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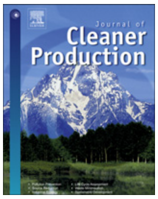

The study of ultrasound-assisted oxidative desulfurization process applied to the utilization of pyrolysis oil from waste tires

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ABSTRACT

In recent years, the increasing world population and rapid industrial development has increased the consumption of fossil fuel-derived oils. In response to the resulting exhaustion of fossil fuel energy, many countries around the world are investigating methods of waste energy recovery and reuse, including oil recovery from the pyrolysis process of waste tires. This study investigates the efficiency of an ultrasound-assisted oxidative desulfurization (UAOD) process in sulfur reduction from diesel oil and the pyrolysis oil from waste tires treatment. The results indicate that the oxidation efficiency increases as the doses of transition metal catalyst are increased. Longer sonication time also enhances the oxidation process, apparently through the biphasic transfer of oxidants, which results in a high yield of organic sulfur oxidation products. The best desulfurization efficiency was 99.7% (2.67 ppm sulfur remaining) and 89% (800 ppm sulfur remaining) for diesel and pyrolysis oils, respectively, via a process executed by two UAOD units connected in series and combined with solid adsorption using 30 g of Al_2O_3 in 6 cm columns. These batch experiment results demonstrate clean waste energy recovery and utilization, while fulfilling the requirements of Taiwan EPA environmental regulations (sulfur concentrations less than 5000 ppm).

1. Introduction

In the past three decades, the increasing world population and rapid industrial developments have drastically increased the consumption of fossil fuel-derived oils. The current use of fossil fuels in various sectors for heat and power generation continues to threaten global stability and sustainability (Dovì et al., 2009; Battaglini et al., 2009). Thus, countries around the world have devoted their resources to solving the shortage of fossil fuel energy and lowering energy costs. In general, the predominant energy policies have been divided into two categories: 1) the development of renewable energy resources and 2) the recycling and reuse of waste energy.

Though by-products, industrial and municipal solid wastes may still possess economic value as energy sources, depending on their quality and market accessibility (Tsai and Chou, 2004; Tsai, 2010). For this reason, researchers have begun to develop chemical treatments for recycling solid wastes to recover their leftover energy (Dodbiba et al., 2008; Stehlik, 2009). The pyrolysis process utilized for oil recovery from the waste of rubber and polymer production and cotton ginning procedures is receiving marked attention in some developed countries (Zabaniotou and Andreou, 2010). However, there is a serious environmental concern that the recovered oils from the pyrolysis of waste tires contain high organic sulfur concentrations in their final products. Upon combustion, the organic sulfur compounds (OSCs) in pyrolysis-recovered oil produces SO_2 and sulfate particulate matter (PM) emissions that endanger public health and welfare (Wan and Yen, 2007). Previous research has shown that such OSCs in petroleum can poison catalytic converters, corrode parts of internal combustion engines, and lead to air pollution. Because the sulfur compounds poison the shift catalyst in the hydrocarbon conversion

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Abbreviations: BTs, Benzothinphenes; DBTs, Dibenzothiophenes; GC/SCD, Gas Chromatograph equipped with a Sulfur Chemiluminescence Detector; HDS, Hydro-Desulfurization; ODS, Oxidative Desulfurization; OSCs, Organic Sulfur Compounds; PM, Particulate Matter; PTA, Phase Transfer Agent; Taiwan EPA, Taiwan Environmental Protection Administration; TMC, Transitional Metal Catalyst; Ts, Thiophenes; UAOD, Ultrasound-Assisted Oxidative Desulfurization.

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process and the electrode catalyst in the fuel cell process, the sulfur content of petroleum fuels utilized in the USA has been decreased to less than 15 ppm. Therefore, in order to improve the life of internal combustion engines and the quality of the air, sulfur removal in any type of burning oil has become an issue of major importance around the world. Furthermore, the Taiwan Environmental Protection Administration (EPA) issued stringent regulations that required the reduction of gasoline sulfur content from 275 to 50 ppm by the year 2007, that of diesel from 350 to 50 ppm and that of heating oil from 350,000 to 5000 ppm by the year 2007. More stringent standards ($<$10 ppm) will be implemented in 2011.

In recent decades, hydro-desulfurization, biocatalytic-desulfurization, liquid/liquid extraction and Oxidative Desulfurization technologies have been developed. In the current industry, hydro-desulfurization (HDS, or distillate hydro-treating) is the largest-scale chemical technique used to remove sulfur from fuel oils. For diesel fuel, recent hydro-desulfurization studies indicate that the organic sulfur compounds remaining at levels lower than 0.1 wt% are alkyl-Dibenzothiophene (DBT) with alkyl substations at the 4- and/or 6-position. These compounds are lower in HDS reactivity and are classified as the most refractory compounds in conventional HDS (Wan and Yen, 2007).

In addition, oxidative desulfurization (ODS) processes have drawn significant attention in the past two decades, and many different ODS technologies have been developed in recent years. Aida and Yamamoto (1994) have reported that peroxyacids are particularly effective oxidants, whereas Collins et al. (1997) recently obtained a DBT conversion of 100% using a phosphotungstic acid/hydrogen peroxide system. Kong et al. (2004) showed the relevant oxidation mechanisms for different sulfur compounds (Fig. 1). In addition, Zannikos et al. (1995) performed a solvent extraction after the oxidation step to reportedly remove 90% of the sulfur in a petroleum fraction under mild conditions. Dolbear et al. (1999, 2000) and Dolbear and Skov (2000) were able to remove refractory sulfur compounds by peroxyacetic acid in the presence of catalysts under ambient temperature and pressure. Moreover, most light gas oil (150 ppm of DBT and 145 ppm of 4,6DMDBT) can be oxidized into sulfones by ozone (Otsuki et al., 1999). The $H_2O_2{-}CF_3COOH$ oxidative system has recently been developed as a new method for super deep desulfurization of diesel (Li et al., 2009).

Despite the progress in ODS method development, the low efficiency of oxidative desulfurization remains a major limitation. Sulfur compounds are known to be slightly more polar than hydrocarbons, with oxidized sulfur compounds like sulfones or sulfoxides being more polar than sulfides. To improve the efficiency of oxidative desulfurization, Mei et al. (2003) and (Wan and Yen, 2007) have utilized these differences to develop an innovative desulfurization technology called Ultrasound-Assisted Oxidative Desulfurization (UAOD), which provides the selective removal of organic sulfur compounds from hydrocarbons by combining procedures of selective oxidation, solvent extraction, and/or solid adsorption (Etemadi and Yen, 2007b). UAOD combines the three complementary techniques of ultrasound, phase transfer catalysis, and transition metal catalysis and can be operated at ambient temperature and atmospheric pressure.

Liquid–liquid extraction, also known as solvent extraction and partitioning, is a method that separates compounds based on their relative solubilities in two different immiscible liquids, usually water and an organic solvent. Highly polar sulfoxides or sulfones can be separated from the nonpolar constituents of oxidized oil via extraction using a polar solvent. Acetonitrile is an optimal choice due to its relatively low boiling point (355 K) and the fact that it can be separated easily from the sulfone solutes by distillation with a boiling point ranging from 550 K to 950 K. Sulfur compounds in light oil are distributed into the acetonitrile phase due to their high polarity (Shiraishi et al., 2002, 1998). Murata et al. (2004) report 80% sulfur removal efficiency from treated oil using solvent extraction with acetonitrile, a result supported by the work of Naito and Hirai (2003). However, the practicality of solvent extraction is hindered by environmental considerations, including the environmental hazards associated with acetonitrile, the possibility of explosions, and the fact that it is non-reusable in this application.

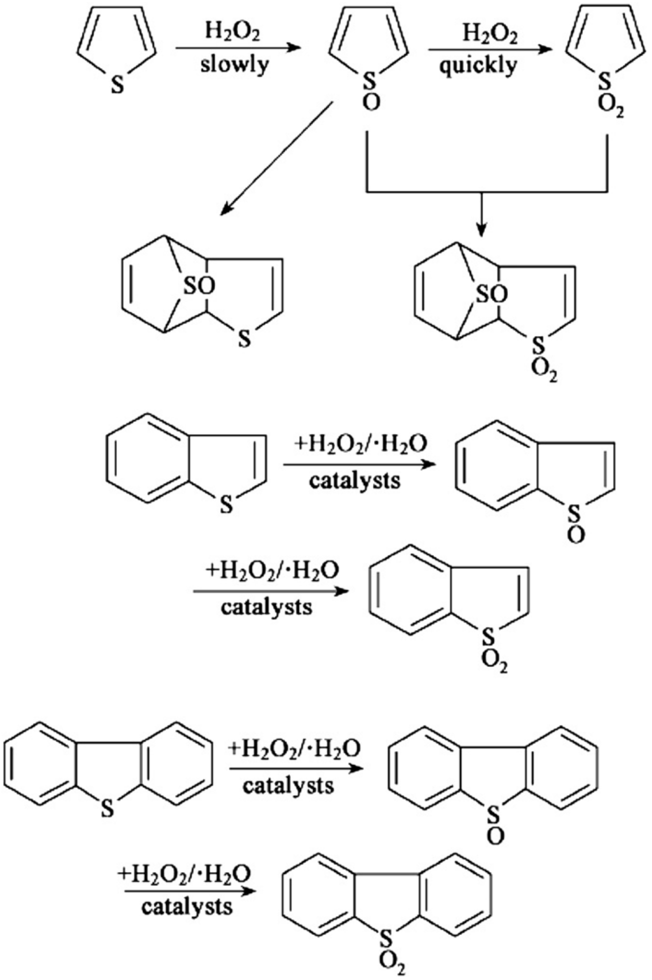

Fig. 1. Oxidation mechanisms of sulfur compounds (Kong et al., 2004).

To avoid the environmental concerns associated with extraction by acetonitrile, an alternative method employing solid adsorption has been investigated as a means of removing organic sulfur compounds from UAOD-treated oil. Studies by Etemadi and Yen (2007a, 2007b) indicate that organic sulfone compounds, which are slightly more polar than organic sulfur compounds (OSCs), can be selectively removed by solid adsorption on alumina oxide at low temperature and atmospheric pressure via UAOD. Similarly, Murata et al. (2004) achieved nearly 100% removal of oxidized sulfur compounds by alumina oxide adsorption. The reusable properties and the high polar adsorption efficiency of alumina oxide demonstrated by these previous studies made it an ideal surface for sulfone removal in this study.

The aim of this research was to determine an effective desulfurization technology to clean waste energy/oil on a relatively small industrial scale. The UAOD process, considered an environmentally safe, clean energy technique, can be up-scaled to a portable, modular continuous flow system. Wan and Yen, (2008) indicated its