Chapter 13

Advances in the Reduction of the Costs Inherent to Fossil Fuels' Biodesulfurization towards Its Potential Industrial Application

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ABSTRACT

Biodesulfurization (BDS) process consists on the use of microorganisms for the removal of sulfur from fossil fuels. Through BDS it is possible to treat most of the organosulfur compounds recalcitrant to the conventional hydrodesulfurization (HDS), the petroleum industry's solution, at mild operating conditions, without the need for molecular hydrogen or metal catalysts. This technique results in lower emissions, smaller residue production and less energy consumption, which makes BDS an eco-friendly process that can complement HDS making it more efficient. BDS has been extensively studied and much is already known about the process. Clearly, BDS presents advantages as a complementary technique to HDS; however its commercial use has been delayed by several limitations both upstream and downstream the process. This study will comprehensively review and discuss key issues, like reduction of the BDS costs, advances and/or challenges for a competitive BDS towards its potential industrial application aiming ultra low sulfur fuels.

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INTRODUCTION

The combustion of fossil fuel generates emissions of sulfur as sulfur dioxide (SO₂), which is corrosive and toxic, and as fine particulate matter of metal sulfates. These emissions are responsible for damage in many different areas. Gaseous chemical compounds of sulfur constitute a major health hazard when present in the air: the large-ring thiophenes, such as dibenzothiophene, abundant in crude oil, are toxic to mammals (Murphy, Amin, Coletta, & Hoffman, 1992); SO₂ gas at high levels can cause bronchial irritation and trigger asthma attacks in susceptible individuals and long-term exposure to combustionrelated one particulate air pollution is an important risk factor for cardio-pulmonary and lung cancer mortality (Pope et al., 2002; Mohebali & Ball, 2008). In addition, incomplete burning of liquid fossil fuels causes emissions of aromatic sulfur compounds to the air (Ho & Li, 2002), and the oxidation of sulfur compounds in the atmosphere eventually leads to aerosol of sulphuric acid. This aerosol causes acid rains, which are responsible for the corrosion of many infrastructures and monuments, and even affect several living organisms including agricultural crops, thus causing direct damage to the economy (Bender & Weigel, 2011). The aerosol is also harmful to the stratospheric ozone contributing to the hole on the Earth's protective ozone layer (Denis, 2010). Lastly, sulfur compounds even prevent functioning of all major pollution control technologies such as automobile catalytic converters (Maricq, Chase, Xu, & Laing, 2002), making it more difficult to fight against pollution.

Since gasoline, diesel and non-transportation fuels account for 75 to 80% of the total refinery products (Babich & Moulijn, 2003), it is only natural that countries find the reductions of sulfur concentration in fuels as the most effective way to decrease the amount of SO_2 emitted in to the air and limit its prejudicial effects (Mohebali, Ball, Kaytash, & Rasekh, 2008).

Therefore, in response to the increasing concerns with environmental and health and effects of the SO_x molecules, several countries have started to impose strict limits on the levels of sulfur present in the fossil fuels. This forced the petroleum industry to develop techniques which remove the sulfur from the fuels, such as hydrodesulfurization (HDS), a process that combines high temperatures and pressures with molecular hydrogen in the presence of complex metal catalysts. However, this process is not very effective at removing heterocyclic sulfur compounds, which can account to up to 70% of the sulfur in petroleum (Borgne & Quintero, 2003), requiring harsher conditions to meet the strict EU sulfur regulations (10 ppm). This deeper desulfurization, with even higher temperatures and pressures, results in an increase of pollution (with $> CO_2$ release), a rise of production costs (resulting from higher energy consumption) and, sometimes, a loss of octane value (Khedkar & Shanker, 2014; Mohebali & Ball, 2008; Srivastava, 2012).

For this reason, oil desulfurization has become an increasingly studied area, and there have been many different approaches to solve these problems, such as the development of new combinations of metal catalysts for HDS, the study of techniques such as catalytic oxidation, desulfurization by adsorption, chemical desulfurization, physical desulfurization, photochemical desulfurization, photocatalytic desulfurization, and biodesulfurization (Srivastava, 2012).

The biodesulfurization (BDS) process consists on the use of microorganisms for the removal of sulfur from fossil fuels. Through BDS it is possible to treat most of the compounds recalcitrant to HDS at mild operating conditions, without the need for molecular hydrogen, or metal catalysts (Mohebali & Ball, 2008). If successfully implemented, it will result in lower environmental costs, with a reduction of 70–80% of CO₂ emissions, smaller residue production, and reduced energy consumption, which in turn translates in reduced capital (two thirds of HDS) and operational costs (10-15% lower) (Kaufman

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