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RESEARCH ADVANCES IN OXIDATIVE DESULFURIZATION TECHNOLOGIES FOR THE PRODUCTION OF LOW SULFUR FUEL OILS

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Abstract.

The oxidative desulfurization (ODS) technology has been widely recognized as one of the most effective methods for the removal of fuel oils, due to the very mild operation conditions it requires. According to the oxidants involved, the ODS methods to date can be divided into the following categories: H_2O_2 oxidation method, organic oxidant method, photochemical oxidation method, as well as those involving the use of plasma or ultrasound. Status of research progress in these ODS methods was systematically reviewed, whereby the future work of importance was proposed.

Key words: low sulfur fuel oil; oxidative desulfurization.

1. Introduction

Oil is the blood of industry and also a principal item reflecting the development level of the national economy. In recent years, due to crude oil reserves, mining conditions and other factors, petroleum products of poor quality are frequently found, especially those with high sulfur content, which has resulted in a series of environmental problems. Much attention has been focused on desulfurization and even deep desulfurization of oil, since the emission of sulfur oxides (mainly SO_2) from oil consumption has been recognized as a precursor of acid rain and also a cause of damage to engine tail gas after-treatment device. In the past decades, more and more stringent legislations on the specifications of sulfur level in oil have been issued in many countries. Production of ultra low sulfur fuel oil is an important task of oil refining industry, and development of deep desulfurization technology has become the target of worldwide researchers.

Sulfur in oil exists in two main forms: the first is termed as „active sulfur" which can react with metal directly, the second is „inactive sulfur" which can not directly react with the metal. Active sulfur includes sulfur, hydrogen sulfide and mercaptan; non-activity include sulfide, carbon disulfide, thiophene (TH), and so on. It is found that sulfur in fluid catalytic cracking (FCC) gasoline , more than 90% sulfur exists in the form of thiophene and its derivatives, while in diesel, thiophene sulfur accounted for 80% of the total sulfur, and benzothiophene (BT) and di-benzothiophene (DBT) accounted for more than 70% of thiophene category [1]. As a result, sulfur of thiophenes removal is the main desulfurization for the study.

At present, oil desulfurization technology can be broadly divided into two categories: hydrodesulfurization (HDS) and non-HDS (NHDS). HDS is a kind of technology. We can gets H_2S when hydrogen adsorbed on catalyst at high temperature and high pressure reacts with sulfur to remove sulfur. HDS is one kind of more mature technology, but there several shortcomings such as a one-time investment, high running costs and needing a lot of hydrogen, all these increased the cost of oil significantly. Non-HDS technology does not use hydrogen source and is in line with the requirements of deep desulfurization, so researchers will focus on non-HDS technology. In the last decade, oxidative desulfurization (ODS) has been studied much. ODS is a kind of technology using oxidants oxidizing organic sulfur to strong polarity matters, and the reaction products can be separated by absorption or extraction. ODS is operated at atmospheric pressure and the standard atmosphere is below 100°C, so it has mild reaction conditions, no needs of hydrogen, and neither of pressure reactor and special operating technology. ODS can remove nitrogen at the same time, and has high selectivity, so that the sulfur compounds (BT, DBT, etc) which are removed difficultly in HDS can be easily removed by oxidation. So ODS is a promising desulfurization technology as its low production cost.

Oxidative desulfurization process principles are as follows: sulfur and oxygen have a similar electronegativity, but oxygen is slightly higher, sulfur and carbon bond almost has nonpolarity, organic sulfides and its corresponding organic compounds have very similar nature, the organic sulfides and hydrocarbons have nearly no differences solubility in polar solvent. Contrarily, the oxygen-containing organic compounds' solubility in polar solvents is greater than its corresponding organic compounds. As a result, when oxygen atoms connected to the sulfur atoms of thiophene compounds, there will be a significant increase of sulfur solubility in polar solvents. In addition, compared to oxygen atoms, the sulfur atoms has d orbit, which makes organic sulfur can be easily oxidized into sulfone and sulfoxide. And connecting a number of oxygen atoms to sulfur atoms of organic sulfur compounds can increase the dipole, thus increasing its solubility in polar solvents [2]. Sulfur content in oil can be reduced through other organic solvents' extraction, thereby reducing the impact on the environment.

Various studies on the ODS process have reported the use of differing oxidizing agents, such as H_2O_2 oxidation method, organic oxidant method, photochemical oxidation method, as well as those involve the use of plasma or ultrasound.

2. H_2O_2 oxidation method

Many oxidizing agents have been reported in ODS process, and H_2O_2 is the main one. After the desulfurization reaction, H_2O_2 decompose to H_2O and O_2, so there is no secondary pollution, and meanwhile oxygen is a kind of favorable oxidant. Proper quantities catalysts can accelerate reaction and increase oxidation efficiency. At present, organic acid and heteropolyoxometalates are catalysts in common use.

H_2O_2—organic acid was the earliest oxidative desulfurization system for molded fuel oil, and the mechanism of reactions is considered as: in the reaction system, H_2O_2 fist reacts with organic acid quickly and generates peroxide acid, and then the acid reacts with non-polar sulfur compounds and form relative sulfone or sulfoxide.

2.1 H_2O_2—acetic acid(AcOH) oxidation system

In 1995, Zannikos et al.[3] dissolved the relevant gas oil in an equal volume of (AcOH) and heating the mixture to 90°C, then a solution of H_2O_2 aqueous hydrogen peroxide was then added drop wise and with stirring over 30min. They discovered that the oxidation process itself led to the removal of a substantial potion of the sulfur without any negative effects in the other properties of the fuel. Further extraction with easily removable solvents such as methanol, N-methylpyrrolidone (NMP) and N, N-dimethylformamide (DMF) could lead to overall desulfurization in excess of 90% at acceptable yields.

In 2002, Shiraishi et al.[4] also applied H_2O_2/AcOH system to the oxidation of desulfurization. They mixed model sulfur compounds (BT, DBT, and their methyl-substituted derivatives) with H_2O_2 solution, and heated to the designated temperature, then added AcOH to the mixture. They found the sulfur content failed to be reduced to the required deep desulfurization level (w=50mg kg^{-1}) only by oxidative desulfurization process. This is why the alkyl-substituted sulfone, produced during the oxidation of sulfur compounds, remained in the resulting light oils, owing to their high hydrophobicity. These, however, may be removed from the light oils by subsequent extraction, using an acetonitrile/water azeotropic mixture, such that the sulfur contents of the light oils were decreased to <50mg kg^{-1}, while maintaining a high oil recovery yield.

Lü Zhi-feng et al.[5] improved H_2O_2/ AcOH system. They developed H_2O_2/acetic anhydride to oxidize diesel, then the oxidized diesel was extracted by ethyl cyanide, adsorbed by adsorbent or distillated to remove the oxidative products. The experimental data showed that oxidation-extraction process was the efficient desulfurization method. Optimal conditions: temperature 80°C, reaction time 2h, and volume ratio of diesel oil: H_2O_2: acetic anhydride was 10:1:1, the total sulfur content of diesel can be reduced from 2623.6mg kg^{-1} to

270.3mg kg^{-1}, the yield of diesel can reach 95.0%. The main oxidative products of sulfur compounds were sulfone, and little SO_4^{2-} can be found in the phase of oxidant.

2.2 H_2O_2—formic acid oxidation system

The reactivity of sulfur compounds for oxidation is increased with the increase of electron density on sulfur atom. The reactivity of DBT derivatives are influenced by the electron donation of substituted methyl groups, and; therefore, the reactivity decreases in the order of 4,6-DMDBT > 4-MDBT >DBT, reversing the order of reactivity for HDS. Otsuki et al.[6] applied H_2O_2 as oxidant, formic acid as catalyst to oxidize the sulfur `compounds. They dissolved 4, 6-DMDBT, 4-MDBT, DBT and BT into ten naphthalene hydrogenation to make the model oil. The results shows that the sulfur oxidation rate decreased in the order: 4,6-DMDBT> 4-MDBT >DBT>BT, and the thiophene derivatives with 5.696 to 5.716 electron density on the sulfur atoms could not be oxidized at 50°C.BT with 5.739 electron density and other benzothiophene and dibenzothiophene with higher electron densities could be oxidized.

Yao Xiuqing et al.[7] applied formic acid as catalyst and H_2O_2 solution as oxidant to oxidize sulfur compounds. Model sulfur compounds of BT, DBT, 4, 6-DMDBT were dissolved in n-heptene to formulate the simulated light oil. The results showed that under the condition of reaction temperature of 60°C, ratio of hydrogen peroxide molar to sulfur molar of 7:1 , volume ratio of hydrogen peroxide to formic acid of 1:1 ,and reaction time of 40min , the desulfurization yields of 4, 6-DMDBT,DBT and BT were 100%, 96% and 58%, respectively. The addition of naphthalene and tetralin made the desulfurization yields of BT decrease, while it made a little increase for the DBT desulfurization yield. They also found both the addition of cyclodexene and indole decreased the removal of BT and DBT, in which desulfurization yield of BT decreased faster than that of DBT.

Lü Zhifeng et al.[8] adopted H_2O_2-HCOOH as oxidation system to oxidize the sulfur compounds in catalytic diesel oil. After oxidation, the oxidized organic sulfur compounds were separated by solvent extraction. The results show that different extracts have different abilities to extract sulfones from the diesel. Among the selected extracts, N, N-dimethyl formamide (DMF) and dimethly sulfoxide (DMSO) are the best. The total sulfur concentration can be reduced from 0.8% to 0.3% when the ratio of extract to diesel is 1:2 (in volume), the content of water in the solvent is 5%, and the extraction time is 10 min.

H_2O_2-organnic acid oxidative system has relatively mild reaction conditions and strong oxidizability, and achieve high desulfurization rate, but the organic acids in the oil-soluble part impact the fuel quality. And the liquid organic acids has several disadvantages such as unrenewable and a high reclaiming cost, so catalyst which can be recovery is one indispensable choice.

2.3 H_2O_2—heteropolyoxometalates oxidation system

Heteropolyoxometalates itself is a solid acid oxidation catalyst, it has several characteristic such as has a large molecular size, good transmission and storage capacity to electrons and protons, high thermal stability, reactivity of "lattice oxygen", high proton acidity and non-toxic, tasteless, non-volatile, so in recent years, it as a kind of functional compounds has received great attention by academia and industry in green chemistry and chemical engineering field. But, the research of using it on oxidative desulfurization is not much. Sulfide is not much research. Heteropolyoxometalates were used as a kind of oxidative desulfurization catalyst in a lot ways, such as it was used alone, loaded to carriers and used with phase transfer catalyst together, and so on. They are introduced below.

2.3.1 Heteropolyoxometalates catalysts

Yazu et al.[9] have done research on organic liquid-liquid biphasic oxidative desulfurization system. In a typical run, DBT was dissolved in *n*-octane as model oil. TPA was dissolved 30% aqueous hydrogen peroxide, which were catalyst and oxidant respectively, then mixed with acetonitrile(MeCN) as dissolvant, they found that, DBT were transferred from oil to MeCN phase which has a higher polarity, and the oxidation happened in MeCN phase. Later, they applied this oxidation system to light oil containing 330 mg kg^{-1} sulfur. When v (oil):v(MeCN) =1:4, reaction temperature was 60°C, the sulfur content in the oil phase can be reduce below 12 mg kg^{-1} .And if the oxidized light oil containing 12 mg kg^{-1} sulfur was treated with equal volume of MeCN, the sulfur content further decreased to 3 mg kg^{-1}.In

2003, they approved the oxidative system above[10]. In the system, DBT were dissolved in tetrad cane as model oil, and ethanol was as solvent, hydrogen peroxide as oxidant. When the reaction temperature was 40°C, the DBT in oil phase can be completely reduced. In 2007, Yazu et al.[11] investigated another organic biphasic oxidative desulfurization system. In this system, the organic sulfur such as BT in octane were oxidized with hydrogen peroxide and TPA catalyst in acetic acid(AcOH)/octane biphasic system. They found, the oxidation reaction happened in AcOH phase, and the most oxidation products were remaining in this phase, resulting in the successive removal of sulfur compounds from the octane phase. When the reaction temperature was 50°C, the BT in the solvent can completely be removed , but if TPA was not applied to this oxidative reaction, the removal of BT was only 8%, so, TPA was one kind of effective oxidative desulfurization catalyst.

2.3.2 Loaded heteropolyoxometalates catalysts

HPA has a relatively small surface and the surface can be easily lost in the process of reaction, so its catalytic role can not be good played, but the load-heteropolyoxometalates catalyst are able to overcome these shortcomings.

In 2003, Yazu et al.[10] applied an immobilized 12-tungstophosphoric acid on an anion exchange resin (TPA/AER) to catalyze the oxidation of DBT and 4,6-DMDBT with H_2O_2 in acetonitrile to give the corresponding sulfones as the major product. The oxidation rates increased with increasing amounts of H_2O_2 and TPA/AER. TPA/AER is reusable since the catalytic activity was not reduced even during the fifth cycle of use. TPA/AER acts as a catalyst for the oxidation of DBT in an octane/MeCN biphasic system as well. The major oxidation products were also the sulfone and distributed in the MeCN phase. They also applied this system to diesel oil containing 330 mg kg^{-1} sulfur, the reduction of the sulfur content was enhanced with increasing amounts of immobilized TPA per unit weight of AER and the sulfur content was reduced to below 50 mg kg^{-1}. The sulfur content was further decreased by solvent extraction with MeCN.

In 2005, Zhang Yanwei et al.[13] prepared $Ti_3(PW_{12}O)_4/SiO_2\text{-}Al_2O_3$ catalytic oxidation-adsorbent by sol-gel method, and applied it to DBT oxidation-adsorption experiment. They found that, under the optional conditions of a reaction temperature of 70°C, a molar ratio of titanium to hydrogen of 3, an adsorbent amount of 5%, a molar ratio of hydrogen peroxide to sulfur of 3 and a reaction time of 2h, the sulfur content in the petroleum ether solution of dibenzothiophene-sulfone reduced from 200 mg kg^{-1} to 2mg kg^{-1} the sulfur removal reached 99%. This said adsorbent also had quite good regenerability.

2.3.3 Cooperation of heteropolyoxometalates and phase transfer catalysts

As the hydrogen peroxide is not soluble in oil phase, gasoline is unable to fully access to oxidants in the reaction process, which slow the reaction speed, and result to an unsatisfying desulfurization result and at the same time increase the amount of oxidant. Phase transfer catalyst (PTC) can improve the poor contact between oil and water. PTC use catalyst speed up the reaction between two reactants in two mutually exclusively soluble solvents (liquid - liquid two-phase system or solid - liquid two-phase system), when the materials react, the actual reactants (such as negative ions) are transferred from one phase to another by catalyst, so that the reactant can meet with the substrate and reacts well.

Collins et al.[14] studied the oxidation of dibenzothiophene with hydrogen peroxide using phosphotungstic acid as catalyst and tetraoctylammonium bromide as phase transfer agent in a mixture of water and toluene. As the reaction exists two competitive reactions: catalysed decomposition of hydrogen peroxide and dibenzothiophene oxidation, so only at suitable conditions, dibenzothiophene yields of 100% be removed. In 2001, Mure Te et al.[15] reported their research that using polyoxometalates to catalyze the oxidation of DBT,4-MDBT and 4, 6 -DMDBT. Hydrogen peroxide was taken as oxidant, tetraoctylammonium bromide was as phase transfer catalyst, and toluene solution was as solvent. They found TPA/H_2O_2 system were significantly more active than their phosphomolybdic counterparts. The temperature was at 50°C, DBT can be removed above 80% in 30 minutes, and 100% in 90 minutes. Huang Dan et al (2006) used DBT/octane as model oil, hydrogen peroxide as oxidant, phosphotungstic acid as oxidation catalyst, and acetonitrile/water azeotropic mixture as extractant. They proposed a new method to improve the reaction and mass transfer performance by adding a surfactant at a little amount in to the reaction system.

For the model system, the reaction time decreased from 24 h to 7 h at 50°C by adding the surfactant of hexadecyltrimethl ammonium bromide (CTAB) into the reaction system, and the sulfur content was detected to be below 1 mg kg^{-1} after only oxidation process. For light oils and diesel oils, the H_2O_2 to oil volume ratio in the oxidation could decrease from 1:1 to 1:25.The quantity of oxidant H_2O_2 decreased significantly, and the desulfurization rate after single-stage oxidation-extraction was above 50%, which was much higher than that of multi-stage extractions without oxidation.

Catalysts assembled in emulsions are found to be potentially recoverable and efficient for a number of catalytic reactions. Li Can et al.[15] designed a kind of catalysts composed of polyoxometalate anions and quaternary ammonium cations according to the catalytic reactions and by optimizing the structures of cations and anions. The catalysts act essentially as surfacants, which are uniformly distributed in the interface of the emulsion droplets, and accordingly behave like homogeneous catalysts. The catalysts show remarkable selectivity and activity in the oxidation of sulfur-containing molecules to sulfone in diesel oil and the selective oxidation of alcohols to ketones, using H_2O_2 as oxidant. After reaction, the catalyst demonstrated over 96% efficiency of H_2O_2 and about 100% selectivity to sulfone for the selective oxidation of sulfur-containing molecules in real diesel. The catalysts can be separated and recycled by a simple demulsification and re-emulsification. Lü Hongying et al.[18] investigated the oxidation of sulfur-containing compounds (BT, DBT, and their derivatives).The sulfur compounds were dissolved in decalin solution to form model oil. The oxidative system composed of 30% hydrogen peroxide , and an amphiphilic catalyst $[C_{18}H_{37}N(CH_3)_3]_4[H_2NaPW_{10}O_{36}]$.The catalyst in the water/oil emulsion system exhibits very high catalytic activity such as all sulfur-containing compounds in the model oil can be selectively oxidized into their corresponding sulfones using hydrogen peroxide as an oxidant, The catalytic oxidation reactivity of sulfur-containing compounds was found to be in the following order:4,6-DMDBT>DBT>5-DBT>BT. The sulfur level of a prehydrotreated diesel can be lowered from 500 to 0.1 mg kg^{-1} after oxidation and then extraction, whereas the sulfur level of a straight-run diesel can be decreased from 6000 to 30 mg kg^{-1} after oxidation and extraction.

2.4 H_2O_2—ionic liquid oxidative system

Wang Jianlong et al.[19] take a kind of ionic liquid as catalyst and extracting agent to reduce the sulfur in model oil. The solution of dibenzothiophene (DBT) dissolved in *n*-octane was used as the model of diesel fuels containing organosulfur compounds, and the 30% (mass fraction) aqueous solution of H_2O_2 was used as oxidant. DBT was removed from the model oil by a combination of both chemical oxidation and solvent extraction with the Brönsted acidic ionic liquid (IL) of N-methyl-pyrrolidonium tetraflouoroborate ($[Hnmp]BF_4$) as extracting agent and catalyst. The experimental results showed that the hydroxyl free radicals produced in [Hnmp] BF_4- H_2O_2system could oxidize DBT to form corresponding sulfone entering IL phase, then S was removed from model oil. In the operation, under the conditions of molar ratio of H_2O_2 to S is 3, reaction temperature 60 , reaction time 1 h and volume ratio of model oil to IL is 1, 1550mg L^{-1} of S in model oil was removed completely. The more the initial concentration of DBT, the more difficult the complete removal of S was. The ionic liquid $[Hnmp]BF_4$ could be recycled 7 times without a significant decrease in the rate of sulfur removal.

He LN et al. [20] synthesized three peroxophosphomolybdates $Q_3\{PO_4[MoO(O_2)_2]_4\}$ (Q =$[(C_4H_9N]^+$, $[C_{14}H_{29}N(CH_3)_3]^+$and $[C_{16}H_{33}NC_5H_5]^+$ and applied them to the catalytic oxidation desulfurization system. The results showed that in the catalytic oxidation desulfurization system containing the peroxophosphomolybdate with short alkyl chain ($[(C_4H_9)_4N]_3\{PO_4[MoO(O_2)_2]_4\}$) and H_2O_2,the process exhibited low sulfur removal (16.8%). However, with addition of 1-butyl-3-methylimidazolium tetrafluoroborate, the extraction and catalytic oxidative desulfurization system remarkably increased the removal of sulfur to 97.3% (with stoichiometric amounts of H_2O_2). The process was superior to the simple extraction with IL (16.3%). The results demonstrated that this desulfurization system could be recycled 4 times with slight decrease in activity. They also found that the catalysts with short alkyl chains exhibited higher catalytic activity than that with long alkyl chain in the system. Moreover, the reactivity of sulfur compound decreased in the order of DBT>4, 6-DMDBT >BT.

2.5 H_2O_2—molecular sieve system

As a kind of catalysts for oxidation reactions, molecular sieve is widely used in the alkylation of aromatics, olefins ethylene, ammonia-oxidation of alkanes and oxidation reactions, and so on. Moreover, the molecular sieve in the oxidation of sulfur also showed good activity and selectivity, at the same time being easy-to-separation and recycling of renewable, so, it received more attention.

Shiraishi et al.[21] investigated the Ti-containing molecular sieve catalysts as oxidative desulfurization catalysts. When sulfur compounds were dissolved in *n*-tetradecane (model light oil), they were oxidized to the corresponding sulfoxides and sulfones in the presence of H_2O_2, and were removed successfully from the oil. However, by use of this basic process, the sulfur concentration of actual light oil failed to be reduced to the required deep desulfurization level (50 mg kg^{-1}). This is why alkyl-substituted sulfoxides and sulfones, produced during the process, are adsorbed on the surface of the catalyst, thus decreasing the catalytic activity. When desulfurization was carried out in the presence of polar acetonitrile solvent, the adsorption of these compounds onto the catalyst was suppressed significantly and the deep desulfurization was achieved successfully. In this process, the denitrogenation of light oil also proceeded effectively. The catalyst recovering showed no decrease in the catalytic activity and could be reused for further desulfurization and denitrogenation of light oil. They [21] also investigated vanadosilicate molecular sieve as a catalyst for oxidative desulfurization catalyst.H_2O_2 was applied as oxidizing agent and the catalytic activities of three kinds of vanadosilicates having different structures and pore-size distributions were compared with those for the corresponding titanosilicates. The oxidation of dibenzothiophene and benzothiophene in acetonitrile was catalyzed more effectively by vanadosilicates than titanosilicates, where the mesoporous vanadosilicate showed the highest activity. The vanadosilicate also accelerated the desulfurization of the actual light oil in an oil/acetonitrile two-phase system: the sulfur content of the oil was decreased successfully from 425 mg.kg^{-1} to less than 50 mg.kg^{-1} (ultradeep desulfurization level). During the process, nitrogen- containing compounds were also removed successfully from the light oil. However, the vanadosilicate, recovered following the reaction, could not be reused for further treatment of light oil. This is because the catalytic activity of the vanadosilicate decreases significantly during the reaction, owing to the dissolution of vanadium species in the silica framework into the acetonitrile solution.

Wang et al.[23] applied Ti-HMS as the catalyst and with H_2O_2 as the oxidant, and studied the oxidative desulfurization of Th, BT, DBT and DMDBT in a model fuel. They found the order of ODS reactivity over Ti-HMS was as follows: DBT>BT>DMDBT>Th, which was determined by the electron density on sulfur atom in thiophene ring and steric hindrance of the sulfur compounds. DMDBT was oxidized more efficiently over Ti-HMS than over TS-1, Ti-β or Ti-MCM-41. The sulfur compounds were oxidized in the channel of Ti-HMS and framework titanium atoms were the active sites. With the decrease of the molar ratio of SiO_2 and TiO_2 from 200 to 25, the DMDBT removal increased from 39.6% to 83.6%. With the increase of relative crystallinity of Ti-HMS from 43.0% to 96.4%, the DMDBT removal increased from 33.0% to 44.8%. When the relative crystallinity of Ti-HMS increased to 100%, the DMDBT removal increased dramatically to 71.4%.Both the mesopore framework and framework titanium atoms were necessary to the ODS of DMDBT.

Cheng et al.[24] investigated an oxidative desulfurization process for model light oil over Ti-MWW. Benzothiophene and dibenzothiophene are oxidized to their corresponding sulfoxides and sulfones, which can be removed by extraction using acetonitrile. The conversion of benzothiophene and dibenzothiophene is 100% and 95%, respectively, at 70°C. The effect of solvent was also studied. Under the same conditions, the conversion of benzothiophene in three solvents is in the order acetonitrile>methanol>water.

As a kind of oxidative desulfurization catalysts, molecular sieves can avoid using toxic substances raw materials, so they are beneficial materials to environment. Moreover they have a good catalytic effect, at the same time, they are applied fully, so, the prospects for development in ODS are very good.

2.6 H_2O_2-ultrasound oxidative desulfurization system

Ultrasound oxidation desulfurization technology is a new desulfurization technology for the desulfurization. Its desulfurization mechanism can be concluded as below: oxidants and raw materials mixed with surfactants in water in a reactor to form a mixture of water phase and organic medium. In the role of ultrasound, the mixture is easy stratified for the water phase and organic phase, and the organic phase is the clean fuel after desulfurization. Moreover, ultrasound will make the local temperature and pressure of the mixture increased rapidly in a short period .At the same time, free radicals And the activation of oxygen were generated in the mixed materials, these substances reacted with sulfides and oxidized them to form sulfate, sulfone and sulfoxide, and these substances were transferred to the water phase. After the solvent extraction sulfate and sulfone were removed. The solvent can be recycling used by regeneration, while sulfuric acid sulfone salt can be used to produce other chemical products.

Sun Mingzhu et al.[25] applied catalytic oxidation which is a non-HDS technology to remove sulfur compounds from diesel fuel. On the basis of catalytic oxidation and solvent extraction, ultrasound irradiation is introduced to provide energy for the reaction, which develops a completely new diesel oil oxidative desulfurization technology. The effects of the selection of extraction catalyst, the volume ratio of extraction solvent to oil, extraction time, extraction times, etc are investigated. The desulfurization results are optimal with ultrasound under the following conditions: taking H_2O_2 as oxidation, phosphoric acid and formic acid as catalysts, the volume ratio of oxidant to oil is 1:10, the molar ratio of H_2O_2 to catalyst is 1:1, the reaction temperature is 50°C, the reaction time is10min, using DMF as the extraction solvent, the ratio of extraction solvent to oil is 1:1, the extraction time is 20 min and extracting twice.

Yen et al.[26] applied ultrasound to remove sulfur. DBT was dissolved into toluene to make a stock solution with a sulfur mass content of 0.4%.A solution containing tetraoctyl- ammonium bromide and hydrogen peroxide containing phosphotungstic acid were added into the reactor. The mixture was irradiated by ultrasound with frequency at 20kHz.The temperature in the reactor was kept at about 73-77°C.It was found that the oxidation of DBT to dibenzothiophene sulfone(DBTO) reached over 85% and 95% within 1 and 3 minutes of ultrasonication, respectively. In 7 minutes, DBT can be completely oxidized to DBTO. In comparison, the conversion of DBT to DBTO in the absence of ultrasound was only 21% in 1 minutes and reached barely above 80% in 7min.For diesel fuels containing various levels of sulfur content, and through the use of catalytic oxidation and ultrasonication followed by solvent extraction, removal efficiency of sulfur-bearing compounds can reach or exceed 99% in a short contact time at ambient temperature and atmospheric pressure. This simple approach can be the basis for obtaining ultra-low sulfur-containing diesel oil. In 2007, they [27] applied the ultrasound-assisted oxidative desulfurization (UAOD) process to a number of diesel fuels containing varying amounts of sulfur content. The transition metal complex and quaternary ammonium salts (QAS) phase transfer agents were applied with aqueous hydrogen peroxide as oxidizing agent. The results showed that the optimized UAOD process followed by extraction can reach or exceed 95% sulfur reduction, or final sulfur concentration less than 15 mg kg^{-1} in a short contact time under ambient temperature and atmospheric pressure. Moreover, high yield of 3-bromobenzothiophene, and 2-bromobenzothiphene sulfone were found from phase transfer agents containing tetraoctylammonium bromide. No contaminates such as brome compound derivates had been isolated when the new fluoride phase transfer agent was used. The experiment also demonstrated that the catalyst could be recovered for reuse. Furthermore, the hydrogen peroxide provides a good performance, and the oxidation will proceed as low as 0.25%.

The ultrasonic oxidation desulfurization has high desulfurization efficiency, but still applied H_2O_2 as oxidant, and at the same time ultrasound device was used, this enhanced the cost and limited the scale of production.

As H_2O_2 was a kind of water-soluble oxidant, so it can easily cause emulsification of oil when added to oil, and it required a long time to mix with the oil sufficiently. Moreover, due to the water-soluble reaction system are in the pan-reactor belonging to intermittent operation process, and it can not be continuous produced, so it is not conducive to the promotion of industrialization. As a result, to find a kind of continuous produced oxidant become the goal of scientists' research.

3. Organic oxidants desulfurization system

Organic oxidants are oil-soluble oxidants, compared to H_2O_2 which is water-soluble agent, they have the following advantages: no water is taken into the oxidation process, no emergence of oil emulsion as a result of the existence of water, a shorter time to mix with the oil well, and the reaction taken place in the tubular reactor continuously, so it is more process-oriented.

Otsuki et al. [28] studied the oxidation of DBT using t-butyl hypochlorite (t-BuOCl) in the presence of several catalysts. Under ambient pressure, and at 30-70 degrees centigrade, more than 90% of DBT could be oxidized in the decahydronaphthalene (decalin) solution. The catalyst was necessary to oxidize dibenzothiophene with t-BuOCl, and gamma-alumina (Al_2O_3) supported catalysts have relatively high activities. At the same time, the activities of the metal-loaded Al_2O_3 catalysts had shown the same activities as those of the Al_2O_3 support, indicating that the Al_2O_3 support itself possessed such activity.

Wang et al. [29] investigated the oxidation of sulfur compounds in kerosene conducted with *tert*-butyl hydroperoxide (*t*-BuOOH) in the presence of various catalysts. The oxidation activities of dibenzothiophene (DBT) in kerosene for a series of Mo catalysts supported on Al_2O_3 with various Mo contents were estimated. The results showed that the oxidation activity of DBT increased with increasing Mo mass content up to about 16 % and decreased when Mo content was beyond this value. The addition of Co and Ni onto the Mo/ Al_2O_3 catalyst led to a significant decrease in the oxidation activity of DBT. The oxidation of BT, DBT, 4-MDBT, and 4,6-DMDBT dissolved in decalin was also carried out on mass fraction of 16% Mo/ Al_2O_3 catalyst with *t*-BuOOH to investigate the oxidation reactivities of these sulfur compounds. The results indicated that the oxidation reactivities of these sulfur compounds decreased in the order of DBT > 4-MDBT > 4,6-DMDBT >>BT. The oxidation activity of each sulfur compound increased with the increasing O/S molar ratio up to the molar ratio O to S of 3 and then leveled off beyond this value.

Ishihara et al. [30] investigated the oxidation of undesirable sulfur compounds present in a desulfurized light gas oil (LGO; sulfur content: 39 ppm).It was performed with tert-butyl hydroperoxide (*t*-BuOOH) as the oxidant in the presence of a mass fraction of 16% MoO_3/Al_2O_3 catalyst. They found that the oxidation activity of the sulfur compounds in the light gas oil increased when the molar ratio of O to S increased up to 15, but the activity slightly decreased for higher ratios. This optimal ratio was significantly higher that the stoichiometric one which equal to 2 due to parallel oxidation reactions of olefins, in the LGO. Further, they compared the oxidation reactivity of DBT, 4,6-DMDBT, and trimethyldibenzothiophene (C_3-DBT), which are refractory compounds present in the light gas oil. The reactivity decreased in the order DBT >>4, 6-DMDBT > C_3-DBT. Then, according to the proposed global process, the previously oxidized molecules in the treated light gas oil were further removed by adsorption over a silica gel at ambient temperature. As a result, the total sulfur content could be decreased after oxidation/adsorption to less than 5 mg kg^{-1}.

Stanger et al.[21] applied silica to catalyze the *tert*-butyl hydroperoxide (TBHP, t-BuOOH) oxidation of DBT and 4, 6-DMDBT to their oxides at 50-90°C. Results showed that sulfur concentrations in simulated hydrotreated petroleum feedstock solutions containing 374 mg kg^{-1} of sulfur as DBT or 4, 6-DMDBT can be reduced to 1 mg kg^{-1} within 40 min at 90°C. As an inexpensive, stable, and recyclable catalyst, silica has several advantages over other catalysts for the oxidation of DBTs to their easily separated oxides as a means of achieving low sulfur levels in petroleum feedstock.

Li et al.[32] did research on the oxidation of DBT in decalin (as solvent) using oil-soluble oxidant cyclohexanone peroxide (CYHPO). The results showed that under the condition of molar ratio of CYHPO to sulfur 2.5:1, reaction temperature 100^{o}C and reaction time 3 h, the desulfurization rate was up to 87%. The little water produced after oxidation was removed by molecular sieve adsorption. The recovery ratio of model oil was up to 98% after the treatment with centrifugation and adsorption.

Zhou et al.[33] investigated the oxidation of DBT in decalin (as solvent) using oil-soluble oxidant *tert*-amyl hydroperoxide (TAHP). They found that under the condition of ratio of TAHP to sulfur 3:1, reaction temperature 90 , reaction time 3 h, the desulfurization rate was up to 95%. The catalyst was necessary to oxidize DBT with TAHP. Weak acid cationic exchange resin of“D113”large aperture acrylic acid series supported MoO_3 catalyst has relatively high activities. After the repetitious use as catalyst for 10 times, it still has good activity.

Zhang et al.[34] did research of oxidative desulfurization on the decalin solution with sulfur compounds of DBT, where the oil-soluble t-butylhydroperoxide (TBHP) was used as the oxidant and the molybdenum oxide (MoO3) catalyst supported on resins was used as catalyst. The results showed that the conversion of DBT could reach 99. 2% at 100^{o}C in 3h using

TBHP in the presence of MoO_3/D113(cationic exchange resins) and MoO_3/D751(a new type cationic exchange resins) catalysts. MoO_3/D113and MoO_3/D751 catalysts had similar catalytic activity, but MoO_3/D113 catalyst had a better selectivity to DBT oxidation and MoO_3/D751 catalyst had a better stability. The non-polar DBT could be converted into polar DBT sulfone, which was easily adsorbed on MoO_3/D113 and MoO_3/D751 catalysts. The activities of MoO_3/D113 and MoO_3/D751 catalysts were not obviously changed after recycling ten times.

Oil-soluble oxidant does not produce a large number of oil-water two-phase in the oxidation process, so as to avoid the production of emulsion. Meanwhile, the reaction can take place in a tubular reactor, so that the process could be carried out in a row.

4. Photocatalytic oxidation desulfurization system

Photocatalytic oxidation of the oil desulfurization is combined with photochemical reaction and liquid-liquid extraction. Under normal temperature and pressure, oil and extractant are added at the same time to begin the photocatalytic oxidation, and the oxidant can be oxygen, hydrogen peroxide, titanium dioxide, and so on. Photocatalytic oxidation desulfurization is a method using high-pressure mercury lamp of visible light or ultra-violet radiation into the polar solvents sulfur compounds, so that the sulfur compounds can be photo-oxidized. This process can be carried out under the normal temperature and pressure, and the sulfur can be extracted by solvent extraction agents, thus greatly reduce the sulfur content to achieve the purpose of desulfurization

Photocatalytic oxidation has the following advantages: no need of catalysts; simple and easy to control reaction; reacted under normal pressure at normal temperature, saving energy; and easily to remove some difficult to removed sulfur compounds such as 4-MDBT, 4, 6-DMDBT, DBT, and so on.

Hirai et al.[35] studied the desulfurization process for DBT and its derivatives such as 4-MDBT and 4, 6-DMDBT by combination of photochemical reaction and liquid−liquid extraction. The DBTs dissolved in tetradecane were quantitatively photodecomposed by the use of a high-pressure mercury lamp and were removed to the water phase as SO_4^{2-} at conditions of room temperature and atmospheric pressure. The order of reactivity for the DBTs was DBT < 4-MDBT < 4,6-DMDBT.They also applied this system to commercial light oil, however, only 22% was removed after 30 h irradiation. They thought this was caused mainly by the depression of the photoreaction of DBT by the presence of aromatic compounds in the light oil.

Hirai et al.[36] investigated a desulfurization process for DBT by a combination of photochemical reaction and liquid-liquid extraction. The DBT dissolved in tetradecane was photodecomposed by the use of a high-pressure mercury lamp and removed into the water phase at conditions of room temperature and atmospheric pressure. The addition of benzophenone (BZP), a triplet photosensitizer, enhanced the removal of DBT from tetradecane. However, the reaction hardly proceeded in the presence of naphthalene (NP), probably because of triplet energy transfer from photoexcited DBT or BZP to ground-state NP. The addition of hydrogen peroxide enhanced the desulfurization of commercial light oil as well as the removal of DBT from tetradecane. They used a 30% H_2O_2 solution to commercial light oil, and 75% sulfur was removed after 24 h photoirradiation, and the sulfur mass content in the light oil was reduced from 2000 mg kg^{-1} to less than 50 mg kg^{-1}.

Yasuhiro et al.[?] used a triplet photosensitizer and hydrogen peroxide in an oil/water two-phase liquid-liquid extraction system for deep desulfurization process for light oil, on the basis of photosensitized oxidation. DBT in tetradecane was effectively desulfurized. This was achieved via the indirect photoexcitation of DBT, using benzophenone (BZP) under photoirradiation conditions of wavelength $\lambda>280$ nm, and the effective oxidation of the excited DBT by H_2O_2, suppressing the photodecomposition of H_2O_2. The desulfurization of commercial light oil was also achieved in this process by the addition of both BZP and H_2O_2, and the sulfur content was reduced from 2000 mg kg^{-1} to 50 mg kg^{-1} by 48 h of photoirradiation. C_5 and C_6 alkyl- substituted DBTs were found to be desulfurized effectively in the presence of BZP and H_2O_2. The photodecomposed sulfur-containing compounds removed into the water phase were separated successfully, using column adsorption with aluminum oxide as the adsorbent.

Zhao et al.[38] applied a desulfurization method for petroleum by gamma rays radiation assisted with peroxide. Thiophene type sulfides were dissolved in *n*-dodecane as the simulation of oil. The results showed that the compounds at low concentration were more degradable effectively than those at high concentration. In addition, the degradation of BT and DBT can be accelerated by adding hydrogen peroxide during the radiation processes. The removal of DBT and BT reached 32.5% and 70.4% respectively by adding hydrogen peroxide compared to 7.8% and 14.6% without hydrogen peroxide respectively. So, hydrogen peroxide showed an apparent synergistic behavior with radiation for degradation of BT and DBT.

Zhao et al.[39] dissolved thiophene into *n*-octane to simulate model oil and studied photosensitized oxidative desulfurization with riboflavin as photosensitizer and O_2 in air as oxidant. A 500W high pressure was used as the light source for irradiation and air was introduced by a gas pump for supplying O_2.With the air flow at 150mL/min, water/oil ratio at 1:1 and riboflavin concentration at 30μmol/L, the desulfurization of thiophene was 85.4% for 3h photoirradiation.

Although the photocatalytic desulfurization method has several advantages such as demanding less investment, a modest reaction conditions, simple process, low-cost for oxidation reaction and easy separation of reaction products, etc, but it has a slow response, the light required for a long time, and the desulfurization mechanism of the photocatalytic oxidation of is still divided, these are subject to further study.

5. Plasma oxidative desulfurization system

Liu et al.[40] studied plasma oxidative desulfurization of organic sulfides in liquid phase. Plasma oxidative desulfurization has high reaction activation and can avoid catalysts poisoning. As the C-S bond is not weak bond, so thiophene generally can not easily be oxidized, but is removed at the existence of plasma and active oxygen, and generated a number of easily separated solid sulfides. The thiophene desulfurization rate can reach close to 80%.Liquid plasma oxidative desulfurization is an effective way to overcame the restrictions of raw materials such as hydrogen, and at the same time got a better desulfurization effect.

6. The future work

In the sulfur compounds desulfurization technologies, though HDS technology for industrial applications is at a dominant position, it has several disadvantages such as harsh conditions, the high cost and can not meet the increasingly stringent environmental regulations on oil products such as low sulfur content requirements, so development of ODS desulfurization technology has great realistic significance. At present, it has made some achievements in this research, but a number of problems have not yet been solved, such as the high amount of oxidants, high-cost, easy deactivation to catalyst, the high cost in solvent extraction, as well as of low oil recovery efficiency, so ODS desulfurization technology is still at laboratory research stage. Comprehensive earlier, we believe achieving practical applications, the following aspects of work is particularly critical to ODS desulfurization technology:

1. the development of high-efficiency, low-cost and high-activity recoverable catalyst to ensure the desulfurization process operation continued efficiently;
2. focus on the development of low-cost oxidant. At the same time, study the kinetics of the system and provide a theoretical basis for the amplification process
3. explored a variety of methods which have good perspective in application (such as surface active agent, reinforcing ultrasound and etc) at the aspect in ODS strengthening and its coupling with adsorption and extraction to improve the general efficiency of desulfurization technology and at the same time to take into account the overall process of technological competitiveness;
4. actively explore and careful evaluate the potential value of new desulfurization technology (such as plasma oxidation, photocatalytic oxidation, etc.) to promote the ODS to innovate continuously and develop in-depth , so as to meet the need of the society.

References

[1] Zheng J H., Remarks on clean fuel production technology[J].Petroleum & petrochemical today, 2003, 11(1): 4-9,

[2] Cui Y., Liu J L., Huang X L et al. Study on diesel desulfurization by selective oxidation/extraction[J]. Petroleum processing and petrochemicals, 2002, 33 (4): 17-20,

[3] Zannikos F., Lois E., Stournas S., .Desulfurization of petroleum fractions of oxidation and solvent extraction[J]. Fuel Processing Technology, 1995, 42(1): 35-45.

[4] Shiraishi Y., Taehibana K., Hirai T., Komasawa I., Desulfurization and denitrogenation process for light oils based on chemical oxidation followed by liquid-liquid extraction [J]. Industrial & Engineering Chemistry Research, 2002, 41(17): 4362-4375.

[5] Lü Z F., Zhan F T., Wang P.,et al., Oxidative desulfurization of straight-run diesel oil by hydrogen-peroxide /acetic anhydride[J].Chemical Engineering of Oil & Gas, 2006, 35(2): 114-117.

[6] Otsuki S., Nonaka T., Takashima N., Oxidative desulfurization of light gas oil and vacuum gas oil by oxidation and solvent extraction[J]. Energy & Fuels, 2000, 14(6): 1232-1239.

[7] Yao X Q., Wang S J., Ling F X et al. Oxidative desulfurization of simulated light oil[J].Journal of fuel chemistry and technology,2004, 32(3):3318-322.

[8] Lü Z F., Zhan F T.,Li L et al. Desulfurization of catalytic diesel oil by hydroperoxide-organic acid oxidation system[J].Journal of the university of petroleum, China(Edition of natural science), 2001, 25(3): 26-30.

[9] Yazu K., Yamamoto Y., Furuya T., et al. Oxidation of dibenzothiophenes in an organic biphasic system and its application to oxidative desulfurization of light oil [J]. Energy & fuel, 2001, 15(6): 1535-1536.

[10] Yazu K., Furuya T., Miki K., Tungstophosphoric acid-catalyzed oxidative desulfurization of light oil with hydrogen peroxide in a light oil/acetic acid biphasic system [J]. Chemistry Letters, 2003, 32(10): 920-921.

[11] Yazu K., Sato S., Sugimoto Y., et al., Tungstophosphoric acid–catalyzed oxidative desulfuriazation of naphtha with hydrogen peroxide in naphtha/acetic acid biphasic system [J]. Journal of the Japan Petroleum Institute, 2007, 50(6): 329-334

[12] Yazu K., Furuya T., Miki K., Immobilized tungstophosphoric acid-catalyzed oxidative desulfurization of diesel oil with hydrogen peroxide[J]. Journal of the Japan Petroleum Institute, 2003, 46(6): 379-382

[13] Zhang Y W., Shen J., Yuan X D., et al.,.Desulfurization by catalytic oxidation and adsorption over $Ti_3(PW_{12}O)_4$[J]. Petroleum process and petrochemicals, 2005, 36(3):20-24.

[14] Collins F M., Lucy A R., Sharp C.,(1997).Oxidative desulphurization of oils via hydrogen peroxide and heteropolyanion catalysis,[J]. Journal of Molecular Catalysis A : Chemical, 1997, 117(1-3): 397-403.

[15] Te M., Fairbridge C., Ring., Oxidation reactivities of dibenzothiophenes in polyoxometalate/H_2O_2 and acid/H_2O_2 systems [J]. Applied Catalysis A:General, 2001, 219(1-2): 267-280. DOI:10.1016/S0926-860X(01)00699-8

[16] Huang D., Wang Y J., Luo G Sh.,et al., A surfactant-enhanced oxidation-extraction process for desulfurization of oils[J].The chinese jounal of process engineering, 2006, 6(3):384-387.

[17] Li C., Gao J B., Jiang Z X., et al., Selective oxidation on recoverable catalysts assembled in emulsions[J]. Topic in Catal, 2005, 35(1-2): 169-175.

[18] Lü H Y., Gao J B., Jiang Z X., et al., Ultra-deep desulfurization of diesel by selective oxidation with $[C_{18}H_{37}N(CH_3)_3]_4[H_2NaPW_{10}O_{36}]$ catalyst assembled in emulsion droplets[J]. Journal of Catalysis, 2006, 239(2): 369-375.

[19] Wang J L., Zhao D Sh., Zhou Er P., Application of Brønsted acidic ionic liquid in extraction and oxidation of dibenzothiophene[J].Acta petrolei sinica(petroleum processing section), 2008, 24(2):227-231.

[20] He L N., Li H M., Zhu W S., et al.,Deep oxidative desulfurization of fuels using peroxophosphomolybdate catalysts in ionic liquids[J], Industrial & Engineering Chemistry Research, 2008, 47(18): 6890-6895.

[21] Shiraishi Y., Hirai T., Komasawa I.,Oxidative desulfurization process for light oil using titanium silicate molecular sieve catalysts[J]. Journal of Chemical Engineering of Japan, 2002,35(12):1305-1311

[22] Shiraishi Y., Naito T., Hirai T., Vanadosilicate molecular sieve as a catalyst for oxidative desulfurization of light oil[J]. Industrial & Engineering Chemistry Research, 2003, 42(24): 6034-6039.

[23] Wang Y., Li G., Wang X Sh., et al., Catalytic oxidative desulfurization of model fuel over Ti-HMS zeolite[J].Chinese journal of catalysis, 2005, 26(7):567-570.

[24] Cheng Sh F., Liu Y M., Gao J B,.et al., Catalytic oxidation of benzothiophene and

dibenzothiophene in moded light oil over Ti-MWW[J], Chinese journal of catalysis, 2006, 27(7):547-549.

[25] Sun M Zh., Zhao D Zh., Sun W W., et al.,Study on the oxidative desulfurization of diesel fuel with power ultrasound[J].Chemistry and adhension, 2008, 30(2):65-68.DOI:CNKI:SUN:HXYZ.0.2008-02-022

[26] Mei H., Mei B W., Yen T F.,. A new method for obtaining ultra-low sulfur dieselfuel via ultrasound assisted oxidative desulfurization[J]. Fuel, 2003, 82(4): 405-414.

[27] Wan M W., Yen T F.,. Enhance efficiency of tetraoctylammonium fluoride applied to ultrasound-assisted oxidative Desulfurization (UAOD) Process[J]. Applied Catalysis A: General, 2007, 319 :237–245.

[28] Otsuki S., Nonaka T., Qian W H., et al.,(2001). Oxidative desulfurization of middle distillate-oxidation of dibenzothiophene using t-butyl hypochlorite[J].Sekiyu Gakkaishi-Journal of the Japan Petroleum Institute, 2001, 44(1): 18-24

[29] Wang D H., Qian W H., Amano H.,. Oxidative desulfurization of fuel oil: part I. oxidation of dibenzothiophenes using *tert*-butyl hydroperoxide[J]. Applied Catalysis A:General, 2003, 253(1): 91–99.

[30] Ishihara A., Wang D H., Dumeignil F.,et al.,.Oxidative desulfurization and denitrogenation of a light gas oil using an oxidation/adsorption continuous flow process[J]. Applied Catalysis A: General, 2005, 279(1-2): 279–287.

[31] Stanger K J**.,** Angelici R J.,(2006).Silica-catalyzed *tert*-butyl hydroperoxide oxidation of dibenzothiophene and its 4,6-dimethyl derivative: a route to low-sulfur petroleum feedstocks[J]. Energy & Fuels, 2006**,** 20(5): 1757-1760.

[32] Li J Y., Zhou X R., Zhao D F., et al.,.Oxidative desulfurization of dibenzothiophene using cyclohexanone peroxid[J].Jounal of fuel chemistry and technology, 2006, 34(2):249-251.

[33] Zhou X R., Li J Y., Zhao C X.,et al.,.Oxidative desulfurization of dibenzothiophene using tert- amylhydroperoxid[J]. Jounal of fuel chemistry and technology,2006, 34(4):506-508.DOI:cnki:ISSN:0253-2409.0.2006- 04-025

[34] Zhang Sh Sh., Zhou X R., Wang J., et al.,.One step catalytic oxidation of dibenzothiophene using t-butyl hydroperoxide over molybdenum oxide catalyst[J].Chemical engineering of oil & gas, 2008, 37(1):1-8.

[35] Hirai T., Ogawa K., Komasawa I.,. Desulfurization process for dibenzothiophenes from light oil by photochemical reaction and liquid-liquid extraction[J]. Industrial Engineering Chemistry Research, 1996, 35(2): 586-589.

[36] Hirai T., Shiraishi Y., Ogawa K.,. Effect of photosensitizer and hydrogen peroxide on desulfurization of light oil by photochemical reaction and liquid-liquid extraction [J]. Industrial Engineering Chemistry Research, 1997, 36(3):530-533.

[37] Shiraishi Y., Hara H., Hirai T., A deep desulfurization process for light oil by photosensitized oxidation using a triplet photosensitizer and hydrogen peroxide in an oil/water two-phase liquid-liquid extraction system[J]. Industrial Engineering Chemistry Research, 1999, 38(4): 1589-1595.

[38] Zhao Y F., Yan N Q., Wu D., et al.,.Investigation on removal of thiophene-type sulfide by gamma rays radiation assisted with hydrogen peroxied[J].Journal of shanghai jiaotong university, 2004, 38(10):1719-1723.

[39] Zhao D S., Li F T., Sun Zh M., et al.,.Photosensitized oxidative desulfurization of thiophene by riboflavin [J].Journal of fuel chemistry and technology, 2008, 36(2):166-169.

[40] Liu W Y., Lei Zh L., Lu W\., et al., Plasma oxidative desulfurization of organic sulfides in liquid phase[J].Chinese journal of applied chemistry, 1997, 14(5):83-85.