

Oxidative Desulfurization of Diesel Fuels Using Air by in-situ Hydroperoxide Generation for Fuel Cell Application

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Introduction

Ultra-low-sulfur diesel which essentially means sulfur levels of 15 ppm or less has been a topic of interest over the past decade due to the strict environmental regulations [1,2]. Under the 80/20 temporary compliance of EPA, 80% of the on-road diesel sold in US is under 15 ppm and by 2012 all diesel sold in US will be under 15 ppm. The potential of developing fuel cell processors using diesel and logistic fuels as feeds are being explored because of their high energy density, safety, ease of handling and storage. However even with the so-called ultra-low-sulfur fuels with only <15 ppmw in diesel fuels or <30 ppmw sulfur in gasoline [2], the sulfur contents are too high and very detrimental to the reforming catalysts in the fuel cell processor and also to the noble metal catalysts in the electrodes of fuel cell [1].

For diesel fuel, removing the last few sulfur compounds down to what is required for fuel cell application [<1 ppmw for proton exchange membrane fuel cell] is still a big challenge because of the alkylated dibenzothiophene especially 4,6-dimethyl dibenzothiophene. Removal of 4,6-DMDBT is much difficult by the conventional hydrodesulfurization process or by adsorption using Ni-based adsorbents [PSU-SARS] since the sulfur atom is sterically hindered by the methyl groups [2]. But the high electron density of sulfur atom in 4,6-DMDBT makes it more favorable for oxidation to 4,6-dimethyldibenzothiophene sulfone [4,6-DMDBTO₂] which are relatively easier to remove by adsorption because of its high polarity. Most of the studies involving oxidative desulfurization employ the use of liquid oxidants which results in storage and handling issues with very little work on air oxidation [3-5]. In this work, hydroperoxides were generated in-situ in diesel fuel by air oxidation of alkyl aromatics which were used for oxidation of the refractory sulfur compounds.

Materials and Methods

Two real diesel fuels were used in this study whose sulfur concentrations were 40 ppmw and 15 ppmw S. Air oxidation of diesel fuel was carried in a batch reactor both catalytically and non-catalytically for generating hydroperoxides in-situ. Sulfur compounds present in the fuel were oxidized using the hydroperoxides generated in-situ at atmospheric pressure and 80°C catalyzed by MoO₃/SiO₂. Adsorption performance of the parent diesel fuel and diesel fuel containing oxidized sulfur compounds were compared. Fuel before and after air oxidation were analyzed for peroxides by ASTM D 3703-99 procedure. Qualitative comparison of sulfur compounds present in the diesel fuel before and after oxidation was carried out by HP 5890 chromatograph (XTI-5, 30 m in length and 0.25 mm in internal diameter) equipped with pulsed flame photometric detector (PFPD). Total sulfur concentration in fuel was analyzed by using Antek 9000 series total sulfur analyzer.

Results and Discussion

Figure 1 shows the PFPD chromatogram of the diesel fuel containing 40 ppmw S at different stages of the reaction. Figure 1 (b) shows the PFPD chromatogram after air oxidation of diesel fuel to produce hydroperoxides in-situ, from the figure it can be seen simultaneous oxidation of sulfur compounds also occurs during air oxidation. Figure 1 (c) shows the PFPD chromatogram of the oxidized sulfur compounds in the diesel fuel after oxidation of sulfur compounds using hydroperoxides generated in-situ which can be seen from the concentration of the peroxide expressed in mg/kg.

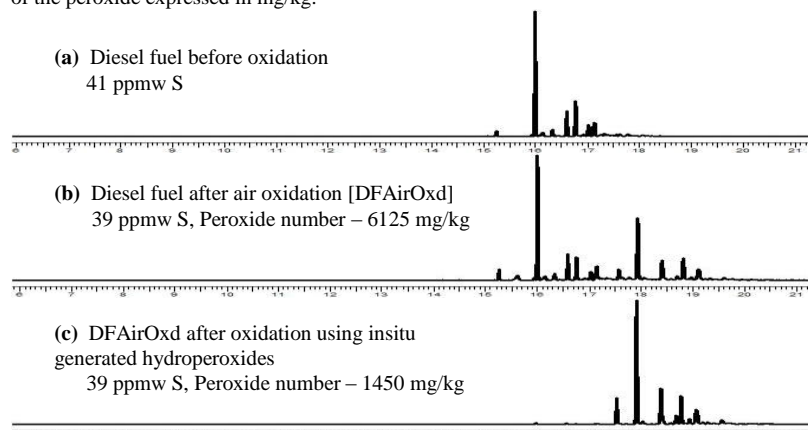


Figure 1. PFPD chromatograms of diesel fuel before and after in-situ oxidation using air.

Oxidation of the sulfur compounds is represented by the formation of new peaks in figure 1 (b) and (c).

Significance

Hydroperoxides can be generated in-situ by air oxidation of alkyl aromatics catalytically/non-catalytically which can be used as effective oxidants for catalytic oxidation of sulfur compounds in diesel fuels. This method has been shown to be effective and can remove sulfur down to <1 ppm level when coupled with selective adsorption.

References

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