

## Oxidative Desulfurization of Fuel Oils

JIANG Zongxuan, LÜ Hongying<sup>a</sup>, ZHANG Yongna, LI Can<sup>\*</sup>

State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China

**Abstract:** Several attractive approaches toward oxidative desulfurization of fuel oils, such as using H<sub>2</sub>O<sub>2</sub>/organic acids, H<sub>2</sub>O<sub>2</sub>/heteropolyacid, H<sub>2</sub>O<sub>2</sub>/Ti-containing zeolites, and other non-hydrogen peroxide systems (e.g., *t*-butyl hydroperoxide etc.) are reviewed. A new alternative oxidative desulfurization process using emulsion catalysts was developed mainly by our group, is introduced in detail. Limitations because of interphase mass transfer are greatly reduced in the emulsion reaction medium. The amphiphilic emulsion catalysts can selectively oxidize the sulfur-containing molecules present in diesel to their corresponding sulfones when using H<sub>2</sub>O<sub>2</sub> as the oxidant under mild conditions. The sulfones in the oxidized fuel oils can be removed by a polar extractant. The sulfur level of a prehydro-treated diesel can be lowered from a few hundred μg/g to 0.1 μg/g after oxidation and subsequent extraction whereas the sulfur level of a straight-run diesel can be decreased from 6000 to 30 μg/g after oxidation and extraction.

**Key words:** oxidative desulfurization; emulsion catalysis; extraction; fuel oil

Much interest has been shown over the last decade for the application of oxidative desulfurization (ODS) to liquid fuels [1–5]. This has been because of the very stringent environmental regulations that have limited the level of sulfur in diesel to less than 15 μg/g since 2006 in the US, less than 10 μg/g since 2005 in Europe, and less than 50 μg/g since 2008 in Beijing and Shanghai in China [6,7]. In addition, trace amounts of sulfur can poison the noble metal catalysts used in the reforming and transforming process of fuels and the electrode catalysts used in fuel cell stacks. Hydrodesulfurization (HDS) is highly efficient for the removal of thiols, sulfides, and disulfides. However, it is difficult to reduce refractory sulfur-containing compounds such as dibenzothiophene and its derivatives especially 4,6-dimethyldibenzothiophene (4,6-DMDBT) to an ultra low level using only conventional HDS [8–12]. Severe operating conditions such as high temperatures, high pressures, and high hydrogen consumption are required for HDS to achieve the ultra-deep desulfurization of diesel. High capital and operating costs are inevitable. Therefore, it is necessary to develop alternative ultra-deep desulfurization processes such as adsorption [1,13–16], extraction [17–20], oxidation [21–25] and bioprocesses [26–30]. Among

these, ODS combined with extraction or adsorption is considered to be one of the most promising processes.

ODS offers several advantages compared with HDS. For example, the refractory-substituted dibenzothiophenes (DBTs) are easily oxidized under low temperature and pressure conditions so expensive hydrogen is not required and, therefore, the capital requirement for an ODS unit is significantly less than that for a deep HDS unit. As the use of expensive hydrogen is avoided, these processes are more suitable for small and medium size refineries; especially those that are isolated and not located close to a hydrogen pipeline [31].

The properties of sulfur and carbon are similar in some ways, e.g., the electronegativity of sulfur is very similar to that of carbon. Therefore, the sulfur-carbon bond is relatively non-polar and sulfur-containing compounds exhibit properties quite similar to their corresponding organic compounds [20]. This is the reason why the solubilities of sulfur-containing compounds and hydrocarbons in polar and non polar solvents are nearly identical.

However, if these sulfur-containing compounds that are present in fuels could be oxidized to their corresponding sulfonates or sulfones their solubility in polar solvents would

Received 10 May 2011. Accepted 18 May 2011.

<sup>\*</sup>Corresponding author. Tel: +86-411-84379070; Fax: +86-411-84694447; E-mail: canli@dicp.ac.cn

<sup>a</sup>Present address: College of Chemistry and Chemical Engineering, Yantai University, Yantai 264005, Shandong, China.

This work was supported by the National Natural Science Foundation of China (20503031, 20673114) and the National Basic Research Program of China (973 Program, 2006CB202506).

Copyright © 2011, Dalian Institute of Chemical Physics, Chinese Academy of Sciences. Published by Elsevier BV. All rights reserved.

DOI: 10.1016/S1872-2067(10)60246-X

increase with an increase in their polarity. The electronic *d*-orbitals of sulfur are available for the oxidation of sulfur-containing compounds that will react with oxidants relatively easily [20]. The dipole moment of the oxidized sulfur-containing compounds increases and they are more soluble in polar solvents.

Generally, desulfurization by selective oxidation involves two main steps: First, the sulfur-containing compounds present in diesel are oxidized to the corresponding sulfoxides and sulfones by an oxidant, and then these sulfoxides and sulfones are removed from diesel by extraction, adsorption, or distillation [32,33].

Currently, the main obstacles to the industrial application of ODS are (1) their low-oxidation activity and their low selectivity for the sulfides present in fuel oils, (2) the difficulties in separation and recovery of the catalysts after the reactions, (3) the low utilization efficiency of  $H_2O_2$ , and (4) the introduction of other components to the oxidation systems [21,25].

Oxidative desulfurization was reported in the literature as early as 1954 [34,35]. However, it was not paid much attention before the current regulations requiring the production of ultra-low sulfur fuel oils. In the last decade many types of oxidative systems have been investigated such as  $H_2O_2$ /organic acids [17,20,36],  $H_2O_2$ /heteropolyacid [3,37],  $H_2O_2$ /Ti-containing zeolites [38–41], and other non-hydrogen peroxide systems (e.g., *t*-butyl hydroperoxide (TBHP),  $O_2$  etc.) [34,42–44]. Some promising systems are discussed below.

## 1 Oxidative desulfurization

### 1.1 $H_2O_2$ /organic acid system

The major organic acids used in ODS are acetic acid and formic acid. For example, conversion/extraction desulfurization (CED) technology began in 1996 when Petro Star Inc. combined conversion and extraction to remove sulfur from diesel fuel [20]. First, the fuel is mixed with  $H_2O_2$ /acetic acid (peroxyacetic acid) and the oxidative reaction takes place below 100 °C under atmospheric pressure. This is followed by a liquid/liquid extraction to obtain a fuel with low sulfur and an extract with high sulfur. Finally, the low sulfur fuel may require additional treatment. The extraction solvent is then removed from the extract for re-use and the concentrated extract is made available for further processing to remove sulfur and to produce hydrocarbon (see Fig. 1).

In a laboratory-scale experiment the fuel did not change significantly and it remained within the quality guidelines. The sulfur levels were markedly reduced from 4720  $\mu\text{g/g}$  to 70  $\mu\text{g/g}$  after processing and the American Petroleum Institute (API) gravity as well as the cetane number improved.

The extraction solvent is also important for the success of this process. In the CED process the production of cost effective solvent cocktails is most important. High desulfurization

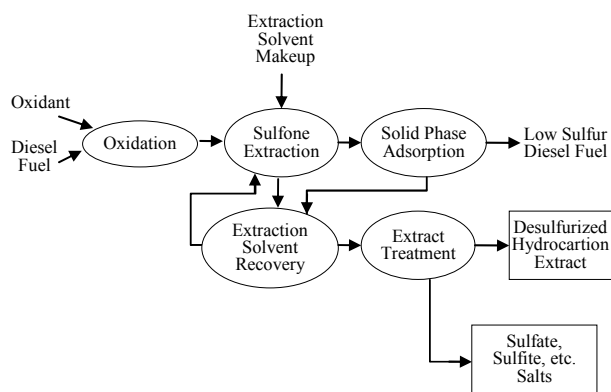


Fig. 1. Simplified diagram of the CED technology [20].

efficiencies are required and only a slight influence on the non-polar fuel constituents is allowed.

The reactivity of the different sulfur-containing compounds including methyl phenyl sulfide, thiophenol, diphenyl sulfide, 4-methyldibenzothiophene (4-MDBT), DBT, benzothiophene (BT), 2-methylthiophene (2-MT), 2,5-dimethylthiophene (2,5-DMT), and thiophene was investigated for selective oxidation using hydrogen-peroxide and formic acid by Otsuki and colleagues [45]. The relationship between the electron densities of the sulfur atoms, which was estimated by molecular orbital (MO) calculations, and the oxidative reactivities of the sulfur-containing compounds was also investigated. The electron densities on the sulfur atom of the sulfur compounds are shown in Table 1. The electron densities of the thiophene derivatives varied between 5.696 (thiophene) and 5.760 (4,6-DMDBT). 2,5-DMT, 2-MT, and thiophene usually oxidize with difficulty because of their lower electron densities. BT (electron density 5.739) and other model compounds with higher electron densities were oxidized to form their corresponding sulfones. These apparent rate constants (*k*) decrease as follows: 4,6-DMDBT > 4-MDBT > DBT > BT. This result indicates that the rate constant increases with an increase in electron density (see Fig. 2).

A hydrogen peroxide and formic acid oxidizing system was also used to study the influence of the solvent on the oxidation rate of the sulfur-containing compounds in the organic phase [46]. The results indicate that heterocyclic sulfur-containing compounds such as benzo- and dibenzothiophene have different kinetic processes compared with thiols and sulfides. The aromaticity of organic solvents has a considerable influence on oxidation rates.

### 1.2 $H_2O_2$ /heteropolyacid system

A new alternative oxidative desulfurization process has been introduced by British Petroleum to avoid the use of organic or inorganic acids [3]. In this process, the oxidation of dibenzothiophene was studied with hydrogen peroxide using phosphotungstic acid as the catalyst and tetraoctylammonium

Download English Version:

<https://daneshyari.com/en/article/60272>

Download Persian Version:

<https://daneshyari.com/article/60272>

[Daneshyari.com](https://daneshyari.com)