

**DEEP EUTECTIC SOLVENTS EXTRACTION OF
DIBENZOTHIOPHENE IN MODEL DIESEL**

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Master of Science

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ABSTRACT

Organic sulfur compounds in diesel fuel produce SO_x during combustion in vehicles, leading to severe environmental pollution and causing health issues. The U.S. Environmental Protection Agency has established increasingly rigid sulfur-content standards, which has led to intense interest in deep desulfurization of diesel fuel. However, current desulfurization technology is not sufficient to achieve the ultralow sulfur diesel (ULSD) required for use in highway vehicles.

Deep eutectic solvents (DESs) appearing at the beginning of this century have become excellent extraction agents for the deep extractive desulfurization process, owing to its low cost, simple and environmentally friendly synthesis process, chemical stability, non-volatility, and being biodegradable. Research shows that DESs have better efficiency than traditional ionic liquids (ILs). Therefore, DESs are better suited for use in desulfurization.

In this study, a new potassium salt-based DES was synthesized using potassium carbonate (K_2CO_3) and ethylene glycol (EG). This type of DES and 30 wt.% H_2O_2 were employed as extractant and oxidant separately for the desulfurization system. Various experiments were carried out on the process of oxidative desulfurization (ODS), extractive desulfurization (EDS) and extractive and oxidative desulfurization (EODS) to find the optimal desulfurization process with this new type of DES. The study found EDS to be the optimal desulfurization process, with a sulfur removal efficiency of 86% at 30 °C after 2 hours, which is higher than most DESs.

Chapter 1. Introduction

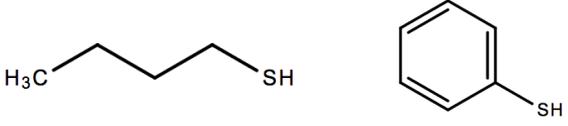
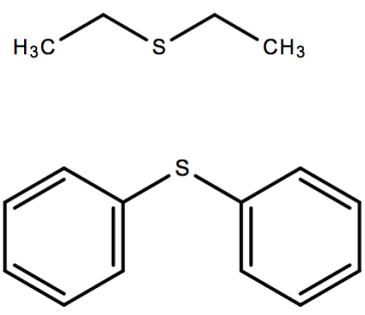
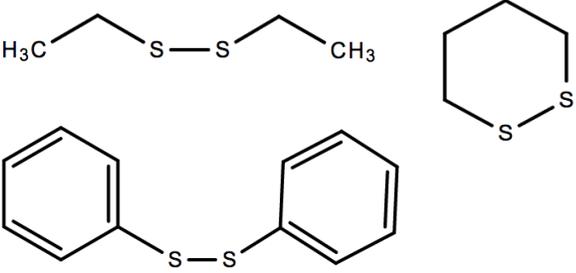
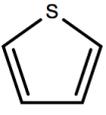
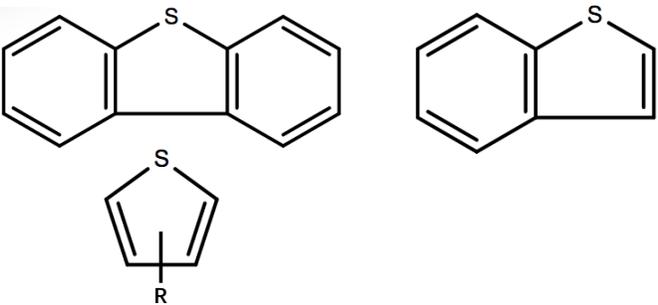
1.1 Overall view of diesel fuel

In general, diesel fuel is a liquid fuel that is used in diesel engines. It was invented by German scientist Rudolf Diesel for his compression-ignition engine in 1892. The most common type of diesel fuel is the petroleum diesel called petrodiesel. It has a kerosene-like odor and is a colorless to brown liquid. Petrodiesel has a typical freezing point around -8°C . The production of diesel fuel is accomplished through the fractional distillation of crude oil, which has a boiling point range of 200°C (392°F) to 350°C (662°F) at ambient pressure. It is a mixture of 75% saturated hydrocarbons and 25% aromatic hydrocarbons containing between 8 and 21 carbon atoms per molecule, typically ¹. The chemical formula for diesel fuel is between $\text{C}_{10}\text{H}_{20}$ and $\text{C}_{15}\text{H}_{28}$. $\text{C}_{12}\text{H}_{23}$ is the average chemical formula ². In the United States, diesel fuel is recommended to be stored in a yellow container to differentiate it from kerosene and gasoline which are stored in blue and red containers, respectively. The combustion products of petrodiesel are water, nitrogen and carbon dioxide. However, sulfur is one of the main pollutants in diesel fuel. Incomplete combustion of diesel engines results in the emission of sulfur oxides (SO_x), nitrogen oxides (NO_x), carbon monoxide, and hydrocarbons, which are the source of soot and fine particles in air pollution. These air pollutants are the main components causing cancer, heart damage, lung damage, and mental functioning problems ³⁻⁴.

1.2 Organic sulfur content

Sulfur presents inorganic and organic forms in diesel, and analyzing the amount of organic sulfurs is considered the key to evaluating the process of desulfurization. Organic sulfur compounds are separated into four groups: thiols (R-SH), sulfides (R-S-R), disulfides (R-S-S-R), and thiophenes. Table 1.1 shows the chemical structures of the major organic sulfur groups in petroleum. Among them, thiophene groups such as benzothiophene, dibenzothiophene, and their derivatives are the most important because their presence makes the desulfurization process more difficult.

Table 1.1 Major organic sulfur in petroleum ⁵

Sulfur compound	General structure	Structural examples
Thiols	R-SH	
Sulfides	R-S-R	
Disulfides	R-S-S-R	
Simple and condensed thiophenes		

1.3 Sulfur regulation

Sulfur contained in fuel leads to the release of sulfur oxide (SO_x) when burning diesel fuel.

It is the most crucial contribution leading to acid rain, air pollution, and human diseases ⁶

because the SO₂ interferes with the catalysts applied in vehicle exhaust treatment systems, resulting in the increased emissions of nitrogen oxides (NO_x) and total suspended solids (TSP). Hence, more and more countries have established rigid rules to lower the sulfur content. Sulfur content in diesel and gasoline has been slowly decreasing and is close to zero level for varieties of applications. In the United States, after October 15, 2006, the U.S. Environmental Protection Agency (EPA) began to phase-in more stringent regulations to lower the amount of sulfur in diesel fuel to 15 ppm. This fuel is known as ultra-low sulfur diesel (ULSD). Use of ULSD has been required of all highway diesel vehicles since 2010. Off-road diesel engine fuels were required to control the level of sulfur to under 500 ppm in 2007, and 15 ppm in 2010. Railway locomotives and marine diesel was limited to 500 ppm of sulfur in 2007, and was further reduced to ULSD (15 ppm) in 2012. There were small refineries exempted from non-road, locomotives, and marine diesel, allowing 500 ppm of sulfur to remain in the system until 2014. After December 1, 2014, all production and import of highway, off-road, locomotive, and marine diesel was required to be ULSD, as shown in Table 1.2 (EPA regulation 2017).

Table 1.2 Highway and Non-road Diesel Fuel Standards

Covered Fuel	2006	2007	2008	2009	2010	2011	2012	2013	2014
Highway Diesel Fuel	80% 15ppm / 20% 500ppm				100% 15 ppm (including small refiner fuel)				
Non-road	N/A	500	500	500	15	15	15	15	15
Locomotive	N/A	500	500	500	500	500	15	15	15
NRLM w/credits (not in NE,MA or AK)	N/A	HS	HS	HS	500	500	500	500	15
ECA Marine Fuel	(no EPA sulfur level requirements)								1000

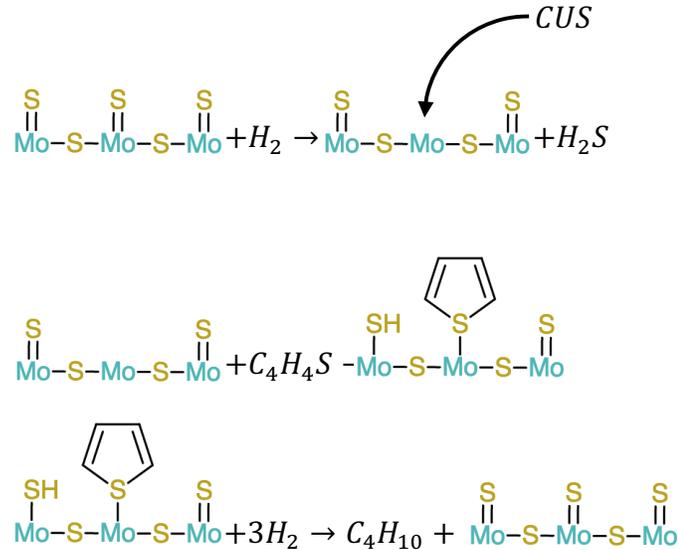
1.4 Current technology

Owing to the stringent fuel regulations, deep desulfurization in fuel is not only a technological challenge but also an economical burden. Nowadays, multiple desulfurization methods have been developed, and determining where these methods can produce ULSD that is economically feasible and can meet the local and global curing standards is the most important step. Hydrodesulfurization (HDS) by catalysis is widely applied in industry ⁷. It is efficient for eliminating thiols, sulfides, disulfides, and some thiophene derivatives. However, it is less effective for removing aromatic sulfur

compounds, such as dibenzothiophene (DBT), and their derivatives. Hence, adsorptive desulfurization, biodesulfurization, oxidative desulfurization, and extractive desulfurization are the leading methods when it comes to the production of ULSD.

1.4.1 Hydrodesulfurization (HDS)

Hydrodesulfurization (HDS) is widely used in catalytic chemistry to remove sulfur from refined oil including gasoline, jet fuel, diesel fuel, and naphtha⁸. Hydrodesulfurization is a hydrogenolysis reaction, which is a type of hydrogenation. It is a process of splitting the C-S chemical bonds and then forming C-H and H-S chemical bonds. The current hydrotreating catalyst is mainly molybdenum disulfide (MoS_2) supported by cobalt or nickel and is reinforced on porous γ -alumina $\text{Co-Mo/Al}_2\text{O}_3$ and $\text{Ni-Mo/Al}_2\text{O}_3$. Additives such as boron, phosphorus, or silica promoters such as $\text{Ni-Co-Mo/Al}_2\text{O}_3$, or improved preparation methods are supported as modifications for hydrotreating catalysts⁷. The edges of the MoS_2 sheet is the active site instead of the basal planes⁹. At the center of the molybdenum disulfide molecules, where the rims of the molybdenum disulfide crystallites form, a stabilized coordinately unsaturated site (CUS) known as an anion vacancy is created. Thus, organic sulfur compounds can bind to the CUS and experience a series of reactions resulting from C-S scission and C=C hydrogenation. The reactions are shown below.



In the industry, hydrotreating, hydroprocessing, hydrocracking, and hydrodesulfurization are the dominant processes employed, since cracking and desulfurization operations occur concurrently in the hydrocracking and hydrodesulfurization process, and it is currently unknown to which is predominant. Hydrotreating refers to mild processes to reduce the sulfur content while hydrocracking involves processes that reduce the boiling range. Although there are around 30 hydrotreating processes applied in the industry, most of them have essentially the same process flow ¹⁰.

The feed (olefin free) is pumped to the required elevated operating pressure and is mixed with a hydrogen-rich gas stream. The collective feedstock is preheated via a heat exchanger prior to being heated by a fired heater to the operating reactor temperature. The heated mixture flows through the fixed-bed reactor at a temperature ranging from 300°C to 400°C. After the hydrodesulfurization reaction starts in this reactor the products are partially cooled by going through the feed preheater and further cooled by a water-cooled heat exchanger. The product stream passes through a pressure controller to decrease the pressure

and then enters a gas separator at 35°C and 3-5 atmospheres of absolute pressure. In the gas separator, most of the gas at the top is unreacted hydrogen and hydrogen sulfide. It goes to an amine contactor to remove the hydrogen sulfide and then is recycled back to mix with the feed for reuse. All excess gas from the separator is combined with the acid gas from the top of the product stripper. The liquid at the bottom in the gas separator vessel flows through a reboiler stripper distillation column. The bottom product from the column yields a final desulfurized liquid product from the HDS unit. The stripper acid gas contains various components such as methane, ethane, propane, hydrogen sulfide, and possibly some butane and other heavier hydrocarbons. The acid gas is sent to a central gas treatment apparatus to remove hydrogen sulfide in the main amine gas treatment apparatus. It is also possible to recover propane, butane, and the like through a series of distillation columns. The remaining methane, ethane, propane, and hydrogen are used in refinery fuel gas systems. The hydrogen sulfide removed and recovered by the amine gas treatment unit is then converted to elemental sulfur in the Claus process unit or converted to sulfuric acid in a wet sulfuric acid process or conventional contact process.

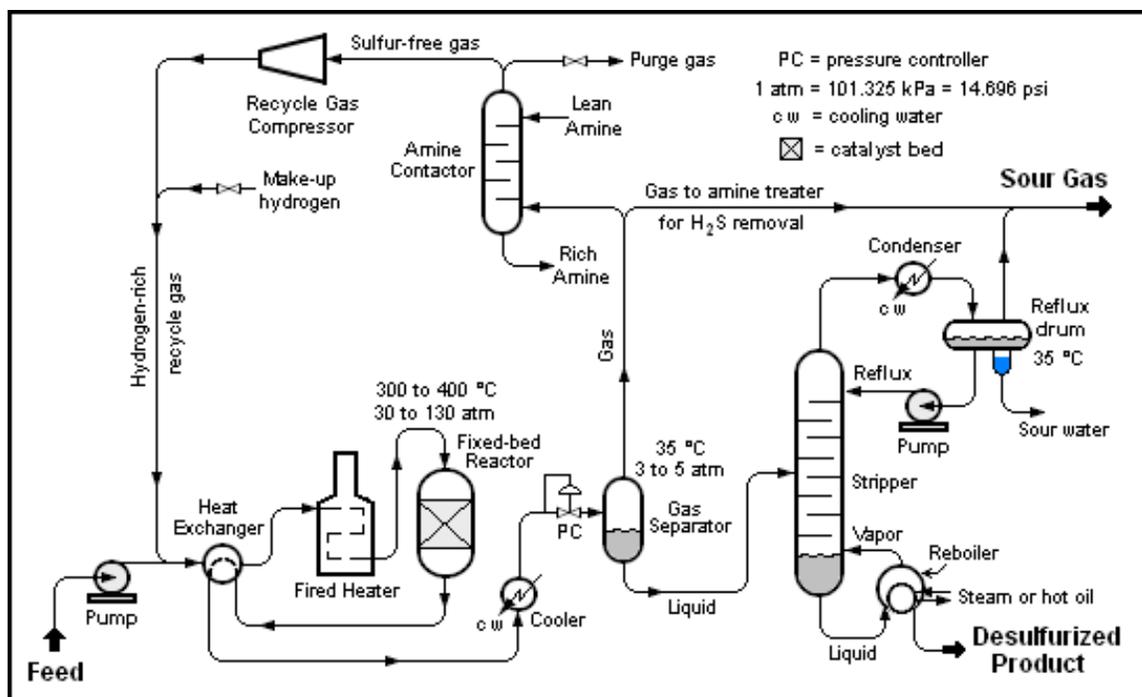


Figure 1.1 HDS process flow

Although the HDS process has been widely applied to produce low sulfur diesel for a long time, not all sulfur compounds are eliminated equally. Thiols, sulfides, and simple thiophenes are easier to remove via the HDS process while condensed thiophenes, benzothiophenes, dibenzothiophenes, and their derivatives protect the sulfur atom owing to the aromatic structure⁵. The reactivity of 4-alkyl DBTs, 6-alkyl DBTs and 4, 6-alkyl DBTs is very low due to the combinations of electronic density, bond order, and spatial, geometric and steric hindrance around the sulfur atom¹¹. The reactivity of DBTs decreases in the sequence of DBT > 4-MDBT > 4,6-DMDBT. To achieve the rigid regulations of diesel fuel standards, deep HDS techniques should be adopted. Its investigation includes the increment of hydrogen, catalyst dosage, and operating pressure and temperatures. An extra 25% to 45% of hydrogen gas is required for lowering sulfur content from 500 ppm_w to 15 ppm_w¹². Hence, the operation fee increases to two times that of the traditional HDS

operational fee since hydrogen usage is the main operation cost for HDS. It is reported that doubling the catalyst dosage can only lower the sulfur content by 100 ppm_w. Therefore, a large increase in catalyst dosage is required to produce ULSD. According to the National Petroleum Council, the operating pressure should be increased from 1100 psi to 1200 psi to produce diesel with no more than 30 ppm_w sulfur. A certain thick-walled reactor is required to withstand such a high pressure, which results in increasing capital and operational costs. Safety with the HDS process is also a major concern while dealing with the required high operating pressure and temperature involving the use of hydrogen gas. There is the possibility of a phenomenon of uncontrollable “hot-spots” as a consequence of reactor wall failure and explosion¹³.

1.4.2 Adsorptive Desulfurization (ADS)

Adsorptive desulfurization is one of the promising approaches for producing ultra-low sulfur diesel that uses adsorbents to selectively remove the organic sulfur compounds (OSCs). ADS has two categories based on the mechanism of the sulfur compound interaction with the sorbent. One of them is adsorptive desulfurization, which the aromatic sulfur compounds enable to be adsorbed on the active sites on the surface of solid adsorbents such as activated carbon¹⁴⁻¹⁵, zeolite-based materials¹⁶⁻¹⁷, or metal–organic frameworks (MOFs)¹⁸⁻¹⁹. Another is reactive adsorption desulfurization, which has chemical interactions between the organic sulfur compounds and the sorbent such as metal oxide²⁰. It is found that the efficiency of adsorptive desulfurization strongly depends on the adsorbent’s properties: adsorption capacity, selectivity for the OSCs, durability, and renewability²¹.

A potential new option for refinery applications is to use a sulfur-selective adsorption unit for ultra-deep removal of organic sulfur following a conventional HDS unit, and this combination can remove all of the sulfur from the liquid fuel products²². The Black and Veatch Pritchard engineering company has developed an adsorption-based desulfurization technology called IRVAD. It is a technology to eliminate various OSCs from refinery streams²³⁻²⁴, shown in Figure 1.2.

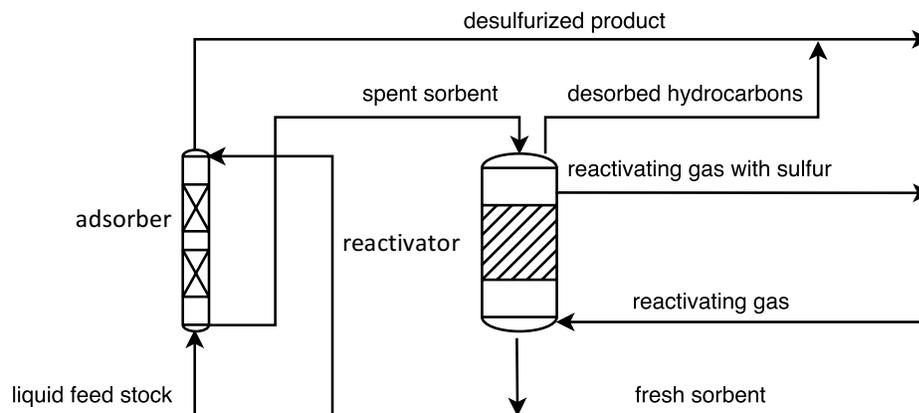
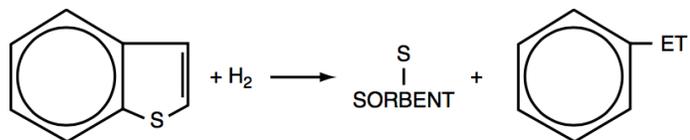


Figure 1.2 Simplified adsorptive desulfurization process flow²¹

A sulfur-rich feedstock enters the bottom of the adsorber, which is a moving bed filled with solid sorbent from the top. The desulfurized hydrocarbon product comes out at the top. The spent sorbent from the bottom of the adsorber goes through a reactivator where the OSCs and some hydrocarbons on the sorbent surface are desorbed by reactivating gas. The reactivating gas with concentrated sulfur is then to be hydrotreated in the next HDS unit and the renewed sorbent is mixed with fresh sorbent and recirculated back to the adsorber. The IRVAD process has at least 90% sulfur removal capabilities. However, its efficiency is limited by the sorbent capacity and its similarity for sulfur compounds. Since the adsorption of dibenzothiophene molecules occurs through the aromatic ring p electrons

parallel to the surface of the catalyst, the adsorbent capacity is quite low. Thus, a large amount of adsorbent is required for the efficient operation of the desulfurization unit. The work of the IRVAD process is currently halted because of the time limit for commercialization of the technology before the introduction of new sulfur levels in Europe and the United States.

Reactive adsorption uses a metal-based sorbent to catch sulfur to form a metal sulfide. It can be described by the following reaction:



The sulfur atom is removed from the benzothiophene molecule and binds together with the sorbent. The rest of the molecule keeps its structure and becomes the final product.

Based on the mechanism of reactive adsorption, Phillips Petroleum Co. USA (now ConocoPhillips) has developed a process called Phillips S-zorb technology applied to remove sulfur from gasoline and diesel fuel²⁵⁻²⁷.

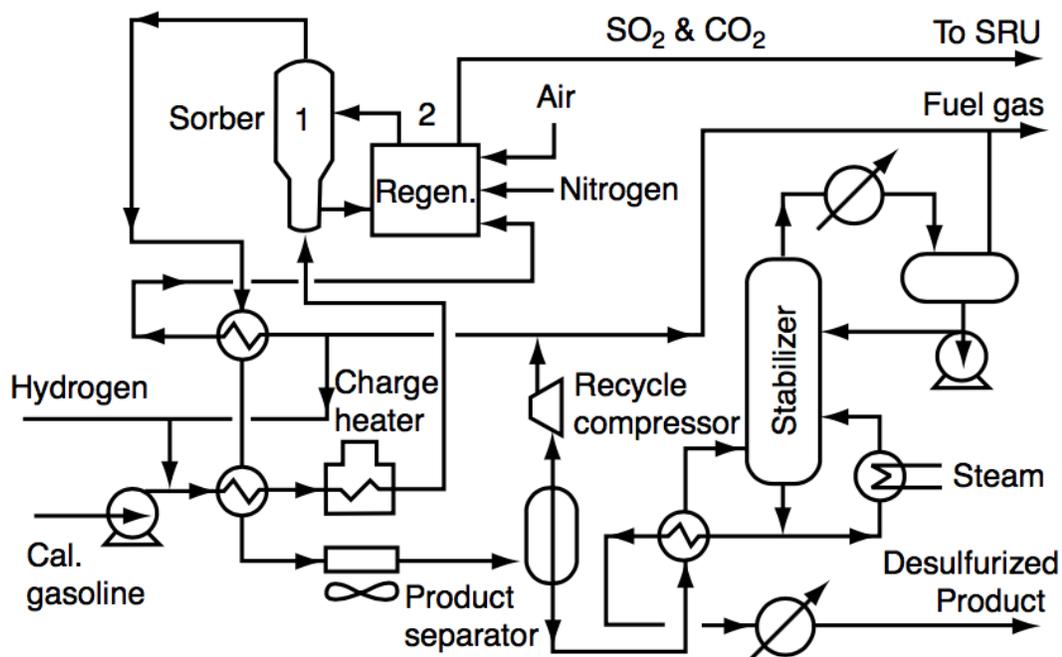


Figure 1.3 S-zorb sulfur removal process and its continuous regeneration

Figure 1.3 indicates the flow scheme of s-zorb gasoline. Gasoline is pumped to the required pressure and then mixed with hydrogen. The mixture is heated by a heat exchanger and charge heater and then enters a fluid bed sorber at the bottom. The operating temperature and pressure of the sorber is 340°C to 410°C and 2 to 20 bar, respectively. The main component of the desulfurization sorbent is zinc oxide, and also includes alumina, silica, and nickel oxide²⁸⁻²⁹. The spent sorbent from the bottom of the sorber flows to the regeneration unit. The desulfurized product from the top of the sorber then cools down by use of a heat exchanger and goes into a separator for separating fuel gas at the top and hydrocarbon stream at the bottom. The hydrocarbon stream flows into a column for further separating pure desulfurized product and fuel gas. The spent sorbent is constantly transferred from the sorber to the regeneration segment. The sulfur is burned by the adsorbent in the separate regeneration vessel and SO₂ is sent to the sulfur unit. The purified

sorbent is further reduced by hydrogen and then the renewed sorbent is recirculated back to the sorber to remove more sulfur. It is claimed that the sulfur removal achieved by this process is 98% with almost 100% hydrocarbon recovery³⁰.

Several studies have found that adsorptive desulfurization desulfurized gasoline or diesel contains no more than 30 ppm_w³¹. Nevertheless, these processes are in need of a particularly synthesized sorbent, which is not commercially obtainable at this stage. In addition to unrealized profits, adsorptive desulfurization is a potential approach owing to its mild operating conditions, environmental friendliness, and its selective removal of refractory thiophenic compounds¹⁴.

1.4.3 Biodesulfurization (BDS)

Biodesulfurization is an enzymatic process that depends on the specificity of microorganisms requiring sulfur for their growth and biological activities to consume the recalcitrant organic sulfur compounds in the diesel or gasoline³². It is theoretically advantageous³²⁻³³: the process conditions are under mild temperature and pressure, which is cost efficient compared with HDS. Also, the enzymes in the microorganisms have extremely high selectivity to OSCs (over HDS); hence, it reduces the unnecessary loss of hydrocarbons and produces low sulfur diesel. It also produces considerably less greenhouse gases³⁴.

There are two types of biodesulfurization processes—destructive pathway and sulfur-specific pathway^{33, 35}. Destructive pathway, also called Kodama pathway, is the process where the carbon skeleton of DBT is not totally oxidized and the C-S bond stays

undamaged. In the sulfur-specific pathway, the carbon skeleton of DBT remains whole and the C-S bond breaks. This is called the 4S pathway (under aerobic conditions). Between the two pathways the sulfur-specific pathway has obtained comparably more attention owing to the high efficiency of reducing of the sulfur content.

The destructive pathway process is divided into three steps including hydroxylation, ring cleavage, and hydrolysis, as shown in Figure 1.5. The Kodama pathway uses a series of enzymes to attack the carbon atoms in the DBT benzene ring to oxidize and destroy the carbon phenyl ring ³⁶. In this pathway, the outer aromatic ring (benzyl ring) of the DBT is first subjected to double oxidation, followed by ring cleavage. This process results in the accumulation of 3-hydroxy-2-formyl-benzothiophene as a water-soluble final product. In this way, there is no desulfurization of the organic sulfur matrix. The oxidation in most cases reaches the step where 3-hydroxy-2-formyl-benzothiophene (HBFT) and pyruvic acid (PA) are produced. The steps after production of HBFT are not fully known. HBFT is chemically unstable and it is most likely mineralized in nature. Several reports indicate that DBT can be utilized via this method by bacterial genera including *Pseudomonas* ³⁷⁻³⁸, *Beijerinckia* ³⁹, and *Rhizobium* ⁴⁰.

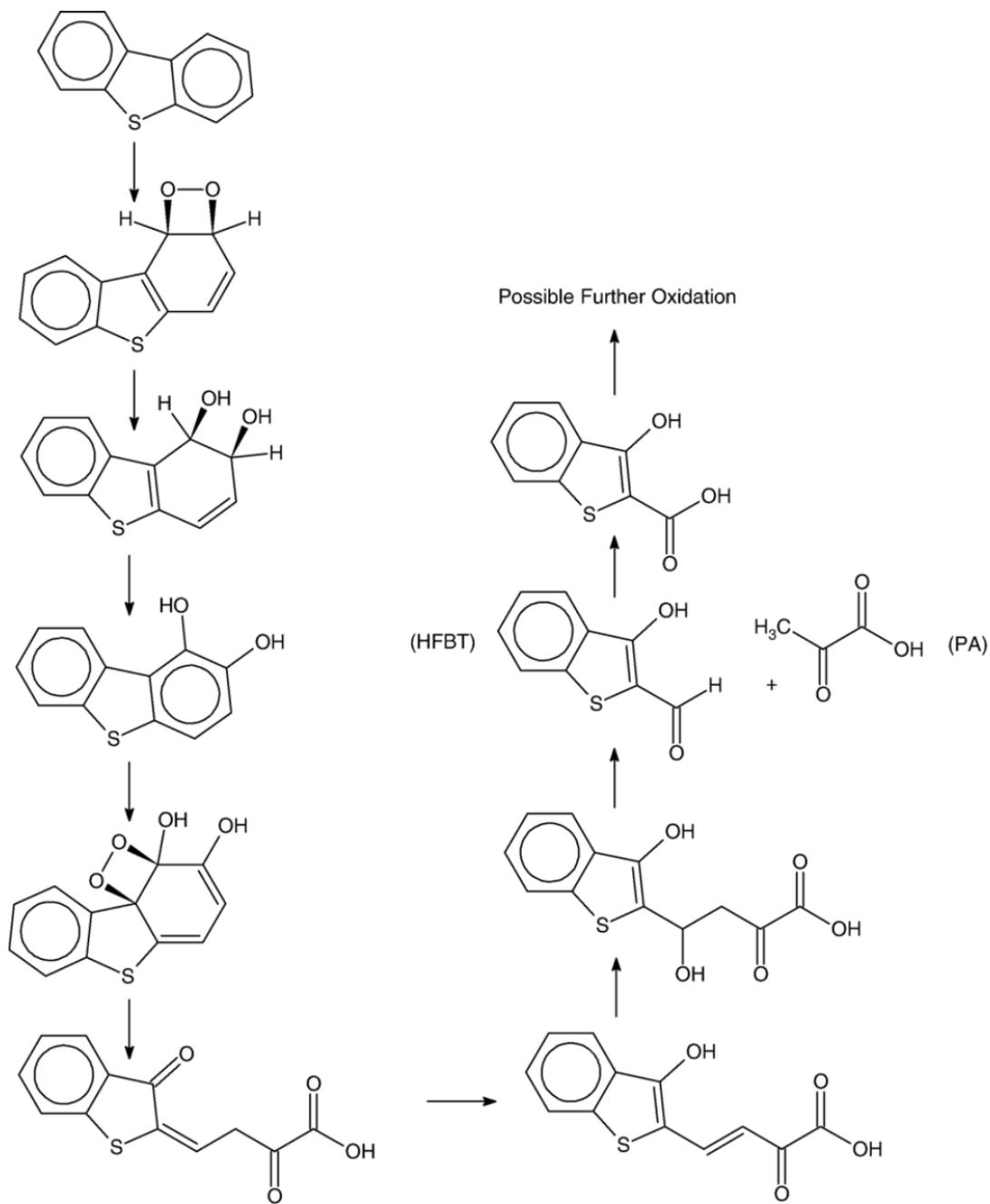


Figure 1.4 Kodama enzymatic pathway on dibenzothiophene³⁶

It is indicated that *Desulfovibrio desulfuricans* M6 convert DBT to biphenyl and H_2S under anaerobic conditions⁴¹. The anaerobic strain could reduce 42% DBT. Some other anaerobic bacterial genera have been reported to follow a different pathway from the

common pathway where biphenyl is not the end product, such as *Desulfomicrobium escambium* and *Desulfovibrio longreachii*⁴². Under anaerobic conditions, the desulfurization of the oil avoids the costs associated with aeration and has the advantage of releasing sulfur as a gas. However, due to low reaction rates, safety, and cost issues, anaerobic BDS methods have not yet been developed⁴³.

The aerobic sulfur-specific pathway is named 4S (sulfoxide–sulfone–sulfinate–sulfate) pathway. It consists of three stages: (i) the DBT ring is oxidized to activate by the sulfur moiety for cleavage; (ii) the cleavage of the DBT occurs between the carbon skeleton and the aromatic sulphinate; (iii) the sulfonate group is removed by bacteria⁴⁴. The DBT sulfur is consecutively oxidized to sulfoxide (DBTO), sulfone (DBTO₂), sulfonate (HPBS), and hydroxybiphenyl (HBP). In the aerobic sulfur-specific pathways, there is almost no reduction in the calorific value of the petroleum products³⁵ as shown in Figure 1.6. There are several microorganism groups that could remove sulfur following the 4S pathways, such as *Pseudomonas* CECT5279⁴⁵ and IGTS7⁴⁶.

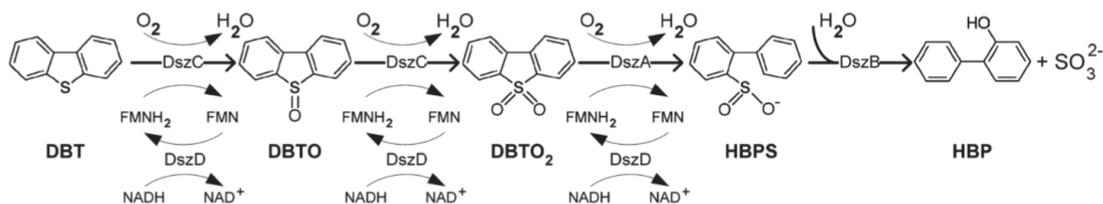


Figure 1.5 The 4S pathway from *Rhodococcus erythropolis* IGTS8 and the enzymes involved in it⁴⁵

The commercial biodesulfurization process is presented in Figure 1.7. The innovation of the process is the employment of multiple-staged airlift reactors to overwhelm poor reaction kinetics at low sulfur concentrations and decrease costs. The growth and

revitalization of cells in the process is a vital step to achieve the long residence time of the biocatalyst required for the commercial process³².

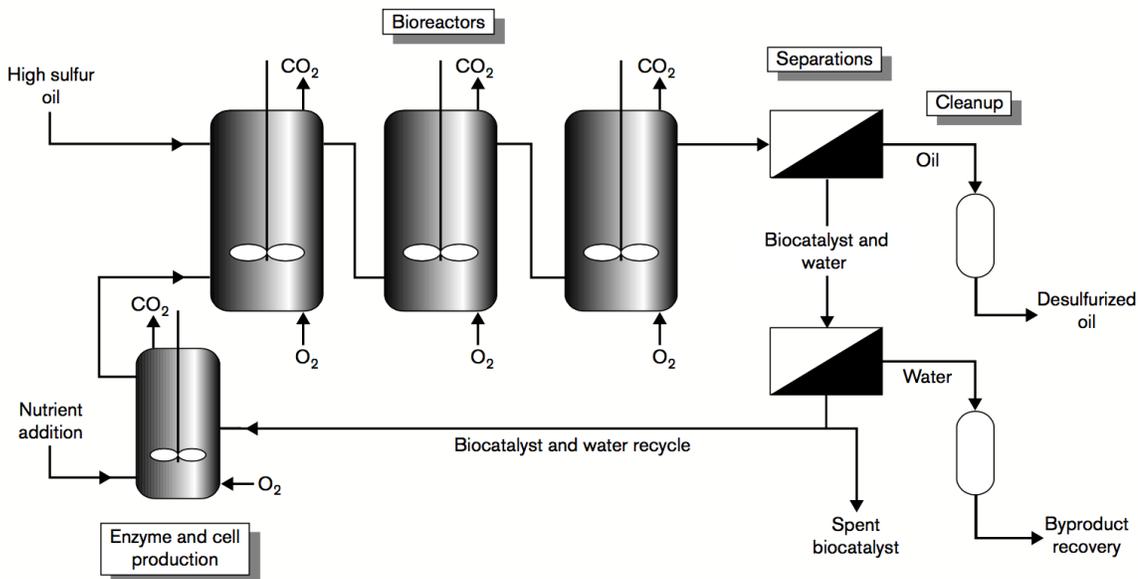


Figure 1.6 Conceptual process flow diagram of BDS³²

BDS can be supplemented by HDS because the steric hindered alkyl DBT is efficiently eliminated via BDS, though it has the lowest reactivity in HDS. Therefore, BDS should be considered to supplement the HDS treatment of stubborn molecules in the existence of complementary technology rather than alternative technology. To achieve very low sulfur content in diesel fuels it has been shown that it is useful to perform a BDS process in combination with the conventional HDS technique.

1.4.4 Oxidative desulfurization with extraction (ODS)

Oxidative desulfurization is a novel technology to selectively oxidize organic sulfur compounds to sulfoxides or sulfones. It includes two stages: (i) oxidization of organic sulfur compounds, and (ii) liquid purification⁴⁷. The process utilizes an oxidant to oxidize

the organic sulfur present in the fuel oil and subsequently removed by adsorption, extraction, distillation, or thermal decomposition^{21, 48-50}. The oxidation of sulfur compounds present in fuels is a critical process for desulfurization. Various studies on the ODS process use different oxidants such as nitric acid/NO₂⁵¹, molecular oxygen⁵²⁻⁵³, hydrogen peroxide⁵⁴⁻⁵⁷, ozone⁵⁸, tert-butyl hydroperoxide (t-BuOOH)⁵⁹, and potassium superoxide⁶⁰. Nitric acid/NO₂ was first studied as an oxidant with methanol as solvent for the ODS process in the 1980s⁵¹. Due to the poor selectivity, low yield, and loss in heating value, this type of oxidant has not been widely used. Murata et al.⁵² reported that the sulfur removal was more than 97%, resulting in less than 5 ppm_w in the oil by using the system consisting of cobalt acetate, aldehyde, and molecular oxygen. It is attractive owing to the availability of the reacting gas and the low cost of gas. The main issues of the process are operation safety, the oxidation of unsaturated aromatic hydrocarbons, and the formation of by-products (CO, CO₂, etc.). T-BuOOH has a low oxidization efficiency compared with other oxidants. Potassium superoxide has high sulfur removal efficiency but it introduces excess K₂CO₃ which may contaminate the oil. Among the oxidants above, hydrogen peroxides show advantages of high oxidation efficiency, affordability, commercial availability, and environmental compatibility.

The second step in ODS is the elimination of the oxidized compound from the fuel oil. It is known that sulfur compounds are slightly more polar than hydrocarbons having similar structures. Also, oxidized sulfur compounds such as sulfones or sulfoxides are substantially more polar than sulfides. It allows the selective removal of sulfur compounds from hydrocarbons by selective oxidation followed by solvent extraction, solid adsorption, or

distillation ⁶¹. The combination of selective oxidation and distillation to remove sulfur is feasible theoretically since the oxidation of sulfur compounds to sulfoxides or sulfones increases their boiling temperature. However, it relies on the fact that the OCSs would only be separated and that their treatment would be done elsewhere. The oxidative distillation desulfurization process is similar to catalytic distillation desulfurization. Solid adsorption is another way to purify the hydrocarbon stream. Silica gel ⁵⁹ is commonly used for adsorbent. However, the liquid hydrocarbon fuels contain not only sulfur compounds but also large amounts of aromatic compounds with aromatic skeletal structures similar to co-existing sulfur compounds, which poses a significant challenge in the development of potent adsorbents with high sulfur adsorption selectivity.

In terms of selective oxidation and liquid/liquid extraction, it is a promising method to remove sulfur in the oil. Some volatile organic compounds (VOCs) are employed as extractants such as N,N-dimethylformamide, dimethyl sulfoxide, methanol, and acetonitrile ⁶². However, the use of VOCs raises safety concerns and environmental contamination risk. Recently, ionic liquids (ILs) and deep eutectic solvents (DESs) have been used as innovative green solvents for liquid/liquid extraction. The ionic liquid is a salt in which the ion coordination is poor resulting in the solvent being liquid at less than 100°C, even at room temperature. At least one of the ions has an off-site charge and one component is organic, which prevents the formation of a stable lattice. As non-aqueous solvents, ILs have many desirable properties including non-volatility, a wide liquid range, low flammability, recyclability, high thermal conductivity, thermal and chemical stability, and easy-handling ⁶³. During the past few years, ILs have become a hotspot in the deep

desulfurization area. Different oxidative desulfurization with ILs systems have been reported. Lo et al.⁶⁴ have indicated that H₂O₂-acetic acid/(bmimPF₆) has a high removal rate of DBT. The Li group has proved that H₂O₂, HPW-CeO₂ and (C₈mim)BF₄ reached a sulfur removal of 99.4%⁶⁵. Therefore, it can be concluded that acidic functionalized ILs could be effectively applied to remove OCSs from fuels⁶⁶. It is also found that acidity is a critical factor affecting the oxidative and extractive desulfurization process. Unfortunately, it is very difficult to control the precise acidity of functionalized ionic liquids. The exorbitant price of ingredients and complex synthesis are other shortcomings. Furthermore, it has low biodegradability and toxicity to ecosystems.

Deep eutectic solvents (DESs) are unique solvents. As ILs analogues, DESs have received lots of attention in recent years because they not only share the excellent properties of chemical stability, low vapor pressure, and design ability, but also have better properties than ILs such as the ease of synthesis, reduced toxicity, being biodegradable, and so on. The efficiencies of the removal of sulfur in oil by some DESs have been reported as substantially higher than those of traditional and functionalized ILs. Therefore, DES is an outstanding extractant for extractive and oxidative desulfurization (EODS) systems.

In summary, the combination of selective oxidative desulfurization with solvent extraction shows overwhelming benefits compared to other types. It is worth doing further research on this type of deep desulfurization.

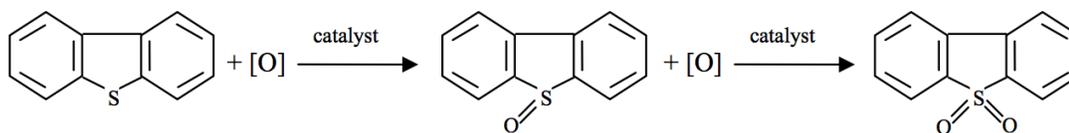
Chapter 2. Theoretical background

2.1 Introduction

As more and more stringent sulfur regulations are developed on diesel, independent traditional HDS is not sufficient to meet the sulfur limitations. Extractive oxidation desulfurization (EODS) has been proved to be viable. In order to improve EODS efficiency and its applicability to diesel it is of great importance to choose the appropriate oxidant and extractant. DESs have an overwhelming benefit over other extractants that could be applied in the EODS system. The basic concepts and their advantages are discussed in this chapter.

2.2 Oxidant selection

Compared with other oxidants, hydrogen peroxide has overwhelming advantages. First, it shows high efficiency in the ODS process, and second, it is less costly than the HDS process because of the absence of hydrogen. Also the by-product is only water so it is environmentally friendly. Recently, it has received increased attention as an oxidant in ODS. Various oxidative systems such as formic acid/H₂O₂⁶⁷, polyoxometalate/H₂O₂⁶⁸, and Ti-containing molecular sieves/H₂O₂⁶⁹ are reported to have good efficiencies to oxidize OSCs to sulfones under mild conditions. The basic reaction scheme is shown in Scheme 2.1.



Scheme 2.1 General reaction of DBT in ODS⁷⁰

2.3 Deep eutectic solvents (DESs)

DESs, as ILs analogues, have emerged at the beginning of this century. In general, a DES consists of two or three cheap, safe, and biodegradable components that are able to associate with each other according to hydrogen-bond interactions to form a eutectic mixture⁷¹. The melting point of the mixture is lower than that of each individual compound because it contains large nonsymmetrical ions that have low lattice energy. DESs consist of hydrogen-bond acceptors (HBA) such as ammonium or phosphonium salt, and hydrogen-bond donors (HBD) such as organic acid, urea, sugars, or alcohols. Conventionally, HBAs are ammonium or phosphonium salt. HBDs are alcohols, organic acid, urea, amides, sugars, or hydrated metal salts of chlorides, nitrates, and acetates⁷²⁻⁷³. In most cases, DESs can be obtained by mixing a quaternary ammonium salt with a metal salt or hydrogen-bonding donor (HBD) having the ability to form a complex with the halide anion of the quaternary ammonium salt. The general formula of DESs is $Cat^+X^-zY^-$ ⁷⁴, where Cat^+ is ammonium, phosphonium, or sulfonium cation; X is a Lewis base, which is generally a halide anion; Y is Brønsted acid; z is the number of Y molecules that interact with the anion. Figure 2.1 summarizes the different quaternary ammonium salts and HBDs that are widely used in formation of DESs.

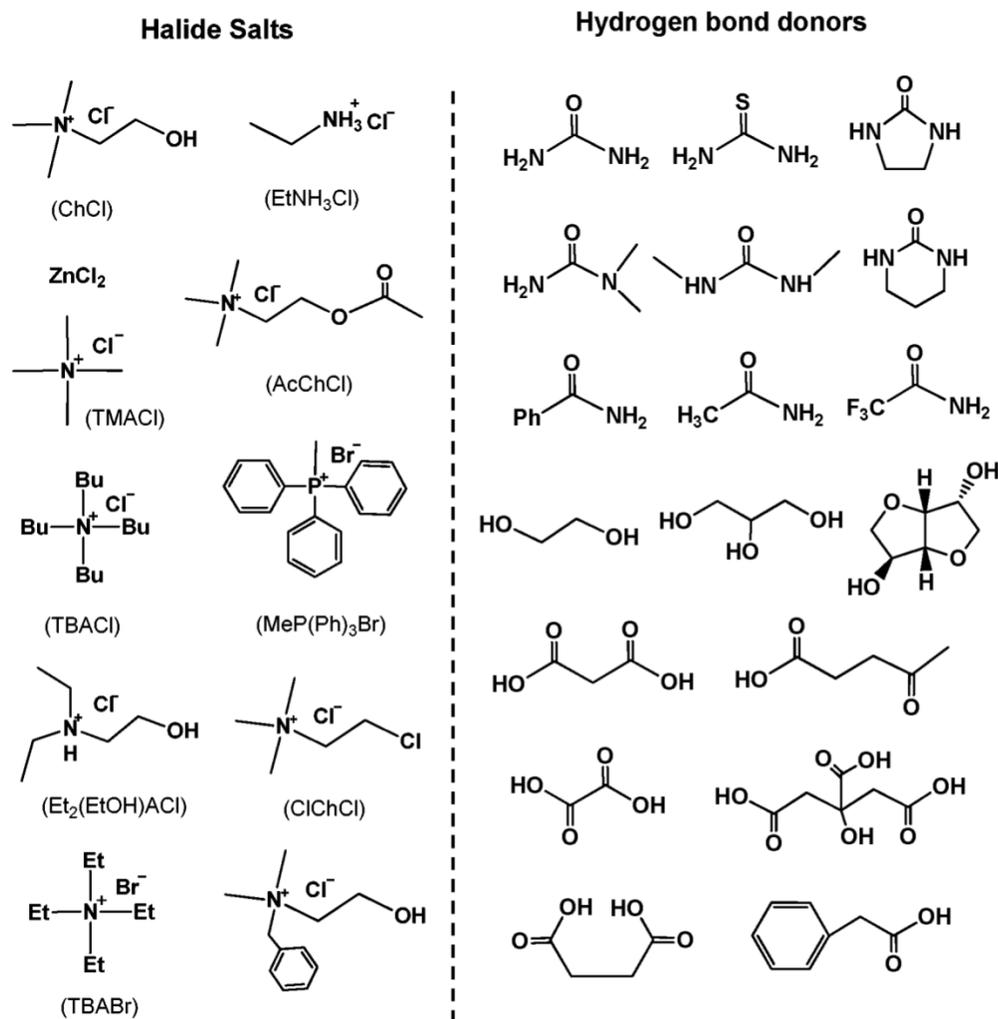


Figure 2.1 Typical structures of the halide salts and HBD used for DES syntheses ⁷¹

DESs exhibit similar physical and chemical properties as traditional ILs such as melting point close to room temperature, undetectable vapor pressure, non-volatility, non-flammability, wide liquid temperature range, and special solubility for many compounds. Despite the fact that they are similar, DESs have better properties than ILs. They are biodegradable and the ingredients of DESs are cheaper than ILs. In other words, DESs overcome the high price and toxicity of ILs. Additionally, synthesis of DESs is 100% atom economic, easily handled, and no purification is required, hence making their large-scale

use feasible. DESs have been applied in many areas such as material preparation ⁷⁵, substance dissolution ⁷⁶, separation processes ⁷⁷, electrochemistry ⁷⁸, catalysis ⁷⁹, and extraction ⁷³.

2.4 Research purpose

In this project, potassium carbonate (K_2CO_3) combined with ethylene glycol (EG) is synthesized. It is a new type of DES since potassium-based salts were not used as an ingredient for DES synthesis. This DES and hydrogen peroxide are employed as extractants and oxidant separately in extractive and oxidative desulfurization (EODS) systems. The reaction mechanism is investigated for understanding and improving the EODS system. Various experiments are carried out to find out the effect factor such as reaction time, system temperature and stirring speed in ODS, EDS, and EODS. Furthermore, the process of ODS, EDS, and EODS are compared to find the optimal desulfurization process with this new type of DES.

Chapter 3. Experiments

3.1 Materials and experimental procedure

3.1.1 Ingredients and equipment

Dibenzothiophene (98%, Sigma-Alorich), Dibenzothiophene sulfone (97%, Sigma-Alorich), n-octane (98+%, Alfa Aesar), acetonitrile (99.8%, Alfa Aesar), Varian star3400 Gas chromatography–mass spectrometry (GC-MS), Agilent 19091S-433 Gas chromatography–mass spectrometry (GC-MS).

3.1.2 Preparation of model oil

Prepare 500 ppm_w model oil by dissolving 0.070g DBT with n-octane into a 200ml flask.

The calculation is presented below:

$$500 \text{ ppm} = \frac{m_{DBT}(g)}{m_{DBT}(g) + m_{n-octane}(g)} \times 10^6 \quad (3.1)$$

$$m_{n-octane} = \rho V = \frac{0.703g}{ml} \times 200ml = 140.6g \quad (3.2)$$

According Equation 3.1 and Equation 3.2, we can get the mass of DBT to be 0.070g.

3.2 Analysis method

Gas chromatography–mass spectrometry (GC-MS) is precise for measuring dibenzothiophene (DBT), which is the main component in ultra-low diesel fuel. In order to get the calibration curve of DBT, 500 ppm_w DBT was diluted into 2 ppm_w, 4 ppm_w, 10 ppm_w, and 20 ppm_w into 5mL flasks, separately. The same amount of 500 ppm_w n-eicosane

was added to these diluted solutions as an internal standard. The proper GC-MS condition is shown below: chromatogram column is HP-5MS (30.0m×250μm×0.25μm), injection volume: 1μL, carrier gas (He): 20 ml/min, the pressure is 8.03 psi, average velocity is 36 cm/sec, the split ratio is 5:1, constant flow mode, inlet temperature is 250°C, detector temperature: 300°C, the column initial temperature is 60°C and hold for 5 min and then heating to 300°C with 20°C/min increase. The delay time is 15 min. The retention time of DBT and n-eicosane is 18.8 min and 19.7 min, respectively. Draw the peak area of DBT versus the concentration of DBT, shown in Figure 3.1. The equation is shown in Equation 3.3.

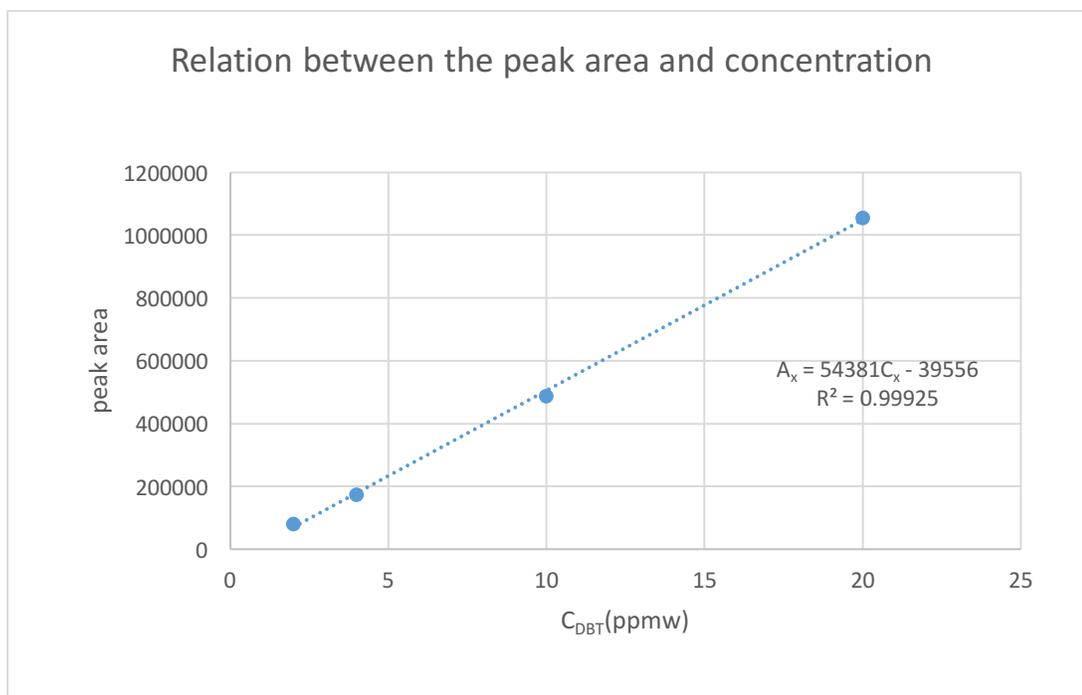


Figure 3.1 Relationship between concentration and peak area

$$A_x = 54381C_x - 39556 \quad (3.3)$$

where,

A_x : peak area of DBT in sample;

C_x : concentration of DBT in sample.

Draw the curve of the ratio of the peak area of DBT to the peak area of n-eicosane versus the ratio of the concentration of DBT to the concentration of n-eicosane. The calibration curve is shown in Figure 3.2. The equation is shown in Equation 3.4.

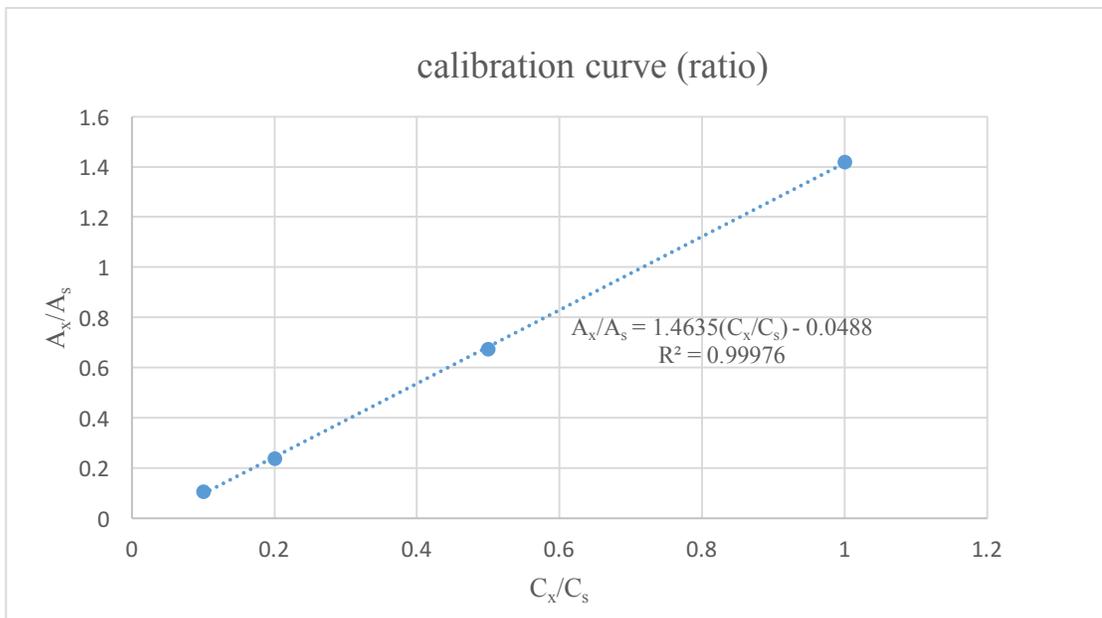


Figure 3.2 correct calibration curve of DBT

As shown in Figure 3.2, the correlation coefficient is 0.99976 and close to 1, which means the linear relationship could represent the calibration curve accurately. Hence, it can be applied for further detection of unknown sulfur amounts in model oil. The calibration curve equation is indicated in Equation 3.4.

$$\frac{A_x}{A_s} = 1.4635 \times \left(\frac{C_x}{C_s} \right) - 0.0488 \quad (3.4)$$

where,

A_x : the peak area of DBT in sample;

A_s : the peak area of n-eicosane in sample;

C_x : the concentration of DBT;

C_s : the concentration of n-eicosane.

The correlation coefficient is 0.99976 while the linear relationship between the peak area of DBT and the concentration of DBT is 0.99925, which is slightly better. The removal percentage of the DBT is represented as X and was calculated as follows:

$$X = \frac{C_0 - C_x}{C_0} \times 100\% \quad (3.5)$$

Where,

C_0 : the initial concentration of DBT in the model oil;

C_x : the concentration of DBT in the oil phase after the reaction began for a certain amount of time.

Since the solvent has little influence on the amount of DBT detected, we use n-octane as the solvent and set the MS scan delay time to 15 min to skip the peak of n-octane and other unnecessary components peaks.

3.3 Experimental design and procedure

3.3.1 DES synthesis

Prepare DES by mixing 1g K_2CO_3 and 8g ethylene glycol (EG) (K_2CO_3 : EG=8) in a 50ml beaker until a homogenous transparent colorless liquid is formed. It is at ambient temperature and atmosphere pressure with a stir speed of 1000 r/min.

3.3.2 Oxidative desulfurization of model oil

9g of 500 ppm_w DBT model oil and 25 μ L 30w% H_2O_2 ($n(H_2O_2)/n(DBT)=10$) were mixed in a 100 ml flask with a water bath at constant temperature for 3h, which is 20°C, 30°C, and 40°C separately. The stir speed is 1000 r/min. The upper phase (model oil) was periodically taken out 0.2mL and diluted into a 5mL flask by adding 0.2mL 500 ppm_w n-eicosane.

3.3.3 Extractive desulfurization of model oil

9g DES prepared in 3.3.1 was mixed with 9 ml 500 ppm_w DBT model oil (DES: model oil=1:1) in a water bath at constant temperature for 3h, which is 20°C, 30°C and 40°C separately. The stir speed is 1000 r/min. The upper phase (model oil) was periodically taken out 0.2mL and diluted into a 5mL flask by adding 0.2mL 500 ppm_w n-eicosane.

3.3.4 Oxidative desulfurization process and extractive process with DES

The mixture containing 9g DES is mixed with 9g model oil (DES: model oil =1:1) and 25 μ L 30w% H_2O_2 ($n(H_2O_2)/n(DBT)=10$) then was stirred vigorously at a certain reaction temperature for 3h; the temperature is 20°C, 30°C and 40°C separately. The stir speed is

1000 r/min. The upper phase (model diesel) was periodically taken out 0.2mL and diluted into a 5mL flask with the additional 0.2mL 500 ppm_w n-eicosane.

Chapter 4. Results and discussion

4.1 Viscosity of DES

Viscosity is one of the most important physical properties for the extraction capacity of DES since viscosity is directly related to molecular gravity so is extraction between DES and DBT. Viscosity indicates the extraction capacity of DES. Furthermore, reliable viscosity data is beneficial for equipment design and fluid flow computations for future industrial applications. According to the temperature effect on viscosity the energy of processing fluids can be reduced. As expected, viscosity of DES decreases as temperature increases, as shown in Figure 4.1. In terms of the viscosity measurement operation of this experiment, owing to the heat transfer loss, there is a difference of around 5°C to 15°C between the sample and water bath. For example, if the measured temperature needs to be 60°C then the water bath temperature should be 70-75°C.

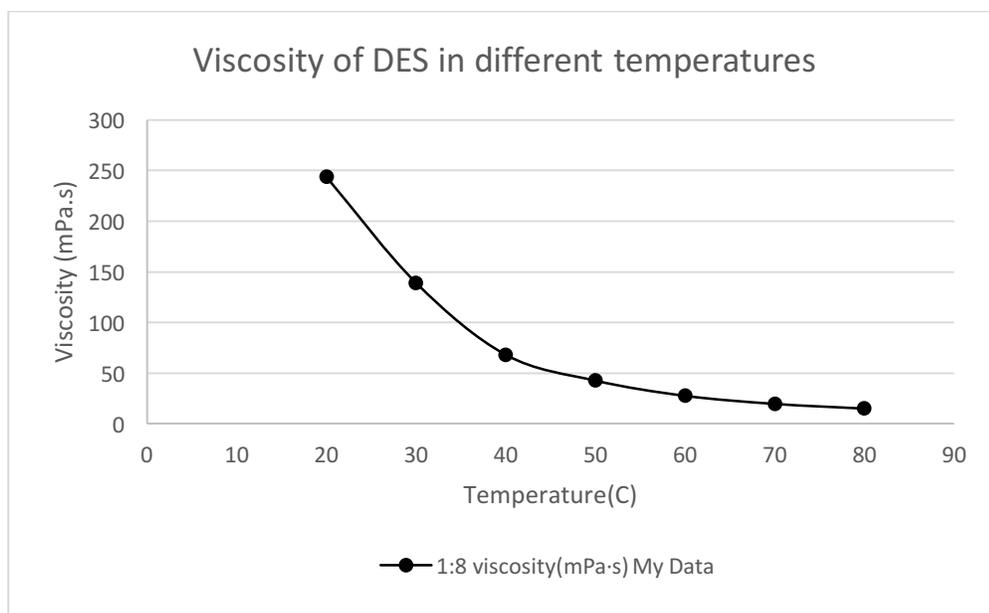


Figure 4.1 Viscosity of DESs in different temperatures

4.2 Extractive desulfurization

4.2.1 Suggested mechanism of the extractive process

In order to get the optimum experiment conditions for extractive desulfurization, it is vital to understand the mechanism of the extractive process. DBT is extracted from oil into the DES phase owing to the comparable strong interaction between DESs and DBT, including CH- π interaction, hydrogen bond, and so on⁸⁰⁻⁸¹. It is reported that the active hydrogen and the sulfur atom in DBT form a hydrogen bond, which turns out to be the main driving force of the extractive process^{80, 82}. This hydrogen-bond interaction allows the sulfur atom to withdraw from the benzene ring and thiophene ring of DBT leading to a reduction of the benzene ring and thiophene ring electron density, and its corresponding hydrogen nucleus electron density.

4.2.2 Time effect of the extractive process

Figure 4.2 indicates the removal of DBT as a function of reaction time at 30°C. It is noticeable that the removal of DBT increases initially and then reaches the highest removal percentage, which is 86% at 2hr. After 2hr, the removal percentage of DBT decreases. It is possible that the prolonged extraction time results in the change of extraction equilibrium. In other words, DBT extracted by DES returns to the oil phase due to the long reaction time. Based on this, it could be concluded that the equilibrium extraction desulfurization time is 2hr. As shown in Figure 4.3, the lowest remaining concentration of DBT is 70.2 ppm_w.

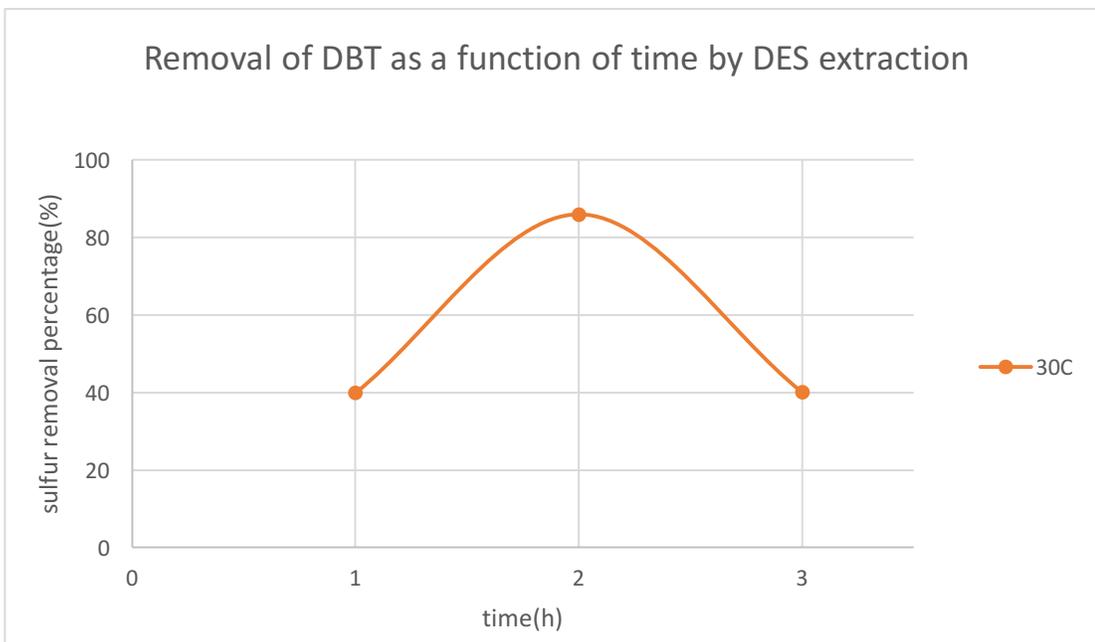


Figure 4.2 Removal of DBT as a function of time by DES extraction

Experiment condition: $T=30^{\circ}\text{C}$, $t=3\text{ h}$, $\text{DBT}=500\text{ ppm}_w$, $m(\text{model oil})=9\text{g}$, $\text{K}_2\text{CO}_3:\text{EG}=1:8$, $m(\text{DES})=9\text{g}$,

$m(\text{model oil}):m(\text{DES})=1:1$

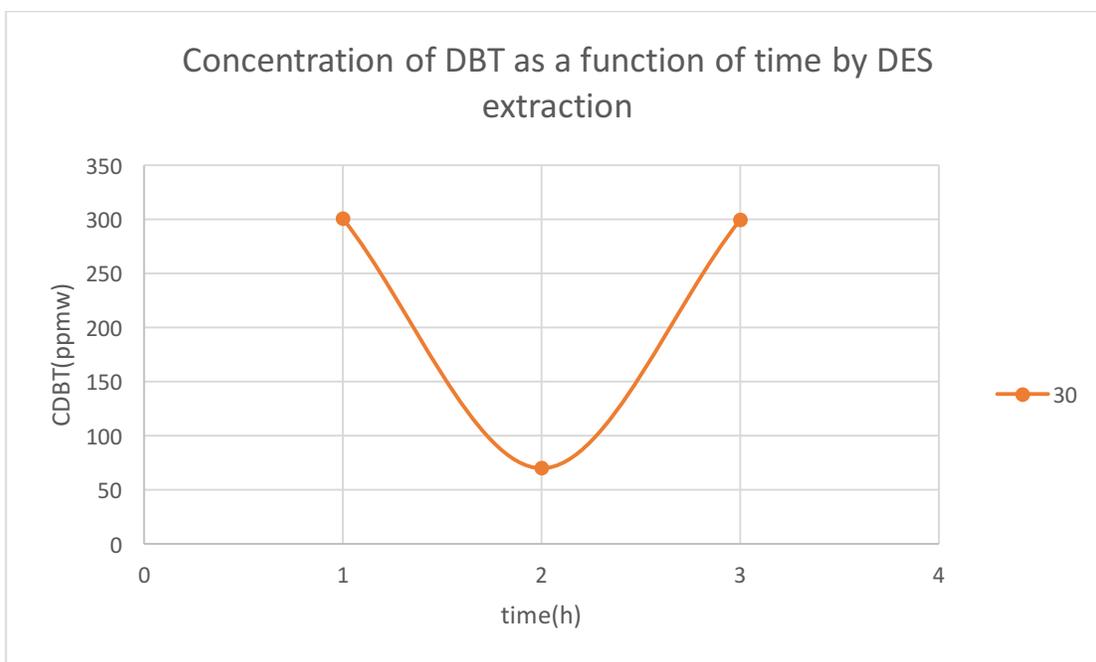


Figure 4.3 Concentration of DBT as a function of time

Experiment condition: $T=30^{\circ}\text{C}$, $t=3\text{ h}$, $\text{DBT}=500\text{ ppm}_w$, $m(\text{model oil})=9\text{g}$, $\text{K}_2\text{CO}_3:\text{EG}=1:8$, $m(\text{DES})=9\text{g}$,

$m(\text{model oil}):m(\text{DES})=1:1$

4.2.3 Temperature effect of the extractive process

System temperature is always important for the industrial extraction process. It is a useful criterion for evaluating the practicality of the extractive desulfurization process being applied in real fuels. As shown in Figure 4.4, the removal percentage of DBT increases in the order of $40^{\circ}\text{C}<20^{\circ}\text{C}<30^{\circ}\text{C}$. Their sulfur removal efficiencies are 33%, 45%, and 86% at 2h, respectively. It is indicated that higher temperatures are not beneficial for the extraction process. From Figure 4.1, it is shown that the viscosity of DES decreases as temperature increases. Hence, it is suggested that higher viscosity of DES leads to better extraction capacity of DES. It could be explained that higher temperature leads to the decline of

molecular gravity and increases the possibility of breaking the hydrogen bond, which is the main driving force for extraction. Furthermore, it is clear that the interaction between the DES and DBT is an exothermic reaction since higher temperature leads to lower removal percentage of DBT. These results provide a potential industrial application process that extraction desulfurization can be applied with an energy saving situation with mild operation conditions. The optimal temperature of extraction is 30°C with the removal of DBT being 86%. It should be noted that the highest extraction efficiency of ILs for a single cycle is no more than 65%⁶⁶. The removal percentage of DBT at 30°C is much higher than at 20°C or 40°C. One possible explanation is that the active site of DES at this temperature has the strongest capacity to extract the S atom from benzene rings and thiophene rings. The interaction between the DBT and DES is performed best at this temperature.

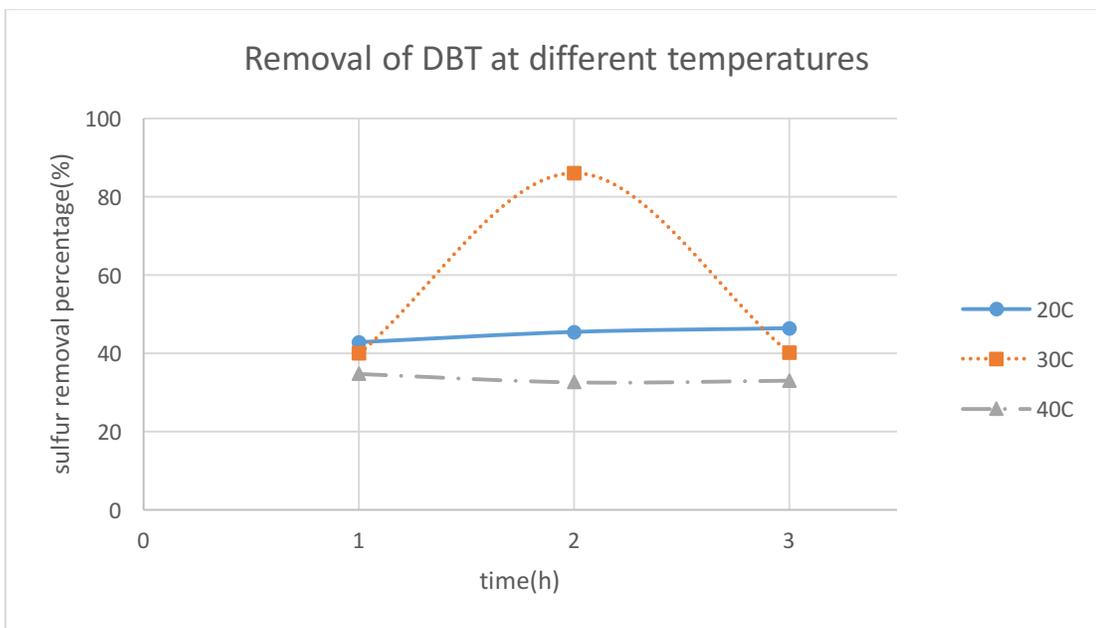


Figure 4.4 Effect of extraction temperature

Experiment condition: $t=3$ h, $DBT=500$ ppm_w, m (model oil) =9g, $K_2CO_3:EG=1:8$, $m(DES)=9$ g, m (model oil): $m(DES)=1:1$

Compared with other DESs, K_2CO_3/EG has better extraction efficiency than most of DESs in one cycle, as shown in Table 4.1. The low cost of ingredients and mild conditions for synthesis are other advantages of K_2CO_3/EG . Therefore, it has major advantages and deserves further investigation.

Table 4.1 comparison of DESs on extraction of DBT

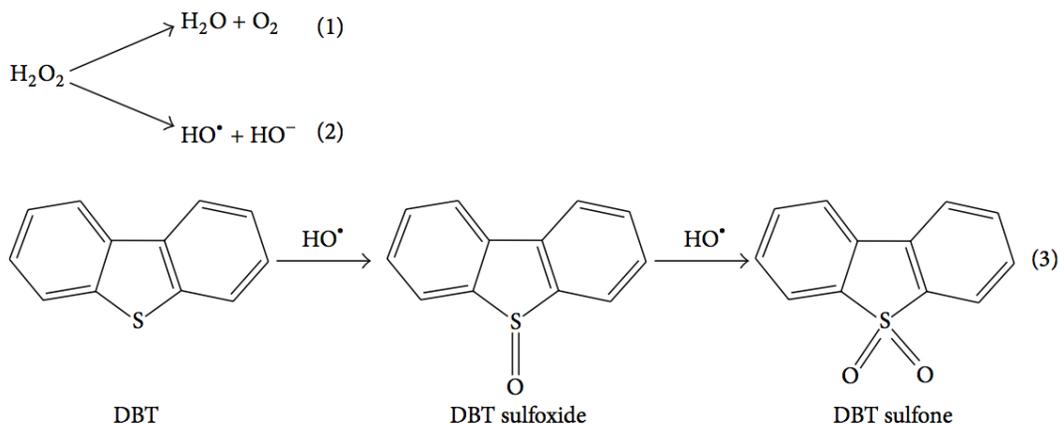
Entry	Types of DESs	DBT removal percentage (%)	Ref.
1	TBAC/PEG	82.83	82
2	TBAC/OXA	29	80
3	TBAC/PEG/ $FeCl_3$	89.53	83
4	ChCl/ $2CH_3COOH$	7.8	73
5	ChCl/ $2PEG$	20.1	81
6	ChCl/ <i>p</i> -TsOH	25.17	84
7	TBAC/ <i>p</i> -TsOH	37.79	84
8	TBAB/ $HCOOH$	80.47	85

4.3 Oxidative desulfurization

4.3.1 Mechanism of oxidation

An appropriate approach is proposed to better understand the mechanism through which sulfur goes to sulfoxide by hydrogen peroxide⁸⁶. As shown in Scheme 4.1, there are two

competing reactions for H_2O_2 depending on the reaction temperature. The first reaction is the thermal decomposition of H_2O_2 , which is an undesirable reaction because it increases the amount of water in the system and reduces the concentration of the oxidant. Therefore, this reaction is not recommended for high temperatures. In reaction (2), hydroxyl groups (OH) are produced, which are strong oxidizing agents. In reaction (3), DBT is oxidized to the corresponding sulfoxide or sulfone.



Scheme 4.1 oxidative reaction of DBT with H_2O_2

4.3.2 Effect of reaction time

Figure 4.5 indicates the concentration of DBT as a function of reaction time at 50°C . As shown in this figure, the concentration of DBT reduces, then slightly increases, as reaction time increases. It could be explained by describing the interactions of oxidizing agents as time proceeds. It is probable that hydrogen peroxide interacts with DBT to produce sulfones. As time goes by, this reaction achieves equilibrium and then it promotes other reactions. After a specific reaction time, the removal of sulfur will not increase with the increase in reaction time, which means that the oxidation system reaches equilibrium and

has the optimal reaction time. The optimal reaction time observed is at 2 hours. Although it can be seen that the concentration of DBT increases as time goes by after the optimum value, the growth is not obvious. The increase in concentration of DBT is owing to the hydrogen peroxide decomposition and, as a result, accelerates the conversion of oxidized sulfur to DBT. In other words, prolonged reaction time results in loss of oxidant, changes in equilibrium, and changes in the reaction medium from oxidation to reduction ⁸⁶.

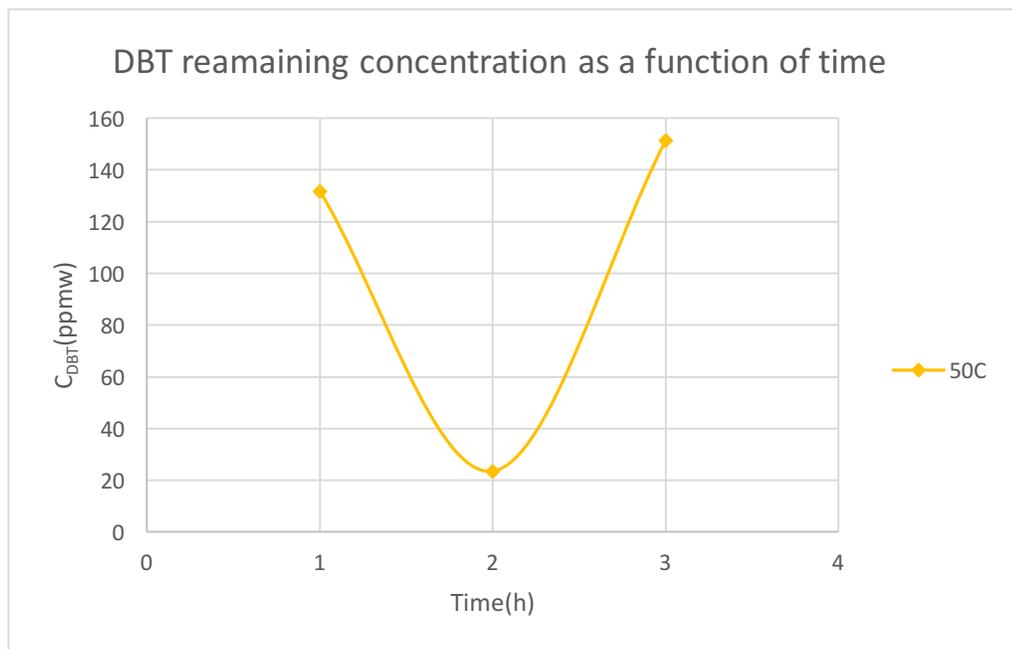


Figure 4.5 DBT remaining concentration as a function of time at 50°C

Experiment condition: $t=3$ h, $DBT=500$ ppm_w, $n(H_2O_2)/n(DBT)=10$, m (model oil) =9 g, V (30%wt H_2O_2) =25 μ L

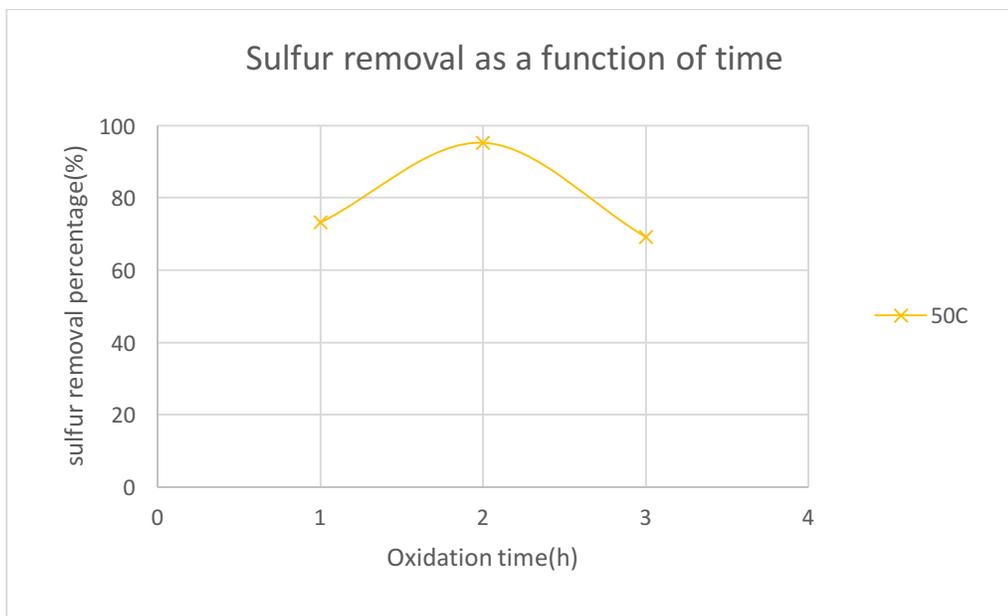


Figure 4.6 DBT removal as a function of time at 50°C

Experiment condition: $t=3\text{ h}$, $T=50^\circ\text{C}$, $\text{DBT}=500\text{ ppm}_w$, $n(\text{H}_2\text{O}_2)/n(\text{DBT})=10$, $m(\text{model oil})=9\text{ g}$, $V(30\%\text{wt H}_2\text{O}_2)=25\ \mu\text{L}$

4.3.3 Effect of reaction temperature and reaction time

The DBT oxidation results with different reaction temperatures under the same conditions are shown in Figure 4.7 and Figure 4.8. As shown in Figure 4.7, the rate of reaction increases when the temperature rises. It is clear that the efficiency of sulfur removal increases with increased temperature, as indicated in Figure 4.8. The sulfur removal efficiency decreases in the order of $50^\circ\text{C}>40^\circ\text{C}>30^\circ\text{C}>20^\circ\text{C}$ at 2hr as shown in Table 4.2. This indicates that the higher temperatures could accelerate the oxidation of DBT⁸⁷. The formation of bubbles during the reaction indicates that the higher reaction temperature stimulates decomposition of hydrogen peroxides. Thus, the decomposition of hydrogen peroxides leads to the reduction of oxidation of DBT. The sulfur removal efficiency

decreases in the order of 40°C>30°C>50°C>20°C at 3hr and the removal of DBT is 99.56%, 71.72%, 69.10% and 45.59%, respectively. Compared to the desulfurization efficiencies in different temperatures and reaction times, the optimal oxidation reaction condition is 40°C at 2hr instead of 3hr in cases where the prolonged reaction time causes the reduction of DBT oxidation.

Table 4.2 Sulfur removal percentage after 2 hours at different temperatures

Temperature (°C)	Sulfur removal percentage (%)
20	30.85
30	48.59
40	77.86
50	95.20

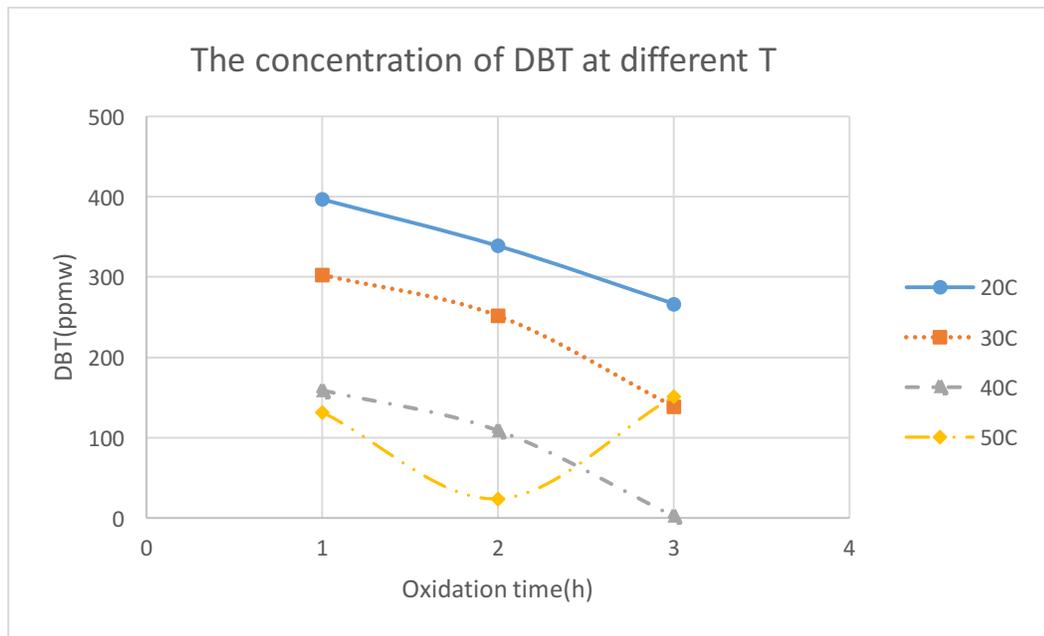


Figure 4.7 the concentration of DBT under oxidation at different temperatures

Experiment condition: $t=3\text{ h}$, $DBT=500\text{ ppm}_w$, $n(H_2O_2)/n(DBT)=10$, $m(\text{model oil})=9\text{ g}$, $V(30\%wt\ H_2O_2)$
 $=25\mu L$

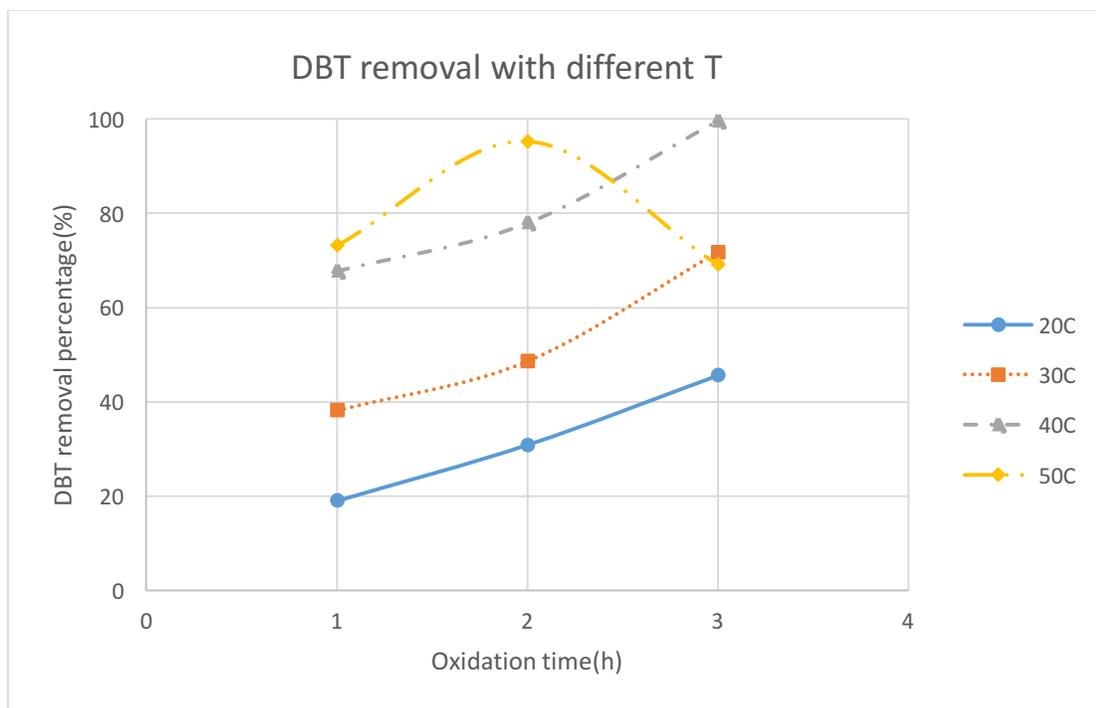


Figure 4.8 DBT removal under oxidation at different temperatures

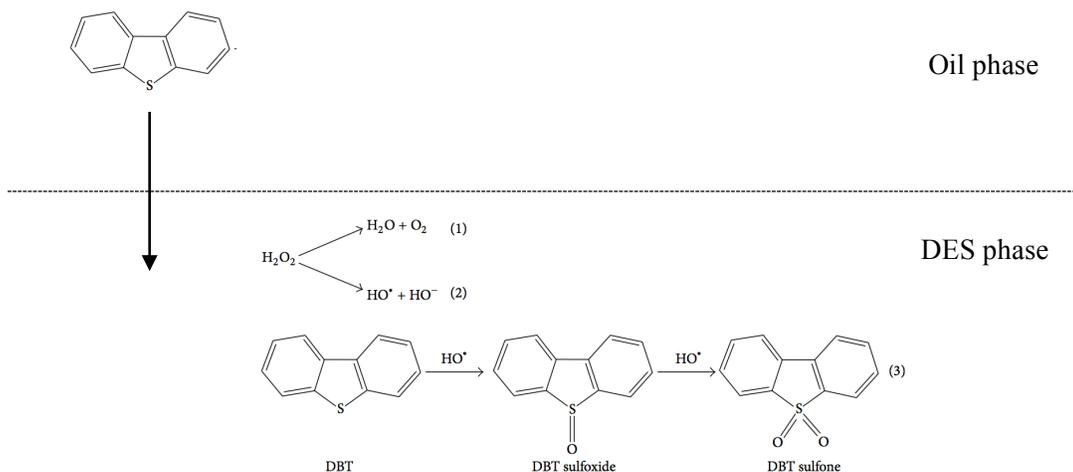
Experiment condition: $t=3\text{ h}$, $DBT=500\text{ ppm}_w$, $n(H_2O_2)/n(DBT)=10$, $m(\text{model oil})=9\text{ g}$, $V(30\%wt\ H_2O_2)$
 $=25\mu L$

4.4 Oxidative and extractive desulfurization

4.4.1 Mechanism of oxidative and extractive desulfurization

It is vital and challengeable to reveal the whole process of oxidative and extractive processes. To clarify the EODS system a mechanism scheme was drawn in Scheme 4.2. The immiscibility of K_2CO_3/EG with model oil results in the formation of biphasic systems. In this system, at the beginning DBT is in oil phase (top) while H_2O_2 is in DES phase (bottom). DBT is extracted into DES phase from oil phase due to the complex interactions

between DES and DBT, such as CH- π interactions, π - π bonds, and hydrogen bonds, etc. These interactions lead to DBT being oxidized, which is conducive to the reaction. Then these active centers can oxidize DBT into sulfoxide DBTO and further to sulfone DBTO₂.



Scheme 4.2 Suggested mechanism of DBT removal by oxidative and extractive process

4.4.2 Temperature effect of oxidative and extractive desulfurization

The effect of system temperature is investigated systematically, as shown in Figure 4.9. It is indicated that the removal percentage of DBT is influenced by both the oxidative process and the extractive process. The DBT removal percentage increases at the beginning until 2hr and then decreases after 2hr at 20°C and 40°C, while the sulfur removal percentage keeps falling at 30°C. Thus, the equilibrium time is at 2 hours. The results also show that the removal of DBT reduces as the temperature decreases at 2hr since the high temperature damages the extraction of DBT. Nevertheless, the higher temperature is more beneficial for the decomposition of hydrogen peroxides. The optimal temperature for oxidative and

extractive processes is 20°C where the removal percentage of DBT is 38%. In fact, the sulfur removal efficiency does not show large differences among these results. It might be attributable to another factor, which is stirring speed. Since the DES phase is immiscible to oil phase, it is important to mix well two phases for extraction of DBT. The low stirring speed causes low DBT removal efficiency while the high stirring speed leads to liquid splash. Limited by the equipment in the lab it is difficult to find a balance stirring speed to mix model oil and DES; as a result, the stirring speed becomes the main effect. The stirring speeds in these experiments are the same, which results in the small difference of DBT removal efficiency, although there is a distinguishable difference in the temperature.

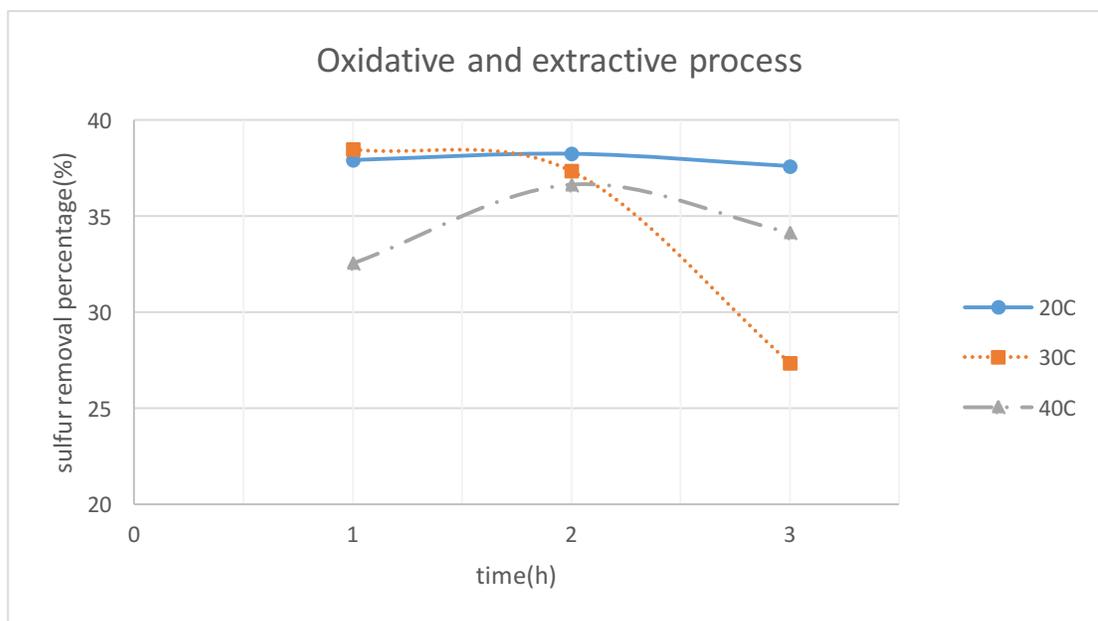


Figure 4.9 Effect of temperature in oxidative and extractive system

Experiment condition: $t=3$ h, $DBT=500$ ppm_w, m (model oil) =9g, $K_2CO_3:EG=1:8$, $m(DES)=9$ g, m (model oil): $m(DES)=1:1$, $n(H_2O_2)/n(DBT)=10$, V (30%wt H_2O_2) =25 μ L

Compared with the separated extractive process, the oxidative and extractive process has comparably lower removal percentage of DBT, which is the opposite of our expectation as shown in Figure 4.10. It might be attributed to the fact that the hydrogen peroxides dissolved into the DES phase, resulting in some extracted DBT returning back to oil phase, which is similar to the desulfurization systems with ILs as extractants⁸⁸. To improve the desulfurization efficiency of the oxidative and extractive system, acidic catalysts are supposed to be added in this system. This enhances the performance of the hydrogen-bond donator (HBD).

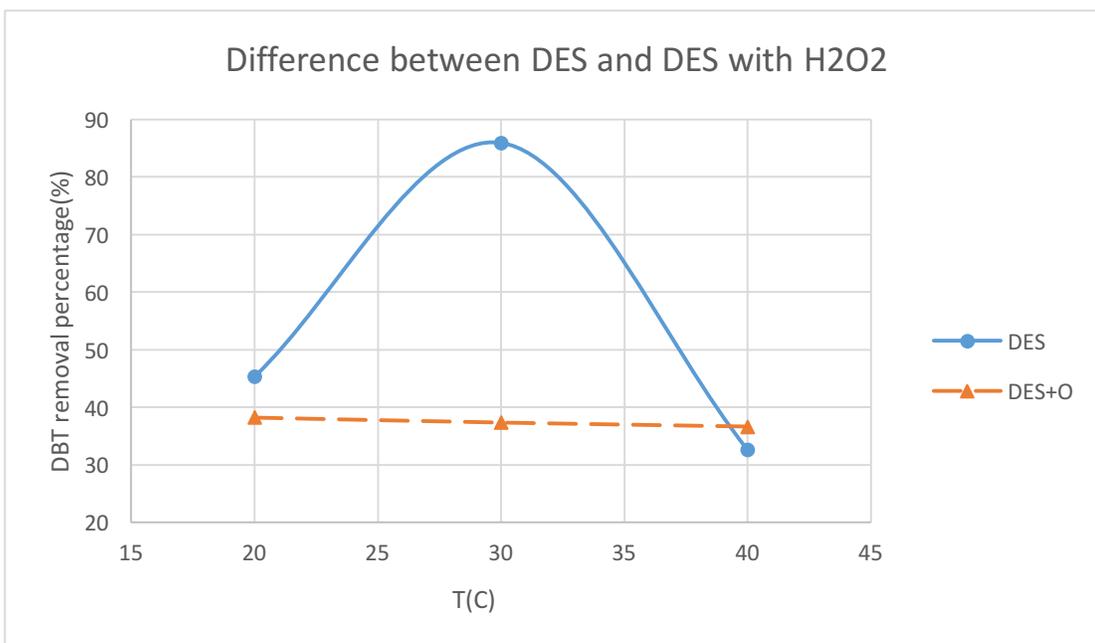


Figure 4.10 DBT removal percentage difference between extraction desulfurization and oxidative/extractive desulfurization

Chapter 5. Conclusions and recommendations

In summary, a new type of “green solvent” named deep eutectic solvents (DESs) have been synthesized by mixing potassium carbonate and ethylene glycol under mild conditions. This type of DES is successfully applied for the deep extraction desulfurization of model oil. In this project, liquid-liquid extraction desulfurization and oxidative desulfurization with extraction are investigated. The optimal experimental conditions for deep desulfurization have been studied in detail, including reaction equilibrium time, reaction temperature, and hydrogen peroxides employment. According to the experimental results, the conclusions and recommendations can be drawn as follows:

1. The optimal experimental condition of K_2CO_3/EG for extraction process is at $30^\circ C$ for 2hr. The removal efficiency of DBT is 86%, which is a better extraction efficiency than most DESs and ILs for single cycle. The removal percentage of DBT increases as the system temperature decreases owing to the high viscosity of DESs at low temperature. Besides, the extraction reaction is an exothermic reaction.
2. Oxidative desulfurization with DESs extraction has the best removal efficiency of DBT if operating at $20^\circ C$ for 2hr. The removal efficiency of DBT in this system is 38%. The lower experimental temperature promotes the higher desulfurization efficiency. Although the removal efficiency is not as high as extraction desulfurization by K_2CO_3/EG , it could be improved by adding a proper acidic catalyst.
3. The mechanism of extraction desulfurization by K_2CO_3/EG and the mechanism of oxidative and extractive desulfurization are investigated, respectively. The hydrogen bond formed between DESs and DBT accounts for the driving force for desulfurization.

4. Stirring speed is an important factor that influences the efficiency of desulfurization. A proper stirring speed and container could promote the extraction capacities of DESs and prevent liquid splash.
5. Hydrogen peroxides dissolved into the DES phase leads to some extracted DBT returning back to oil phase. As a consequence, extractive and oxidative desulfurization has lower removal efficiency than extractive desulfurization.

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