

Chapter 10

Molecularly Imprinted Polymer Nanofibers for Adsorptive Desulfurization

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ABSTRACT

Desulfurization of fuel oils is an essential process employed in petroleum refineries to reduce the sulfur concentration in fossil fuels in order to meet the mandated environmental protection limit of 10 ppm sulfur. The hydrodesulfurization (HDS) process, which is currently being employed for desulfurization, is limited in treating refractory organosulfur compounds as it only reduces sulfur content in fuels to a range of 200-500 ppm sulfur. Oxidative desulfurization (ODS) is considered a new technology for desulfurization of fuel oils as the process is capable of desulfurizing fuels to reach the ultra-low sulfur levels and can serve as a complementary step to HDS. The chapter discusses, briefly, the oxidation of refractory sulfur compounds found in fuels using vanadium as a catalyst to form organosulfones, a first step in ODS process. The chapter also discusses, in detail, the chemistry involved in molecular imprinting of organosulfones on functional polymers, and the electrospinning of the polymeric matrix to produce molecularly imprinted nanofibers employed for selective adsorption of organosulfones from the oxidized mildly hydrotreated fuels, a second step in the ODS process. Chemical interactions, apart from the imprinting effect, that can be exploited in molecularly imprinted polymers for selective extraction of organosulfones, such as hydrogen bonding, π - π interactions, van der Waals forces and electrostatic interactions, were discussed by employing density functional theory calculations. The possibilities of electrospinning on a large scale as well as prospects for future industrial applications of functional molecularly imprinted nanofibers in desulfurization are also discussed.

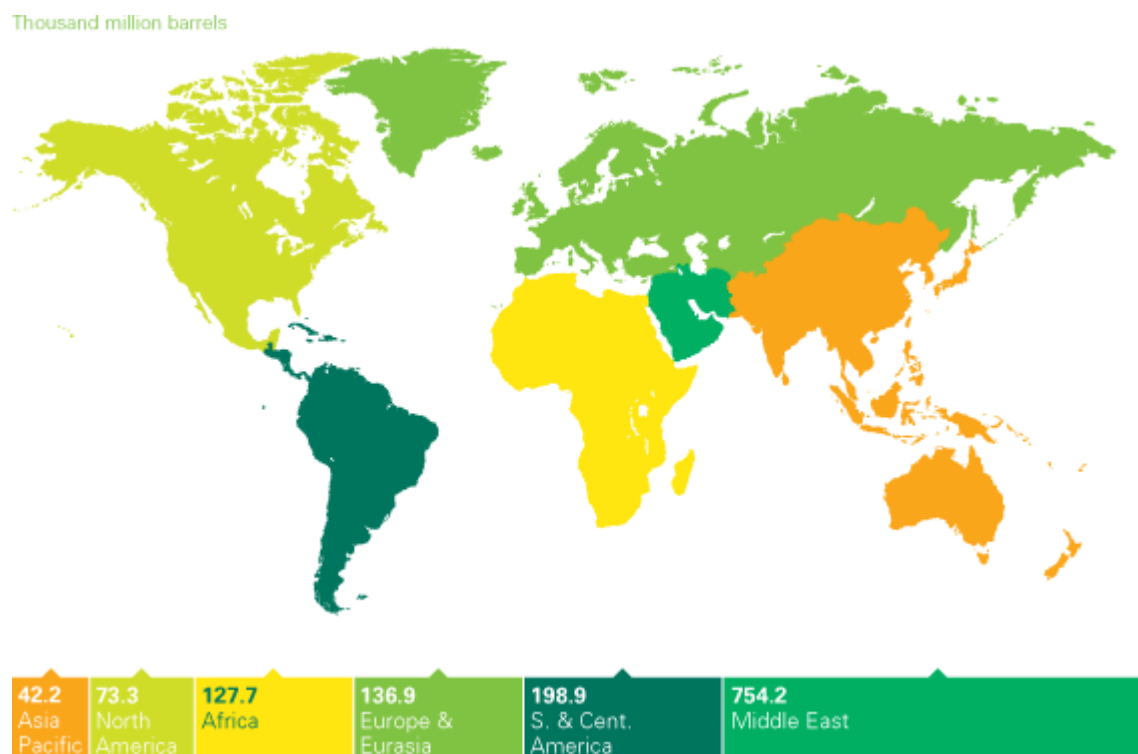
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INTRODUCTION

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, and the 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 reserves 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.

However, it is known that over 70% of the world's oil reserves tend to be of heavier and sourer composition, i.e. have a high sulfur content. The sulfur content distribution in some crude oil reservoirs around the world is depicted in Figure 2. It can be seen that the sulfur content of crude oils varies appreciably from one reservoir to another. The low sulfur containing crude oils are referred to as sweet oils, while the high sulfur containing crude oils are referred to as sour crudes and are less desirable due to the high cost involved in refining the oils (Source: EPA, 2013; Crude oil reserve, 2013). Sulfur oxides are produced from fuel containing sulfur compounds during combustion and these emissions constitute a serious environmental hazard 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,

Figure 1. Crude oil reserves distribution around the continents of the world
(Source: EPA, 2013; Crude oil reserve, 2013).



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