Environmental Protection Research
https://ojs.wiserpub.com/index.php/EPR/

UNIVERSAL WISER
PUBLISHER

Short Communication

In-situ Formation of Sulphur-Trapped Petroleum Coke via Thermal Cracking of Vacuum Residue: A Practical Approach to Reduce Environmental Pollution

Supriyo Majumder*, **Shalini Gupta, Chiranjeevi Thota, Bharat L. Newalkar**

Corporate R&D Centre, Bharat Petroleum Corporation Limited, Greater Noida, Uttar Pradesh, India
E-mail: supriyomajumder@bharatpetroleum.in

Received: 8 May 2023; **Revised:** 26 July 2023; **Accepted:** 19 September 2023

Abstract: Environmental regulations restrict the use of high-sulphur petroleum coke as a solid fuel due to the emission of a substantial amount of sulphur oxides (SOx) upon combustion. Therefore, the free sulphur present in petroleum coke needs to be reduced to achieve lower SOx emissions. This paper describes a novel and efficient method for the trapping of free sulphur in petroleum coke during its formation from vacuum residue in the presence of an additive. Among the various additives tested, calcium oxide (10 wt%) was found to be most effective for maximum trapping of free sulphur in petroleum coke. This sulphur-trapped petroleum coke reduces SO_2 emissions by 67% upon combustion; hence, it can be used as a better fuel than regular high-sulphur petroleum coke. Thus, by replacing regular petroleum coke with this newly developed sulphur-trapped petroleum coke, environmental pollution can be reduced significantly.

***Keywords*:** petroleum coke, sulphur reduction, vacuum residue, calcium oxide

1. Introduction

In Asia, India is the second-largest consumer of petroleum coke after China. The annual consumption of petroleum coke in India is around 14.44 million metric tonnes (MMT), according to the latest statistics compiled by the Ministry of Petroleum and Natural Gas, Government of India. However, the production of petroleum coke in the country is only 12.45 MMT (worldwide production is 134 MMT as of 2016 data); hence, there is a substantial demand and supply gap, and the excess consumption is catered to through imports from global sources. The cement, power, and steel industries are the predominant consumers of petroleum coke. Additionally, the chemical, brick, and textile industries are also significant consumers of this material.

Although petroleum coke is an inexpensive fuel material, its high content of sulphur restricts its wide use as a fuel due to the emission of a substantial amount of sulphur oxides (SOx) upon combustion, creating tremendous environmental pollution. The SOx emission from petroleum coke is directly related to the amount of easily combustible free sulphur compounds present in it. The sulphur content of petroleum coke varies from less than 1% to more than 10%, mainly depending on the sulphur content of the petroleum feedstock [1]. Sponge coke contains approximately 4 to 6 wt% of sulphur and is used as a fuel material. However, petroleum coke with less than 4% sulphur is generally blended with a high-sulphur variant to achieve the desired sulphur level in the blended product. Needle coke, primarily used for making electrodes, contains less than ~ 1% of sulphur. Most of the sulphur species in petroleum coke exist as

DOI: https://doi.org/10.37256/epr.3220232992

organic sulphur bound to the carbon matrix of the coke [2]. A small amount of sulphur (in general, no more than 0.05% of the total sulphur) also exists as inorganic sulphur in the coke. Major organic sulphur components in petroleum coke are believed to be thiophenes, benzothiophenes, and dibenzothipthiophenes, as these are the predominant species in heavier hydrocarbon fractions. Some organic sulphides may also be present as side chains of aromatic or naphthenic molecules.

Due to environmental regulations, petroleum coke with higher levels of sulphur is not suitable for industrial use as fuel due to the emission of substantial amounts of pollutants upon combustion. Hence, desulphurisation of petroleum coke is a challenge for refiners and, therefore, an active area of research. Methods for desulphurisation of petroleum coke involve extraction with a suitable polar solvent, high-temperature calcination, hydrodesulphurisation, microbial desulphurisation, oxidative desulphurisation, and alkali calcination [3, 4]. Extractive desulphurisation of petroleum coke is the most convenient way to reduce sulphur, but the method is inefficient, and a maximum of 20% reduction in sulphur level can be achieved [5]. However, extractive desulphurisation efficiency can be improved with pre-oxidised petroleum coke, and up to 76% desulphurisation was reported [6]. The desulphurisation of petroleum coke via calcination at an elevated temperature has been extensively investigated. Ibrahim [7] reported that the desulphurisation efficiency of Syrian petroleum coke reaches 80% at 1,375 °C and further increases to 88% at 1,425 °C. Although high-temperature calcination substantially reduces sulphur content in petroleum coke, the method is energy-intensive and may not be viable economically. The desulphurisation of petroleum coke can be achieved at a lower temperature in the presence of hydrogen. Gillot et al. [8] reported a 50% reduction in sulphur at 800 °C and a 92% reduction at 1,300 °C. Later, Saha and Tollefson [9] heated petroleum coke to 800 °C for 90 min in the presence of hydrogen flow and observed 86.6% desulphurisation efficiency. Although desulphurisation in the presence of hydrogen is efficient, the method is a potential safety hazard with H_2 as a reducing agent. Bio-desulphurisation (BDS) of petroleum coke was reported by Agarwal et al. [10], where the authors developed an integrated approach via nitric acid pre-treatment followed by BDS using Pantoea agglomerans D23W3 and removed almost 50% sulphur from the petroleum coke. Desulphurisation of petroleum coke via calcination in the presence of an excess amount of alkali is known to reduce the sulphur content of petroleum coke substantially [11, 12]. In a recent development, researchers found that with an alkali-to-coke ratio of 2, a reaction temperature of 500 °C, and a reaction time of 2 h, the desulphurisation of petroleum coke reached 98% when NaOH powder was used as an alkali source [13]. Although the alkali calcination technique reduces sulphur content in petroleum coke to a large extent, the method is not economically viable due to the stoichiometric use of caustic. Moreover, the method produces a large quantity of hazardous alkali waste, which is difficult to handle and dispose of. Desulphurisation of petroleum coke in the presence of ammonia has been reported lately [14], in which more than 80% of organic sulphur was removed at 800 °C.

The key concern in the use of petroleum coke as an industrial fuel is the emission of SOx upon combustion. Moreover, SOx production is directly proportional to the amount of free sulphur (easily combustible) present in the petroleum coke. Therefore, a viable option could be the trapping of the free sulphur present in petroleum coke as inorganic sulphide or sulphate, which may not liberate SOx upon combustion. Although most of the reported petroleum coke desulphurisation techniques deal with the post-treatment of the material, very limited reports are available regarding the in-situ trapping of sulphur in petroleum coke during its formation from vacuum residue. In-situ formation of sulphur-trapped petroleum coke is advantageous over post-treatment methods as the process is less capex-intensive and existing hardware in delayed coking plants can be utilised for the same. As a result, the trapping of the free sulphur in petroleum coke during its formation is a unique but economically viable proposition.

This paper describes lab-scale studies on the in-situ formation of sulphur-trapped petroleum coke from vacuum residue via thermal cracking in the presence of commercially available additives. Experiments were carried out systematically to optimise the quantity of additive that can be employed for significant trapping of free sulphur in petroleum coke. Moreover, these sulphur-trapped petroleum cokes were tested for SOx emissions upon combustion.

2. Materials and methods

A vacuum residue sample was collected from BPCL Bina Refinery (BR), India, and the specification of the sample is given in Table 1. Other chemicals were purchased from commercial vendors and used as is in the reaction without any further purification. The sulphur content of petroleum coke samples was analysed using a sulphur analyser (LECO

Corporation, Model TruSpec S) following ASTM D 4239-C. SO_2 emissions post-combustion of petroleum coke were analysed with the analyser (Yokogawa, Model IR200).

Table 1. Specification of BR vacuum residue

BR vacuum residue properties	
Specific gravity (g/cc)	1.0196
Total sulphur (wt%)	5.19
Sodium (ppmw)	15
Asphaltenes (wt%)	21
Conradson carbon residue (wt%)	23.99
Distillation (SIMDIST)	
5% recovery	562 °C

Note: SIMDIST = Simulated distillation

3. Experimental details

3.1 *Preparation of sulphur-trapped petroleum coke*

Experiments were carried out in a 500-ml autoclave (high-pressure and high-temperature batch reactor). In a typical experiment, 100 g of vacuum residue (preheated to 120 °C in an oven) and 5 g of additive were charged in an autoclave (a list of additives used in the process is given in Table 2). The mixture was slowly heated to 470 °C at a rate of 5 °C/min with continuous mechanical stirring. The autoclave was heated further and kept at 470 °C for 1 hour before cooling to room temperature. Liquid products were collected from the fractionator. The solid petroleum coke formed in the autoclave was collected and mixed with 100 mL of toluene. The mixture was refluxed for 2 h, cooled to room temperature, and filtered. The solid was washed with toluene and dried in an oven at 150 °C for 6 h. Dried petroleum coke samples were crushed to powder and analysed for sulphur content. A photo of the laboratory experimental setup is given in Figure 1.

3.2 *Combustion of petroleum coke*

A quartz reactor was charged with 100 mg of petroleum coke. The reactor was heated to 150 °C for 1 h in the presence of a continuous flow of N_2. The gas was changed to zero air, and the reactor was heated further to 600 °C at a rate of 10 °C/min. The produced gas mixture was passed through a SO_2 analyser.

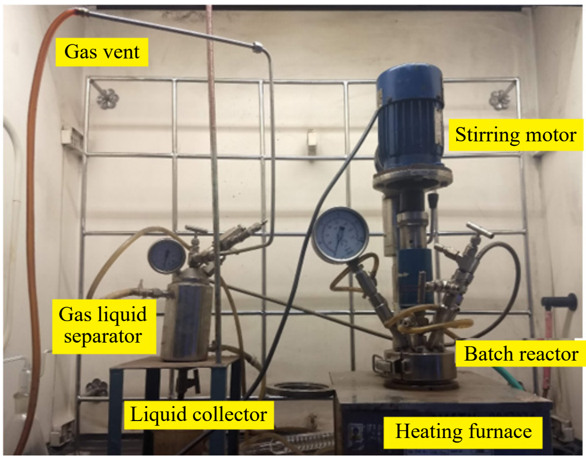


Figure 1. Laboratory experimental setup

4. Results

Alkali and alkaline earth metal oxides, hydroxides, and carbonates are capable of de-sulphurising a variety of organo-sulphur compounds, such as mercaptans, organic sulphide, and thiophenes, when mixed with petroleum pitch, coal tar pitch, and coke at elevated temperatures [15]. Interestingly, some of these sulphur compounds are also predominant in heavier hydrocarbon fractions, like vacuum residue. Hence, we explored alkaline earth metal oxide and their precursors as additives for the formation of sulphur-trapped petroleum coke during the thermal cracking of vacuum residue. The sulphur trapping efficiency of various alkaline earth metal compounds is given in Table 2. Petroleum coke produced via the thermal cracking process without any additive contains 7.54 wt% sulphur (Table 2, Entry 1). This is regarded as the free sulphur present in petroleum coke. However, the addition of 2.5 wt% of CaO or $Ca(OH)_2$ (Table 2, entries 2 and 3) produced petroleum coke with 6.30% and 6.62% free sulphur content, respectively. $CaCl_2$ (Table 2, Entry 4) was also quite efficient in the formation of petroleum coke with a lower sulphur content (6.43%). Other calcium salts were not effective, and only 3.8% trapping of the sulphur content was observed with $Ca(NO_3)_2$ (Table 2, Entry 5). $CaCO_3$, which is known to reduce sulphur content in petroleum coke upon calcination at 1,000 °C, is also found to be an efficient additive (Table 2, Entry 6) when mixed with vacuum residue prior to thermal treatment, and 16.8% sulphur was trapped. MgO was found to be less effective compared to calcium variants (Table 2, Entry 7). The lower reactivity of MgO compared to CaO is possibly due to the higher lattice energy in the former compared to the latter. Similar observations were also reported in the hydrolysis of alkaline earth metal oxides, in which MgO is hydrolysed slowly to $Mg(OH)_2$, whereas CaO readily reacts with water to form $Ca(OH)_2$ [16].

Table 2. Desulphurisation efficiency of various alkaline earth metal compounds

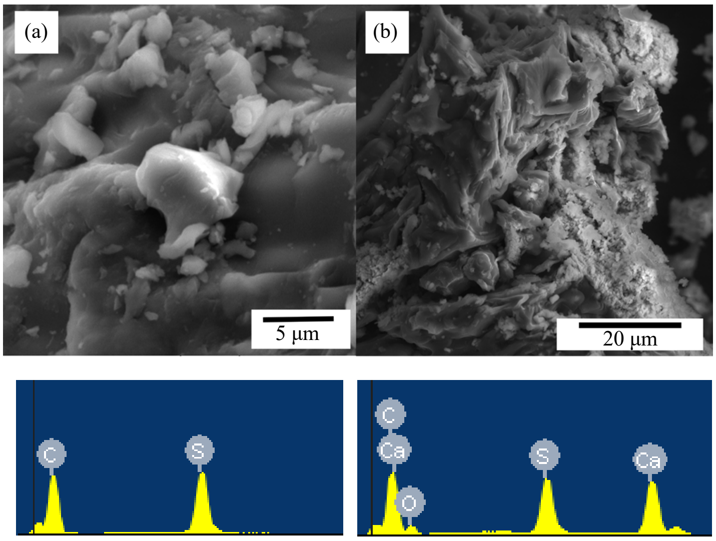
Entry	Additive used (2.5 wt%)	Free sulphur (wt%)	Sulphur trapped (%)
1	No additive	7.54	0
2	CaO	6.30	16.5
3	$Ca(OH)_2$	6.62	12.2
4	$CaCl_2$	6.43	14.7
5	$Ca(NO_3)_2$	7.25	3.8
6	$CaCO_3$	6.27	16.8
7	MgO	6.91	8.5

Considering availability, cost effectiveness, and in-situ sulphur removal efficiency, the preferred choice is CaO. CaO is conveniently provided as lime or may be derived from materials such as limestone or dolomite. However, other calcium compounds ($CaCl_2$ and $CaCO_3$) can also be used. The extent to which sulphur trapping can be achieved with varying amounts of CaO in vacuum residue (VR) was investigated, and the results are presented in Table 3. The results indicate a higher amount of sulphur can be trapped in petroleum coke with an increase in additive concentration in vacuum residue. The use of 10 wt% CaO resulted in a maximum 63.6% reduction in combustible sulphur content (Table 3, Entry 4). Attempts to further increase the CaO quantity resulted in irreproducible results, presumably due to improper mixing with vacuum residue, and were not explored further considering the economics of the process.

Table 3. Effect of CaO concentration on sulphur content in petroleum coke

Entry	Sample name	CaO used (wt%)	Free sulphur (wt%)	Sulphur trapped (%)
1	VR-2.5	2.5	6.30	16.5
2	VR-5	5	5.16	31.6
3	VR-7.5	7.5	4.05	46.3
4	VR-10	10	2.74	63.6

To understand the difference in morphology, scanning electron microscopy (SEM) analysis (Figure 2) was carried out on petroleum coke formed with and without the CaO additive. A smooth and uniform surface (Figure 2(a)) was observed for petroleum coke when no additive was used for thermal coking. However, the surface appeared to be significantly rough when it was produced in the presence of 10% CaO (Figure 2(b)). This sudden change in the coke morphology was thought to originate from the reaction of matrix-bound sulphur with CaO. Furthermore, elemental analysis of the SEM images confirms the trapping of sulphur inside CaO.



Element	Weight (%)
C K	92.53
S K	7.47

Element	Weight (%)
C K	64.44
O K	21.94
S K	6.01
Ca K	7.61

Figure 2. SEM images and energy dispersive X-ray (EDX) analysis of (a) petroleum coke without additive and (b) petroleum coke with 10% CaO

The key objective of this study was to trap sulphur in petroleum coke in the presence of an additive so that upon combustion it doesn't emit SOx, an environmental pollutant. As the petroleum coke formed in the presence of additives contains a lower amount of free sulphur, it is expected to emit a lower amount of SOx upon combustion. Therefore, sulphur-trapped petroleum coke is suitable as a solid fuel with a better emission profile. To examine the extent of SO_2 emission from sulphur-trapped petroleum coke compared to regular petroleum coke, combustion studies at a temperature between 400 and 600 °C are carried out, and the SO_2 produced is analysed with a Yokogawa SO_2 analyser. To determine the total amount of SO_2 generated, the concentration of SO_2 is plotted against time (Figure 3). The area under the curve represents the total amount of SO_2 produced upon combustion. The dilution effect of the additive was nullified with a proportional increase in petroleum coke quantity. These results are presented with supporting information. Petroleum coke produced from vacuum residue in the presence of 10% CaO resulted in a 67% reduction in SO_2 when compared with regular petroleum coke. This result correlates well with the sulphur content (Table 3, Entry 4) obtained from the sulphur analyser.

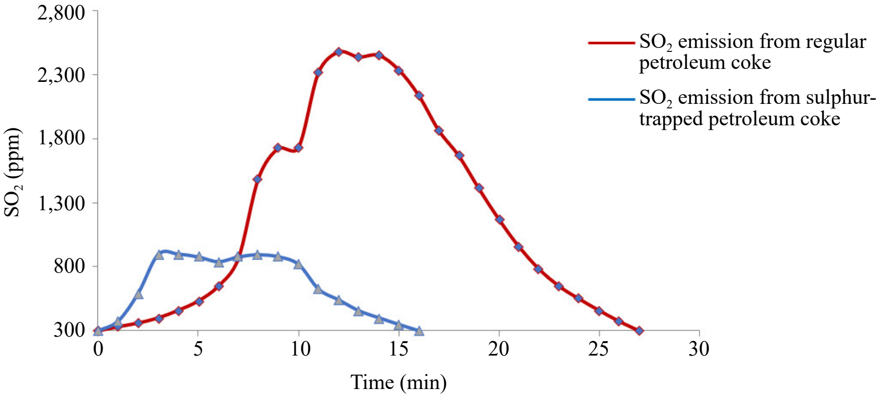


Figure 3. SO_2 emission comparison from petroleum coke and sulphur-trapped petroleum coke

The reduction in sulphur content in petroleum coke can be attributed presumably to the formation of CaS during thermal cracking. Upon combustion, the CaS present in the solid coke gets oxidised to $CaSO_4$, releasing substantial heat energy and stabilising the sulphur content of the fuel in the ash.

Finally, we have compared different petroleum coke desulphurisation methods reported over the past two decades (Table 4). Although calcination in the presence of excess alkali was found to remove most of the sulphur from petroleum coke, the process generates substantial caustic waste and may not be viable for industrial practice. Hydrodesulphurisation and high temperature calculation are also efficient in removing the sulphur to a large extent. Unfortunately, higher operating costs due to the use of hydrogen and calcination at elevated temperatures make these processes economically challenging. Microbial desulphurisation as well as sulphur removal through solvent extraction are less efficient. Moreover, all these reported methods deal with the post-treatment of the petroleum coke and hence require additional hardware, leading to increased capital costs. Interestingly, the in-situ trapping of free sulphur in petroleum coke reported here traps sulphur to a large extent during the formation of petroleum coke from vacuum residue. Therefore, no additional setup is required, and existing delayed coker plants in petroleum refineries can be utilised to produce petroleum coke with low combustible sulphur. To the best of our knowledge, this is the first report on the in-situ trapping of sulphur in petroleum coke during its formation from vacuum residue.

Table 4. Comparison of different methods for petroleum coke desulphurisation

Sl No	Petroleum coke desulphurisation methods	Sulphur removal (%)
1	Solvent extraction	15 to 20
2	Calcination at a high temperature	40 to 88
3	Hydrodesulphurisation	50 to 92
4	Microbial desulphurisation	up to 50%
5	Desulphurisation in the presence of NH_3	80%
6	Alkali calcination	up to 98%
7	In-situ trapping of free sulphur (this work)	up to 67%

5. Conclusions

The presence of free sulphur in petroleum coke restricts its wide use as a solid fuel due to the emission of SOx upon combustion. We have developed a novel and efficient protocol to trap free sulphur present in petroleum coke during its formation from vacuum residue. CaO was found to be the most suitable additive for in-situ trapping of free sulphur present in petroleum coke. The sulphur-trapped petroleum coke generated with 10% CaO reduces SO_2 emissions by 67% upon combustion. Therefore, replacing regular petroleum coke with this newly developed sulphur-trapped petroleum coke has the potential to mitigate environmental pollution to a large extent. Further study is being conducted in our lab to understand the economic feasibility of the process for large-scale implementation. Moreover, we are evaluating the production of sulphur-trapped petroleum coke in our delayed coker pilot plant using powdered CaO as an additive, and the results of this study will be communicated in the future.

Conflict of interest

There is no conflict of interest for this study.

Acknowledgments

The authors thank BPCL management for permission to publish the research work. The authors also thank Dr. K. Chaitanya Kumar for the help with SEM EDX analysis and BR for providing vacuum residue and sulphur content analysis. The authors also thank Dr. Durgaiah Chevella for the help in manuscript preparation.

References

[1] Stanford Research Institute. *Petroleum coke: Process economics program*. Report number: 72-a, 1976.

[2] Feintuch HM, Bonilla JA, Godino RL. FW delayed-coking process. In: Meyers RA. (ed.) *Handbook of petroleum refinery processes*. New York, United States: McGraw-Hill; 1986. p.43-49.

[3] Al-Haj-Ibrahim H, Morsi BI. Desulphurization of petroleum coke: A review. *Industrial & Engineering Chemistry Research*. 1992; 31(8): 1835-1840. https://doi.org/10.1021/ie00008a001

[4] Gagnon A, Backhouse N, Darmstadt H, Ryan E, Dyer L, Dixon DG. Impurity removal from petroleum coke. In: Sadler BA. (ed.) *Light Metals 2013*. New York, United States: Springer; 2013. p.1057-1062. https://doi.org/10.1007/978-3-319-65136-1_178

[5] Phillips CR, Chao KS. Desulphurization of Athabasca petroleum coke by (a) chemical oxidation and (b) solvent extraction. *Fuel*. 1977; 56(1): 70-72. https://doi.org/10.1016/0016-2361(77)90045-X

[6] Ibrahim HA. Upgrading of Syrian petroleum coke by pre-oxidation. *Periodica Polytechnica Chemical Engineering*. 2011; 55(1): 21-25. https://doi.org/10.3311/pp.ch.2011-1.04

[7] Ibrahim HA. Thermal treatment of Syrian sponge coke. *Journal of King Saud University-Engineering Sciences.* 2006; 18(2): 261-269. https://doi.org/10.1016/S1018-3639(18)30839-0

[8] Gillot J, Lux B, Cornuault P, Du Chaffaut F. Changement de structure lors de la desulphuration de coke de petrole [Change in structure during desulfurization of petroleum coke]. *Carbon*. 1968; 6(3): 389-394. https://doi.org/10.1016/0008-6223(68)90034-1

[9] Saha C, Tollefson EL. Hydrodesulphurization of athabasca fluid coke-conversion and mechanism. *The Canadian Journal of Chemical Engineering*. 1995; 73(2): 211-219. https://doi.org/10.1002/cjce.5450730207

[10] Agarwal P, Sharma DK. Studies on the desulphurization of petroleum coke by organorefining and other chemical and biochemical techniques under milder ambient pressure conditions. *Petroleum Science and Technology.* 2011; 29(14): 1482-1493. https://doi.org/10.1080/10916460902839230

[11] George ZM, Schneider LG, Tollefson EL. Desulphurization of a fluid coke similar to the Athabasca oil sands coke. *Fuel*. 1978; 57(8): 497-501. https://doi.org/10.1016/0016-2361(78)90161-8

[12] Lee SH, Choi SC. Chemical activation of high sulfur petroleum coke by alkali metal compounds. *Fuel Processing Technology*. 2000; 64(1-3): 141-153. https://doi.org/10.1016/S0378-3820(00)00070-9

[13] Wang MH, Yang A, Wang M, Zhang XY, Zhai YC. Desulphurization of petroleum coke via alkali calcination. *Advanced Materials Research.* 2014; 997: 526-529. https://doi.org/10.4028/www.scientific.net/AMR.997.526

[14] Xiao J, Zhang Y, Zhong Q, Li F, Huang J, Wang B. Reduction and desulfurization of petroleum coke in ammonia and their thermodynamics. *Energy & Fuels*. 2016; 30(4): 3385-3391. https://doi.org/10.1021/acs.energyfuels.5b02929

[15] Berg L, Berg JW. *Removal of sulphur from petroleum coke with lime*. US4981667A (Patent) 1990.

[16] Brett NH. Magnesium and alkaline-earth oxides. In: Brook RJ. (ed.) *Concise encyclopedia of advanced ceramic materials*. Amsterdam, Netherlands: Elsevier; 1991. p.283-286. https://doi.org/10.1016/C2009-1-28294-3