

Chapter 12

Nanotechnology Applied to the Biodesulfurization of Fossil Fuels and Spent Caustic Streams

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ABSTRACT

The use of nanostructured materials in combination with desulfurizing microorganisms is a promising technique that would improve the desulfurization processes of gaseous fuels, oil, and some wastewater. Nanoparticles are highly versatile and tunable depending on the necessities of each particular contaminated media. The chapter shows the current technological options for the biodesulfurization of natural gas, oil and wastewater produced from the petroleum refining, where the application of nano-sized materials combined with desulfurizing microorganisms would improve the desulfurization capacities. In addition, advantages, disadvantages and opportunities of this hybrid technology are presented.

INTRODUCTION

Sulfur in Gaseous Fuels

The world's energy requirements have strongly increased due to the growing industrialization, especially in emerging economies. Fossil fuels still represent the main energy source around the world. Among these various energy sources, gaseous fuels have been increasingly used because of their easier exploitation and their somewhat more environmentally friendly impact (i.e. natural gas). However, these gaseous fuels

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commonly contain significant concentrations of hydrogen sulfide (H_2S), and other sulfur species such as carbon disulfide (CS_2), carbonyl sulfide (COS) and organic sulfides (see Table 1). On the other hand, non-fossil fuels used such as coal, oil, peat, wood, and other organic materials contain sulfur, which is released as SO_2 after combustion. In combination with the humidity of the atmosphere, SO_2 produce the recurrent problem of acid rain that can cause severe damage to ecosystems. Sulfur poisoning of chemical catalyzer is another frequent problem during cracking and refining of crude petroleum.

Spent Caustic Streams

The spent caustic streams are wastewater originated from petroleum refining process. In petroleum refining, H_2S is removed from fuel gases by scrubbing into a sodium hydroxide solution, producing sulfides (HS^- and S^{2-}). The resulting sulfidic caustic aqueous solution can contain sulfide concentrations exceeding 2 - 3 w/w ($0.6 - 0.9 \text{ mol L}^{-1}$), at pH greater than 12 and even other organic sulfur and aromatic compounds (Sipma, *et al.* 2004). Maintaining these streams under alkaline conditions would limit the emission of foul sulfide odorants. Olmos, *et al.* (2004) reported a characterization (Table 2) of spent caustic and sour waters produced in a Mexican petroleum refinery.

The aim of this chapter is to show the current technological options for the biodesulfurization of fossil fuels such as natural gas, oil and wastewater produced from the petroleum refining, where the application of nano-sized materials combined with desulfurizing microorganisms would improve the desulfurization capacities. In addition, advantages, disadvantages and opportunities of this hybrid technology are presented.

BACKGROUND

Conventional Desulfurization Methods

Several inorganic materials have been used for effective sorption of sulfur related compounds from fossil fuels in the recent years. Metal oxides of Fe, Zn, Mn, Mo, V, Ca, Sr, Ba, Co, Cu, Si and W have been particularly used for sulfur scavenging (Meng, *et al.* 2009). The general equation for desulfurization reactions is:

Table 1. Typical compositions of various gaseous fuels

Gaseous Fuels	Composition (% v/v)							
	Other S*	H_2S	H_2	CO_2	CH_4	N_2	CO	HC**
Natural gas	≈ 0.25	3.8–8.6	≈ 0.3	2–18	36–71	54–58	—	≈ 3.0
Distillery Biogas	≈ 0.003	1.2–2.5	≈ 0.04	22–28	58–64	1.5–5	—	—
Refinery fuel gas	≈ 0.03	4.5–7.5	≈ 20	11–15	≈ 1.5	50–59	≈ 18	≈ 2
Coke oven gases	≈ 0.03	0.3–4.8	≈ 15.0	24–28	≈ 50	≈ 0.15	≈ 10	≈ 0.02
Coal gasification	≈ 0.017	0.6–2.0	≈ 21	15–26	5–26	≈ 27	9–22	≈ 0.6

(González-Sánchez & Revah, 2006).

* CS_2 , Mercaptans, and thiophene, **HC Hydrocarbons.

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