

Perspective

# Biodesulfurization Processes for the Removal of Sulfur from Diesel Oil: A Perspective Report

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**Abstract:** The presence of elevated levels of sulfur in diesel oil results in an increased sulfur content in the process stream, which poses significant risks to human health, animals, the environment, vehicles, and infrastructure. Sulfur is a major contributor to particulate matter (PM) and total PM emissions. The level of pollutants emitted is correlated to the sulfur content in diesel fuel. Consequently, regulations regarding the sulfur content in crude oil products, particularly in diesel oil, have become increasingly stringent. Refiners are working to develop sulfur-free fuels with less than 10 ppm of sulfur. To address the impending threats to human health and the environment, and the impact of climate change on property, eco-friendly desulfurization techniques such as biodesulfurization (BDS) are being explored. Several bacterial species have been identified for the BDS of diesel oil, but extensive studies are needed to fully understand the mechanism. Further research on BDS is also required to make it more attractive and competitive in industrial applications. Combining BDS with other technologies for the desulfurization of diesel oil can potentially reduce operating costs and improve resource allocation, making this innovation a viable option for industry.

**Keywords:** biodesulfurization; sulfur; dibenzothiophene; diesel fuel; recalcitrant organosulfur



**Citation:** Mamuad, R.Y.; Choi, A.E.S. Biodesulfurization Processes for the Removal of Sulfur from Diesel Oil: A Perspective Report. *Energies* **2023**, *16*, 2738. <https://doi.org/10.3390/en16062738>

Academic Editors: Antonio Zuorro, Athanasios I. Papadopoulos and Panos Seferlis

Received: 30 January 2023

Revised: 13 March 2023

Accepted: 14 March 2023

Published: 15 March 2023



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## 1. Introduction

Sulfur and its derivatives are in the top three common substances in the crude oil and petroleum industry ranging from 0.03% to 7.89% (*w/w*) [1]. Aside from the damages sulfur dioxides brought to catalytic converters in vehicles, severe ecological contamination that impacts the health of people and animals happens when sulfur-containing oil is directly combusted, as a large amount of sulfur dioxide is emitted to the environment [2]. Sulfur in different forms of oxides in the atmosphere generates acid rain when reacting with water vapor. Acid rain can damage the flora and fauna in our ecosystems, can even cause faster corrosion in buildings and metallic structures, and can cause bankruptcy in agriculture due to the reduced efficiency of photosynthesis processes [3]. Sulfur dioxide (SO<sub>2</sub>) also contributes to smog containing sulfur derived from the elevated level of sulfur oxides (SO<sub>x</sub>) present in the atmosphere and is exacerbated by dampness and particulate matter (PM). Sulfur was reported as one of the principal sources of particulate matter in the airspace. About 2% of sulfur-containing substances in diesel oil are immediately transformed into sulfate PM [4]. To solve this issue, sulfur content regulation in crude oil products, particularly in diesel oil, has become increasingly stringent [5]. Refineries are also undertaking initiatives to make advances in producing fuels within the standard sulfur level (less than 10 ppm). A nonstop worldwide campaign aiming at a lower sulfur content in diesel oil is underway and several nations have adopted policy initiatives to require stricter emission standards. More countries are decreasing the sulfur level in diesel and at the same time implementing stricter emission standards. Fuel quality improvements can sometimes outpace emission standards. For example, Euro IV low-sulfur diesel was adopted in most European countries when Euro III emission standards were still in place [6]. Strata's

advisors confirmed the nonstop campaign worldwide towards lesser sulfur content in diesel oil and identifies several nations that have placed themselves along policy initiatives to require progress soon. Among the top 100 countries, European countries dominated the top 40, and the Philippines was one of the countries newly added in 2019 and ranked at 76th place in the year 2022 [7]. Numerous innovations have been created to develop better techniques for achieving ultra-deep desulfurization. Among these are improving hydroprocessing infrastructure, improving hydroprocessing catalysts, having additional steps for removing refractory sulfur-containing compounds, and improving the quality of feedstocks [8].

Sulfur is a critical polluting component in diesel and has been the object of stringent regulation. Regular grades of diesel contained as much as 5000 ppm of sulfur while low-sulfur grades contain no more than 500 ppm sulfur. Ultra-low sulfur contains a maximum of 15 ppm and diesel contains less than 10 ppm [9]. The sulfur-containing compounds include thiols, thiophenes, substituted benzo and dibenzo thiophenes (BTs and DBTs), benzonaphthothiophenes (BNT) and many more complex molecules [10]. Recalcitrant organosulfur oil compounds in the form of BTs, DBTs, alkyl DBTs and its derivatives are the primary sulfur-containing compounds in diesel oils that need to be removed to achieve a sulfur-free diesel oil [11]. Diesel sulfur contents of 1000 ppm, 350 ppm and 19 ppm were found to emit sulfur compounds and the PM formed after combustion that pose hazards to humans, the environment and in diesel engines [12]. Multiple refinery strategies and recent technologies have been developed that can be used to remove sulfur [13]. Numerous studies have been conducted to remove these compounds of sulfur from diesel oil. Hydrodesulfurization (HDS) is conventionally applied in the industry but has the disadvantage of operating in extreme conditions and requires expensive catalysts and equipment [14]. HDS goes through the process at an elevated temperature (290–455 °C) and elevated pressure (150–3000 lb/in<sup>2</sup>). This method also displays difficulty in removing one of the major sulfur compounds in diesel oil which is DBT [15]. Adsorptive desulfurization (AD), on the other hand, has the advantage of high sulfur removal efficiency and operates under low conditions but the utilization of this method in actual fuel oil is not yet successful, aside from its poor reusability [16]. Extractive desulfurization has the advantage of operating at ambient conditions and has low energy requirements, but the disadvantage is the high solvent cost and the generation of secondary pollutants [17,18]. One of the favorable approaches in the desulfurization of diesel oil, and the focus of the studies at present, is oxidative desulfurization [19]. This is due to its high efficiency, high selectivity, cost-effectiveness, operation on moderate conditions, usually at low temperature (less than 100 °C) and atmospheric pressure, and its high recyclability [20]. However, the problem with catalytic oxidative desulfurization is the difficulty in catalyst preparation and requirement for the utilization of corrosive oxidants. The new method which opens the way for an alternative potential desulfurization strategy is biodesulfurization (BDS) that utilizes the diverseness of microorganisms; the method only requires mild, ambient conditions of pressure and temperature and solved the dilemma of high-cost catalysts [21]. BDS' greater advantage is the possibility of desulfurizing BTs and DBTs and alkylated derivatives while restoring the calorific value of oil in an economical, effective, and environmentally friendly way [3].

Considering the vast advantages of using the BDS process as a purification technique for diesel oil, this paper aims to provide information about the recent technologies involved in the BDS of diesel oil. It will focus on presenting the emerging trends of diesel oil and its production. This paper will also present an overview of the different desulfurization technologies, but focus on the BDS method as a diesel purification technique. A detailed mechanism of BDS will also be discussed, the bacteria utilized for BDS, the techno-economic perspective of utilizing BDS compared to other desulfurization methods, and the present update on the possibility of utilizing this method in the industry.

### 1.1. Effects of Sulfur

High sulfur content in diesel oil leads to the high sulfur content of substances in the process stream. These sulfur-containing compounds are dangerous to humans, animals, the environment, vehicles, and infrastructure. The consequence of sulfur to health, property, and the environment was identified and will be discussed in this section.

#### 1.1.1. Effects on Human and Animal Health

Internal combustion engines use diesel oil to power many automobiles and generators. Sulfur is identified as one of the principal sources of PM and total PM emissions. The quantity of the said pollutants is correlated to the quantity of sulfur in diesel fuel. A study conducted by U.S. Environmental Agency (USEPA) found out that 2% of the sulfur in diesel fuel is modified as direct PM. PM is the most dangerous vehicle emission to humans and animals. It has been found out that PM with a particle size of less than 2.5 microns in aerodynamic diameter (PM 2.5) is also carcinogenic [22]. PM 2.5 is related to lung cancer and cardiopulmonary mortality. Furthermore, non-stop exposure to PM 2.5 brings about a series of chronic illnesses which involve infections in the respiratory system, aggravating current asthma, congenital heart disease, deep-rooted bronchitis, and cerebrovascular diseases [4].

#### 1.1.2. Effects on Environment and Infrastructure

Oxides of nitrogen (NO<sub>x</sub>), SO<sub>2</sub>, and PM are the substances present in flue gas from combustion in a diesel engine. If these gases are present in the atmosphere and react with water, oxygen, and other chemicals, this will lead to the generation of acid compounds known as the precursors to acid rain and smog. Acid rain, particularly in the form of sulfuric and nitric acids, causes the fast deterioration of buildings and property, destroys forests, pollutes lakes, and harms agricultural areas. Acid rain can damage the environment by disturbing the natural balance in the ecosystem through unbalanced chemicals, and decrease biodiversity [23]. Smog containing sulfur, also known as London smog, is generated due to the substantial quantity of SO<sub>x</sub> in the atmosphere. Sulfurous smog is a serious air pollutant that causes irritation to the human eyes, nose, and lungs [24]. Aside from the damaging effect of compounds containing sulfur in the environment, sulfur is also disastrous for combustion engines. The generation of oxyacids of sulfur from combustion products leads to corrosion of the internal combustion engine. Sulfur also affects the performance of air pollution control devices since sulfur intensely adsorbs onto a catalyst, which is metal, and this condition inhibits the adsorption of other air pollutants such as carbon monoxide, nitrogen oxide, and hydrocarbons. Sulfur-containing compounds also deactivate the catalysts that are utilized in upgrading hydrocarbons [25].

When acid rain falls to the ground in the form of sulfuric acid, it can fall on statues, buildings, and other man-made infrastructure and damage their surfaces. These acidic compounds can also wear down metal and cause paint and stone to depreciate faster. Acid rain could also damage the exteriors of buildings and other pieces of architecture such as monuments. The consequence of this damage can be expensive since damaged materials need to be restored, or worse, restructured, and the rapid deterioration of infrastructure causes an increase in maintenance costs [26].

#### 1.1.3. Effects on the Economy

A negative impact on the economy of nation can be observed when sulfur-containing compounds are present in fuel at high concentrations because vast area are affected if these sulfur compounds are emitted into the atmosphere. Huge economic losses associated with acid rain were recorded while a high economic impact can be achieved if sulfur in the diesel fuel is removed, most especially if the cost of desulfurization technologies decreases [27].

### 1.2. Sulfur Content Regulations

The quantity of sulfur present in diesel fuel before USEPA began regulating the sulfur content in diesel was about 5000 parts per million (ppm). Regulations on sulfur levels in diesel by the EPA started in 1993. Two different sources were the focus of the USEPA in standardizing diesel, particularly on its sulfur content in road (or highway) vehicles, and in non-road engines and equipment. The EPA started to specify more strict policies to lessen the quantity of sulfur in petroleum products. In diesel fuel, 15 ppm of sulfur content at the start of 2006 was regulated. It is expected that the decrease in sulfur content in diesel and other petroleum products will give way to the utilization of state-of-the-art emission control techniques intended to decrease PM emissions from diesel-consuming machines. The European Union established this transformation and it is being implemented in North America at present. Since 2007, the demand for environmentally friendly fuels has created an upgraded emission quality to be applied to vehicles in the US. More countries are taking the initiative through policy making to decrease the sulfur present in diesel fuel. Refineries are also undertaking initiatives to make advances in the production of fuels within the standard sulfur level (less than 10 ppm).

## 2. Information and Emerging Trends of Diesel Oil and Its Production

The term diesel was named after the inventor and German engineer Rudolf Diesel. Diesel fuels are mixtures of complex hydrocarbons, containing all the classes of hydrocarbons such as paraffins, naphthenes, aromatics, and in small concentrations, olefins [28]. Diesel, the customary name for diesel fuel oil, is utilized in compression ignition engines in motor vehicles. In 1892, Diesel patented his original design. The diesel fuel that is refined comes from crude oil and biomass material. The majority of the diesel fuel manufactured in the United States is from the purification of crude oil. About 11 to 12 gallons of diesel fuel from each 42-gallon (U.S.) barrel of crude oil is manufactured in US petroleum refineries [29].

Diesel fuel used by the end user started as crude oil mined underground, the product of many decomposing plants and animals combined with elevated pressure and heat. After the crude oil has been collected, it is brought to a petroleum refinery for further processing, namely separation, conversion, and purification. In large distillation towers, the separation process takes place. Usually, the oil is subjected to extremely high heat until the material splits into different phases, but is usually in the form of gases and liquids. The separation of products occurs due to a temperature gap from the top and bottom of the distillation equipment. The output or by-products varies from propane gas around the top, diesel in between and lubricants near the base. Conversion is the next procedure in diesel production, which requires the application of a catalyst to several heavy fuel oils from the fractional distillation process. The purpose of this method is to generate more gasoline, diesel, and propane. Purification is the concluding method in the operation, and customarily requires desulfurization [30].

One of the major reasons why the international economy is kept moving is because of petroleum products, especially diesel fuel. Because of diesel fuel, a lot of consumer goods can be transferred around the world, electric power generation is harnessed, and improved efficiency in farms outputs is achieved. Diesel fuel performs an important function in improving the worldwide economy and quality of life. Diesel engines are utilized globally for shipment, the production of goods, electricity generation, building construction, and agriculture. There are many types of diesel engines present, and they are categorized according to their purpose. Starting from little, fast-moving diesel injection engines to low-velocity direct-injection behemoths with cylinders one meter (three feet) in diameter. Their profitability can be defined by their efficiency, economy, and reliability [31].

Diesel oil is associated with crude oil. Globally, liquid fuel consumption in the US Energy Information Administration forecast will increase from an average of 99.4 million barrels per day (*b/d*) in 2022 to 100.9 million *b/d* in 2023, which is 0.4 million *b/d* higher than in last month's outlook. The higher consumption forecast is primarily driven by

upward revisions to global economic growth. The sudden fall in demand for crude oil in 2020 happened because of economic flexibility influence of the COVID 19 epidemic, along with global stoppages throughout the world [32]. Nevertheless, in comparison with the demand of 84.8 M barrels per day in 2012, the demand has still followed an ascending path over the past few decades [33].

Crude oil has become a significant commodity because of its use in diverse processes and in diverse forms in many applications. The transportation division is regarded as the biggest consumer of fuel worldwide. About one third of the demand for oil worldwide is accounted for by the transportation sector, mostly because of the reliance on motors that need fuel from petroleum. The organization of petroleum-exporting countries, or OPEC, forecasts demand will reach 109 million barrels of oil globally per day by 2045. The fuels for transportation such as gasoline and diesel are expected to continue to be the most in-demand products. The demand for diesel and gas oil is predicted to reach 30 million barrels per day in 2045, higher from 26.4 million barrels in 2019 [34].

### 3. Existing Technologies for Desulfurization of Diesel Oil

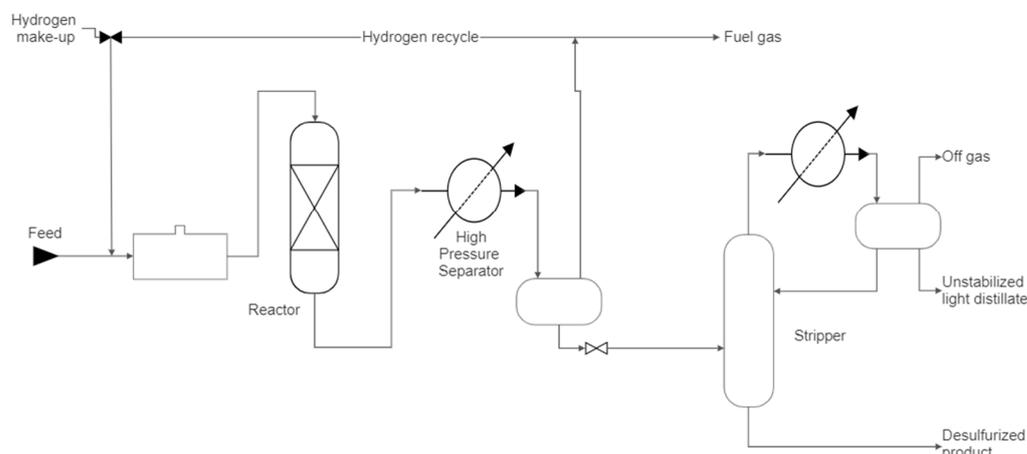
The advantage diesel oil has is energy conservation, economy, environmental protection, safety, durability, and high performance. Along with the development of diesel engine technologies, diesel oil has been widely utilized as the fuel of equipment such as diesel motor cars, boats, and ships, mine power units, and drilling wells. Due to the sulfur in the diesel oil that generates sulfur oxide during elevated temperature combustion, it not only corrodes the component of motor car engine but can be discharged into the air. This can consequently lead to the formation of acid rain. In addition, the efficiency of diesel oil catalysis after-treatment devices is also affected since the catalytic hydro-dearomatization catalyst is poisoned by sulfur. In view of the harm of sulfur in diesel oil, sulfur content has become a topic of domestic and international interest in the reduction diesel oil and a lot of countries are also becoming more stringent in their sulfur content index requests regarding diesel oil [17].

Diesel oil is seen as an all-round fuel since it is used in most transportation engines. It is also considered as the largest source of air pollution due to the serious health impacts brought by the sulfur-containing compounds emitted by the diesel engine. Diesel-fueled engines were found to also emit NO<sub>x</sub> that can form harmful ground level ozone aside from fine particles. Different techniques of refining diesel fuel are available, particularly those related to the removal of sulfur used to reach the allowable amount of sulfur content in diesel oil of about 10 ppm.

#### 3.1. Hydrodesulfurization (HDS)

Hydrodesulfurization, a method for removing sulfur in petroleum products and natural gas is a form of catalytic chemical process and it is shown in Figure 1. Eliminating the sulfur lessens the SO<sub>2</sub> emissions brought by utilizing diesel fuels in the automotive industry, residential areas, and industrial furnaces. Several organo-sulfur compounds are transformed to H<sub>2</sub>S and sulfur-free organic compounds in the HDS process. This process is being carried out via catalytic treatment with hydrogen at elevated pressures of between 150 psi and 3000 psi and elevated temperatures of between 290 °C and 455 °C, using metal catalysts such as CoMo/Al<sub>2</sub>O<sub>3</sub> or NiMo/Al<sub>3</sub>O<sub>3</sub>. Refineries may produce extremely low sulfur diesel by controlling the hydrotreatment conditions and using appropriate catalysts. A two-step deep desulfurization process is enough to meet the 10 ppm sulfur requirement for diesel fuel. The initial step reduces the sulfur concentration of the diesel fuel to below 250 ppm and the second step produces diesel products with a sulfur concentration of 10 ppm [35]. The currently common heterogeneous catalyst that can meet the requirement to remove most of the organosulfur compounds is Ni/Mo (or Mo/Co) sulfide. At present, modeling studies based on homogeneous catalysis have contributed a great deal to understanding the mechanism of HDS. During these studies, several other reactions of thiophenes in organic transition metal complexes were discovered. These have led to the

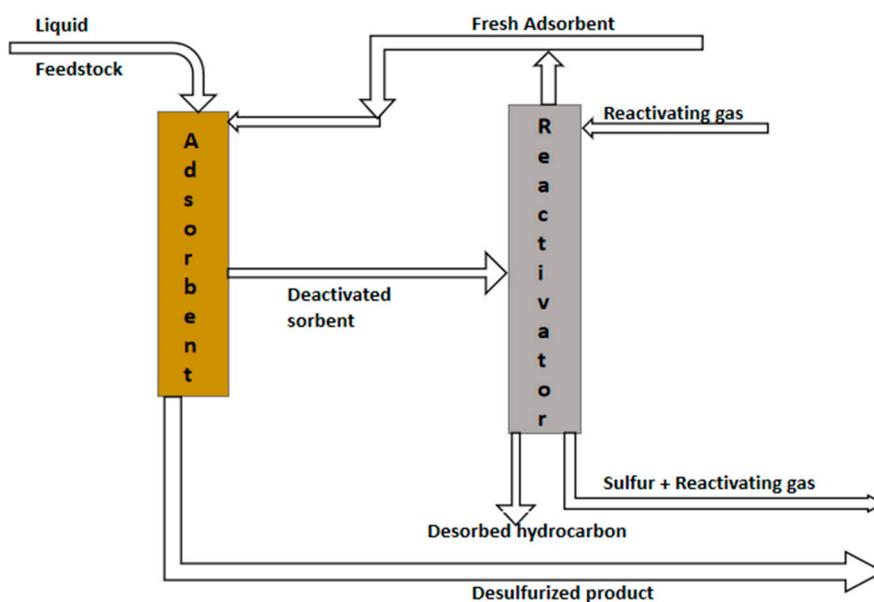
utilization of specific reactions of coordinated thiophenes for the synthesis of organosulfur compounds that are difficult to prepare through other methods [36].



**Figure 1.** Hydrodesulfurization flow diagram.

### 3.2. Adsorptive Desulfurization (ADS)

Adsorptive desulfurization (ADS) is emerging as a low-cost alternative to ultra-deep hydrodesulfurization. Over-sulfated chondroitin (OSC) undergoes surface assimilation into a specified solid adsorbent in adsorptive desulfurization to create zero- or low-sulfur fuel. Adsorptive desulfurization is categorized into two groups based on the interactivity between OSCs and the adsorbent. The two categories are direct adsorption desulfurization and reactive adsorption desulfurization. AD is a modern technology for eliminating sulfur from petroleum distillates. AD is one of the focuses and interests of researchers at present due to it being economical in nature, easy to carry out, and the fact it can be utilized by different fuel processors. AD is concerned with contacting fuel with an activated/functionalized adsorbent to eliminate the sulfur from the fuel, as shown in Figure 2. The advantage of AD is its non-requirement of hydrogen, operation under mild conditions of temperature (room temperature to around 100 °C), and the ability of the adsorbent to be recycled, which makes it an economical method of removing the sulfur from diesel fuel [16].

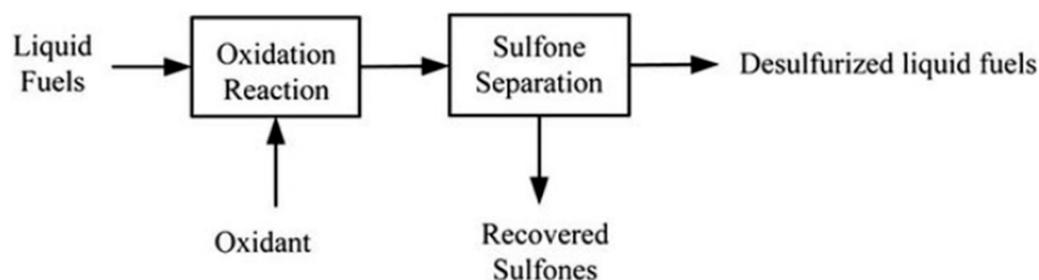


**Figure 2.** Adsorptive Desulfurization flow diagram.

The latest development in ADS that improved ADS' performance with respect to selectivity, stability, and reusability is the incorporation of metal with the existing materials used as adsorbents. Examples of adsorbents are zeolites, metal oxide, metal-organic frameworks, mesoporous material, and carbon [37]. Another innovation that is being carried out in ADS is the regeneration studies on the several types of adsorbent materials. This technique is partially successful, while the application of bacterial treatments as a standalone or combined approach, which is known to be bioregeneration of the spent adsorbent, is found to have potential [38].

### 3.3. Oxidative Desulfurization (ODS)

The process where the sulfur compounds decompose to their corresponding sulfoxides (1-oxides) and sulfones (1, 1-dioxides) is called ODS, as shown in Figure 3. The difference between ODS and HDS method is the sulfur compounds. The sulfur compounds in ODS are reduced to form  $\text{SO}_2$ . The deduction of sulfur in ODS is performed at low pressure and temperature ( $\sim 50^\circ\text{C}$ ). It is also conducted using moderate operating conditions and an expensive catalyst, specifically hydrogen, is no longer needed to carry out the procedure. However, the problem with this technique is that it uses large quantity of oxidizing agent and requires a separation technique to collect the catalysts. The reaction's selectivity and activity are slow, and therefore an extended reaction time is needed. The most promising outcome was completed by the oxidation of peroxyacid ( $\text{HCOOH}/\text{H}_2\text{O}_2$ ). Sulfones and sulfoxide removal was implemented when oxidation was performed. First, extraction was carried out to achieve a sulfur concentration level of 7.0 ppm, after which is adsorption with silica gel to attain a 0.0% sulfur content [39]. A recent innovation in ODS that focused on selectivity and economics is catalytic ODS. It reduces the leaching of active species and has the potential to recover and reuse the catalyst for successive transformation. Catalytic ODS utilizes mesoporous silicate that aids in easy surface modification by bringing it into contact with organosilanes and initiating the immobilization of homogenous catalysts [40].



**Figure 3.** Oxidative desulfurization flow diagram.

### 3.4. Desulfurization of Diesel Fuel Using Ionic Liquids (ILs)

Another technique used in the removal of sulfur from diesel fuel is using ILs as a solvent for sulfur extraction. This technique is a form of oxidative or extractive desulfurization [41]. A wide scope of IL-based experimental areas has been identified due to the disparity of feasible IL forms. There are unlimited number of ILs that can be synthesized to be utilized for this purpose. ILs are also known to be “task-specific” and “designer solvents.” The chemical form of an IL can be rearranged and the physicochemical properties can be changed in accordance with the boundary conditions given by the desired operation [42]. Identifying the procedure of the reaction among the sulfur compounds as solutes and ILs as solvent is crucial due to the extraction efficiency and recyclability of ILs and relies on their interaction mechanism. Another factor is the quantity of feasible combinations between anions and cations in IL being unlimited, and it being extremely hard to screen the individual experiment. ILs consist of complex ions with several types of reaction. In this form, any solute molecule will have varied solute–solvent reactions because of the several electron-leaving, electron-giving, basic, and acidic properties. Hydrogen bonding occurs due to the giving of the cation part of ILs to the S atom in aromatic

S compounds. Another reason hydrogen bonding happens is the effects of anion and dilution [41]. A study conducted on the desulfurization process of simulated gasoline and diesel, as well as with real samples, confirmed the capability of ILs as a solvent for the extractive removal of sulfur from petroleum products [43]. The IL-based desulfurization technique is becoming a popular method nowadays because of its numerous advantages and promising performance [44]. Some advantages of ILs are their non-volatility, wide range, high thermal and chemical stability, their ability for regeneration, and reusability. The substantial number of species and designability of ILs create numerous options suitable for desulfurization [45].

### 3.5. Biodesulfurization

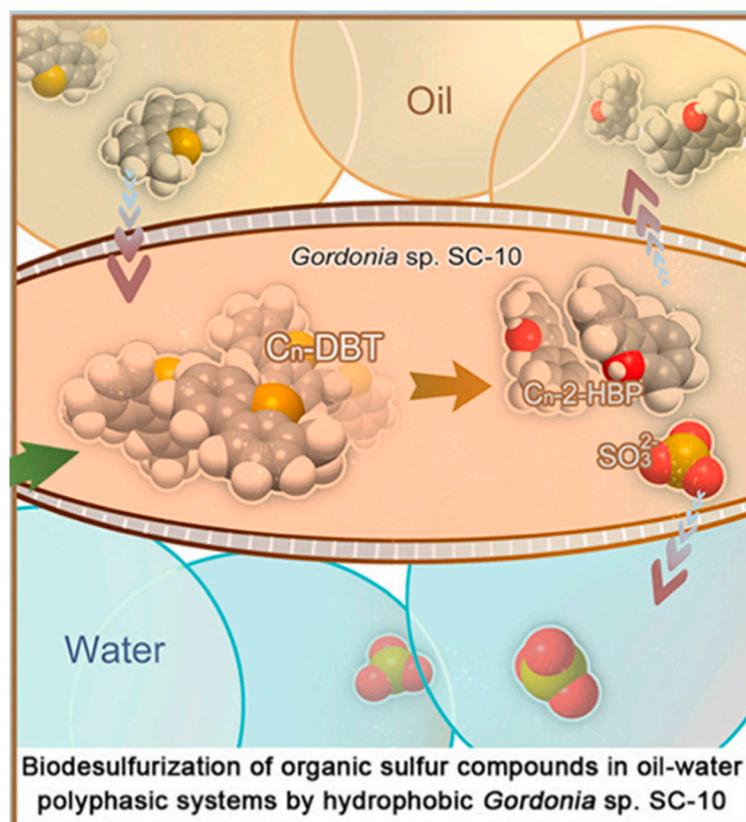
The utilization of microorganisms that could selectively extract atoms of sulfur from organosulfur compounds is the process known as BDS. It is an innovation that complements the conventional hydrodesulfurization of fuels. Sulfur is selectively oxidized through the enzymes present in the bacteria by cutting carbon–sulfur bonds. Among the many advantages of BDS are its operation at ambient temperatures and atmospheric pressures, and it demanding lower energy than conventional HDS methods to meet the current regulatory standards of sulfur in diesel fuel. BDS is also economical since it produces an ample amount of CO<sub>2</sub> when in connection with HDS without requiring hydrogen. Furthermore, a certain amount of key sulfur-containing compounds that cannot be removed with the HDS process can be eliminated by BDS. It was also found that HDS can be replaced by BDS or that the two desulfurization processes can be utilized at the same time [4].

Another technology related to biodesulfurization is the application of catalytic processes by utilizing enzymes or catalytic agents to improve the performance of the process [40]. The development of heterogeneous bio-nanocatalysts delivers an improved performance of biodesulfurization. This is because the lignin nanoparticles functionalized with concanavalin A, a renewable and efficient platform for the layer-by-layer immobilization of the enzyme, are utilized for the process [46].

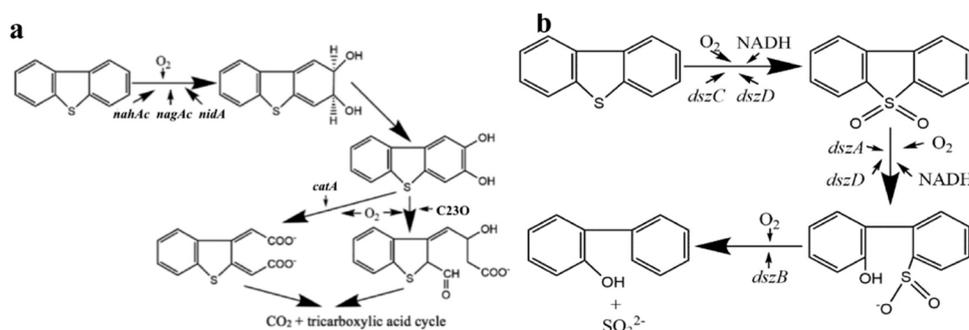
The impending harm towards human health and the environment as well as property brought by climate change led to the focus on techniques for the desulfurization of diesel fuel which are environmentally friendly, such as BDS. With this, the call for utilizing such technologies on the industrial level is important and must be the greatest preference for emergent nations [3]. To upscale BDS, an excellent knowledge and familiarity of interactions is required [47].

Multiple microbial species that go through DBT-BDS have been observed and researched extensively such as *Rhodococcus* sp. [48], *Gordonia* sp. [49], *Nocardia* sp., *Pseudomonas* sp. [50], *Sphingomonas* sp. [51], *Mycobacterium* sp. [52], *Brevibacillus* sp. [53], and *Bacillus subtilis* sp. [54]. The biodesulfurization process that illustrates how sulfur is selectively oxidized through the enzymes present in the bacteria *Gordonia* sp. by cutting carbon–sulfur bonds is shown in Figure 4.

In BDS, there are two pathways that are widely established and utilized. The first is the oxidative C-C cleavage pathway, also known as the Kodama Pathway, and the second is the sulfur-specific pathway, or the 4S metabolic pathway, as shown in Figure 5. The pathway referred to by the oxidative cleavage of DBT is the Kodama pathway. It is the pathway of a destructive ring where the bond between the C-C backbone of one of the benzene rings is cleaved selectively by a subsequent series of oxidation processes. The C-S bond is kept intact in the partially cleaved ring [55].



**Figure 4.** Biodesulfurization process [2]. Permission obtained through Rights Link<sup>®</sup>.



**Figure 5.** Functional genes for the degradation of DBT (dibenzothiophene) by the Kodama pathway and the 4S pathway. (a) Kodama pathway; (b) 4S pathway [56]. Permission obtained through Rights Link<sup>®</sup>.

Numerous studies acknowledge that multiple microbial species are able to utilize DBT via the aforementioned pathway, including *Pseudomonas* [57]. Following the cleavage of the ring, deoxygenation in this pathway also initially takes place at the peripheric aromatic ring (benzyl ring) of DBT. This interaction leads to 3-hydroxy-2-formyl-benzothiophene build up as a water-soluble end product and it is impossible for the desulfurization of the organosulfur substrate to take place in this pathway [22]. On the other hand, the sulfur-specific pathway has gathered extensive attention worldwide as it eliminates sulfur from DBT through C-S bond disintegration while keeping the carbon skeleton undamaged. 2-hydroxybiphenyl (2-HBP) is the output in this pathway and sulfur is liberated as  $\text{SO}_3$ , with the advantage of keeping the calorific value of fossil fuel [3]. The 4S pathway is a four-step enzymatic pathway that converts DBT to 2-hydroxybiphenyl (HBP) and sulfate (Figure 5). The first two steps are the conversion of DBT to DBT sulfoxide (DBTO) and then to DBT sulfone (DBTO<sub>2</sub>). These steps are catalyzed by the enzymes DszC monooxygenase and DszD oxidoreductase in synchrony. The third step is the conversion of DBTO<sub>2</sub> to 2-(2'-

hydroxyphenyl) benzene sulfinate (HBPS), which is catalyzed by DszA monooxygenase and DszD oxidoreductase in synchrony. The last step is the conversion of HBPS to HBP and sulfite by DszB desulfinate [58].

#### 4. Recent Studies on BDS

Some microbial species have been found out that can selectively desulfurize DBT and its derivatives in diesel oil. Several studies also reported that there are identified bacterial species that can desulfurize a range of sulfur compounds in diesel oil. By screening the research studies conducted from 2006 to 2023, BDS studies focusing on the removal of DBTs were identified and they are shown in Table 1.

**Table 1.** Microbial strains capable of desulfurizing DBTs.

Microbial Strain	Optimum Conditions				References
	Sulfur Conc (ppm)	Temperature (°C)	Final Sulfur Conc (ppm)	% Efficiency of Bacteria	
<i>Erithrobacter</i> spp. NISOC-03	3000	30	1080	64	[59]
<i>Gordonia alkanivorans</i> 1B	37	37	8.5	77	[60]
<i>Rhodococcus erythropolis</i> IGTS8	10	30	2	80	[61]
<i>Sulfolobus solfataricus</i> P2	55.28	78	6.36	88.5	[62]
<i>Rhodococcus erythropolis</i> MTCC3552	92.13	50	1.01	98.9	[63]
<i>Arthrobacter sulfureus</i> MTCC3332	92.13	50	0.68	99.26	[63]
<i>Gordonia rubrotica</i> MTCC 289	92.13	50	0.55	99.4	[63]
<i>Rhodococcus erythropolis</i> MTCC3951	92.13	50	0.37	99.6	[63]
<i>Rhodococcus erythropolis</i> SHT87	552.78	30	0	100	[64]
<i>Desulfobacterium anilini</i>	-	30	-	82	[65]
<i>Rhodococcus erythropolis</i> FSD-2	198	30	11.88	94	[66]
<i>Spingomonas subarctica</i> T7b	280	27	114.8	59	[67]
<i>Rhodococcus erythropolis</i> XP	259	30	14.25	94.5	[10]
<i>Pseudomonas delafieldii</i> R-8	591	30	313.05	47.03	[5]
<i>Gordonia</i> sp. SC-10	167.7	30	19.62	88.3	[2]
<i>Bacillus subtilis</i> DSMZ 3256	1842	30	1270.98	31	[68]
<i>Rhodococcus erythropolis</i> PTCC1767	1842	30	1178.88	36	[68]
<i>Bacterium achromobacter</i> sp.	92.13	37	6.54	92.9	[69]
<i>Rhodococcus globerulus</i> DAQ3	16,100	30	14,183.46	11.90	[70]
<i>Rhodococcus erythropolis</i> HN2	630	30	25.2	96	[53]
<i>Rhodococcus erythropolis</i> HN2	690	60	27.6	96	[71]
Combination of <i>Alphaproteobacteria</i> , <i>Gammaproteobacteria</i> and <i>Actinobacteria</i>	100	30	25	75	[11]
<i>Gordonia</i> sp. Sc-10	10.2	30	5	50.98	
	194.7	30	30.4	84.39	[72]
	3035.3	30	1792.8	40.93	

Several microbial species have been identified to be able to transform DBT or to utilize it as their source of sulfur in their growth metabolism such as *Rhodococcus*, *Arthrobacter*, *Pseudomonas*, *Gordonia*, *Bacillus*, and *sulfobulus* [4]. DBT is commonly utilized as a typical organo-sulfur compound when conducting research studies on BDS [63]. DBT and its derivatives make up a total of 70% of the sulfur content in diesel fuel and it is known as the main organo-sulfur compound. Furthermore, another advantage of DBT is it can be managed easily, unlike other sulfur-containing substances, since it is a non-cancer-causing agent and does not pose hazards to human health [73]

*Rhodococcus* species are commonly utilized for BDS since they are suitable for hydrocarbon metabolism and this bacteria species displays a promising result in BDS, as presented in Table 1. The *Rhodococcus* strain achieved as high as 100% and as low as 80% BDS efficiency for sulfur concentrations at 10 ppm to 552.78 ppm. A low BDS efficiency utilizing *Rhodococcus* species can be observed when a high concentration of sulfur is involved in the process. At 1842 ppm and 16,100 ppm of sulfur considered in the BDS process, only 36% and 11.9% efficiency were achieved, respectively. Bacteria species such as *Gordonia*, *Arthrobacter*, and *Desulfobacterium* also give a high BDS efficiency ranging from 77% to 99.4%, with a sulfur concentration of 37 ppm to 167.7 ppm. Other bacteria species give less than 70% BDS efficiency with sulfur concentrations of more than 280 ppm. Among these

are *Bacterium Achroacter* and *Spingomonas*. *Pseudomonas* and *Bacillus* species also gave low BDS efficiency but involved high concentrations of sulfur. For *Pseudomonas* sp., the BDS efficiency was 47.03% with a sulfur concentration of 591 ppm, while *Bacillus* sp. gave an efficiency of 31% at a sulfur concentration of 1842 ppm.

## 5. Industrial View on Biodesulfurization

There are emerging issues with BDS that can be realized regarding its application on an industrial scale. There are several challenges that can be identified in the utilization of BDS technology by the industry. Although BDS can successfully achieve 100% efficiency, the process is only applicable to a low sulfur concentration in diesel. Improving the performance of BDS for a high sulfur concentration in diesel is still needed. Another major problem that was identified in its industrial application is the slow kinetics of the BDS process [74]. Several studies have been conducted that focus on adopting innovations like immobilization, the utilization of nanotechnology, biphasic systems, genetic engineering, and the use of surfactants to enhance the BDS performance and address this issue [75]. Cell immobilization technology gives a potential solution, since it allows the cell system to be used multiple times and relieves feedback inhibition toward cells caused by metabolic products [76]. A study conducted on the BDS of DBT through immobilized cells achieved 100% efficiency, and was reusable up to four times [77]. Another problem is the high price of culture media when growing bacteria. However, studies have been conducted using carbon sources that are derived from industrial agricultural products which can function as an alternative to lessen its cost [76]. The cost of microorganisms can be a hindrance in utilizing BDS in industry. The immobilization of cells has been suggested and further study on its recyclability could be conducted to find a feasible solution to its cost problem.

At present, the coupling of other desulfurization technologies with BDS could be a novel approach for the industry to produce clean and green fuels. Successful studies on the coupling of desulfurization technologies have been conducted. A study was successfully conducted on the removal of sulfur from heavy oil and light crude oil through BDS, reactive adsorption, oxy-desulfurization, photo-desulfurization, and solvent extraction [78]. Recent technologies are the utilization of nano-adsorbents which are found to enhance the transfer of DBT from bacteria [4]. Another technique is the application of catalytic processes [40] and the development of heterogenous bio-nanocatalysts that show an improved performance of biodesulfurization [46], which could be a significant factor for application in industry. However, further investigation to address the different challenges specified in conducting BDS at an industrial scale is needed to assure its successful implementation.

## 6. Conclusions and Future Perspective

This perspective paper has pointed out that sulfur causes serious damages to human life, property, and the environment. At present, the desulfurization method employed for petroleum distillates that is used at the industrial scale is HDS. The problem with HDS is it is an energy-intensive process aiming at a low-sulfur petroleum distillate product. A 10 ppm sulfur target in the HDS process requires a three times greater amount of catalyst in volume, a higher quantity of hydrogen gas as a catalyst, 30–60% higher, a 25 °C to 50 °C increase in temperature, and an increase in H<sub>2</sub> pressure which is about 10 MPa to 30 MPa compared with the production of 500 ppm petroleum distillate products [37]. High operating and investment costs are needed when working at such high operating conditions. Another problem with the HDS process is the compound of sulfur formed in the process, H<sub>2</sub>S. The formation of H<sub>2</sub>S also creates another environmental issue. Several species of bacteria utilized for the BDS of diesel oil have been presented and show promising results in terms of sulfur removal from diesel oil. Coupling with other desulfurization technologies in diesel oil, such as HDS, can be considered, since the process operating cost can be reduced. The process economics can be improved if this innovation successfully materializes. It has been recommended that a deep understanding of the BDS mechanism in coupling with HDS requires extensive studies. Moreover, research on BDS is still needed to make it

competitive and attractive for the industry, either when utilizing BDS alone or coupling it with other desulfurization technologies.

**Author Contributions:** Conceptualization, R.Y.M. and A.E.S.C.; formal analysis, R.Y.M.; investigation, R.Y.M.; resources, A.E.S.C.; data curation, R.Y.M.; writing—original draft preparation, R.Y.M. and A.E.S.C.; writing—review and editing, R.Y.M. and A.E.S.C.; visualization, R.Y.M.; supervision, A.E.S.C.; project administration, A.E.S.C.; funding acquisition, A.E.S.C. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research received no external funding.

**Data Availability Statement:** Not applicable.

**Conflicts of Interest:** The authors declare no conflict of interest.

## References

1. Javadli, R.; de Klerk, A. Desulfurization of heavy oil. *Appl. Petrochem. Res.* **2012**, *1*, 3–19. [CrossRef]
2. Chen, S.; Zang, M.; Li, L.; Chen, J.; Liu, Q.; Feng, X.; Sun, S.; Zang, C.; Zhao, C. Efficient Biodesulfurization of Diesel Oil by *Gordonia* Sp. SC-10 with Highly Hydrophobic Cell Surfaces. *Biochem. Eng. J.* **2021**, *174*, 108094. [CrossRef]
3. Kalita, M.; Sangannavar, P.A.; Chutia, M.; Jha, D.K.; Sathyanarayana, K.; Kumar, J.S.; Subrahmanyam, G. *Microbial Biodesulfurization: A Sustainable Technology for Refining Fossil Fuels*; Elsevier Inc.: Amsterdam, The Netherlands, 2022; ISBN 9780323905909.
4. Sadare, O.O.; Obazu, F.; Daramola, M.O. Biodesulfurization of Petroleum Distillates—Current Status, Opportunities and Future Challenges. *Environments* **2017**, *4*, 85. [CrossRef]
5. Guobin, S.; Huaiying, Z.; Jianmin, X.; Guo, C.; Wangliang, L.; Huizhou, L. Biodesulfurization of Hydrodesulfurized Diesel Oil with *Pseudomonas Delafieldii* R-8 from High Density Culture. *Biochem. Eng. J.* **2006**, *27*, 305–309. [CrossRef]
6. Xie, Y.; Posada, F.; Minjare, R. Diesel Sulfur Content impactson Euro VI Soot-Free Vehicles: Considerations for Emerging. *Front. Environ. Sci. Eng.* **2020**, *10*. Available online: <https://theicct.org/publications/diesel-sulfur-content-soot-free-emerging-markets> (accessed on 3 March 2023).
7. Stratas Advisors. *11 Countries Move Up in Top 100 Ranking on Diesel Sulfur Limits*; Stratas Advisors: Houston, TX, USA, 2018; p. 3.
8. Dembaremba, T.O.; Majodina, S.; Walmsley, R.S.; Ogunlaja, A.S.; Tshentu, Z.R. Perspectives on Strategies for Improving Ultra-Deep Desulfurization of Liquid Fuels through Hydrotreatment: Catalyst Improvement and Feedstock Pre-Treatment. *Front. Chem.* **2022**, *10*, 807225. [CrossRef] [PubMed]
9. Britannica. Diesel Fuel. *Br. Ed. Encycl.*. 2023. Available online: <https://www.britannica.com/technology/diesel-fuel> (accessed on 17 February 2023).
10. Yu, B.; Xu, P.; Shi, Q.; Ma, C. Deep Desulfurization of Diesel Oil and Crude Oils by a Newly Isolated *Rhodococcus Erythropolis* Strain. *Appl. Environ. Microbiol.* **2006**, *72*, 54–58. [CrossRef]
11. Awadh, M.; Mahmoud, H.; Abed, R.M.M.; El Nayal, A.M.; Abotalib, N.; Ismail, W. Diesel-Born Organosulfur Compounds Stimulate Community Re-Structuring in a Diesel-Biodesulfurizing Consortium. *Biotechnol. Rep.* **2020**, *28*, e00572. [CrossRef]
12. Zhao, H.; Ge, Y.; Wang, X.; Tan, J.; Wang, A.; You, K. Effects of Fuel Sulfur Content and Diesel Oxidation Catalyst on PM Emitted from Light-Duty Diesel Engine. *Energy Fuels* **2010**, *24*, 985–991. [CrossRef]
13. Lee, H.; Kang, S.; Jin, Y.; Jung, D.; Park, K.; Li, K.; Lee, J. Systematic Investigation of the Extractive Desulfurization of Fuel Using Deep Eutectic Solvents from Multifarious Aspects. *Fuel* **2020**, *264*, 116848. [CrossRef]
14. Optenhostert, T.; Puthenkalam, S.; Stegmann, N.; Steffen, M.; Schmidt, W. Catalytic Hydrodesulfurization of Gaseous Fuels with Autogenously Formed Hydrogen. *Chem. Ing. Tech.* **2021**, *93*, 1028–1032. [CrossRef]
15. Abid, M.F.; Ahmed, S.M.; AbuHamid, W.H.; Ali, S.M. Study on Novel Scheme for Hydrodesulfurization of Middle Distillates Using Different Types of Catalyst. *J. King Saud Univ. Eng. Sci.* **2019**, *31*, 144–151. [CrossRef]
16. Ganiyu, S.A.; Lateef, S.A. Review of Adsorptive Desulfurization Process: Overview of the Non-Carbonaceous Materials, Mechanism and Synthesis Strategies. *Fuel* **2021**, *294*, 120273. [CrossRef]
17. Li, Y.; Zhang, Y.; Wu, P.; Feng, C.; Xue, G. Catalytic Oxidative/Extractive Desulfurization of Model Oil Using Transition Metal Substituted Phosphomolybdates-Based Ionic Liquids. *Catalysts* **2018**, *8*, 639. [CrossRef]
18. Zhang, B.; Jiang, Z.; Li, J.; Zhang, Y.; Lin, F.; Liu, Y.; Li, C. Catalytic Oxidation of Thiophene and Its Derivatives via Dual Activation for Ultra-Deep Desulfurization of Fuels. *J. Catal.* **2012**, *287*, 5–12. [CrossRef]
19. Rajendran, A.; Cui, T.Y.; Fan, H.X.; Yang, Z.F.; Feng, J.; Li, W.Y. A Comprehensive Review on Oxidative Desulfurization Catalysts Targeting Clean Energy and Environment. *J. Mater. Chem. A* **2020**, *8*, 2246–2285. [CrossRef]
20. Choi, A.E.S.; Roces, S.; Dugos, N.; Wan, M.W. Adsorption of Benzo thiophene Sulfone over Clay Mineral Adsorbents in the Frame of Oxidative Desulfurization. *Fuel* **2017**, *205*, 153–160. [CrossRef]
21. Martínez, I.; Mohamed, M.E.S.; García, J.L.; Díaz, E. Enhancing Biodesulfurization by Engineering a Synthetic Dibenzothiophene Mineralization Pathway. *Front. Microbiol.* **2022**, *13*, 987084. [CrossRef]
22. Mohebbi, G.; Ball, A.S. Biodesulfurization of Diesel Fuels—Past, Present and Future Perspectives. *Int. Biodeterior. Biodegrad.* **2016**, *110*, 163–180. [CrossRef]

23. Bradford, A.; Briggs, B. Acid Rain: Causes, Effects and Solutions. *Live Science*. 16 March 2022. Available online: <https://www.livescience.com/63065-acid-rain.html> (accessed on 17 February 2023).
24. Mahima, K. Science behind Smog and Ominous Implications. *Down to Earth*. 2 April 2018. Available online: <https://www.downtoearth.org.in/blog/air/science-behind-smog-and-its-ominous-implications-60080> (accessed on 17 February 2023).
25. Ashok, B.; Kumar, A.N.; Jacob, A.; Vignesh, R. *Emission Formation in IC Engines*; Elsevier Inc.: Amsterdam, The Netherlands, 2021; ISBN 9780128239551.
26. Wu, X.; Gao, M.; Guo, S.; Maqbool, R. Environmental and Economic Effects of Sulfur Dioxide Emissions Trading Pilot Scheme in China: A Quasi-Experiment. *Energy Environ.* **2019**, *30*, 1255–1274. [[CrossRef](#)]
27. Martin, S.A.; Gallaher, M.P.; O’Connor, A.C. *Economic Impact of Standard Reference Materials for Sulfur in Fossil Fuels*; Institute of Portland Metropolitan Studies: Portland, OR, USA, 2000.
28. Ackland, J.; White, J.; Waibel, R.T.; Londerville, S.B. Fuels. In *The Coen & Hamworthy Combustion Handbook*; CRC: Boca Raton, FL, USA, 2013; pp. 71–94. [[CrossRef](#)]
29. U.S. Energy Information Administration (EIA). Diesel Fuel Explained. 2021. Available online: <https://www.eia.gov/energyexplained/diesel-fuel/> (accessed on 17 February 2023).
30. Chianelli, R.R.; Berhault, G.; Raybaud, P.; Kasztelan, S.; Hafner, J.; Toulhoat, H. Periodic Trends in Hydrodesulfurization: In Support of the Sabatier Principle. *Appl. Catal. A Gen.* **2002**, *227*, 83–96. [[CrossRef](#)]
31. Bacha, J.; Freel, J.; Gibbs, A.; Gibbs, L.; Hemighaus, G.; Hoekman, K.; Horn, J.; Ingham, M.; Jossens, L.; Kohler, D.; et al. *Diesel Fuels Technical Review*; Chevron Corporation: San Ramon, CA, USA, 2007; pp. 1–116.
32. U.S. Energy Information Administration (EIA). *Short-Term Energy Outlook*; U.S. Energy Information Administration (EIA): Washington, DC, USA, 2023.
33. Choi, A.E.S.; Roces, S.A.; Dugos, N.P.; Wan, M.-W.W. Parametric Screening Analysis for the Oxidative Desulfurization of Diesel Oil. *Chem. Eng. Trans.* **2021**, *88*, 91–96. [[CrossRef](#)]
34. Sönnichsen, N. Daily Global Crude Oil Demand 2006–2026. *Statista*. 7 March 2023. Available online: <https://www.statista.com/statistics/271823/daily-global-crude-oil-demand-since-2006/> (accessed on 7 March 2023).
35. Piemonte, V. Desulfurization from Gas Oil: Sulfur Removal of Gas Oil to 10 ppm. *J. Clean Energy Technol.* **2013**, *1*, 2–7.
36. Yang, Y.; Kadam, V.D.; You, J. *Thiophenes and Their Benzo Derivatives: Reactivity*, 4th ed.; Elsevier Ltd.: Amsterdam, The Netherlands, 2021; ISBN 9780128186565.
37. Saha, B.; Vedachalam, S.; Dalai, A.K. Review on Recent Advances in Adsorptive Desulfurization. *Fuel Process. Technol.* **2021**, *214*, 106685. [[CrossRef](#)]
38. Omar, R.A.; Verma, N. Review of Adsorptive Desulfurization of Liquid Fuels and Regeneration Attempts. *Ind. Eng. Chem. Res.* **2022**, *61*, 8595–8606. [[CrossRef](#)]
39. Farshi, A.; Shiralizadeh, P. Sulfur Reduction of Heavy Fuel Oil by Oxidative Desulfurization (ODS) Method. *Pet. Coal* **2015**, *57*, 295–302.
40. Capecci, E.; Piccinino, D.; Bizzarri, B.M.; Botta, L.; Crucianelli, M.; Saladino, R. Oxidative Bio-Desulfurization by Nanostructured Peroxidase Mediator System. *Catalysts* **2020**, *10*, 313. [[CrossRef](#)]
41. Mohammadi, P. Ionic Liquids for Desulfurization. In *Ionic Liquid-Based Technologies for Environmental Sustainability*; Elsevier: Amsterdam, The Netherlands, 2022; pp. 61–74; ISBN 9780128245453. [[CrossRef](#)]
42. Hosseini, A.; Khoshima, A.; Sabzi, M.; Rostam, A. Toward Application of Ionic Liquids to Desulfurization of Fuels: A Review. *Energy Fuels* **2022**, *36*, 4119–4152. [[CrossRef](#)]
43. Francisco, M.; Arce, A.; Soto, A. Ionic Liquids on Desulfurization of Fuel Oils. *Fluid Phase Equilib.* **2010**, *294*, 39–48. [[CrossRef](#)]
44. Desai, K.; Dharaskar, S.; Khalid, M.; Gedam, V. Effectiveness of Ionic Liquids in Extractive–Oxidative Desulfurization of Liquid Fuels: A Review. *Chem. Pap.* **2022**, *76*, 1989–2028. [[CrossRef](#)]
45. Bhutto, A.W.; Abro, R.; Gao, S.; Abbas, T.; Chen, X.; Yu, G. Oxidative Desulfurization of Fuel Oils Using Ionic Liquids: A Review. *J. Taiwan Inst. Chem. Eng.* **2016**, *62*, 84–97. [[CrossRef](#)]
46. Crucianelli, M.; Bizzarri, B.M.; Saladino, R. SBA-15 Anchored Metal Containing Catalysts in the Oxidative Desulfurization Process. *Catalysts* **2019**, *9*, 984. [[CrossRef](#)]
47. Feng, S.; Yang, H.; Zhan, X.; Wang, W. Enhancement of Dibenzothiophene Biodesulfurization by Weakening the Feedback Inhibition Effects Based on a Systematic Understanding of the Biodesulfurization Mechanism by *Gordonia* Sp. through the Potential “4S” Pathway. *RSC Adv.* **2016**, *6*, 82872–82881. [[CrossRef](#)]
48. Maghsoudi, S.; Vossoughi, M.; Kheirloomoom, A.; Tanaka, E.; Katoh, S. Biodesulfurization of Hydrocarbons and Diesel Fuels by *Rhodococcus* sp. Strain P32C1. *Biochem. Eng. J.* **2001**, *8*, 151–156. [[CrossRef](#)]
49. Chang, J.; Kim, Y.J.; Lee, B.H.; Kho, K.-S.; Rye, H.W.; Chang, Y.K.; Chang, H.N. Production of a Desulfurization Biocatalyst by Two-Stage Fermentation and Its Application for the Treatment of Model and Diesel Oils. *Biotechnol. Progr.* **2001**, *17*, 876–880. [[CrossRef](#)]
50. Mingfang, L.; Jianmin, X.; Zhongxuan, G.; Huizhou, I.; Jiayong, C. Microbial Desulfurization of Dithiophene and 4,6-Dimethyldibenzothiophene in Dodecane and Straight-Run Diesel Oil. *Korean J. Chem. Eng.* **2003**, *20*, 2169–2183. [[CrossRef](#)]
51. Darzins, A.; Mrachko, G.T. Sphingomonas Biodesulfurization Catalyst. U.S. Patent 6133016, 17 October 2000.

52. Srinivasaraghavan, K.; Sarma, P.M.; Lal, B. Comparative Analysis of Phenotypic and Genotypic Characteristics of Two Desulfurizing Bacterial Strains, Mycobacterium Phlei SM-120 and Mycobacterium Phlei GTIS10. *Lett. Appl. Microbiol.* **2006**, *42*, 483–489. [[CrossRef](#)]
53. Abo-State, M.A.; El-Gendy, N.S.; El-Temtamy, S.A.; Mahdi, H.M.; Nassar, H.N. Modification of Basal Salts Medium for Enhancing Dibenzothiophene Biodesulfurization by *Brevibacillus invocatus* C19 and *Rhodococcus erythropolis* IGT58. *World Appl. Sci. J.* **2014**, *30*, 133–140.
54. Kirimura, K.; Furuya, T.; Nishii, Y.; Ishii, Y.; Kino, K.; Usami, S. Biodesulfurization of Dibenzothiophene and Its Derivatives through the Selective Cleavage of Carbon-Sulfur Bonds by Moderately Thermophilic Bacterium *Bacillus subtilis* WU-S2B. *J. Biosci. Bioeng.* **2001**, *91*, 262–266. [[CrossRef](#)] [[PubMed](#)]
55. Kodama, K.; Umechara, K.; Shimizu, K.; Nakatani, S.; Minoda, Y.; Yamada, K. Identification of Microbial Products from Dithiophene and Its Proposed Oxidation Pathway. *Agric. Biol. Chem.* **1973**, *37*, 45–50. [[CrossRef](#)]
56. Wang, L.; Ji, G.; Huang, S. Contribution of the Kodama and 4S Pathways to the Dibenzothiophene Biodegradation in Different Coastal Wetlands under Different C/N Ratios. *J. Environ. Sci.* **2019**, *76*, 217–226. [[CrossRef](#)] [[PubMed](#)]
57. Hou, Y.; Kong, K.; Yang, J.; Zhang, J.; Shi, D.; Xin, W. Biodesulfurization of Benzothiophene by Immobilized Cells of *Pseudomonas Stutzeri* UP-1. *Fuel* **2005**, *84*, 1975–1979. [[CrossRef](#)]
58. Abin-Fuentes, A.; Mohamed, M.E.S.; Wang, D.I.C.; Prather, K.L.J. Exploring the Mechanism of Biocatalyst Inhibition in Microbial Desulfurization. *Appl. Environ. Microbiol.* **2013**, *79*, 7807–7817. [[CrossRef](#)]
59. Papizadeh, M.; Roayaei Ardakani, M.; Motamedi, H. Growth-Phase Dependent Biodesulfurization of Dibenzothiophene by *Enterobacter* sp. Strain NISOC-03. *Pollution* **2017**, *3*, 101–111. [[CrossRef](#)]
60. Alves, L.; Melo, M.; Mendonça, D.; Simões, F.; Matos, J.; Tenreiro, R.; Gírio, F.M. Sequencing, Cloning and Expression of the Dsz Genes Required for Dibenzothiophene Sulfone Desulfurization from *Gordonia alkanivorans* Strain 1B. *Enzyme Microb. Technol.* **2007**, *40*, 1598–1603. [[CrossRef](#)]
61. Caro, A.; Boltes, K.; Letón, P.; García-Calvo, E. Dibenzothiophene Biodesulfurization in Resting Cell Conditions by Aerobic Bacteria. *Biochem. Eng. J.* **2007**, *35*, 191–197. [[CrossRef](#)]
62. Gün, G.; Yürüm, Y.; Dinler Doganay, G. Revisiting the Biodesulfurization Capability of Hyperthermophilic Archaeon *Sulfolobus solfataricus* P2 Revealed DBT Consumption by the Organism in an Oil/Water Two-Phase Liquid System at High Temperatures. *Turk. J. Chem.* **2015**, *39*, 255–266. [[CrossRef](#)]
63. Bhanjadeo, M.M.; Rath, K.; Gupta, D.; Pradhan, N.; Biswal, S.K.; Mishra, B.K.; Subudhi, U. Differential Desulfurization of Dibenzothiophene by Newly Identified MTCC Strains: Influence of Operon Array. *PLoS ONE* **2018**, *13*, e0192536. [[CrossRef](#)]
64. Davoodi-Dehaghani, F.; Vosoughi, M.; Ziaee, A.A. Biodesulfurization of Dibenzothiophene by a Newly Isolated *Rhodococcus Erythropolis* Strain. *Bioresour. Technol.* **2010**, *101*, 1102–1105. [[CrossRef](#)]
65. Aribike, D.S.; Susu, A.A.; Nwachukwu, S.C.U.; Kareem, S.A. Microbial Desulfurization of Diesel by *Desulfobacterium Aniline*. *Acad. Arena* **2009**, *1*, 11–14.
66. Zhang, Q.; Tong, M.Y.; Li, Y.S.; Gao, H.J.; Fang, X.C. Extensive Desulfurization of Diesel by *Rhodococcus erythropolis*. *Bioethanol. Lett.* **2007**, *29*, 123–127. [[CrossRef](#)] [[PubMed](#)]
67. Gunam, I.B.W.; Yaku, Y.; Hirano, M.; Yamamura, K.; Tomita, F.; Sone, T.; Asano, K. Biodesulfurization of Alkylated Forms of Dibenzothiophene and Benzothiophene by *Sphingomonas Subartica* 17b. *J. Biosci. Bioeng.* **2006**, *101*, 322–327. [[CrossRef](#)]
68. Boshagh, F.; Mokhtarani, B.; Mortaheb, H.R. Effect of Electrokinetics on Biodesulfurization of the Model Oil by *Rhodococcus Erythropolis* PTCC1767 and *Bacillus Subtilis* DSMZ 3256. *J. Hazard. Mater.* **2014**, *280*, 781–787. [[CrossRef](#)]
69. Bordoloi, N.K.; Sudhir, R.K.; Chaudhuri, M.K.; Mukherjee, A.K. Deep-Desulfurization of Dibenzothiophene and Its Derivatives Present in Diesel Oil by a Newly Isolated Bacterium *Achromobacter* sp. to Reduce the Environmental Pollution from Fuel Combustion. *Fuel Process. Technol.* **2014**, *119*, 236–244. [[CrossRef](#)]
70. Yang, J.; Yongqi, H.; Dishun, Z.; Shaozhao, W.; Lau, P.C.K.; Marison, I.W. Two-Layer Continuous-Process Design for the Biodesulfurization of Diesel Oils under Bacterial Growth Conditions. *Biochem. Eng. J.* **2007**, *37*, 212–218. [[CrossRef](#)]
71. Nassar, H.N.; Ali, H.R.; El-Gendy, N.S. Waste Prosperity: Mandarin (*Citrus Reticulata*) Peels Inspired SPION for Enhancing Diesel Oil Biodesulfurization Efficiency by *Rhodococcus Erythropolis* HN2. *Fuel* **2021**, *294*, 120534. [[CrossRef](#)]
72. Chen, S.; Zhao, C.; Liu, Q.; Zhang, X.; Sun, S.; Zang, M. Biodesulfurization of Diesel Oil in Oil-Water Two Phase Reaction System by *Gordonia* sp. SC-10. *Biotechnol. Lett.* **2019**, *41*, 547–554. [[CrossRef](#)] [[PubMed](#)]
73. Pokethitiyooka, P.; Tangaromsuk, J.; Kruatrachue, M.; Kalambaheti, C.; Borole, A.P. Biological Removal of Organic Sulphur by Bacterial Strains Isolated in Thailand. *Sci. Asia* **2008**, *34*, 361–366. [[CrossRef](#)]
74. Agarwal, M.; Dikshit, P.K.; Bhasarkar, J.B.; Borah, A.J.; Moholkar, V.S. Physical Insight into Ultrasound-Assisted Biodesulfurization Using Free and Immobilized Cells of *Rhodococcus Rhodochrous* MTCC 3552. *Chem. Eng. J.* **2016**, *295*, 254–267. [[CrossRef](#)]
75. Martínez, I.; Mohamed, M.E.S.; Rozas, D.; García, J.L.; Díaz, E. Engineering Synthetic Bacterial Consortia for Enhanced Desulfurization and Revalorization of Oil Sulfur Compounds. *Metab. Eng.* **2016**, *35*, 46–54. [[CrossRef](#)] [[PubMed](#)]
76. Alves, L.; Paixão, S.M. Enhancement of Dibenzothiophene Desulfurization by *Gordonia alkanivorans* Strain 1B Using Sugar Beet Molasses as Alternative Carbon Source. *Appl. Biochem. Biotechnol.* **2014**, *172*, 3297–3305. [[CrossRef](#)] [[PubMed](#)]

77. Dai, Y.; Shao, R.; Qi, G.; Ding, B.-B. Enhanced Dibenzothiophene Biodesulfurization by Immobilized Cells of *Brevibacterium Lutescens* in N-Octane–Water Biphasic System. *Appl. Biochem. Biotechnol.* **2014**, *174*, 2236–2244. [[CrossRef](#)]
78. Agarwal, P.; Sharma, D.K. Comparative Studies on the Bio-Desulfurization of Crude Oil with Other Desulfurization Techniques and Deep Desulfurization through Integrated Processes. *Energy Fuels* **2010**, *24*, 518–524. [[CrossRef](#)]

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