Oxidative Desulfurization of heavy oils: Mini Review

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Abstract: Various strategies for desulfurization of heavy oil were analysed and critically evaluated the feasibility of the various methods for heavy oil. The widely used methods like hydrodesulfurization (HDS) is not efficient enough to remove sulphur compounds to meet the new requirements of sulphur standard. The demanding rules imposed on the heavy oil has made researchers to find alternate methods like oxidative desulfurization. The scope of the present review is to provide a brief analysis of present catalytic oxidation techniques: methods like Bronsted lewis acid catalytic oxidation, heteropoly acid (HPA) catalytic oxidation, ionic liquid catalytic oxidation, molecular sieve catalytic oxidation and titanium catalytic oxidation routinely used for ODS process.

Key Words: Hydrodesulfurization, Alternative desulfurization, Sulfur Compounds, Oxidative desulfurization, Heavy oil

1. Introduction

The increasing demand for the heavy oil and diminishing reserves made the use of low-quality fuels inevitable. The utilization of low-quality fuel leads to emission of toxic gases, which is threat to environment and as well to the human beings causing health issues.[1] Further, the sulfur compounds present in low-quality fuel poisons the noble metal catalysts in refining industries leading to diminishing profits.[2] Due to these reasons, the environmental protection agencies (EPA) imposed stringent conditions on the sulfur level of heavy oil. Through the years the rules are tightening, and no wonder liquid fuels with zero sulfur becomes mandate in the coming years.[3]. Traditionally the organosulfur compounds are removed from the heavy oil by hydrodesulfurization method using a sulfided catalyst. During hydrodesulfurization process, sulfur compounds converted into aliphatic hydrocarbons by elimination of H_2S gas. Inspite of industrialized and well optimized process, HDS has several demerits like use of expensive hydrogen, high temperature and pressure, selectivity issues and failure to remove refractory sulfur compounds.[4],[5],[6]. Literature has revealed many other alternative methods to treat refractory sulfur compounds such as oxidative desulfurization (ODS), adsorptive desulphurization and extractive desulfurization.[7],[8],[9]. Studies have shown that oxidative desulfurization (ODS) has been mentioned as the best technique due to the mild operation conditions. Remarkably, through the years the number of papers steadily increased to satisfy the needs of environmental protection agencies (EPA) to reduce the sulfur levels in heavy oils.[10]

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1.1 Sulfur in Crude Oil

High sulfur content in oil, results in poor quality which leads to catalyst poisoning, environment pollution and other consequences. Sulfur mainly exists in two forms organic and inorganic, inorganic sulfur such as hydrogen sulfide and pyrite present in suspension. Whereas the main source of sulfur found in heavy oil present in the organic form such as thiophenes and benzothiophene. Significantly, oil with higher amounts of sulfur compounds found to possess high viscosities and higher densities, generally aliphatic sulfur compounds are easily removed in desulfurization process. On the other hand, the removal efficiency is reduced for sulfur contained in aromatic rings, such as thiophene and its benzologs, due to delocalization of n-electrons on sulfur atoms generating more resonance structures and extra stability. The removal efficiency of sulfur compounds purely dependent on chemical nature.

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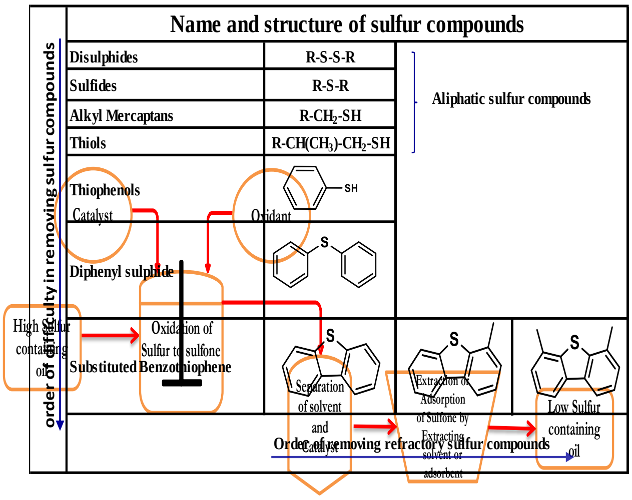

Figure-1: Commonly available sulfur compounds in the crude oil and the order of difficulty in removing different organosulfur compounds

The boiling range of sulfur compounds purely depends on nature and concentration, in turn higher the boiling point of sulfur compounds more difficult to remove and turn into refractory sulfur compounds. Generally, a trend has been observed that as higher the complexity of sulfur compound in crude oils, higher the viscosities and higher densities is found. The order of difficulty in removing different organosulfur compounds shows that refractory sulfur compounds are difficult to remove compared to aliphatic sulfur compounds **(Figure-1).**

1.2. Description of ODS

During ODS process the sulfur compounds are removed by oxidation reaction in presence of a suitable oxidizing agent with or without catalyst. The process involves sequential oxidation. In brief, ODS mainly include two stages: (i) Oxidation of sulfur compound to sulfones and (ii) solvent extraction to remove sulfones as mentioned in **(Figure-2)**.Sulfones can be separated from the heavy oils by adsorption, solvent extraction or by thermal distillation. Adsorption is a process where suitable adsorbents like zeolites etc are used for adsorption. In the solvent extraction the polar & non-polar solvents are used for extraction of the sulfones. Thermal distillation is a process of separating sulfur free oil based on the difference in boiling point of respective sulfones. Through the years various oxidants reported in literature. Among many oxidants, the H_2O_2 is repeatedly gained importance as better oxidant as it is having more active oxygen and leaves water as by product.[11]. Furthermore, the strong affinity of sulfur for oxygen and high oxidation potential of sulfur are added advantage for selective oxidation of ODS.

Figure-2: Schematic representation of sulfur removal in the oxidative desulfurization process

2. Catalytic Oxidation System

2.1. Acetic Acid/Formic Acid/PTC Catalytic Oxidation System

The utility of metal catalysts can be circumvented using simple Bronsted acids, chiefly HCOOH and CH_3COOH often known for years to assist ODS in presence of H_2O_2 through the formation of active peroxyacids. Consequently, these acids may be considered as metal free and cost-effective catalysts. Despite the apparent benefits of this Bronsted acid-peroxide oxidation system, the ODS process has certain demerits, such as oil soluble organic acid catalysts, not recoverable and affects the oil properties. Therefore, alternative metal free catalysts highly necessitated to avoid these demerits. Recently few reports explored the role of different activated carbon in assisting the performance of COOH-H_2O_2 ODS system based on surface adsorption phenomenon.

M. Te et al [12] studied sulfur removal from heavy oil using an oxidant-extractive system with formic acid and H_2O_2 system. The oxidation of most refractory sulfur compounds 4,6-DMDBT oxidized to > 95% conversion. As the formic acid is small molecule, the peracid formed with can interact with sulfur without any steric hindrance. Mamaghani et al. [13] studied the removal of DBT with promising oxidation system consisting of hydrogen peroxide, formic acid, and sulfuric acid, where sulfuric acid acts as catalyst and to increase the acidity of media. Detailed study has been performed with respect to each parameter like qty of sulfuric acid, ratio of solvent and temperature by using response surface methodology. Remarkable model was established for sulfur removal against the effective parameters. Despite the evident benefits of this liquid acid-peroxide oxidation system, the ODS process has certain disadvantages, like carry over of oil soluble organic acid as a catalyst in the reaction mixture which causes separation problems and affects the fuel properties of diesel oil. Furthermore, oil soluble organic acid catalysts are not fully recoverable and are non-renewable. Therefore, recoverable, and recyclable catalysts are better alternatives for the fuel oil refining industries.

Sayudi et al [14] explored the use of two alternative oxidants system ($KMnO_4/H_2O_2$) in combination with formic acid and acetic acid as catalyst for oxidative desulphurization. The objective of research was to compare the study of two alternative oxidants ($KMnO_4/H_2O_2$) on ODS and examine the effect of two acid catalysts acetic acid and formic acid.

2.2. Polyoxometalates (POM)/PTC/ H_2O_2 oxidation system:

POM catalysts are a cluster of early transitional metal ions and polyoxoanions and classified into isopolyanions, have one metallic element and heteropolyanions additionally have one hetero atom. In addition, they are versatile catalysts due to their multiple functional active sites. POM and HPA are having similar type of structures, due its unique properties, these catalysts in the ODS process have attracted significant attention as green catalysts in combination with H_2O_2 oxidant. Generally, Keggin, Anderson and Dawson, type POMs are frequently used as the catalysts. Due to high thermal stability and ease of synthesis, Keggin type is very familiar among the POM ODS catalysts.

F.M. Collins et al [15] exclusively investigated sulfur removal with hydrogen peroxide using Phosphotungstic acid as catalyst and tetraoctylammonium bromide as phase transfer catalyst. The catalyst system inhibits the decomposition of H2O2, thereby converting the thiophene nucleus containing sulfur compound into sulfones. Further the sulfur compounds can be separated by adsorption on silica gel. M.A.

Rezvani et.al [16] prepared novel catalyst bearing the composition of tetra(*n*-butyl) ammonium salt of iron^{III}-substituted phosphotungstate@lead lead oxide composite. In depth analysis of catalyst and catalyst activity evaluated using CH_3COOH/H_2O_2 oxidizing agent at 60 °C. Furthermore, the various relative experiments were carried out to investigate the efficiency of catalyst. In addition, mechanism and recyclability of catalyst has been studied.

R. Ghubayra, et al [17] investigated keggin-type of heteropoly acids adsorbed on activated carbon (HPA/C). The new modified HPA catalyst is more active compared to other recently reported catalysts. The high catalytic activity is due to adsorption of HPA on to pores of carbon support which prevents leaching of catalyst. Further, step by step mechanism has been proposed by which is different from homogeneous-catalyzed ODs reaction.

2.3. Ionic Liquid Catalytic Oxidation System

Ionic liquids (ILs), a class of new emerging green solvents, own exclusive properties, such as low melting point, negligible vapor pressure, excellent thermally stability and especially adjustable structure by changing components of cations and anions. In recent research, some studies have reported that the extractive combined with catalytic oxidative desulfurization (ECODS) strategy gaining importance in desulfurization process.

J. Wang et al.[18] investigated the application of novel Lewis acidic ionic liquids synthesized with organic base and lewis acid(ODBU]Cl/nZnCl2) have been developed and utilized with hydrogen peroxide (H_2O_2,30Wt %) as an oxidant for model oils. The desulfurization conditions were optimized by varying the proportion of lewis acid. The critical reaction parameters such as temperature, molar ratios of reagent and molar ratios of oxidant. Furthermore, the recyclability of novel catalyst has been studied. The removal efficiency of BT, DBT, 4-MDBT, and 4,6-DMDBT from model fuel were 93%, 97%, 94%, and 95%, respectively

Dharaskar et al [19] experimented the ODS process using imidazolyl ionic liquids with composition of 1-butyl-3-methylimidazolium tetrafluoroborate for extractive desulfurization of liquid fuel. Detailed analysis of synthesized ionic liquid was captured, in addition its properties like conductivity, solubility and viscosity analysis were carried out. Further, recycling of ionic liquids carried out without regeneration of catalyst upto four times. Significantly, through the years numerous research studies have been conducted using ionic liquid in catalytic ODS of fuel oil.

Shao et al. [20] investigated series of the imidazolium-based phosphoric ionic liquids were synthesized and used for extractive oxidative desulfurization of heavy oils. Among several catalysts screened, the hexaammonium heptamolybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}·4H_2O$) as catalyst and 30 wt % hydrogen peroxide (H_2O_2) solution as oxidant found to be best system for efficient removal of sulfur system. Furthermore, the effects of the of ionic liquids, ILs/oil mass ratio, reaction temperature, reaction time, and regeneration of ionic liquid on the thiophene nucleus sulfur removal were investigated in detail.

2.4. Molecular Sieve Catalytic Oxidation System

Zeolites can be modified with different metal ion such as Fe2+, K+, Ag+, Cu+, Ni2+, Zn2+, andCe4+ and Pd2+ by ion exchange or impregnation methods. Modified zeolites with these metal ions increase the selectivity and adsorption capacity. The adsorption on zeolites mainly occurs by reactive adsorption, selective adsorption, and π-complexation with sulfur compounds used by zeolites for the removal of sulfur compounds.

Tian et al. [21] studied, structured CeY(meso-CeY) zeolite demonstrated higher desulfurization performance compared to microporous CeY in the presence of solvent. Furthermore, the structural characterization specifies that the mesopore present in zeolites is benefit to the selective adsorption desulfurization, due to swelling up of pores. The paper mentions the preparation of structures CeY zeolites and characterization of prepared zeolites.

Sun et al. [22] investigated the use of modified NaY zeolites with 0.09 M NaOH (NaY-0.09) aqueous solution and transition-metal ions. The resultant modified zeolites (NaY-0.09) has the sulfur removal efficiency reached upto 99.9% with much higher adsorption capacity per gram. The modified zeolites (NaY-0.09) on TPD analysis indicated that formation of mesopores and increase in number of weak lewis acid sites, which improved the desulfurization activity.

Dasgupta et.al [23] investigated vapor phase adsorptive desulfurization process on commercial grade diesel with NiY zeolite. The paper mentions advantages over fixed bed adsorptive desulfurization such as easy regeneration at minimum temperature wave between adsorption and regeneration. Further, the zeolite exhibited multi cycle stability.

2.5. Titanium Catalytic Oxidation System

The TS-1 catalyst system gained importance during recent times for the removal of sulfur compounds. However, the TS-1 catalyst for ODS is limited by low catalytic activity and long reaction times. Recently, solutions have been proposed to address these drawbacks found in TS-1 mediated ODS method, like addition of polar solvents, preparation of mesoporous TS-1 and adding metal nanoparticles on TS-1 surface. However, TS-1 as the catalyst still faces many obstacles for industrialization because of difficulty in catalyst separation, long reaction times, high efficiency, and recyclable catalyst, and developing an environment friendly and cheap catalyst.

Zhao et al. [24] examined desulfurization of diesel oil using Ti-containing zeolite photocatalysts with hydrogen peroxide as oxidant. Detailed study has been carried out with respect to amount of photocatalyst and hydrogen peroxide concentration. Further the oxidized sulfur compounds are easily removed due to solubility in water. The achieved rate of sulfur reduction for DBT was 90% and the catalyst was found to be reusable several time.

Yang et al. [25] studied the oxidative desulfurization with mesoporous titanium silicalite-1(TS-1) using a hybrid SiO2–TiO2 xerogel for removal of sulfur refractory compounds from model oil. Comparatively the M-TS-1 has demonstrated more activity than TS-1, due to presence of significantly enlarged mesopore volume than that of conventional TS-1. The characterization revealed the best texture properties and high crystallinity of M-TS-1.

Khorrami and Aghbolabagh [26] reports oxidative-extractive desulfurization using new organic-inorganic hybrid catalyst ($TBAPW_{11}Zn@TiO_2@PAni$). The synthesized new catalyst showed high stability and reusable upto five times without loss of activity. Detailed study has been carried out with respect to time, temperature, and amount of catalyst.

3. Conclusions:

Hydrodesulfurization is a well-established and industrialized technique which employs the use of hydrogen at high pressure and temperature, ultimately increasing the initial and operating investment cost. Through the years, many literature papers has been published of alternative methods to treat refractory sulfur compounds, where HDS process not found to be effective, such as extractive desulfurization, bio desulfurization, extraction with ionic liquids, selective adsorption, and oxidative desulfurization have been proposed in complementary, or as alternatives, to HDS. Amongst these methods, the oxidative desulfurization process has gained more attention due to its mild operating condition and high sulfur removal efficiency. Significantly, through the years the number of papers on ODS steadily increased to satisfy the needs of EPS agencies on reduction of sulfur levels in heavy oil. Knowing the fact, this review has categized the types of ODS catalyst and briefly reviewed about metal free catalyst, POM's, ILS, and molecular sieve catalytic system. However, several initiatives have been proposed to address these drawbacks found in the ODS method, which include developing a cost effective, high efficiency, and recyclable catalyst, and developing an environment friendly and cheap oxidizing agent. Apart from these challenges, the more critical challenge is the scale up of the catalytic oxidative desulfurization process due to some major obstacles, such as low selectivity for the sulphides present in feed and recovery of the used catalysts after the reaction.

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