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Review

Biodesulfurization of diesel fuels – Past, present and future perspectives

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ABSTRACT

The world focus on environmentally friendly fuels requires refiners to convert the increasingly poor-quality crude oil into high-quality finished products. Refineries are facing many challenges including heavier crude oils and increased fuel quality standards. Global society is moving towards zero-sulfur fuel and hydrodesulfurization (HDS) is the most common technology used by refineries to remove sulfur from intermediate streams. However, HDS has several disadvantages and therefore recent research has focused on improving HDS catalysts and processes and also on the development of alternative technologies. Among the alternative technologies one possible approach is biodesulfurization (BDS). BDS is a process that is based around bacterial potential. In this process, bacteria remove organosulfur from oil fractions without degrading the carbon skeleton of the compounds. BDS operates at ambient temperature and pressure with high selectivity, resulting in decreased energy costs, low emission and no generation of undesirable side-products. For assessing the potential of BDS as a biorefining process, pilot plants have been operated. The results obtained for BDS may be generally applicable to other areas of biorefining. In this review the history, current status and future challenges of BDS will be discussed. The integration use of BDS systems with existing HDS technology is discussed as a future approach by the oil industry, providing an efficient and environmentally friendly approach to desulphurization.

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1. Introduction

Sulfur is the third most abundant heteroatom in crude oil and can vary from 0.05% to 10% of the composition. The types of sulfur compounds vary greatly within a crude supply (Blumberg et al., 2003). In addition to elemental sulfur, sulfate, sulfite, thiosulfate and sulfide, together with more than 200 sulfur-containing organic compounds have been identified in crude oils (Ma, 2010). Sulfur-containing heterocyclic compounds are among the most potent environmental pollutants. Reducing sulfur levels in fuels can decrease harmful emissions in three ways: (i) directly reducing sulfur dioxide (SO_2) and sulfate particulate matter (PM), (ii) achieving better performance from the emissions control systems, especially catalysts, and (iii) enabling the use of new emission control technologies such as diesel PM filters, NOx absorbers and selective catalyst reduction systems (Stanislaus et al., 2010).

Conventional HDS processes have been employed by refineries to remove organic sulfur from liquid fuels for several decades. This technology is economic in terms of removal of a number of classes of compounds containing sulfur, other than refractory organic sulfur compounds (Breysse et al., 2003). Deep desulfurization of diesel fuel has become an important research subject due to the upcoming legislative regulations to reduce sulfur content. However, to meet the challenges of producing ultraclean diesel fuels, especially with sulfur content lower than 15 ppm, both capital investment and operational costs would be high due to more stringent operating conditions. Consequently, several alternative approaches have been used, including selective adsorption, extraction by ionic liquid, oxidative desulfurization and BDS.

Microbial desulfurization of organosulfur pollutants is attracting more attention because of cost effectiveness and environmental friendliness. However, this technology is not yet available for large-scale applications, so future research must investigate modifications of this process for industrial applications (Xu et al., 2006). Several previous reviews outline progress in microbial desulfurization from the basic and practical point of view (McFarland et al., 1998; Monticello, 1998; McFarland, 1999; Ohshiro and Izumi, 1999; Tong et al., 2001; Acero et al., 2003; Gray et al., 2003; Gupta et al., 2005; Kilbane, 2006; Soleimani et al., 2007; Mohebali and Ball, 2008; Xu et al., 2009; Debabov, 2010; Nuhu, 2013; Boniek et al., 2015). A recent mini-review on the role of biotechnology in the petroleum industry (Bachmann et al., 2014) highlighted the potential significance of BDS although few details were presented. In this current review, attention is focused solely on the biodesulfurization of diesel fuels as an alternative technology, which has become an important research subject.

2. Sulfur in petroleum and its fractions

In crude oil, sulfur is present in soluble organic form, the principal generic groups being: (i) aliphatic and aromatic thiols and their oxidation products (disulfides); (ii) aliphatic, aromatic and mixed thioethers, and (iii) heterocyclics based on the thiophene ring: thiophene itself, benzothiophene (BT), dibenzothiophene (DBT), and their alkyl substituted derivatives (Oldfield et al., 1998). The most abundant form of sulfur in petroleum is usually the thiophenic form. Thiophenic sulfur often comprises 50%–95% of the sulfur in crude oil and derived fractions, and alkylated DBTs are the most common organosulfur compounds typically found in crude oil and fractions used to produce diesel (Kilbane and Le Borgne, 2004). In other words the organosulfur compounds found in crude oil are generally classified into two types: non-heterocyclics and heterocyclics. The former comprise thiols, sulfides and disulfides. Cyclic or condensed multicyclic organosulfur compounds are referred to as sulfur heterocyclics (Mohebali and Ball, 2008).

3. Air pollution as a result of fuel combustion

A typical flue gas from the combustion of fossil fuels will contain quantities of NO_X, SO_2 and particulate matter (PM); these gases react in the atmosphere with water, oxygen and other chemicals to form a mild solution of sulfuric and nitric acids. The acid rain dissolves buildings, kills forests and poisons lakes as well as damaging agricultural areas located downwind of combustion facilities (Mohebali and Ball, 2008). Acid rain also damages the environment by upsetting the natural balance of chemicals and can decrease biological diversity of the ecosystems. Traces of sulfur present in the diesel fuels poison the oxidation catalysts in the emission control system and reduce their effectiveness for the oxidation of harmful carbon monoxide, hydrocarbons and volatile organic matter (Stanislaus et al., 2010).

Sulfur is one of the key causes of PM and total PM emissions are proportional to the amount of sulfur in the diesel fuel. According to the U.S. Environmental Protection Agency (USEPA), approximately 2% of the sulfur in the diesel fuel is converted to direct PM emissions. PM has been found to be a human carcinogen (Stanislaus