SYNTHESIS AND APPLICATION OF GLYCERIN PITCH-DERIVED ACTIVATED CARBON FOR MODEL FUEL OIL DESULFURIZATION AND ELECTRODE USE

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by

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ADS	Adsorptive desulfurization
ACs	Activated carbons
DBT	Dibenzothiophene
SO_2	Sulfur dioxide
HDS	Hydrodesulfurization
ppm	parts per million
ppmw	parts per million by weight
H_2S	Hydrogen sulfide
EDLC	Electric double layer capacitor
FESEM-EDX	Field Emission Scanning Electron Microscopy – Energy Dispersive X-Ray
FTIR	Fourier Transform Infrared Spectroscopy
XRD	X-ray diffraction
TGA	Thermal Gravimetric Analysis
UV-Vis	Ultraviolet–visible spectroscopy
MOF	Metal-organic frameworks
H_3PO_4	Phosphoric acid
$Fe(NO_3)_2$	Iron (III) nitrate
PTFE	Polytetrafluoroethylene
pH_{PZC}	Point of zero change

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SINTESIS DAN APLIKASI SISA GLISERIN-KARBON AKTIF UNTUK PENYAHSULFURAN MODEL MINYAK BAHAN API DAN PENGGUNAAN ELEKTROD

ABSTRAK

Penyahsulfuran bahan api adalah penting bagi mematuhi peraturan alam sekitar dalam mengurangkan kandungan sulfur untuk mengurangkan pencemaran udara dan melindungi kesihatan manusia. Penyahsulfuran penjerapan (ADS) telah muncul sebagai kaedah yang berkesan dan cekap untuk menyingkiran sebatian sulfur daripada bahan api diesel. Kaedah ini memerlukan keupayaan penjerapan, seperti karbon aktif (ACs) untuk menangkap sebatian yang mengandungi sulfur secara selektif. Karbon aktif dihasilkan daripada sisa gliserin, iaitu sumber semula jadi dan bahan buangan industri. Agen pengaktif iaitu asid fosforik (H_3PO_4) dan ferum nitrat ($Fe(NO_3)_3.9H_2O$) telah dimanfaatkan dalam kaedah impregnasi basah. Matlamat utama kajian ini adalah untuk menekankan keupayaan karbon aktif gliserin sebagai bahan penyerap yang handal dan mesra alam untuk mencapai piawaian sulfur yang rendah bagi bahan api. Teknik-teknik pencirian seperti diffraksi sinar-X (XRD), analisis penyerapan nitrogen (NA), mikroskopi pengimbasan medan elektron-emisi pemantulan tenaga-X (FESEM dan EDX), spektroskopi transformasi fourier inframerah (FTIR), dan analisis termogravimetri (TGA) telah digunakan. Karbon aktif yang diimpregnasikan dengan asid fosforik menunjukkan kawasan permukaan yang tinggi (860 m^2/g) dan struktur berpori (0.4012 cm^3/g), ciri ini memudahkan penyerapan yang berkesan bagi sebatian sulfur seperti DBT. Pelbagai parameter dioptimumkan untuk meningkatkan kecekapan proses penyahsulfuran penjerapan termasuk kepekatan pengimpregnasi, suhu kalsinasi, suhu tindak balas, pH larutan,

masa larutan, jumlah penyerap dan kepekatan DBT dengan menggunakan bahan api diesel model sebanyak 100 kepekatan sulfur (ppm). Kajian tersebut akhirnya mengenal pasti parameter optimum untuk proses ADS, termasuk kepekatan impregnasi sebanyak 40%, suhu kalsinasi sebanyak 700 °C, suhu tindak balas sebanyak 30 °C, pH larutan sebanyak 4, masa larutan sebanyak 60 minit, jumlah adsorben sebanyak 0.5 gram, dan kepekatan DBT permulaan sebanyak 100 ppm. Ciri khusus yang telah ditetapkan ini dapat memberi impak yang tinggi dalam keupayaan menangkap DBT dari bahan api model diesel, memberikan wawasan baharu untuk menyelenggara proses penyerapan yang optimum dalam aplikasi penapisan bahan api. Hasil penemuan menunjukkan bahawa penggabungan fosforus meningkatkan kebolehan pilihan mekanisme ADS untuk penyingkiran DBT sehingga 87.78 % dan berupaya menyahsulfurisasi bahan api diesel sebenar. Kajian kinetik menunjukkan bahawa proses penjerapan mematuhi kinetik tertib pseudo kedua dan mematuhi model isoterma penjerapan Langmuir. Karbon aktif telah menunjukkan potensi untuk digunakan sebagai elektrod superkapasitor dengan kapasitan mencecah 0.65719 $\mu F/cm^2$, seperti yang ditentukan oleh voltametri kitaran. ini diperhatikan semasa penyiasatan terhadap pengaruh kandungan PTFE (10%) dan kadar imbasan (5 mV/s) Keputusan ini menunjukkan bahawa sisa gliserin boleh digunakan secara langsung sebagai pelopor yang bagus untuk pengeluaran karbon aktif berkualiti tinggi.

SYNTHESIS AND APPLICATION OF GLYCERIN PITCH-DERIVED ACTIVATED CARBON FOR MODEL FUEL OIL DESULFURIZATION AND ELECTRODE USE

ABSTRACT

Desulfurization of fuel is crucial in meeting environmental regulations in reducing the sulfur content to minimize air pollution and protect human health. Adsorptive desulfurization (ADS) has emerged as a viable and efficient method for sulfur compounds removal from diesel fuel. This method requires the ability of adsorbents, such as activated carbon (ACs) to selectively capture sulfur-containing compounds. Activated carbons was produced from glycerin pitch, a natural resource and industrial waste material, through the wet impregnation method employing activating agents, namely phosphoric acid (H_3PO_4), and ferum nitrate ($Fe(NO_3)_3.9H_2O$). The primary aim of this study is to emphasize the potential of glycerin pitch activated carbon as an efficient and eco-friendly material means to attain ultra-low sulfur fuel standards. The prepared activated carbons were characterized by X-Ray Diffraction (XRD), nitrogen absorption analysis (NA), field emission scanning electron microscopy-energy dispersion X-ray (FESEM and EDX), fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA). ACs impregnated with phosphoric acid have exceptionally high surface area (860 m^2/g) and porous structure (0.4012 cm^3/g) which provides ample sites for adsorption of sulfur compounds such as dibenzothiophene (DBT). A set of parameters including impregnation concentration, calcination temperature, reaction temperature, pH solution, contact time, adsorbent dosage and initial dibenzothiophene (DBT) concentration were studied to find the optimum conditions for the ADS process by

using 100 ppm model diesel fuel. The study ultimately identified the optimum parameters for the ADS process, which included an impregnation concentration of 40%, a calcination temperature of 700 °C, a reaction temperature of 30 °C, a pH solution of 4, a contact time of 60 minutes, and adsorbent dosage of 0.5 grams, along with initial DBT concentration of 100 ppm. These specific conditions were determined to yield the highest efficiency in removing DBT from the model diesel fuel, providing valuable insights for optimizing the adsorption process in fuel purification applications. The findings revealed that the inclusion of phosphorus enhanced the selectivity of the ADS mechanism for DBT removal up to 87.78 % and capable to desulfurize the real diesel fuel. Kinetic studies demonstrated that the adsorption process adheres to second-pseudo-order kinetics and conforms to the Langmuir adsorption isotherm model. The ACs demonstrated potential application as supercapacitor electrode with the specific capacitance of the device up to 0.65719 $\mu F/cm^2$, as determined by cyclic voltammetry. This was observed during the investigation into the influence of PTFE content (10%) and scan rates (5 mV/s). These results suggest that glycerin pitch waste can be directly utilized as a sustainable precursor for the production of high-quality activated carbons.

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Crude oil contains a diverse range of hydrocarbons, a significant level of organic sulfur, nitrogen, and oxygen-containing molecules, which are the primary contaminants in determined the oil quality. When combustion of fuels occurred, sulfur was emitted as sulfur dioxide (SO_2), a colourless, bad-odour toxic gas that has been one of the major sources that contribute to air pollution as it forms a thick smog and haze that brought a negative impact on both the health and environment (Azadi et al., 2023). A strict environmental regulation regarding the amount of sulfur in the transportation fuel has been limited to be about 10 ppm in many countries by 2010 (Stanislaus et al., 2010). European countries already applied new Euro 5 low-sulfur diesel fuel in 2013. Meanwhile Euro 3 emission standards were still used n in many countries, especially in South America, Africa, southeast Asia, and the Middle East (Xie et al., 2020). The conventional method for removing sulfur dioxide, hydrodesulfurization (HDS), has been found to be incompatible with the removal of sulfides, which is necessary to produce diesel fuel with a very low sulfur content. An alternate solution was needed to overcome some of the disadvantages associated with hydrodesulfurization.

Adsorptive desulfurization (ADS) was observed as a promising desulfurization method. ADS had several advantages over other desulfurization methods due to its outstanding desulfurizing effect and simple operation (Chen et al., 2020). Furthermore, the adsorptive desulfurization approached had gained popularity due to its ability to easily adsorb sulfur compounds using activated carbons (ACs) as its adsorbents. ACs are popular adsorbents due to their remarkable application in separation and purification technologies, as well as for their excellent adsorption performance. Adsorption performance was determined by the adsorbent's surface properties, such as pore volume, specific surface area, pore size, and pore size distribution (Jha et al., 2019). Apart from it, ACs was readily applied in electrochemical capacitors as the main active electrode component or support. This is attributed to its exceptional characteristics, including a high surface area.

1.1.1 Sulfur

The Sustainable Development Goals for 2030 prioritised a clean energy and environment. Sulfur containing compounds are one source of contamination towards the global environment (Saha et al., 2021). Organic and inorganic sulfur compounds existed in separate forms (Figure 1.1). Thiols, sulphides, and thiophene compounds make up the organic group (Svinterikos al., 2019). These are the primary sulfur sources found in crude oil. On the other hand, the inorganic category comprised elemental sulfur, hydrogen sulfide, and pyrites, which are typically encountered in dissolved or suspended particle forms (Haruna et al., 2022). Organic sulfur compounds such as benzothiophene, dibenzothiophene (DBT), and thiophene are abundant in crude oil-derived transportation fuels (Wang et al., 2010). The combustion of these compounds resulted in the production of poisonous gases such as SO_2, which posed a serious hazard to human health and well-being. It also acts as a precursor to acid rain and had caused corrosion issues in pipeline, pumping, and refining equipment (de Luna et al., 2018). The removal of these compounds from transportation fuels and other petroleum products was imperative to safeguard both human health and the environment.

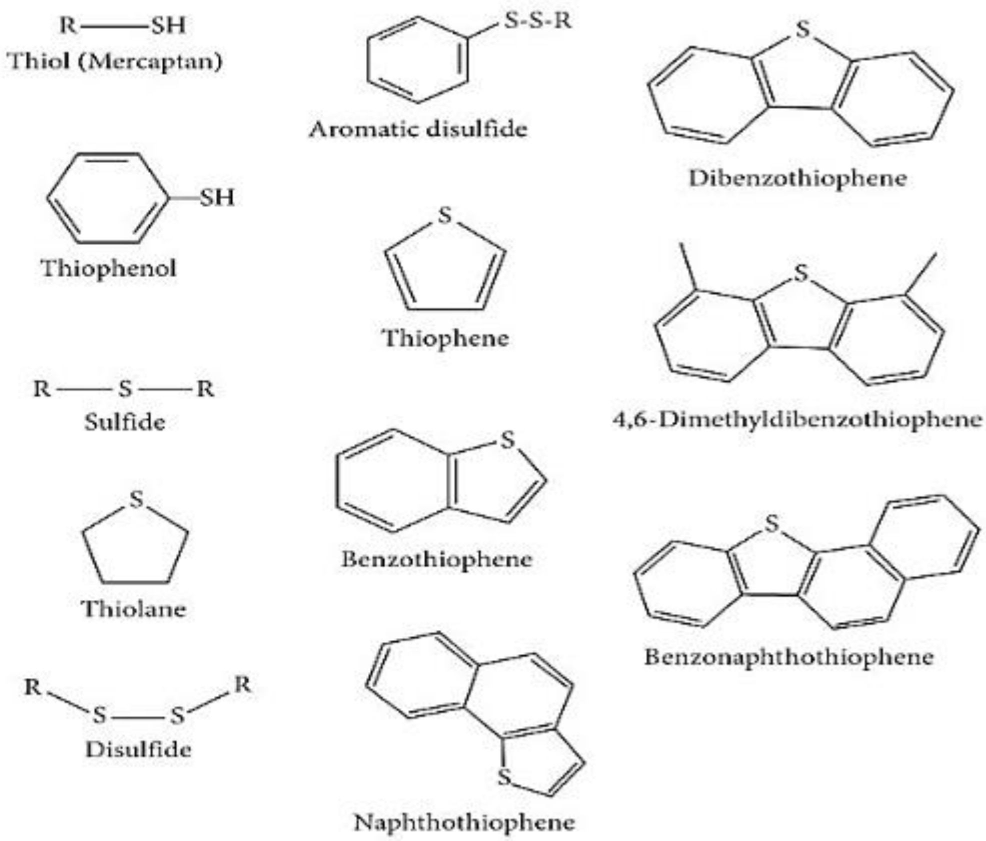

Figure 1.1 Organic sulfur compounds (Svinterikos al., 2019

Considering the harmful impacts of sulfur compounds on the environment, most countries had imposed strict limits on the amount of sulfur allowed in fuel to ensure the environment sustainability. Beginning in 2006, the United States Environmental Protection Agency (USEPA) implemented a strict environmental regulation limiting the amount of sulfur in diesel fuel to produce environmentally friendly fuel oil with a sulfur content ranging from 10 to 15 ppm in order to reduce harmful emissions (Singh et al., 2023). Many countries have limited the sulfur concentration to 10 ppm in 2016. Most of the countries have adopted ultra-low sulfur content standard way before Malaysia. Thailand adopted Euro 2 Standards way back in 2002, Hong Kong moved a step forward to Euro 3 Standards in 2002, meanwhile, Singapore, South Korea and Taiwan have migrated to Euro 4 Standards in the same year. Malaysia government started enacted the introduction of sulfur-free fuel with the Euro 2 Standards (500 ppm) in 2007. Since then, Malaysia begins to improve and updated their fuel quality (Francesch-Huidobro et al., 2014). In April 2020, despite the challenges posed by the Covid-19 pandemic, the government announced the nationwide replacement of Euro 2M diesel with Euro 5-grade diesel at retail petrol pumps. This transition had been carried out in full compliance with the Environmental Regulations of 2007 and the Environmental Quality Regulations of 2021. The adoption of Euro 5 diesel throughout the country was expected to have a positive impact on air quality, as this cleaner fuel had a significantly lower sulfur content of 10 ppm compared to Euro 2M's sulfur content of 500 ppm, leading to an overall improvement in the atmospheric conditions (Bernama et al., 2021). Malaysia had moved its ranking and listed among the countries that successfully achieved a low-level sulfur content as depicted in Figure 1.2. However, there are still refractive sulfur compound remained in diesel even after it reach ultra-low sulfur. These sulfur compounds were difficult to remove using current technologies. Besides, the current technique required high cost since it used pressure and hydrogen gas to operate. Therefore, a new alternative technology was introduced to overcome this problem.

The reduction of sulfur emissions to zero is expected to be achieved in the near future (de León et al., 2019). New environmental regulations imposed stringent requirements on the fuel industry in terms of the allowable sulfur content in fuels, with the goal of eventually reaching 0% sulfur content. The International Maritime Organization issued a global regulation in 2020 that will significantly reduce marine fuel sulfur concentrations from 3.50% to 0.5% to reduce harmful sulfur oxide emissions (Yu et al., 2023). China's national VI standard, which required a sulfur content of 1 ppmw had been implemented as the most recent vehicle emission standard. In addition, many governments worldwide had implemented regulations to restrict the sulfur content of fuels (Zhao et al., 2023).

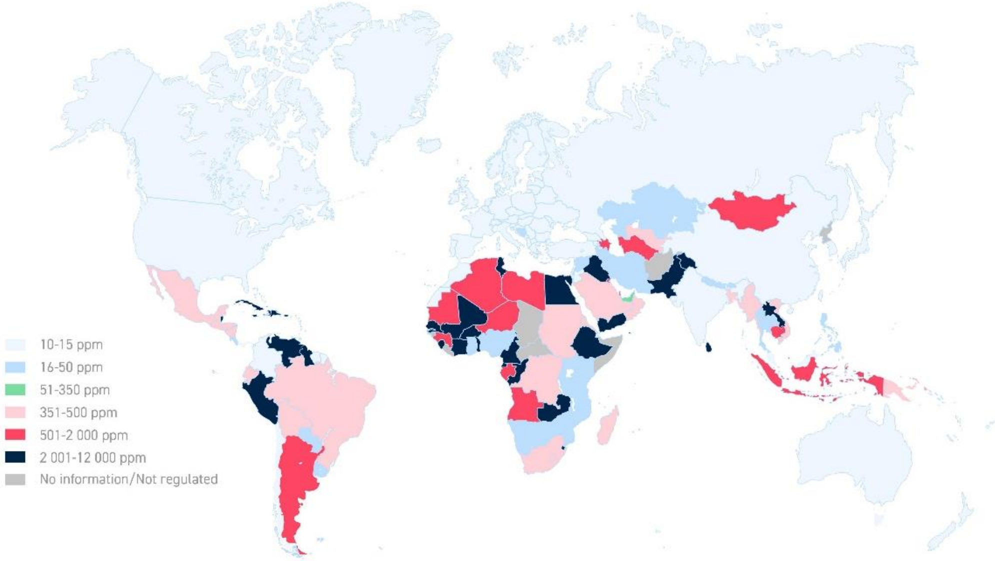

Figure 1.2 Global diesel sulfur level in 2023 (Stratas Advisors 2023)

1.1.2 Adsorptive Desulfurization

There efforts had been undertaken to discover a fast and effective desulfurization technology to tackle the high sulfur content present in diesel fuel. In order to ensure the sulfur level in diesel fuel complied with the government's rules. Adsorptive desulfurization (ADS) is a non-HDS approach had emerged as a promising ultra-clean technology for reducing SO_2 emissions and enhanced the quality of fuel oil. Adsorption had gained recognition as an efficient, cost-effective, sustainable, and environmentally friendly method for sulfur removal from crude oil and its derivatives (Gooneh-Farahani et al., 2023). In selecting an adsorbent for ADS, it is crucial to choose one with specific features that can be highly selective, as the efficiency of desulfurization heavily relied on its textural characteristics to ensure the effective removal of sulfur compounds. A suitable adsorbent should possess a large surface area, a significant pore volume, mesoporous structure, and high concentration of active sites on its surface (Mirshafiee et al., 2023). Various sorbent materials were utilized as adsorbents for thorough desulfurization processes. These materials included activated carbon, silica gel, zeolites, metal oxide nanoparticles, metal-organic frameworks, and amorphous silica-alumina materials (Saleh et al., 2018). The process of adsorptive desulfurization (ADS) begins with sulfur contaminants transferred from the fluid stream to the outer surface and subsequently diffused through the pores of the adsorbent.

1.1.3 Activated Carbon

Activated carbon (ACs) had a wide range of applications, including water treatment, air purification, and use as a catalyst in the chemical industry. The chemical and physical characteristics of this material enabled a broad spectrum of applications in both environmental and industrial contexts. Its large surface area resulted in a high adsorption capacity, allowed it to leach pollutants from environmental matrices (Younes et al., 2022). ACs exhibited several distinct advantages that made them superior compared to other types of adsorbents. These advantages included a high removal rate, the ability to address multiple types of pollution simultaneously, the elimination need minimal energy consumption, and the renewability of activated carbon as well as the recycling ability (Tian et al., 2022). The material chosen used in production of activated carbon was a critical decision as it significantly influenced the properties and cost of the end product. Generally, any readily available and cost-effective materials with high carbon content and low inorganic content were suitable as ACs precursors. Consequently, a wide range of precursors had been explored, including coconut shells, wood, petroleum pitch, biomass wastes, algae, and coffee grounds (Gonçalves et al., 2019). An essential aspect in the production of activated carbons was to ensure that they possessed an abundance of oxygen-containing groups, high porosity, and strong thermal stability. These characteristics were crucial for ACs to serve as primary adsorbents and provide the effective removal sites for SO_2 (Sun et al., 2020).

1.1.4 Glycerin pitch

Global energy consumption was increase rapidly, with industries contributed to approximately 50% of the world's energy usage. Malaysia had earned its reputation as the one of the largest producer and exporter of palm oil globally, boasting a production of 17.73 million tonnes of palm oil. The growth of Malaysia's palm oil industry had been remarkably rapid over the last four decades, and it was anticipated that the country would maintain an average production of 15.4 million tonnes of palm oil between 2006 and 2012. The figure rose steadily to reach 76.39 million tons in 2021, driven by the increased demand for biodiesel and oleochemicals (Armylisas et al., 2023). The production of various products from palm-based oleochemicals also resulted in the generation of multiple waste streams within the oil palm industry.

Glycerine pitch is a by-product collected during the distillation process in the production of refined glycerine. It is mainly composed of glycerol, fatty acids, and triglycerides. However, glycerine pitch faced limitations in alternative applications due to its substantial dust and contaminant content, along with high alkalinity and organic components. These properties posed environmental risks, potentially contaminating natural resources, soil, waterways, and groundwater if not treated properly (Hazimah et al., 2023). Presently, Malaysia's primary methods for treating glycerine pitch involved either incineration or sealing it in drums before landfill disposal. There are several attempts using glycerin pitch as a valuable source employed glycerine pitch can be employed as a medium in the fermentation process to produce liquid biofertilizer. Meanwhile, Hock et al., (2022) produced activated carbon from glycerin pitch for methylene blue removal after being distillate via zinc chloride activation. Moreover, glycerin pitch can be used as a sole binder to produce roofing tile (Teoh et al., 2021). These efforts eventually increased the glycerine pitch's economic value and built a workable waste management strategy for it. Glycerin pitch can be a significant challenge in the production of activated carbon for the desulfurization process, but effective methodology can help to ensure that the final product is high quality and able to meets sulfur regulatory standards.

1.1.5 Electrochemical Capacitor

Electrochemical capacitors had garnered significant attention in the realm of advanced energy storage due to their impressive attributes, including extensive cycle life, long-term durability, and exceptional specific power (Devi et al., 2023). Capacitors are considered a highly promising application due to their excellent power density across a broad spectrum of operating conditions. They had found widespread uses in electronic products, backup power systems, telecommunications, and hybrid electric vehicles over the past few decades. The performance of capacitors depended significantly on the active material used in their construction (Luo et al., 2022). The performance of electrode capacitors relied on the structure and morphological characteristics of the electrode materials. Typically, carbon nanotubes, activated carbon, and graphene oxide are frequently employed as active materials for constructing electrode capacitors because of their cost-effectiveness, prolonged stability, and exceptional power density (Elanthamilan et al., 2022).

Activated carbons had gained considerable attention as electrode materials for capacitors among various other materials. Their exceptional characteristics, including surface area, porosity, cost-effectiveness, and superior electrochemical stability, are vital factors contributing to their relatively high electrical conductivity. Consequently, the surface charge of ACs can be easily controlled by applying electric potential or current to facilitate ion storage. Leveraged the synergy of these superior features makes ACs well-suited for use in energy storage applications as electrodes for capacitors (Hou et al., 2012).

1.2 Problem Statements

Hydrodesulfurization is the traditional approach to reduce sulfur levels in diesel fuel. Unfortunately, it presents significant drawbacks in terms of operational cost and harsh processing conditions. Moreover, it less effective in eliminate organosulfur compounds from fuel, particularly refractory species like DBT. It's noteworthy that all fuel stations in Malaysia had already transitioned to using Euro 5 diesel, which contains only 10 ppm of sulfur. However, the economic viability of HDS becomes a pressing concern. Thus, there is a critical need to explore alternative or complementary processes that offer improved efficiency and sustainability in sulfur removal from diesel oil.

ADS stands out as a highly promising and efficient method for eliminating pollutants. It notable benefits including low cost, superior efficiency, and straightforward operational procedures. These benefits can be harnessed by finding the right adsorbent material that excels in sulfur removal and electrode performance.

There was various type of adsorbents like activated carbon, silica, metal-organic framework, zeolites and others.

It is important to find adsorbent that have exceptional adsorption capacity, highly versatile and can effectively adsorb a wide range of contaminants, can be regenerated and reused multiple times, cost-effective and compatible with a wide range of treatment processes and equipment. Most of the adsorbents doesn't have enough requirements as mentioned. A comprehensive examination of the adsorbent's properties will elucidate the underlying reasons for activated carbon's continued preference over alternative adsorbents.

Another thing to consider is choosing precursor for synthesize of ACs. Usually, ACs created from natural sources give a low surface area and pore structure. It is important to find natural sources that exhibit an exceptionally high surface area and have highly porous nature to maximize the adsorption capacity. Traditional organic materials such as rice husk, coconut shells, and coffee bean waste have been extensively used, the potential of alternative precursors like glycerin pitch remains relatively unexplored. The knowledge choosing glycerin pitch from industrial waste as ACs precursor and used in desulfurization process are limited.

The synthesis ACs must be able to desulfurize all the contaminants present in fuels. Unlike some alternative adsorbents, activated carbon exhibits versatile adsorption capabilities, making it suitable for comprehensive desulfurization processes. Additionally, activated carbon can be regenerated and reused, enhancing its cost-effectiveness and sustainability in fuel treatment applications.

Moreover, activating agent selected must be able to enhance the texture and overall effectiveness adsorption of ACs. Choosing the right activating agent is crucial for improving the texture and overall effectiveness of activated carbons in adsorption processes. The activating agent plays a key role in creating pores within the ACs structure, increasing its surface area and enhancing its ability to capture contaminants. Therefore, the choice of activating agent is essential in maximizing the efficiency of ACs in adsorption applications, ensuring cleaner and safer environments.

Another problem is the ability of synthesized ACs to be able to be used in supercapacitors. The synthesized ACs are expected to have a good electrochemical property, conductivity, and to ensure reliable performance in electrode applications.

Addressing these challenges is essential for unlocking the full potential of glycerin pitch-derived activated carbon as a multifunctional material for both desulfurization and electrode applications.

1.3 Objectives of Research

The objectives of this study are:

1. To synthesis and characterize activated carbon derived from crude glycerin pitch.
2. To study the desulfurization performance of activated carbon towards of model and real fuel.
3. To evaluate adsorption behaviour of activated carbon.
4. To study the potential of AC as electrode material.

1.4 Scope of Study

The objectives of this study were achieved by focusing on four main scopes. First scope was synthesis of activated carbon derived from glycerin pitch through chemical activation. Glycerin pitch used as a natural carbon source in the production of activated carbon. The main components of glycerin pitch, such as glycerol, fatty acids, and triglycerides, undergo thermal decomposition during carbonization, leading to the formation of carbonaceous residues. These residues, when subjected to chemical and physical activation, undergo further structural rearrangement and pore development, resulting in the creation of activated carbon with desirable adsorption properties. The activation process involves the introduction of activating agents at high temperatures to create a porous structure within the carbonaceous material, thereby increasing its surface area and adsorption capacity. The process utilized is known as the wet chemical impregnation method, employing phosphorus and iron as activating agents. Through careful control of processing parameters such as activation temperature, and activating agent concentration, glycerin pitch can be effectively utilized as a precursor for the production of activated carbon with tailored properties suitable for various applications, including fuel treatment, and energy storage. The prepared activated carbons undergo various characterization techniques to verify properties of the synthesized activated carbon, including surface area, pore size distribution, morphology, functional groups, and elemental composition. Activated carbons were characterized by using nitrogen adsorption/desorption technique, x-ray diffraction (XRD), field emission scanning electron microscope with energy dispersive X-ray spectroscopy (FESEM-EDX), fourier-transform infrared spectroscopy (FTIR), and thermogravimetric analysis (TGA).

The second scope to assess the desulfurization efficacy of activated carbon towards both model and real fuel samples. Adsorptive desulfurization method was employed to remove the sulfur contaminant in both model and real diesel. Desulfurization experiments were conducted using activated carbon synthesized previously and the performance was evaluated under controlled conditions. A few experimental setups will be devised to find the optimised desulfurization efficiency. The parameters include effect of reaction temperature (30, 50 and 80 °C), pH (2, 4, 6, 8, 10, 12), dosage (0.05, 0.1, 0.3, 0.5, 0.8, 1.0), contact time (15, 30, 45, 60, 75, 90, 105, 120 min), initial sulfur concentration (100, 300, 500, 700 and 900 ppm), and recycle test. The optimized desulfurization process, developed through experimentation, was applied to desulfurize actual diesel samples. Both the untreated diesel and the desulfurized diesel underwent X-ray fluorescence (XRF) analysis to detect any variations in sulfur concentrations. This research activities provide valuable insights into activated carbon's desulfurization potential and its applicability in addressing sulfur emissions from fuel sources.

The third scope was the kinetics and adsorption behaviour of ACs in removing target pollutants from aqueous solutions. It involves conducting kinetic studies to assess the rate of pollutant removal using both pseudo-first order and pseudo-second order kinetic models. The pseudo-first order model assumes a rate-limiting step of adsorption onto a finite number of active sites, while the pseudo-second order model considers chemisorption between adsorbate and adsorbent as the rate-determining step. Furthermore, adsorption studies were conducted using Langmuir and Freundlich isotherm models to analyse the equilibrium adsorption behaviour of the adsorbent. The Langmuir model describes monolayer adsorption, providing insights into maximum adsorption capacity, while the Freundlich model characterizes multilayer adsorption, elucidating adsorption affinity and heterogeneity. By comprehensively investigating both kinetics and adsorption behavior, this research aims to offer valuable insights into the potential application of activated carbon material for sulfur removal in aqueous environments.

The last scope was the investigation on the potential of activated carbon as an electrode material for energy storage applications. The scope of research involves comprehensive characterization of ACs to assess its suitability for use in electrochemical devices. Key aspects of the investigation include evaluating the electrochemical properties of ACs, such as capacitance, through electrochemical testing and analysis. Additionally, the research explored the influence of scan rates (5, 20, 50, 100 mV/s) and binder contents (10, 15, 20, 25, 30 %) on the supercapacitance values. By systematically studying these factors, this research aims to provide valuable insights into the potential of ACs as an electrode material for enhancing energy storage efficiency and sustainability.

1.5 Significance of Study

An important concern associated with diesel fuel in Malaysia pertain to the existence of organosulfur compounds, which had the potential to diminish the quality of diesel. At present, the predominant approach for sulfur reduction in diesel fuel is predominantly centered around hydrodesulfurization. However, HDS had been found to be less effective in addressing this issue. Adsorptive desulfurization method is introduced by using activated carbon as adsorbent to produce low sulfur diesel. This study is significant because ADS technique applied had a simple operation process compared to HDS. ACs can be prepared using common chemical solution and do not require high condition of temperature and pressure. ADS also effective in removing sulfur and had high ability to extract aromatic compound in a short time. Furthermore, ADS is environmentally friendly approach since it utilized glycerin pitch waste as the sources to synthesize adsorbents and it can be reused again several times. Moreover, the removal of impurities from diesel fuel can result in an increase in the price of diesel fuel, ultimately contribute to the improvement of the country's economy. Hence, this research holds significant importance in addressing the existing desulfurization techniques to meet the Euro 5 specifications. This aligned with broader environmental goals aimed at mitigating pollution and promoting the use of cleaner fuels for a more sustainable environment. The ADS process had the potential to produce green diesel and can be considered as a green and sustainable technology. This project's distinctiveness stems from the absence of prior research on the utilization of activated carbon derived from glycerin pitch for desulfurization purposes.

CHAPTER 2

LITERATURE REVIEW

2.1 Desulfurization Techniques

Hydrodesulfurization widely used industrial process for removing sulfur compounds from crude oil and other hydrocarbon feedstocks. The HDS process involved the use of hydrogen gas and a catalyst, typically composed of metals such as molybdenum or cobalt supported on alumina or silica, to break down sulfur-containing compounds, such as thiols, sulfides, and thiophenes, into hydrogen sulfide (H_2S) and other byproducts. H_2S then removed from the hydrocarbon stream through various separation techniques, such as absorption, adsorption, or chemical conversion (Javadli et al., 2012). The HDS process occurred at high temperature and pressure to maintain the hydrogen gas in a liquid state, allowed it to penetrate the hydrocarbon molecules and react with the sulfur compounds. The catalyst was essential for facilitating the reaction between the hydrogen and sulfur compounds and ensuring high selectivity towards sulfur removal. HDS was a highly effective method for removing sulfur compounds from crude oil and other hydrocarbon feedstocks.

However, it had several drawbacks (Marafi et al., 2019). Hydrodesulfurization is a complex process that involved high production costs and requires significant material consumption. The increased demand for heavy crude oil has resulted in a shortened catalyst lifespan at refineries. Additionally, HDS requires hydrogen (H_2), which significantly drives up production costs. Effectiveness of HDS was limited in removing aromatic sulfur compounds.

A new alternative of desulfurization process called extraction desulfurization had been introduced. Desulfurization via extraction depends on the solubility of the organosulfur compounds in certain solvents (Seredych et al., 2012). Extractive desulfurization was an attractive method because of it was a straightforward industrial application and it dot not had requirement for H_2. The solvent reacted with the sulfur compounds to form a product that can be easily separated from the material. It was a purely physical extraction. However, the solubility of organosulfur compounds in the solvent restricted the effectiveness of extractive desulfurization. It was crucial to select a suitable solvent that can effectively undergo physical separation from the oil. The choice of solvent should have low equilibrium solubility in the oil and exhibit low viscosity to facilitate the extraction of sulfur from the oil.

Meanwhile, oxidative desulfurization process involved a chemical reaction between an oxidant and sulfur that facilitates desulfurization (Betiha et al., 2018). The sulfur-containing compounds in diesel fuel were first oxidized using an oxidant, such as hydrogen peroxide, ozone, or air, in the presence of a catalyst. The oxidized sulfur compounds then reacted with the solvent, which is usually polar, to form soluble sulfones that can be easily separated from the fuel using conventional methods, such as distillation. One of the biggest difficulties of oxidative desulfurization was the selectivity of the oxidation reaction, as the oxidant can react with other components of the fuel and produce unwanted byproducts.

Another approach for desulfurization was biological desulfurization. It was a process extracted the sulfur from fossil fuels without causing the hydrocarbon chains to break or altering the carbon structures (Sarda et al., 2012). Biodesulfurization occurred at low temperatures and pressures in the presence of microorganisms capable of metabolizing sulfur compounds. This process enables the direct desulfurization of crude oil by selecting suitable microbial species. There are two main types of biological desulfurization: aerobic and anaerobic. Aerobic desulfurization used bacteria that can metabolize sulfur compounds in the presence of oxygen, while anaerobic desulfurization used bacteria that can metabolize sulfur compounds in the absence of oxygen. However, there were also some challenges associated with biological desulfurization, including the need for careful control of the growth conditions of the microorganisms and the potential for microbial contamination of the fuel. The process also relatively slow and may not be suitable for large-scale industrial applications (Cattaneo et al., 2023).

The various methods for desulfurization present different approaches with distinct advantages and limitations. HDS is a widely used industrial process due to its effectiveness in sulfur removal, but it suffers from high costs, short catalyst lifespan, and limitations in removing aromatic sulfur compounds. Extraction desulfurization offers a simpler alternative without requiring hydrogen, but its effectiveness is limited by solvent solubility constraints. Oxidative desulfurization faces challenges in selectivity during oxidation reactions. Biological desulfurization presents an intriguing approach by utilizing microorganisms, but it is hindered by slow process rates and potential for microbial contamination. Among these methods, adsorptive desulfurization stands out as the most promising due to its versatility, cost-effectiveness, and ability to selectively remove sulfur compounds without altering the hydrocarbon structure. Additionally, adsorptive desulfurization does not require high temperatures or pressures, making it suitable for a wide range of applications and offering potential for integration with existing industrial processes.

2.1.1 Adsorptive Desulfurization System

HDS widely used technology for sulfur removal from petroleum fractions. Alternative sulfur removal method was introduced to overcome HDS method.

Adsorptive desulfurization was the among the top techniques used to remove sulfur-containing compounds from liquid fuels. ADS was often conducted using solid sorbents with varying levels of porosity and functionalities to achieve maximum adsorptive capacity. The adsorbents played an important role in selective adsorb sulfur compound. Each adsorbent material had its own strengths and weaknesses and suitable for different applications.

The choice of adsorbent for ADS depended on several factors such as the type and concentration of pollutants to be removed, the flow rate and temperature of the air stream, and the desired level of pollutant removal efficiency. It important to select an adsorbent that is effective, cost-efficient, and environmentally sustainable for the specific application. Prior literatures had focused on the typically used adsorbent within the procedure of adsorptive desulfurization of sulfur compound.

2.1.2 Adsorbent for Adsorptive Desulfurization

There were few types of adsorbents had been approached to achieve a low sulfur level. Metal-organic frameworks (MOF) were one of the adsorbents that had captured the attention of researchers due to their growing potential in various applications such as storage, adsorption, catalysis, and separation processes. MOF used in ADS systems have high selectivity and adsorption capacity for certain types of pollutants, including volatile organic compounds, carbon dioxide, and sulfur dioxide. Anyhow, MOF was unstable under certain conditions, such as high temperatures or exposure to moisture (Ahmed et al. 2014). MOFs' remarkable selectivity can be attributed to their exceptional porosity, including both micro and mesoporous characteristics, as well as their ability to adjust their structure to accommodate different shapes and sizes. The performance of MOF was enhanced by altering chemical nature by employing methods such as grafting, post-synthetic modification with functionalized organic linkers, and integrating active species (Khan & Jhung et al. 2017).

A detailed exploration by Zhou et al. (2023) provided the potential of titanium-based metal-organic frameworks (Ti-MOF) as a material for effective adsorptive desulfurization. Ti-MOF was made of Ti_8O_8 ring-shaped cluster and 2-aminoterephtalic acid, which contain a functionalized metal–organic backbone that was expected to bring adsorption properties. They achieved an equilibrium adsorption amount (q_e) of 112 mg/g for the adsorption of DBT. Another MOF, CPO-27-Ni, was synthesized using solvothermal method by Yan et al., (2023). They considered CPO-27-Ni as a promising adsorbent for adsorptive desulfurization applications. As a result, they reported a 0.2981 mmol S/g in desulfurization activity. Additionally, after three cycles of adsorption and regeneration, the loss in desulfurization efficiency was minimal. Mguni et al., (2021) also synthesized Ni-based-MOF exhibited a high overall adsorptive activity of 4.14 mg S/g with the addition of formic acid.

Zeolites had been recognized for their significant adsorption capacities and their potential to adsorb organosulfur compounds. Zeolites were a type of crystalline aluminosilicate mineral with a highly ordered porous structure (Pérez-Botella et al., 2022). They were composed of silica and alumina tetrahedra linked together to form a three-dimensional framework with regular channels and cavities. Synthetic and natural zeolites were frequently used in adsorptive desulfurization, but the utilization of natural zeolites in adsorption studies is relatively uncommon. One of the reasons for this rarity could be attributed to the challenges associated with purifying natural zeolites, as they often contain numerous impurity phases within their primary structure.

Xiao et al., (2022) were successfully fabricated zeolite nanocrystals, ZSM-5, using via condensed viscous powder system through steam-assisted gel crystallization. The preparation of ZSM-5 zeolites for adsorptive desulfurization from fuel requires careful controlled of several parameters, including the choice of synthesis method, surfactant template, and synthesis conditions. With proper understanding and control of these parameters, the preparation process was facile and controllable. The desulfurization activity of ZSM-5 zeolites was conducted using fixed-bed adsorption experiments with 1.0 g of adsorbents with selected particle sizes of 0.250-0.425 mm. ZSM-5 zeolite achieved adsorption capacity of 0.0550 mmol S/g for the adsorption of thiophene of 500 ppmw. Zhang et al., (2023) synthesized a different type of zeolite by incorporating cuprous oxides into the pores of zeolite Y. This involved ion exchange, where Cu^{2+} ions were introduced into the pores of zeolite Y. Some of the Cu^{2+} ions were then reduced to cuprous oxide using sodium borohydride as a reducing agent. The results showed that the zeolite adsorbent demonstrated outstanding desulfurization performance with a capacity of 20.0 mg of sulfur per gram (20.0 mg S/g) for DBT and could be regenerated and reused for up to 15 cycles.

Metal oxide-based adsorbents had been explored for ADS due to their appealing characteristics, including straightforward synthesis methods, strong structural stability, and resistance to common solvents (Jing et al., 2023). Among the most employed metal oxide adsorbents are Al_2O_3, SiO_2, ZnO, TiO_2, and mixed metal oxides. One advantage of using metal oxide adsorbents was their high adsorption capacity and selectivity for certain pollutants. However, there were also some limitations to using metal oxide adsorbents in ADS systems by controlling their selectivity and activity towards specific pollutants.

A TiO_2-SiO_2 mixed metal oxide-based adsorbent with high surface area mesopores was studied for ADS by Qin et al., (2018). The ADS of the metal oxide adsorbent achieved an impressive 99% removal of sulfur desulfurization efficiency with sulfur concentration of 500 ppm. This exceptional desulfurization performance was attributed to the modification of TiO_2 with SiO_2. It resulted in a material with a large specific surface area and significant surface acidity. In accordance with the Lewis acid-base theory, it was observed that most thiophene-based sulfur compounds in fuels act as Lewis bases, made them readily adsorbable by Lewis acidic sites. The enhanced desulfurization performance was attributed to the increased presence of Lewis acid sites when TiO_2 was modified with SiO_2, along with the concurrent generation of Bronsted acid center. The adsorption efficiency study of mixed metal oxide was continued by Watanabe et al., (2021). They synthesized Ti-Ce oxide-based adsorbent through a urea precipitation method from aqueous solutions of inorganic salts. Cerium (IV) oxide, titanium (IV) oxide, and their mixed oxide were utilized in this synthesis process. The Ti-Ce mixed oxide adsorbents typically exhibit higher desulfurization efficiency than single oxide adsorbents due to their synergistic effects. It has been found that Ti cations on the surface of Ti-Ce mixed oxides provide the Lewis acid sites that enable the coordination of the sulfur-containing species through the lone pairs of electrons on the sulfur atoms. Meanwhile Ce cations, on the other hand, provide the necessary oxygen vacancies that allow for the adsorption of sulfur-containing species by creating surface oxygen vacancies and increasing the surface area of the mixed oxide adsorbent. The Ti-Ce oxide adsorbents were reported to significantly reduce the sulfur content in fuel, decreasing it from

1055 to less than 1 ppmw in multiple cycles of adsorption within a fixed-bed flow system.

Silica is a type of adsorbent made from a naturally occurring mineral. It was a porous material with a large surface area, which made it an excellent adsorbent (Zhu et al., 2015). The adsorption characteristics of silica gel were attributed to its expansive surface area and the existence of polar groups on its surface. One of the advantages of silica gel as an adsorbent was its ability to be regenerated and reused. After it had adsorbed a substance, the silica gel can be heated to drive off the adsorbed molecules and restore its adsorption capacity. Kaur et al., (2022) discussed the synthesis and application of SBA-15 supported benzoxazolium-based ionic liquids in adsorptive desulfurization. SBA-15 was a type of mesoporous silica material that has a highly ordered pore structure, made it an ideal support for the immobilization of ionic liquids. SBA-15 achieved a remarkable 78.9% sulfur removal of DBT within a 100-minute timeframe and could be reused up to ten times.

Ionic liquids had played a crucial role in ADS studies by offering space and accommodation for thiophene compounds (Su et al., 2004). Ionic liquids with high π-electron density assisted in the removal of sulfur molecules through π-π stacking interactions within the molecules. In a separate study, Zhang et al., (2018) synthesized an adsorbent for the adsorptive desulfurization of dibenzothiophene. This adsorbent was created by functionalizing metal onto poly-ionic liquids that were grafted onto silica gel, denoted as P-4. The researchers synthesized the polyionic liquids using a combination of polyethylene glycol and ionic liquids, which were then functionalized with metal phthalocyanine complexes. P-4 adsorbent efficiently showed 52.41 mg/g DBT was adsorbed through ADS by using optimal amount of adsorbent 10 g/100 mL of model oil.

Activated carbon (ACs) is an amorphous form of carbon treated specially to produce a large surface area and a well-developed internal pore structure. It is a microcrystalline, non-graphite, amorphous, tasteless, form of carbon. It is a diverse adsorbent containing up to 90% carbon with unique textural properties which include a high degree of porosity and high surface area. There are a few classifications of ACs, such as powdered activated carbon, granulated activated carbon, pellet activated, carbon, activated carbon cloths, fibrous activated carbon, and extracted activated carbon. Due to its versatility, many researchers have sought to lower costs associated with activated carbon by either using inexpensive source materials to produce carbon or by conducting surface modifications. Most of the times, ACs may be produced from industrial byproducts, agricultural waste, and livestock (Azeez & Ganiyu, 2018)

In a study of Mhemed et al., 2020, spent coffee grounds was used as a precursor for the preparation of ACs as it a cost-effective and sustainable material. The production of spent coffee grounds was abundant that it made 748,000 tons per year. Spent coffee grounds were first dried before was mixed with a solution of phosphoric acid. Then the mixture was introduced into a horizontal tubular furnace and heated from room temperature to desired temperature at a heating rate of 5 °C/min^{-1} for 120 min. The obtained products were used to desulfurize 100 ppm thiophene compound. The optimum spent coffee grounds ACs exhibited the highest adsorption capacity, with up to 2.23 mmol/g. Brewer's spent grains (BSG) were utilized for AC production, and silver nanoparticles were chosen for sorbent modification to enhance its activity in eliminating DBT components. The study reported that BSG-AC exhibited an adsorption ability of 80% when tested with an initial concentration of 100 ppm of DBT. The regenerated BSG-AC was then reused