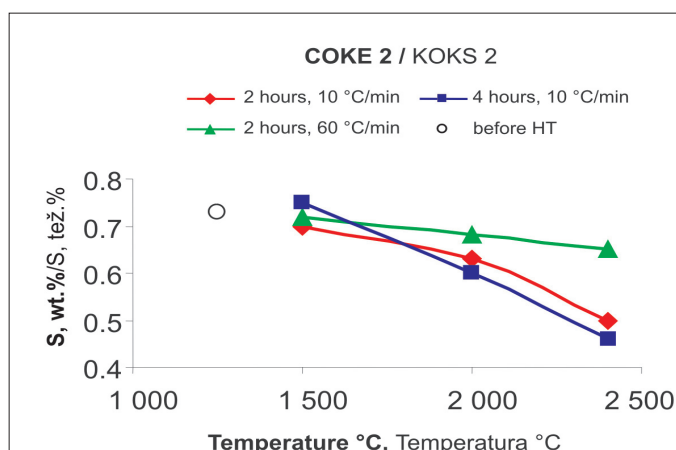


Fig. 2. Change of sulphur content by HT (coke 2)
Sl. 2. Promjena sadržaja sumpora nakon TO koksa 2

Table 3. Properties of coke as a function of heat treatment temperature and heat-soak time (heating rate of 10 °C/min)

Sample	Properties	1 500 °C		2 000 °C		2 400 °C	
		2 hrs	4 hrs	2 hrs	4 hrs	2 hrs	4 hrs
Coke 1	Mass loss, mgg ⁻¹	2.3	3.1	8.2	13.6	14.8	19.7
	Ash, wt. %	0.12	0.11	0.105	0.104	0.102	0.10
	Density, kgm ⁻³	2 088	2 088	2 091	2 095	2 096	2 100
Coke 2	Mass loss, mgg ⁻¹	4.0	4.1	5.8	6.4	12.1	13.8
	Ash, wt. %	0.104	0.94	0.097	0.091	0.090	0.89
	Density, kgm ⁻³	2 138	2 137	2 148	2 150	2 168	2 173

Table 4. Types of sulphur compounds identified in the ash of coke (heating rate of 60 °C/min)

Sample	Chemical type of sulphur						
	Before HT	After HT					
		1 500 °C		2 000 °C		2 400 °C	
		2 hrs	4 hrs	2 hrs	4 hrs	2 hrs	4 hrs
Coke 1	Ni ₃ S ₂ CaSO ₄ FeS S	Ni ₃ S ₂ TiS	NiS ₂ TiS	NiS ₂	CaSO ₄	βNi ₇ S ₆ CaSO ₄	βNi ₇ S ₆
Coke 2	NiS K ₃ Na(SO ₄) CaSO ₄ TiS S	NiS TiS K ₃ Na(SO ₄)	Ni CaSO ₄ S	TiS NiS	NiS	α Ni ₇ S ₆	α Ni ₇ S ₆

method (XRD) using Philips-Norcelo device and applying CoK α radiation.

RESULTS AND DISCUSSION

Results of investigation of the change in sulphur content in analyzed petroleum cokes are shown in Figures 1 and 2. It is evident that the increase in heating temperature results in gradual decrease of sulphur content regardless of the heat-soak time and rate of sample heating. Higher separation of sulphur from coke 1 was recorded during slower (heating rate of 10 °C/min) and shorter (2 hours) heating. From the initial 1.67% of sulphur in coke 1 only 0.91% of sulphur remained after HT at 2 400 °C (Figure 1). Similar results (Figure 2) were obtained for coke 2 which contained 0.73% of sulphur before heat treatment. In view of the lower initial content, after heating of coke 2 at 2 400 °C the sulphur content diminished to 0.65-0.46% depending of heat treatment conditions.

These results are supplemented by the analysis of mass loss, ash content and density, shown in Table 3.

In difference to change in sulphur content, increase of heating temperature results in higher mass loss and diminished ash content. After longer heating (4 hours) loss of mass is higher and ash content in coke is lower. These results can be explained by separation of additional components (other than sulphur) from coke. Earlier investigation showed that heat treatment leads to partial separation of metallic and non-metallic components from coke.¹²

The data from Table 2 show differences in other properties of analyzed cokes (density, content of volatile substances and certain metals) before HT. Namely, the properties of coke depend on the type and properties of the coking feedstock. The content of aromatic hydrocarbons is higher in cokes produced by thermal cracking of the feedstock, while naphthenes predominate in cokes produced by vacuum distillation of the feedstock. Coke 1 is produced from the feedstock with higher sulphur content (1.3%, Table 1). Decanted oil, and atmospheric residue in particular, have higher sulphur and metal content in different chemical forms in comparison with pyrolysis

Table 5. Types of sulphur compounds identified in the ash of coke (heating rate of 10 °C/min)

Sample	Chemical type of sulphur						
	Before HT	After HT					
		1 500 °C		2 000 °C		2 400 °C	
		2 hrs	4 hrs	2 hrs	4 hrs	2 hrs	4 hrs
Coke 1	Ni ₃ S CaSO ₄ FeS S	Ni ₃ S ₂	NiS ₂	NiS ₂	CaSO ₄	βNi ₇ S ₆	βNi ₇ S ₆
Coke 2	NiS K ₃ Na(SO ₄) ₂ TiS S	NiS TiS	NiS	Na ₂ SO ₄ NiS	NiS	Na ₂ SO ₄ α Ni ₇ S ₆	α Ni ₇ S ₆

residue.^{13,15} Atmospheric residue and decanted oil have less aliphatic compounds than the pyrolysis residue. Aliphatic character is expressed by the presence of numerous side chains consisting of 2-4 atoms, which mutually bond aromatic compounds and contribute to higher density. Table 2 demonstrates that density of coke 1 amounts to 2 086 kgm⁻³ and density of coke 2 (produced from a mixture of atmospheric residue, pyrolysis residue and decanted oil) is 2 126 kgm⁻³.

Tables 4 and 5 shows inorganic compounds of sulphur obtained by XRD analysis of ashes of the analyzed cokes after HT at different heating rates (60 °C/min and 10 °C/min). Presence of elemental sulphur, sulphides (Ni₃S₂ and FeS) and sulphate CaSO₄ was determined in coke 1 before HT. In coke 2 are present elemental sulphur, sulphides (NiS, TiS), and sulphates CaSO₄ and K₃Na(SO₄)₂. The identified sulphur compounds in cokes are either originally present or are a consequence of coke transformation into ash (mostly sulphates). After faster heating (60 °C/min), higher separation of sulphur from both cokes was recorded only above 2 000 °C, which is indicated by the higher number of identified compounds (Table 4). Table 5 shows types of sulphur compounds after slower heating (10 °C/min) of the same coke samples. The table shows somewhat lower number of identified sulphur compounds in comparison with the same samples subjected to heating at higher heating rates. The results are in agreement with the results of change in sulphur content of coke after HT (Figures 1 and 2), where lower content of sulphur was recorded after slower heating.

According to the data from literature¹⁷, application of heat treatment up to 1 000 °C results in separation of sulphur in the form of H₂S. Elemental sulphur is separated between 1 000 - 1 300 °C, and partly metallic sulphides above 1 500 °C.

The obtained results show that after heat treatment of coke up to 2 400 °C, inorganic sulphur mostly remains in the form of metallic sulphides. Separation of sulphur depends on the stability of compounds and on possible

transformations under high temperature conditions. Stability of sulphur compounds at higher temperatures is affected by the strength of bonds between sulphur and carbon, particularly in heterocyclic rings of organic compounds. For example, sulphur present within thiophene rings is chemically and thermodynamically more stable than sulphur associated with the core of aromatic compounds. Accordingly, partial disassociation of otherwise stable C-S bonds in organic structures of coke occurs only at high temperatures (2 100 - 2 200 °C). Some authors explain the stability of sulphur compounds by the fact that sulphur atom can have 2, 4 and 6 valence bonds, whose breaking requires more thermal energy than the breaking of single bonds in, for example, hydrogen.^{1,8,10}

Irreversible expansion of coke volume is possible during heat treatment (1 400 - 2 000 °C) due to the pressure of separated sulphur compounds and nitrogen (so-called coke „puffing“). It is accompanied by the change in structure and the change of certain coke properties (higher porosity, lower density, strength, electrical and thermal conductivity), which is particularly important for petroleum coke used in the production of graphite products (such as carbon electrodes, construction products). Irreversible expansion of carbon during heat treatment can be reduced or arrested by slow heating or addition of inhibitors such as certain metals and their compounds. If coke “puffing” was caused by separation of sulphur, iron and its compounds are most often used as inhibitors.^{3,5,9}

CONCLUSION

Results of investigation demonstrated that during heat treatment (up to 2 400 °C), partial desulphurization of analyzed petroleum cokes took place. In addition to temperature, separation of sulphur from petroleum coke is also affected by heat-soak time and heating rate. Slightly higher separation of sulphur was achieved when shorter heat-soak times at slower heating rates were applied.

According to the results of phase analysis, before HT sulphur is present in elemental form and in the form of metallic sulphides and sulphates. After the heating of pe-

troleum coke, partial separation and transformation of inorganic sulphur compounds takes place and sulphides are the most stable compounds (identified even after HT at 2 400 °C). Separation of sulphur depends on the composition of the coking feedstock and strength of C-S bond in the coke structure. Longer heat-soak time results in higher loss of mass, and in higher density of coke. In view of that, it can be concluded that risk factors for possible "coke puffing" caused by separation of sulphur, particularly in the case of heating of coke 2, are lower.

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