Chapter 6
Coordination Polymers and Polymer Nanofibers for Effective Adsorptive Desulfurization

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ABSTRACT

Desulfurization of fuel oils is an essential process employed in petroleum refineries to reduce the sulfur content to levels mandated for environmental protection. Hydrodesulfurization (HDS), which is currently being employed, is limited in treating refractory organosulfur compounds and only reduces the sulfur content in fuels to a range of 200-500 ppmS. In this chapter, several scientific and technological advances reported in the literature for the desulfurization of fuels are reviewed and discussed. Amongst these techniques, oxidative desulfurization (ODS) and adsorptive desulfurization (ADS) are proposed as additional steps to complement HDS in meeting the mandated ultra-low sulfur levels (10 ppmS). In the ODS technique, refractory organosulfur compounds are oxidized to organosulfones, followed by solvent extraction

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or adsorption of the organosulfones. The chemistry involved in the development and fabrication of sulfur/sulfone responsive adsorbents is also discussed. The use of molecular imprinted polymers (MIPs) and coordination polymers (CPs) for the selective adsorption of organosulfone compounds (in ODS) and/or organosulfur (in ADS) offers various properties such as imprinting effect, hydrogen bonding, π-π interactions, van der Waals forces, π-complexation, and electrostatic interactions. CPs, in particular metal organic frameworks (MOFs), have been reported to possess suitable features to overcome most of these challenges associated with adsorptive ultra-deep desulfurization when design strategies to achieve good selectivity are strictly followed. Matching the sizes of the cavities to the critical dimensions of the sulfur containing compounds (SCCs), using suitable metal centres which allow for coordinative interaction with the SCCs and using linkers with suitable functionality as to enhance specific interaction (dispersion forces) with the SCCs were considered to be pivotal features to prioritize. The prospects for the use of MIPs and CPs for future industrial applications in desulfurization are envisaged.

INTRODUCTION

Crude oil is a complex blend containing thousands of hydrocarbons, non-hydrocarbon compounds and heavy metals (Sami *et al*. 1994). The hydrocarbons are mixed with variable quantities of sulfur-, nitrogen-, and oxygen-containing compounds. Crude oil is expected to be the source of energy in the world for several decades to a century. Crude oil reserves are distributed around all the continents (Figure 1). The Middle East has the highest reserves of over 750 thousand million barrels and the Asia Pacific region having the least reverses of just over 40 thousand million barrels of oil. Generally, crude oils are refined to separate the complex mixture into simpler fractions that can be used as fuels, lubricants, and as intermediate feedstock for petrochemical industries.

The sulfur content distribution in some crude oil reservoirs around the world is depicted in Figure 2. The sulfur content of crude oils varies appreciably from one reservoir to another. Over 70% of the world's oil reserves are classified to be of heavier and sourer composition, meaning they have a high sulfur content. The low sulfur-containing crude oils are referred to as sweet oils and are more desirable due to fewer costs during refinery processes, of which removal of sulfur is an important step. (Source: EPA, 2013; Crude oil reserve, 2013). Removal of sulfur has become important over the years since sulfur oxides produced from the combustion of fuel containing the sulfur compounds are emitted into the atmosphere, constituting serious environmental hazards such as acid rain and the generation of airborne particulate (such as smog and sulfates). Sulfur oxides also poison and deactivate catalytic converters in vehicles, while smog and particulates, on the other hand,