Chapter 1
Sulfur in Petroleum:
Petroleum Desulfurization Techniques

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ABSTRACT

This chapter describes the occurrence of organosulfur compounds in petroleum, their detrimental effects and various techniques for removal of these compounds. The sole commercial desulfurization process i.e. HDS is broadly discussed in terms of reaction conditions, different types of catalysts used, reactor design and mechanistic pathways in the process. The shortcomings of HDS and needs for developing new desulfurization techniques is also described. Various newly developed research techniques for desulfurization are also discussed with their technical backgrounds, commercial overview, advantages and shortcomings in the light of literature reports. These techniques include, Adsorptive desulfurization, Bio-desulfurization, Precipitative desulfurization, and Oxidative desulfurization with its sub types like ODS using H2O2- Polyoxometalates (POM), ODS with Ionic liquids, Photo-oxidative desulphurization and Ultrasound Assisted ODS.

INTRODUCTION

Sulfur occurs in crude petroleum in different forms and in varying quantities. But in petroleum the presence of sulfur compounds is undesirable because of several reasons, such as causing corrosion problems, deactivating catalysts in various refining processes and contributing to environmental pollution. The problem of environmental deterioration is increasing steadily as the energy demand increases with growth of the world's population; therefore, worldwide environmental regulation authorities are imposing strict regulations to limit the amount of sulfur in petroleum based liquid fuels.

At present, the commonly used industrial process for removal of sulfur from petroleum is hydrodesulfurization (HDS), which involves treatment of petroleum fractions in a special reactor at high temperature (300-500 ^{o}C) in the presence of a catalyst and hydrogen gas under high partial pressure (30-300 psi). The requirements of HDS process make it a too expensive operation. Furthermore, HDS cannot eliminate certain refractory sulfur compounds from petroleum and therefore cannot attain low level desulfurization

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under its normal operating conditions. Thus, petroleum desulfurization is a challenging task for the refiners under the current environmental regulations. Keeping in view this scenario, worldwide researchers are striving to develop new desulfurization techniques that are cost effective and more efficient than HDS. In this regard, several new techniques for desulfurization of petroleum have been introduced, including extractive desulfurization, adsorptive desulfurization, desulfurization by polymer membranes, precipitative desulfurization, bio-desulfurization and oxidative desulfurization. All these techniques are still in stages of technological improvements since each one has its own advantages and drawbacks.

This chapter gives detailed account of different types of sulfur compounds occurring in petroleum, their hazardous effects and various processes used for desulfurization of petroleum. The main objectives of this chapter include,

- To identify the nature and types of different sulfur compounds presents in crude petroleum and their distribution in distillate fractions.
- To know various problems associated with sulfur compounds present in petroleum.
- To understand the technological background of different desulfurization techniques and identify the limitations of each.
- To highlight the developments occurred in different desulfurization processes over the past few decades.

1. OCCURANCE OF SULFUR IN PETROLEUM

In crude petroleum, sulphur exists as a non-hydrocarbon constituent in different concentrations. Petroleum crudes obtained from different oilfields contain different quantities and types of sulphur compounds. Generally in heavier crude oil, the proportion and complexity of the sulphur compounds is usually greater than the lighter crudes. The concentration of sulphur in crude petroleum may range from trace amounts to as high as 8 wt%, depending upon its source e.g. the sulphur content in some light Pennsylvanian crude is about 0.05%, in heavy Mexican or Mississippi crude as high as 5% or even more, whereas Middle East crude contain about 2.1% sulfur (Birch et al., 1925).

Based on their nature, sulfur compounds in petroleum, may be divided in two categories i.e. sulfur in organic form and in inorganic form. In inorganic form sulfur is present as H_2S, elemental sulphur, and pyrites which are dissolved or suspended in crude petroleum. In organic form the sulphur is bounded to a hydrocarbon molecule as a heteroatom, these compounds may be classified as thiols, sulfides, thiolanes, thiophenes, benzothiophenes, benzonapthothiophenes and their alkylated derivatives (Agarwal et al., 2009).

On the basis of their reactivity, sulphur compounds occurring in crude petroleum may be classified in two classes, namely active sulfur and inactive sulfur compounds. Active sulfur compounds are those which directly react with metals and causes corrosion, including H_2S, mercaptans, elemental sulphur and lower sulphides. The active sulfur compounds impart corrosive action to the sour crudes, but due to their high reactivity these compounds can be easily removed from petroleum. The second class, inactive sulfur compounds cannot react readily with metals and it includes aromatic sulphur compounds i.e. thiophene, benzothiophene, dibenzothiophenes, benzonapthothiophenes and their alkyl substituted derivatives, etc.