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Adsorptive Desulfurization of Diesel over Imidazolium-Functionalized Carbon Nanospheres: Evaluation of Physicochemical Properties and Emission Simulation

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Abstract

This study investigates the desulfurization of commercial diesel through adsorption using functionalized imidazolium ionic liquid carbon nanospheres (CNSs-IL) and evaluates its effects on engine performance and emissions. CNSs were characterized using FTIR, XRD, and SEM-EDX analyses. The adsorption process was optimized by studying parameters such as temperature, contact time, agitation speed, and CNSs-IL dosage. Under optimal conditions (50°C, sorbent-to-diesel ratio of 0.05, agitation speed of 350 rpm, and 150 min), the sulfur content was reduced to 31 ppm, with additional reductions in nitrogen and aromatic contents. The desulfurized diesel underwent comprehensive characterization and was tested in a diesel engine alongside commercial diesel. Performance tests revealed reduced brake-specific fuel consumption and lower emissions of SO_2, CO, and NOx. Numerical simulations, validated by experimental in-cylinder pressure data, closely aligned with the experimental findings, highlighting a 33% reduction in CO emissions and a 21.37% reduction in NOx emissions for the desulfurized fuel compared to commercial diesel. These results confirm that desulfurized diesel produced using CNSs-IL meets physico-chemical standards and enhances engine performance while significantly reducing environmental pollutants, making it a viable and sustainable alternative to conventional diesel.

Keywords: *Diesel; Adsorptive desulfurization; Carbon nanospheres; Ionic liquid; Simulation.*

1. Introduction

Diesel engines are widely utilized for their high efficiency and durability, making them indispensable in industries, transportation, and various sectors of society. However, they are significant contributors to harmful emissions, including smoke and nitrogen oxides (NOx), which pose serious environmental and health risks [1-2]. Moreover, sulfur compounds present in transportation fuels exacerbate these challenges. During combustion, sulfur compounds produce sulfur oxides (SOx), leading to acid rain, accelerating the corrosion of fuel-handling components, and poisoning catalysts used in refining processes. Common sulfur species in middle distillates, such as diesel and kerosene, include straight-chain compounds (e.g., thiols and thioethers) and cyclic aromatic compounds like thiophene, benzothiophene, and dibenzothiophene, the latter being classified as refractory polyaromatic compounds due to their chemical stability and resistance to removal [3-4].

Despite advancements in alternative energy technologies, transportation fuels remain a serious element of global energy consumption, particularly in aviation, heavy transport, and power generation. Rising diesel prices, declining petroleum reserves, and increasingly stringent emission regulations have intensified the need for innovative solutions. Governments worldwide are enforcing lower sulfur content thresholds for transportation fuels, mandating levels as low as 10–20 ppm [5]. Achieving these standards requires innovative desulfurization techniques and advanced fuel treatment methods to mitigate the environmental impacts of sulfur emissions. At the same time, efforts to reduce harmful emissions from diesel engines have focused on improving engine technologies and reformulating fuels to enable cleaner combustion. These strategies, combined with the development of clean fuels, are essential for addressing the dual challenges of environmental sustainability and energy security.

Several processes are used to reduce sulfur content in diesel, including hydrodesulfurization, oxidative desulfurization, microbial desulfurization, oxidative-extractive desulfurization, oxidative-emulsion desulfurization and adsorptive desulfurization [6-10]. However, these methods have drawbacks, such as high temperature and pressure for hydrodesulfurization, long treatment times for microbial and extractive desulfurization, and additional unit operations and costs for oxidative and emulsion-based processes. Catalyst modifications have improved some methods, but core issues like high process conditions remain unresolved [11]. Among these, adsorptive desulfurization is more cost-effective and efficient, operating at lower temperatures and pressures without requiring additional unit operations.

Adsorptive desulfurization is considered a highly viable approach for eliminating sulfur compounds from fuel, offering advantages from economic, technical, and environmental perspectives. The efficiency of this method is strongly influenced by the type of adsorbent utilized. Both carbon-based and non-carbon-based materials are often modified to create mesoporous adsorbents with enhanced surface area and porosity [12].

The carbon-based materials are recognized for their cost-effectiveness, chemical and thermal stability under anoxic conditions, adjustable surface area influenced by the choice of carbonaceous precursors and preparation methods, ease of modification, and strong adsorption capacity for both aromatic and refractory sulfur compounds [13].

The objectives of this study are to evaluate the desulfurization of commercial diesel fuel using metal-carbon-based nanocomposites and to assess the regenerable performance of functionalized carbon nanosphere sorbents synthesized from asphaltene fractions via the pyrolysis process. The sorbents were characterized before and after each desulfurization stage using various analytical techniques and procedures. The adsorption process was conducted using real commercial diesel in the presence of carbon nanospheres, followed by an evaluation of the treated diesel's properties and a simulation of its emissions.

2. Materials and methods

2.1. Materials

Asphaltene deposits samples sourced from the Hassi-Messaoud petroleum field were supplied by the Sonatrach society. All chemicals such as surfactants 1-propylamine-3-methylimidazolium bromide, dicyclohexylcarbomiide), ethanol, sulfuric acid, nitric acid, and dimethylformamide were purchased from Sigma Aldrich (Saint Louis, MO). The commercial diesel was supplied by Algiers refinery and its proprieties are listed in Table 1.

2.2. Preparation and functionalized of CNSs-IL

Carbon nanospheres (CNSs) were synthesized via pyrolysis, following methods from our previous research [14]. The asphaltene fraction deposits were reacted with a Fe/SiO_2 solution in a quartz reaction tube (27 mm x 120 mm) inside a furnace at 1000°C for 90 minutes, using nitrogen as a carrier gas at a flow rate of 60 mL/min. After the reaction, the product was cooled to room temperature under a nitrogen atmosphere.

The resulting solid was oxidized using a concentrated acid mixture of H_2SO_4 (65%) and HNO_3 (98%) in a 3:1 volume ratio. The mixture was briefly sonicated and then refluxed under magnetic stirring at 60°C for 5 hours in an oil bath. The treated CNSs were washed with distilled water until a neutral pH was achieved and subsequently dried under vacuum at 70°C.

To prepare CNSs-IL, 5 mg of oxidized CNSs, 10 mg of 1-propylamine-3-methylimidazolium bromide (IL), and 10 mg of dicyclohexylcarbodiimide were mixed in 10 mL of dimethylformamide (DMF) via ultrasonication for 20 minutes. The mixture was stirred vigorously at 60°C for 24 hours. The resulting suspension was centrifuged at 4000 rpm for 30 minutes, and the settled material was filtered. The product was washed sequentially with DMF, ethanol, and deionized water, and then dried at 70°C overnight, yielding a black powder.

2.3. Adsorption experimental procedure

Adsorption experiments were conducted in Erlenmeyer flasks, where a fixed volume of adsorbate solutions with varying initial concentrations was mixed with a known mass of adsorbent and stirred using a magnetic stirrer. The prepared mixtures were agitated until equilibrium was achieved. For the initial setup, 100 g of diesel fuel and 0.5 g of selected imidazolium ionic liquid functionalized carbon nanospheres (CNSs-IL) were added to the diesel fuel and stirred vigorously. After 10 minutes, the solid CNSs-IL were filtered out for further characterization. The treated diesel was then washed with double-distilled water, dried, and stored for subsequent analyses.

2.4. Characterization techniques

The carbon nanosphere-based materials were characterized using a Scanning Electron Microscope (SEM) (Zeiss Supra 55 VP, Germany) equipped with an Energy Dispersive X-ray (EDX) analyzer to study their structural and morphological properties and to determine the elemental composition and distribution. Surface functional groups were analyzed using Fourier Transform Infrared Spectroscopy (FTIR) (Frontier 01, PerkinElmer, USA), with IR spectra collected via the KBr pellet method over a wavelength range of 400–4000 cm^{-1}. Powder X-ray diffraction patterns of prepared sample were taken by a two-circle (2θ-θ) X-ray powder diffractometer (X'Pert PRO XRD PW 3040 system) using Copper kα1 of wavelength 1.54056×10-10 m, and kα2 of wavelength 1.544426×10-10 m. The scan was taken between 2θ of 10° and 2θ of 45° at increments of 0.04° with a count time of 4 seconds for each step. Surface area and porosity parameters, including the BET surface area (SBET), total pore volume (Vp), microporous surface area (Smicro), micropore and mesopore percentages, and average pore diameter, were determined from nitrogen adsorption isotherms at 77 K using a Micromeritics Tristar 3020 Plus.

The physicochemical properties of diesel were determined using ASTM standard methods. SARA analysis for saturates, aromatics, resins, and asphaltene content was performed via TLC-FID/FPD using a Iatroscan-MK6 instrument, following ASTM D2007. Metallic elements were analyzed with a Buck Scientific VGP-210 flame atomic absorption spectrometer. Elemental composition (C, H, N, and S) was measured using an Elementar Vario-Micro analyzer and Spectroil-M spectrometers. The composition of diesel products was analyzed using liquid gas chromatography coupled with mass spectrometer. The GC-FID process for diesel started at 50°C (2 min hold), 130°C (2 min hold), 180°C (2 min hold) at a rate of 5 °C/min and the temperature was elevated to 290 C at 5°C/min.

2.5. Test engine specifications and its testing method

This section investigated the performance and exhaust emissions of desulfurized diesel in comparison to Algerian commercial diesel. The tests were conducted on a single-cylinder, air-cooled Lister Petter ST1 diesel engine. Performance testing was carried out at the engine's standard operational speed of 1500 rpm, with the injection timing precisely set to 20° before the top dead center. Throughout the experiments, injection timing and pressure profiles were carefully monitored for diesel samples, with a specific focus on engine operation under a 50% load condition. The detailed engine specifications and fuel injection system parameters are provided in Table 1, offering a comprehensive overview of the setup and testing conditions.

Table 1. Operating conditions of diesel engine test.

Parameter	Specification
Engine type	Lister Petter Type ST1
Governor type	Mechanical centrifugal type
Range of nozzle opening	16.5–24.5 Mpa
N◦ of strokes	04
Stroke length	88.50 mm
N° of cylinders	01
Cylinder bore	95.25 mm
Power rating	Petter Type ST1
Compression ratio	18 :1
Bowl depth	15.10 mm
Upper bowl diameter	45.00 mm
Air measurement device	Diaphragm
Dynamometer based on eddy currents	
Model maximum power	EurothermPARVEX 42 kw
Fuel injection system specifications	
Injection duration	20°
Diameter of the nozzle hole	0.25 mm
Injection timing for fuel	20°BTDC
Included spray angle	125°
Number of nozzle holes	03

2.6. Exhaust emission analyzer

A Greenline 8000 exhaust gas analyzer was employed to measure emissions from the test engine. This analyzer is capable of detecting carbon monoxide (CO), sulfur dioxide (SO_2), and nitrogen dioxide (NO_x) emissions with a sensitivity of ±1 ppm, as well as oxygen (O_2) and carbon dioxide (CO_2) emissions with a sensitivity of ±0.1%. During the performance tests, the engine was run until it reached its operating temperature. The probe of the gas analyzer was then inserted into the exhaust pipe, and emission data were recorded. The analyzer generated printed results for subsequent analysis.

3. Results and discussion

3.1. Characterization of synthesized ionic liquid functionalized carbon nanospheres (CNSs-IL)

The morphology of carbon nanospheres synthesized by the pyrolysis of asphaltene fraction at 1000°C for 20 min was examined, as shown in Figure 1(a-b) at magnifications of 10 µm and 5 µm. The results indicated that the material is composed of uniformly shaped spherical particles. The particles exhibit a natural tendency to cluster together, forming agglomerates, which aligns with findings from previous studies [15]. Additionally, the nanospheres were observed to connect in patterns resembling necklaces or beads, forming extended, continuous structures. The images (Figure 1) reveal that the morphology of the CNSs remains largely unchanged following IL modification. This indicates that a thin layer of IL is deposited on the surface of the CNSs. As illustrated in Figure 2(b), the elemental composition analysis indicates that the carbon nanospheres primarily contain carbon, with trace amounts of oxygen. The insert in Figure 1b presents the EDX spectrum of the NCSs-IL materials, confirming the presence of carbon and oxygen. The existence of oxygen leads to availability of oxygenated functional groups on CNSs surface. No other detectable contaminants were observed, with the detection limit being within ±0.01%.

The structural characterization of CNSs-IL products synthesized at 1000°C under nitrogen atmosphere was performed using FTIR spectroscopy in the spectral range of 4000–400 cm^{-1}. The FTIR spectrum of the CNSs sample (Figure 1c) reveals an absorption peak at 1654.93 cm^{-1}, attributed to the aromatic C=C stretching vibration characteristic of the carbon skeleton.

For the CNSs sample, which exhibited the most well-defined carbon nanostructure, a peak at 1654.93 cm⁻¹ was observed, indicating a strong aromatic C=C stretching band with minimal vibrations from carbonyl, hydroxyl, amide, or amine groups (Figure 1c) [15]. In Figure 1, low intensities observed in the spectral region of 3600–3000 cm⁻¹ correspond to the presence of hydroxyl (OH) and amine (NH) groups. Aliphatic stretching vibrations of alkanes are identified at 2800 cm⁻¹ and 3000 cm⁻¹, with deformation peaks noted at 1458.68 cm⁻¹ and 1372.88 cm⁻¹, while the peak at 1109 cm⁻¹ corresponds to the C-O stretching vibration.

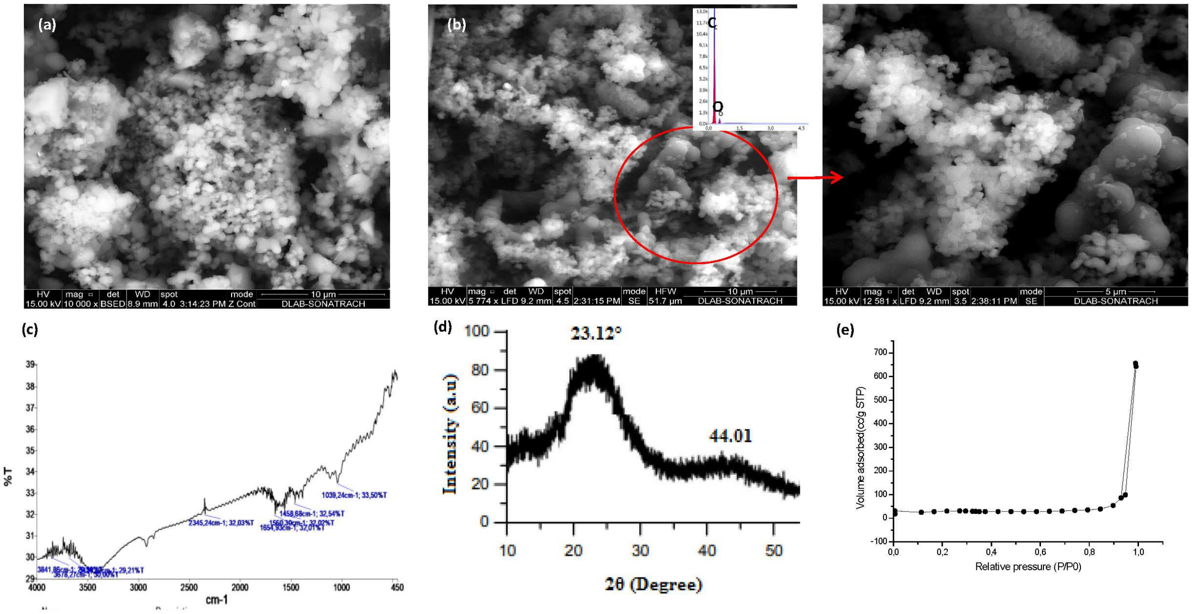
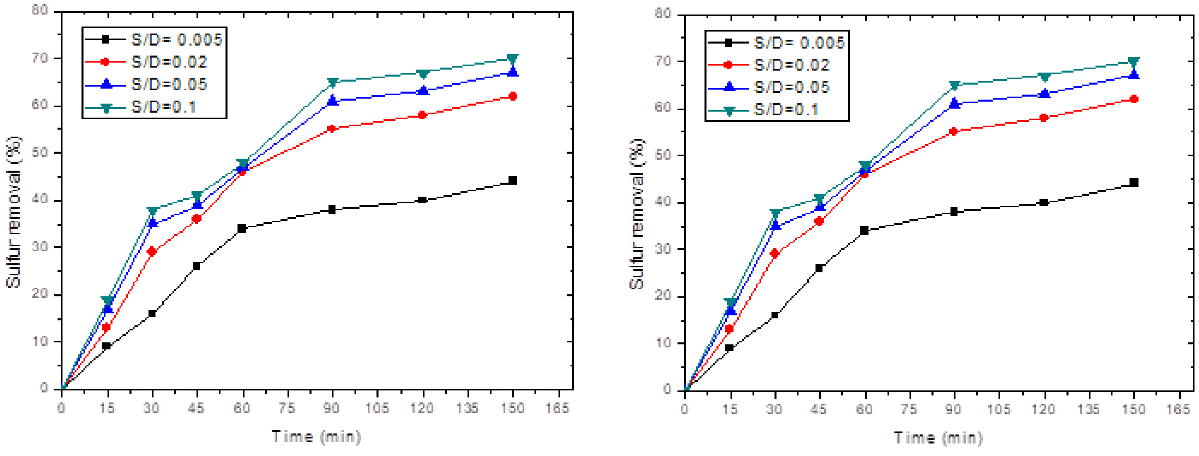


Figure 1. Characterization of prepared carbon nanospheres: (a) SEM of CNSs, (b) SEM-EDX pf CNSs-IL, (c) FTIR OF CNSs-IL, (d) DRX and (e) Nitrogen adsorption–desorption isotherms of the CNSs-IL.

The XRD spectrum of CNSs-IL (Figure 1d) exhibits two Bragg peaks at 2θ = 23.12° and 44.01°, corresponding to the (002) and (101) planes, respectively. The peak at 23.12° indicates a significant presence of amorphous material associated with multi-walled carbon nanotubes, while the peak at 44.01° suggests a hexagonal graphite lattice [14].



a b

Figure 2. Characterization of prepared carbon nanospheres: (a) SEM of CNSs, (b) SEM-EDX pf CNSs-IL, (c) FTIR OF CNSs-IL, (d) DRX and (e) Nitrogen adsorption–desorption isotherms of the CNSs-IL.

The pore structure properties of the CNSs, including BET-specific surface area, pore volume, and average pore diameter, were analyzed using N_2 adsorption-desorption techniques (Figure 1e).

The N_2 adsorption-desorption isotherms for CNSs-IL synthesized at 1000°C demonstrated a notable increase in nitrogen adsorption volume from 100 to 500 cm^3/g as the relative pressure rose from 0.8 to 1. This increase, driven by capillary condensation, suggests that the CNSs-IL possess a mesoporous structure capable of accommodating substantial nitrogen adsorption. These mesopores are likely formed by inter-particle voids (textural mesopores) between the primary particles. The surface area was fond to be 165 m^2/g with a pore volume of 0.8 cm^3/g and mean pore diameter of 19 nm.

3.2. Adsorptive desulfurization of commercial diesel using CNSs-IL

This section examines the impact of various operating parameters on the adsorptive treatment efficiency for diesel fuel desulfurization. The effect of adsorbent dosage was investigated at room temperature (25°C), with four CNSs-IL dosages (0.5, 2, 5, and 10 g) using 100 g of diesel and an agitation speed of 250 rpm (Figure 2a). Results show that sulfur compound removal increased with higher adsorbent dosages due to the larger surface area and higher density of oxygen-containing functional groups introduced by acid treatment and the functionalization by ionic liquid. However, after 120 min of reaction, the desulfurization rate stabilized, likely due to surface saturation. Final sulfur removal percentage after 150 min were 70.1% for the highest mass ration of sorbent/diesel (S/D=0.1 wt/wt) dosage and 44.03% for the lowest S/D=0.005 wt/wt.

The impact of temperature (20°C to 55°C) and agitation intensity (150 to 700 rpm) on desulfurization was also assessed (Figure 2b). Sulfur removal improved with increasing temperature, reaching 95.01% at 55°C after 150 min with an adsorbent-to-fuel mass ratio of 0.05. Enhanced performance at elevated temperatures was attributed to improved diffusion rates and increased kinetic energy, promoting stronger adsorbate interactions with the CNSs-IL surface. Higher agitation speeds further enhanced sulfur removal by improving turbulence, reducing boundary layer thickness, and facilitating adsorbate diffusion, which accelerated sulfur molecule diffusion toward the CNSs-IL surface [13]. Physical contact between the stir bar and CNSs-IL further reduced particle size, exposing more adsorption sites. A reaction temperature of 50°C was identified as optimal, achieving high efficiency while preserving fuel quality and considering economic and environmental constraints. At 55°C, a slight reduction in adsorption capacity was observed (95.01%), likely due to desorption phenomena.

3.3. CNSs-IL reusability and recyclability

Reusability is a significant factor for assessing the industrial and economic viability of a catalyst. Consequently, we examined the performance of the CNSs-IL sorbent over multiple usage cycles through recycling and reutilization techniques. The ionic liquid functionalized CNSs was regenerated by washing with ethanol. Each reuse cycle was conducted under identical conditions to the initial cycle.

As illustrated in Figure 3 a, the efficiency of adsorptive desulfurization progressively declined from cycle 1 to cycle 3 when using non-regenerated CNSs-IL, likely due to the saturation of sorbent sites. Conversely, the recycled CNSs-IL maintained its activity for at least five cycles with minimal performance loss. This recyclability highlights the CNSs-IL's potential as a cost-effective catalyst for repeated desulfurization processes.

As can be observed in Figure 4, the presence of residual elements such as iron, zinc, and sulfur on the CNSs-IL after the adsorptive desulfurization process indicates that the synthesized CNSs-IL have successfully adsorbed both metals and sulfur compounds simultaneously. This observation is further supported by the EDX analysis, as depicted in Figure 4.

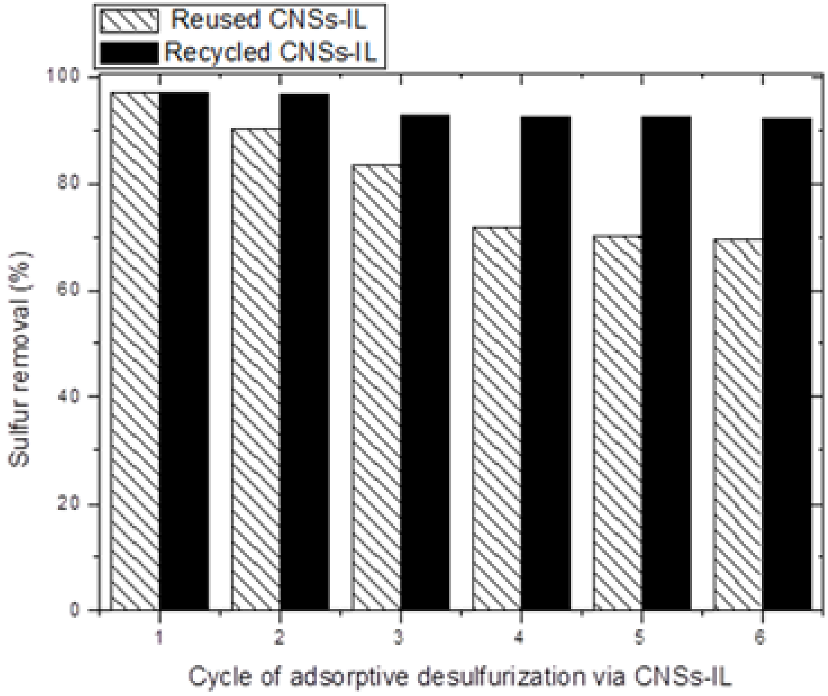


Figure 3. Recycling and reutilization of CNSs-IL effect on the desulfurization of diesel. Experimental Conditions: V_{diesel} = 100 mL with the initial sulfur content of 557 ppm; CNSs-IL/Diesel=0.05; T=50°C for 1.5 h, agitation speed= 350 rpm and pH=7.

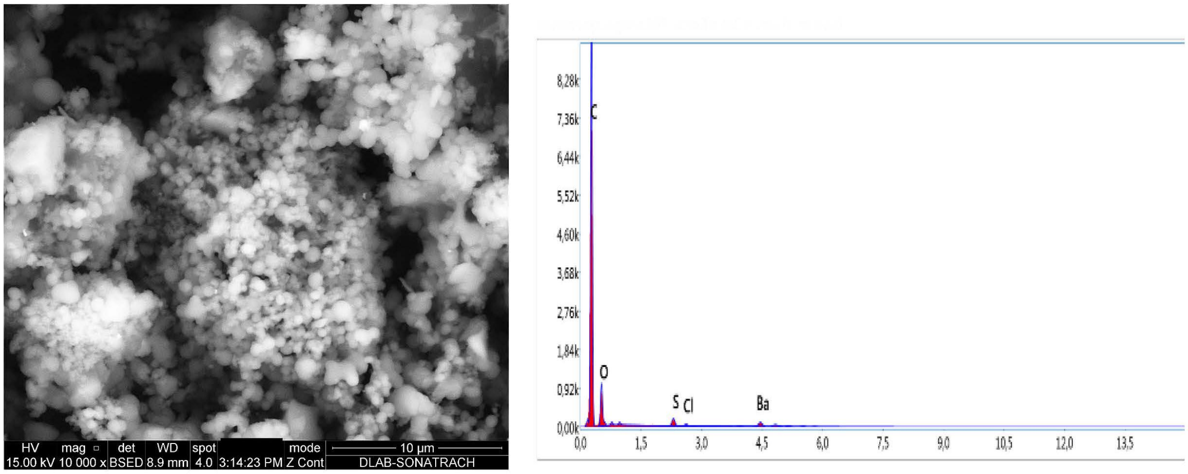


Figure 4. SEM-EDX analysis of CNSs-IL after adsorption process using commercial diesel.

3.4. Effect of the adsorptive desulfurization on the specifications of diesel

The quality of fuels plays a decisive role in their commercial viability, and as such, the properties of commercial diesel were evaluated before and after microwave treatment (Table 2). The distillation characteristics of both treated and untreated diesel remained relatively consistent. However, a significant decrease in the content of aromatic and naphthene compounds was observed. Specifically, the content of aromatic compounds reduced from 17.05 to 15.51 vol%, and naphthene compounds decreased from 20.74 to 10.49 vol%. This finding aligns with the results reported in literature, who noted an increase of over 2 wt% in saturated hydrocarbons and a 17 wt% reduction in aromatic hydrocarbons during a similar treatment [16]. As indicated in Table 2, more than 95% of sulfur compounds were efficiently removed from diesel, compared to nitrogen-containing compounds. Furthermore, the adsorptive desulfurization treatment did not significantly affect the fuel parameters such as density, kinematic viscosity, flash point, water content, and calorific value, indicating that fuel specifications remained unchanged and they are reasonably in the range of diesel fuel standard values.

Table 2. Physicochemical proprieties of commercial transportation fuels used in this work.

Propriety	Method	$Diesel^{BT}$	$Diesel^{AT}$
Density at 15°C, g/mL	ASTM D-1298	0.8271	0.8125
Viscosity, (m/s^2) at 20°C	ASTM D-445	4.169×10^{-6}	4.335×10^{-6}
Color	ASTM D-1500	0.5	0.1
Distillation range (°C)	ASTM D-86		
Initial point		162	180
5%		178	198
10 %		189	215
20 %		208	248
30 %		225	264
50 %		255	281
70 %		288	295
80%		315	336
90 %		329	353
95 %		350	358
Final point (°C)		371	376
Residue (vol %)		1.5	1.5
Flash point (°C)		66	64
Freezing point (°C)	ASTM D-2386	- 14	-15
Water content (wt. %)	ASTM D-6304	22	26
Total acid number (mg KOH/g)	ASTM D-1319	0.0029	0.0030
Total nitrogen content (wt. %)	ASTM D-3228	0.125	0.052
Total sulfur content (wt. %)	ASTM D-4294	0.621	0.031
Aromatic (vol %)	ASTM D-1319	18.9	7.46
Paraffins (vol%)	ASTM D-1319	75.2	89.73
Naphtenes (vol%)	ASTM D-1319	5.6	2.81
Olefines (vol%)	ASTM D-1319	0.3	
Calorific value, MJ/kg	ASTM D 4529-01	43.2745	43.2127

BT: before and AT: after adsorptive desulfurization process using CNSs-IL.

The chemical composition of the treated diesel fuel was analyzed using GC-MS spectroscopy, which revealed the dominance of paraffins (C_7–C_{25}), aromatics, and polyaromatics (Fig. 5).

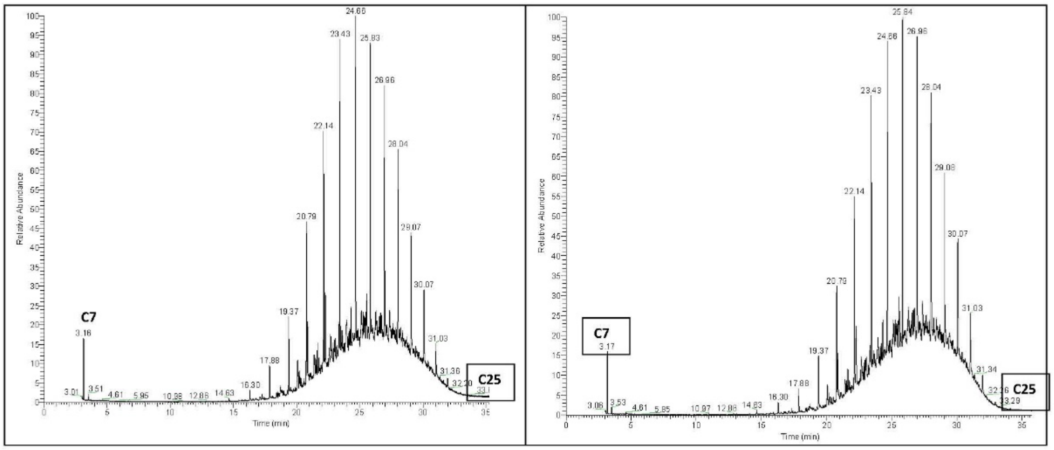


Figure 5. CG-MS chromatograms of commercial diesel (a) before and (d) after adsorptive desulfurization.

For enhanced detection of heteroatoms and polyaromatics, liquid-liquid extraction with dimethyl sulfoxide was employed, as reported in previous studies. GC-MS analysis confirmed the presence of the sulfur-containing compounds, such as dibenzothiophene (DBT), nitrogen-containing compounds like indole and carbazole derivatives, and polyaromatics such as naphthalene and anthracene. Successful elimination of sulfur-, nitrogen-containing and metals compounds was achieved using adsorptive desulfurization without adversely affecting diesel quality, unlike hydrodesulfurization (HDS), which often operates under harsher conditions.

3.5. Engine performance and exhaust gas tests

The impact of desulfurized and treated diesel on engine performance and exhaust emissions were examined in this section. Figure 6 a-b indicate variations of brake specific fuel consumption and brake mean effective pressure with engine speed, respectively. It is observed from these figures that the brake mean effective pressure for the desulfurized diesel are slightly higher than those of commercial diesel, while the brake specific fuel consumption is lower than that of commercial diesel. There is no significant difference in performance parameters when the desulfurized and commercial diesel are used in the engine. The brake specific fuel consumption represents the ratio of fuel consumption to the engine's brake power, serving as an indicator of the fuel required to generate a unit of power. In general, the brake specific fuel consumption exhibits an inverse relationship with engine brake power. On average, the brake specific fuel consumption during desulfurized utilization was found to be 3.2% lower than that of commercial diesel. This reduction is probably due to the removal of heavy molecules from treated diesel, which enhances combustion efficiency [16]. As observed in Figure 6b, the brake mean effective pressure rises with the engine speed and then reaches the minimum value at speed of 2500 rpm. These tests outcome clearly indicate that desulfurized diesel positively impacts engine performance parameters, confirming its suitability as a fuel for diesel engines without any operational concerns.

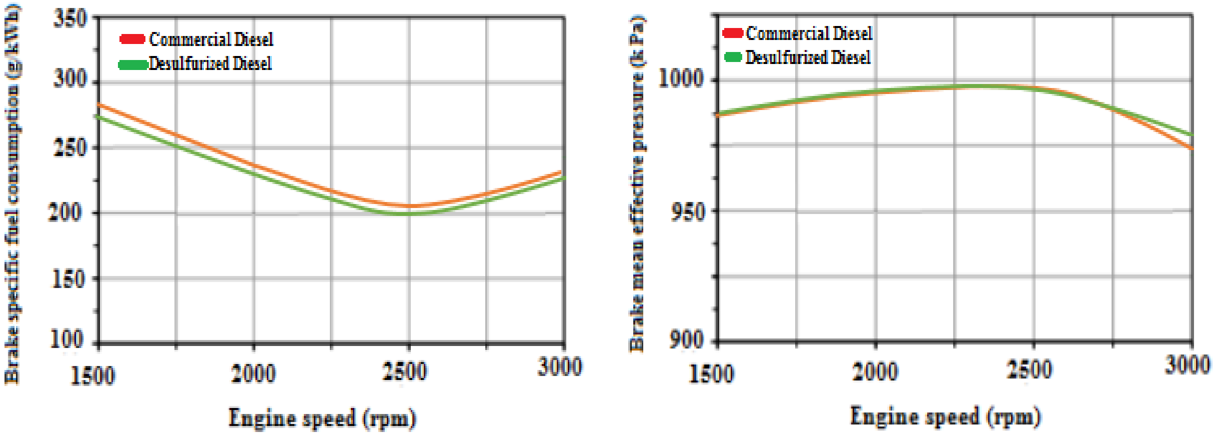


Figure 6. Effects of desulfurized diesel on (a) the brake specific fuel consumption and (b) the brake mean effective pressure.

During the combustion process in engine, various compounds are emitted, including CO_2, H_2O, O_2, and N_2, which are typical by-products of combustion and undesirable substances such as CO, NOx, SO_2, unburned hydrocarbons (HC), particulate matter, and other emissions are also generated. These pollutants not only negatively impact the environment but can also reduce combustion efficiency. Herein, the exhaust emissions of SO_2, CO, and NOx were measured for desulfurized and commercial diesel using an exhaust gas analysis device. The variations in these emissions with engine speed are presented in Figures 7, providing insights into the comparative performance of the fuels and their environmental impact. The sulfur content of Diesel was reduced to 31 ppm through adsorptive desulfurization onto CNSs-IL, as detailed in Table 2. As can be seen in Figure 7a, the combustion of desulfurized diesel in the test engine resulted in lower SO_2 emissions compared to commercial diesel. In parallel, NOx emissions for desulfurized diesel were lower than commercial diesel emissions at engine speeds exceeding 2000 rpm, with minimum values of 53 ppm for desulfurized and 71 ppm for commercial diesel observed at 1750 rpm (Figure 7b). The CO emission from the engine functioned with the desulfurized diesel is lower than those of commercial diesel for the considered engine speeds (Figure 7c).

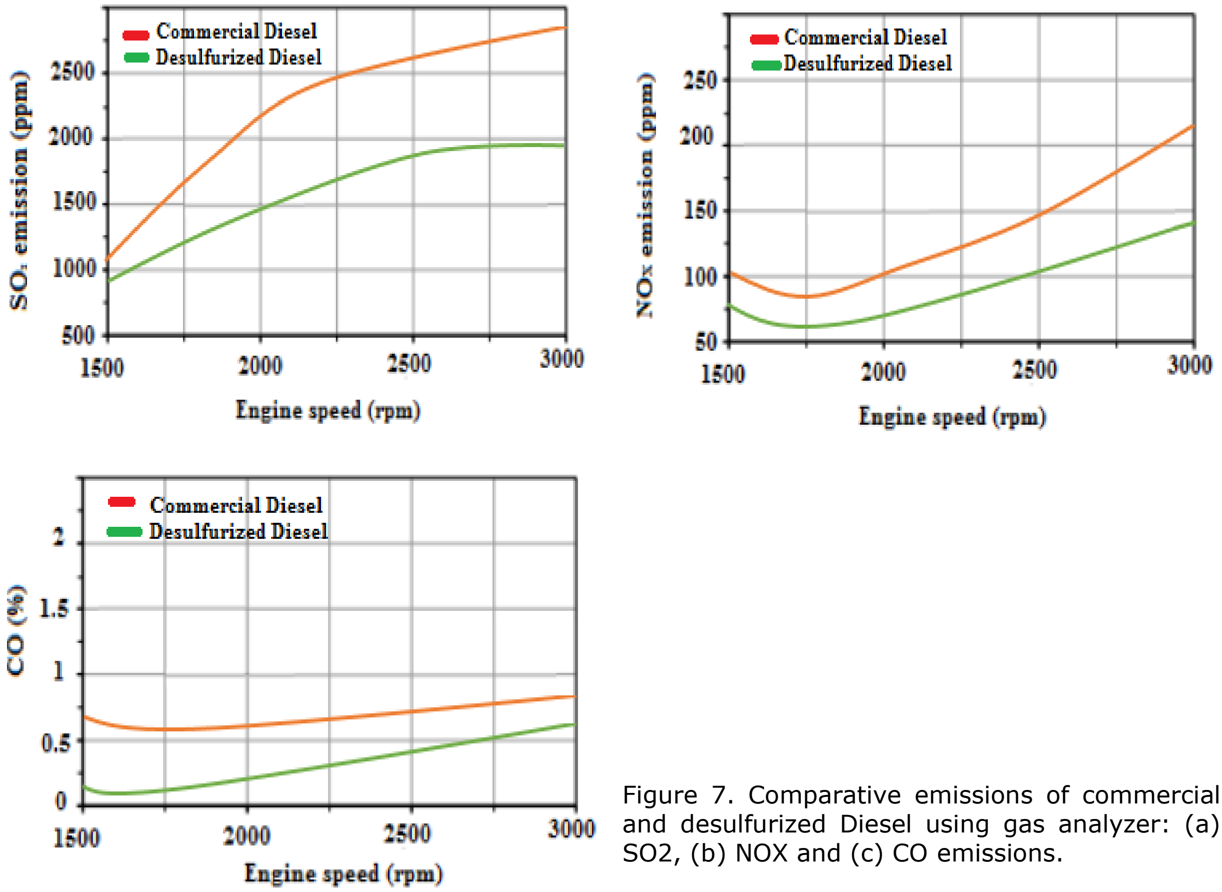


Figure 7. Comparative emissions of commercial and desulfurized Diesel using gas analyzer: (a) SO2, (b) NOX and (c) CO emissions.

3.6. Computational combustion and gas emissions simulation of a diesel engine

The numerical analysis for this work was performed using the CONVERGE 3.2 simulation software, which is a robust 3D-computational fluid dynamics (CFD) tool specifically designed for analyzing chemically reactive flows. The governing mass transport equations, represented as compressible equations, can be solved using the software's integrated physical and chemical models including: the KH-RT breakup model for spray atomization, the RNG k−ε turbulence model for flow dynamics, the CTC-Shell model for combustion processes, the Zel’dovich mechanism for NO formation, and a soot emission model based on the Hiroyasu formation model [17-18]. To ensure accurate simulations of complex fluid behavior and chemical reactions, thermodynamic properties such as viscosity, latent heat of vaporization, vapor pressure, and density of the desulfurized and commercial diesel were incorporated into CONVERGE's fuel library (liquid.dat) to model the desulfurized diesels’ performance and emissions characteristics under various operating conditions.

As shown in Figure 8, it clear that NOx emissions are significatively reduced at full engine load as well as CO emissions. However, this reduction depends on the engine conditions such as: temperature in engine cylinder, air flow. As can be seen, a high level of agreement between simulated and experimental values confirmed the accuracy of the numerical frameworker obtained in this work.

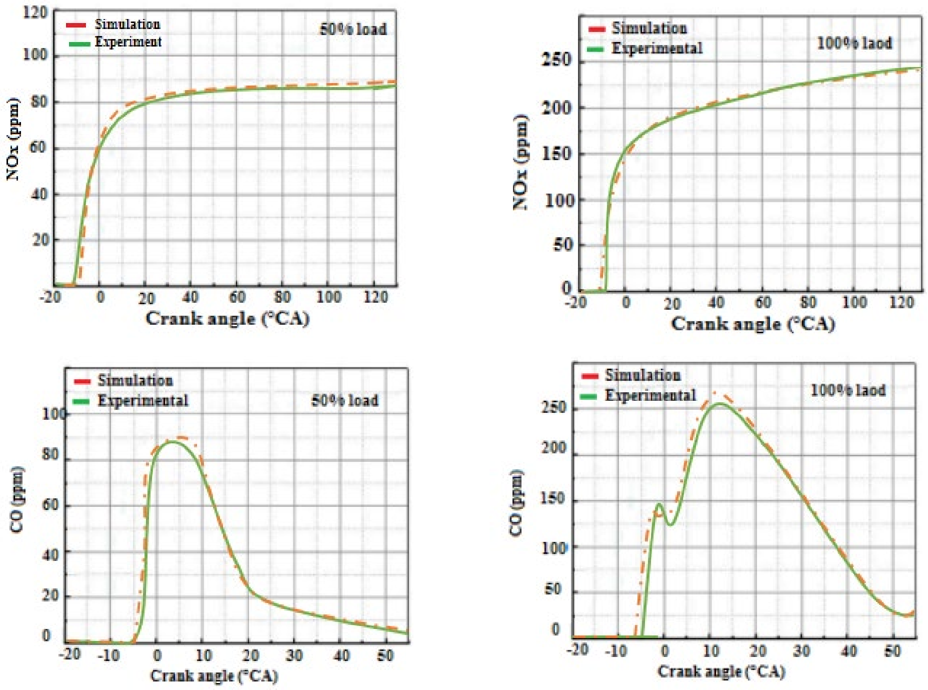


Figure 8. Simulated and experimental gas emission as function of crank angle at 50% and 100% load conditions: (a) NOx emissions and (b) CO emissions.

Figure 9 despites the variation in NOx and CO emissions as a function of the crank angles for both the commercial and desulfurized diesel. The decrease in NOx emissions in desulfurized diesel can be attributed to its decreased oxygen content after adsorption process via CNSs-IL (Figure 9a). Considering both CO and NOx emissions, desulfurized diesel demonstrates a more reasonable performance, achieving a significant reduction in CO emissions by 33 % and a in NOx emissions by 21.37% compared to commercial diesel.

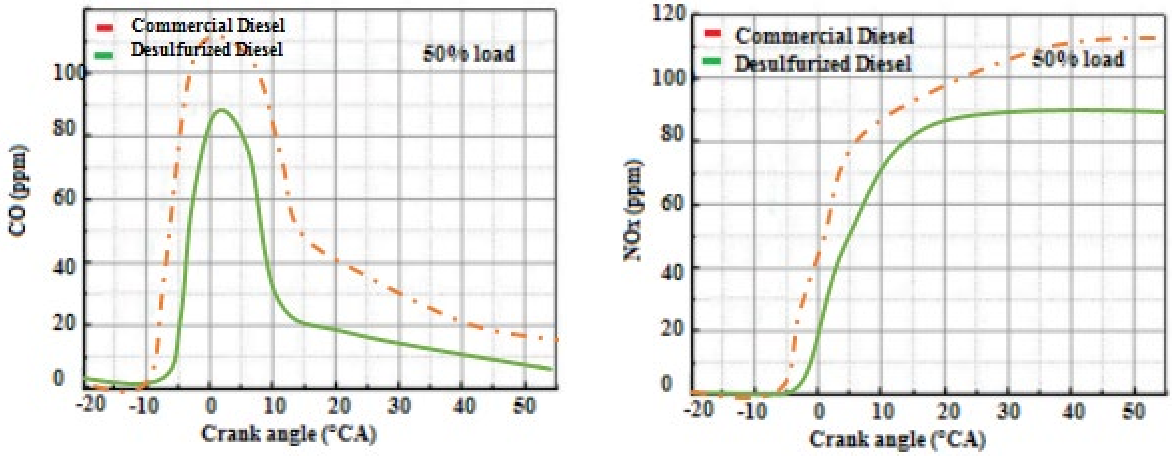


Figure 9. Comparison of gas emissions of commercial and desulfurized diesel: (a) CO emissions and (b) NOx emissions.

4. Conclusion

In conclusion, the work demonstrates that desulfurization of commercial diesel using functionalized imidazolium ionic liquid carbon nanospheres (CNSs-IL) is an effective method for significantly reducing sulfur, nitrogen, and aromatic contents in diesel fuel. The adsorption process, optimized under specific conditions, successfully decreased the sulfur content to 31 ppm while maintaining fuel integrity. Engine performance tests revealed that the desulfurized diesel not only met the required physico-chemical standards but also outperformed commercial diesel in terms of reduced brake-specific fuel consumption and lower emissions of SO_2, CO, and NOx. The numerical simulations further validated the experimental results, highlighting reductions of 33% in CO emissions and 21.37% in NOx emissions, thus underscoring the environmental advantages of the desulfurized fuel. Overall, this work confirms that the desulfurized diesel is a viable alternative for use in diesel engines, combining enhanced environmental sustainability with reliable engine performance.

References

[1] Mesdour S, Boufades D, Moussiden A, and Hamada B. Extractive dearomatization, denitrification, and desulfurization of gas oil fractions by a mixed extractant of N, N-methylpyrrolidone, N, N-dimethylformamide, and ethylene glycol via microwave radiations. Petroleum Science and Technology, 2019; 37(15): 1755-1762.

[2] Mesdour S, Lekbir C, Doumandji L, and Hamada B. Microwave-assisted extractive catalytic-oxidative desulfurization of diesel fuel via a VO(acac)2/ionic liquid system with H_2O_2 and H_2SO_4 as oxidizing agents. Journal of Sulfur Chemistry, 2017; 38(4): 421-439.

[3] Benmabrouka H, Mesdour S, Boufades D, Moussiden A, Berrabia N, Tliba L, and Hamada B. Vanadium-catalyzed extractive oxidesulfurization of commercial diesel in ionic liquid with combined oxidizing agents. Petroleum Science and Technology, 2019; 37(6): 662-670.

[4] Gunam IBW, Sitepu A, Antara NS, Triani IGAL, Arnata IW, and Setiyo Y. Bacterial desulfurization of dibenzothiophene by Pseudomonas sp. strain kwn5 immobilized in alginate beads. J Teknol., 2021; 83(2): 107–115.

[5] Agarry SE, Salam KK, Alade AO, and Oyelakin MA. Adsorptive desulfurization of diesel with modified pig dung: experimental design with optimization, kinetics, isotherms, and thermodynamics studies. Discover Applied Sciences, 2024; 6(8): 390.

[6] Bedoud K, Mesdour SHN, Boufades D, Moussiden A, Benmabrouka H, Hamada B, and Kaddour O. Process parameters and intensification effects of microwave exposure applied for the extractive oxidation of diesel: an optimization using response surface methodology. Petroleum Chemistry, 2024; 1-17.

[7] Gheni SA, Awad SA, Ahmed SMR, Abdullah GH, and Al Dahhan M. Nanoparticle catalyzed hydrodesulfurization of diesel fuel in a trickle bed reactor: experimental and optimization study. RSC Adv., 2020; 10(56): 33911–33927.

[8] Baklashkina KA, Samborskaya MA, Krivtsova KB, and Kraevskaya IO. Advantages of combining different processes for diesel fuel desulfurization. Petroleum & Coal, 2023; 65(1).

[9] Mesdour SHN, Boufades D, Boussak H, Saoud A, Demim S, Benmabrouka H, and Hamada B. Efficient removal of sulfur and nitrogen compounds from actual fuels by oxidation-extraction process using acid combinations. Materials Today: Proceedings, 2022; 49: 1118-1123.

[10] Chen K, Li W, Biney BW, Li Z, Shen J, and Wang Z. Evaluation of adsorptive desulfurization performance and economic applicability comparison of activated carbons prepared from various carbon sources. RSC Adv., 2020; 10(66): 40329–40340.

[11] Hammadou née Mesdour S, Boufades D, Boussak H, Moussiden A, Benmabrouka H, Demim S, and Kaddour O. Potential application of carbon nanospheres as adsorbents for the simultaneous desulfurization and demetallization of transportation fuels. Fullerenes, Nanotubes and Carbon Nanostructures, 2022; 30(4): 419-427.

[12] Hammadou née Mesdour S, Boufades D, Dahou M, Moussiden A, Boussak H, Demim S, and Linda LS. Synthesis and functionalization of carbon nanospheres from asphaltene fractions for crude oil upgrading and viscosity reduction. Fullerenes, Nanotubes and Carbon Nanostructures, 2024; 32(9): 851–865.

[13] Güzel B, Celebi N, and Yıldırım G. Synthesis and spectroscopic studies of carbon nanosheets (CNSs) produced by pyrolysis of phthalazinium betaines at relatively lower temperatures. Chemical Papers, 2019; 73: 2007-2017.

[14] Arpa O, Yumrutaş R, and Kaşka Ö. Desulfurization of diesel-like fuel produced from waste lubrication oil and its utilization on engine performance and exhaust emission. Applied Thermal Engineering, 2013; 58(1-2): 374-381.

[15] Bousbaa H, Benayad Z, and Naima K. Numerical analysis of fuel type effects on combustion and emissions of a turbocharged direct injection engine. Energy Thermofluids Eng., 2022; 2: 31–38.

[16] Tripathi G, Sharma P, Dhar A, and Sadiki A. Computational investigation of diesel injection strategies in hydrogen-diesel dual fuel engines. Sustainable Energy Technologies and Assessments, 2019; 36: 100543.

[17] Bousbaa H, Benayad Z, and Naima K. Numerical analysis of fuel type effects on combustion and emissions of a turbocharged direct injection engine. Energy Thermofluids Eng., 2022; 2: 31–38.

[18] Tripathi G, Sharma P, Dhar A, and Sadiki A. Computational investigation of diesel injection strategies in hydrogen-diesel dual fuel engines. Sustainable Energy Technologies and Assessments, 2019; 36: 100543.

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