Fuel Processing Technology 98 (2012) 30–38

Contents lists available at SciVerse ScienceDirect

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

Review

A review of electrochemical desulfurization technologies for fossil fuels

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ARTICLE INFO

Article history:
Received 21 April 2011
Received in revised form 9 January 2012
Accepted 22 January 2012
Available online 20 February 2012

Keywords:
Electrochemical desulfurization
Fossil fuel
Heavy crude oil
Coal
Catalysts

ABSTRACT

Desulfurization is an important process for crude oil upgrading. Electrochemical desulfurization technologies have advantages over conventional hydrodesulfurization technologies in terms of low temperature and pressure operation with high product selectivity and therefore less energy consumption. In this paper the authors reviewed the research done in the past decades on electrochemical desulfurization for fossil fuels. The principles, electrochemical methods, electrochemical reactors, catalysts and electrolytes employed in the electrochemical desulfurization process were discussed; and future research work is recommended.

Contents

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0378-3820/$ – see front matter.
doi:10.1016/j.fuproc.2012.01.022

1. Introduction

As conventional oil reserves deplete, unconventional oil reserves including heavy oil, extra heavy oil, and oil sands and bitumen, which comprise of 70% of the world's total oil resources, are becoming more important [1,2]. With rising oil prices, the production of synthetic crude oil from unconventional resources such as oil sands is becoming increasingly economically viable [1]. However, these unconventional oils contain fairly large quantities of contaminants such as sulfur, nitrogen, nickel, and vanadium. For example, a sulfur content of 4.86 wt.% was reported for Athabasca oil sand bitumen [3]. Typical organic sulfur containing compounds in oil include thiophene, benzothiophene, dibenzothiophene, benzonaphthothiophene, dinaphthothiophene, mercaptans, and sulfides. In addition, oil contains inorganic sulfur such as elemental sulfur, and sulfides [4].

The combustion of high sulfur content fossil fuels can release harmful sulfur oxides into the air and therefore pose serious environmental problems. Thus, great efforts have been made to decrease the sulfur content in fossil fuels. Currently the widely used technology is hydrodesulfurization (HDS). HDS is a process in which crude oil is heated at high pressures and temperatures in the presence of hydrogen and catalysts. The resulting products are low sulfur oil and hydrogen sulfide gas that is removed in a post treatment step via the Claus process. However, HDS faces problems of high energy consumption, high cost of raw materials, and undesired by-product formation. In addition, while the goal is to obtain a low-sulfur fuel product, HDS can lead to a loss in octane (for gasoline) due to saturation of the olefins present in naphthas. Thus other desulfurization techniques with low cost and low energy consumption are needed.

Electrochemical desulfurization (ECDS) technology has been explored to remove sulfur by the electrochemical oxidation or reduction of sulfur compounds in fossil fuels [5–7]. This technology is able to remove sulfur at relatively low temperatures and pressures, which potentially makes the process much less energy intensive and more economical than conventional technologies. In ECDS, there is also a degree of freedom to control products by adjusting the applied potential. Promising results have been reported using this technique. However, the ECDS technology is still in its early development stage, and further research is needed to push this technology toward commercialization. With the intension to facilitate the research and development, we reviewed the progress of this technology, and discussed the principles and technology development for the electrochemical desulfurization of fossil fuels. As the organic compositions of coal, petroleum products, and bitumen are similar, a method for one can provide insight into methods for the others. In this review particular attention is paid to the desulfurization of petroleum feedstocks, including those derived from oil sands bitumen.

2. Principles of electrochemical desulfurization

2.1. Oxidation and reduction of organic sulfur compounds

Electrochemical desulfurization is based on the reduction and/or oxidation of sulfur-containing compounds in fossil fuels. The electrochemical cathodic reduction of organic sulfur compounds (expressed as R-SH) leads to the formation of H_2S, as shown in Eq. (1):

$$R-SH+2H^{+}+2e^{-}=R-H+H_2S. \quad (1)$$

The resulting H_2S can be removed by a gas/liquid separation process.

The electrochemical anodic oxidation of organic sulfur compounds is expressed as Eq. (2):

$$R-SH+4OH^{-}-4e^{-}=RH+SO_2+2H_2O. \quad (2)$$

In Eq. (2), SO_2 represents RSH oxidation products, which might be O-containing RSH molecules (e.g. RSO_xH). The addition of oxygen to sulfur-containing compounds increases the polarity of the sulfur compounds so that they can be removed by extraction with polar solvents or by adsorption with polar adsorbents.

2.1.1. Reduction of sulfur compounds

Using sulfur model compounds such as thiophene and benzothiophene, the concept of electroreductive desulfurization of heavy hydrocarbons seems to be feasible [8–11]. Although electroreductive desulfurization enables easy separation of the resulting H_2S from the hydrocarbon feed, it has been found that the hydrocarbon feed may also polymerize, and sulfur oligomers may form and remain entrained in the polymerized hydrocarbon feed [12]. In addition, strong electrochemical reducing conditions can lead to contaminant deposition on the catalyst surface, severely deactivating the catalyst over time. In aqueous media under strong reducing potentials, hydrogen may evolve and clean the catalyst surface, although there is also a risk that the evolved hydrogen may cause problems for the catalyst's desulfurization efficiency. In their investigation of the electrochemical reaction of thiophenol derivatives on Pt, Vieira et al. [13] found that the derivatives required potentials much lower than the hydrogen adsorption/evolution potential on a Pt catalyst, resulting in much lower desulfurization efficiencies due to competition between the derivatives and hydrogen evolution.

2.1.2. Oxidation of sulfur compounds

Electrooxidative desulfurization has the advantage of not forming H_2S, a highly toxic gas. However like electroreductive techniques, electrooxidation can result in the formation of sulfur oligomers. In inventions that implemented electrooxidative desulfurization [14–19], sulfur was removed through physical separation of the formed sulfur

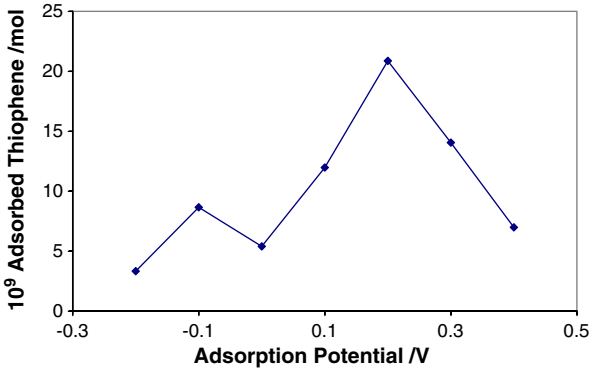

Fig. 1. The amount of thiophene adsorbed vs. the adsorption potential.
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