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Synthesis and application of functionalized polymers for the removal of nitrogen and sulfur species from gas oil

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ABSTRACT

Functionalized polymers, which consist of polymer support, linker, and π-acceptor, have shown promising results in removing nitrogen and sulfur compounds from heavy gas oil via charge transfer complex (CTC) mechanism. In this work, the effect of polymer support in the efficiency and selectivity of the functionalized polymers toward nitrogen removal was studied by synthesizing three different polymers, consisting of hydrophilic and hydrophobic polymer supports, with the same linker and π-acceptor. Hydrazine (-H_2N-NH_2) and 2,4,5,7-Tetranitro-9-fluorenone (TENF) were chosen as the common linker and π-acceptor, respectively. The polymer supports were: polyacrylamide (PAM), polystyrene-co-divinylbenzene (PS-DVB), and polyglycidyl methacrylate-co-ethylene glycol dimethacrylate (PGMA-co-EGDMA). In the first stage, the functionalized polymers, PGMA-NN-TENF, PS-NN-TENF, and PAM-NN-TENF, were synthesized and characterized using different methods and techniques including Fourier Transform Infrared Spectroscopy (FT-IR), Brunauer-Emmett-Teller (BET), Scanning Electron Microscopy (SEM), Thermogravimetric Analysis/Differential Thermal Analysis (TGA/DTA), CHNS elemental analysis, and Nuclear Magnetic Resonance (NMR) spectroscopy. A Nitrogen/Sulfur analyzer was used to determine total nitrogen and sulfur adsorption by the synthesized polymers in 4 different feeds: model compound (MC), light gas oil (LGO), heavy gas oil (HGO), and a blend of heavy and light gas oil (BGO). Results have shown that PGMA was the best polymer support with LGO, HGO, and BGO feeds, while PS-DVB showed the highest nitrogen removal with MC feed. The higher efficiency and selectivity of PGMA-NN-TENF toward nitrogen species, in the presence of sulfur and other aromatic species in the feed, were due to the combination of hydrophilic nature and high surface area of PGMA-NN-TENF compared to other polymers. Modifying the pretreatment conditions of the polymers with BGO feed showed that increasing temperature, contact time, and polymer to oil ratio increased the efficiency of the PGMA-NN-TENF polymer.

1. Introduction

One of the major problems facing the hydrotreatment process of heavy crude oil is the high sulfur and nitrogen content compared to conventional crude oil. The presence of sulfur compounds in fuel reduces fuel quality and releases pollutants to the atmosphere, thus the standards and regulations for sulfur content are becoming progressively stricter in order to produce cleaner fuels. Moreover, studies have shown that nitrogen species have been identified as a strong inhibitor of hydrodesulfurization HDS reactions [1–6]. Nitrogen compounds poison or inhibit HDS catalysts, effect the stability of the fuel during storage [7], and lower the quality of the fuel by the formation of insoluble sediments and gums [8]. Looji et al. [9] and Laredo et al. [10] found that nitrogen compounds can lower the reaction rate in the deep HDS even when they are present in low concentration. Caeiro et al. [11] showed that the increase of nitrogen compound in the feed, increases coke formation and decreases gasoline yield. The inhibition effect of nitrogen compounds is due to the competitive adsorption between aromatic nitrogen and sulfur species over active sites [6,12]. Both basic and non-basic nitrogen compounds showed inhibition effect on HDS process with the effect of the basic nitrogen compounds, such as indoline, slightly higher than their parent non-basic compounds, indole [10]. However, the inhibition effect of non-basic nitrogen compounds can be stronger when it is converted to basic nitrogen compound via hydrogenation process or by adsorption on HDS catalyst [5,10,13,14]. In addition, Li et al. [13] found that non-basic nitrogen compounds, such as carbazoles, cycloalkyl-carbazoles, benzocarbazoles, and cycloalkyl-benzocarbazoles, are dominant in coker gas oil and are hard to convert into smaller molecules, thus resulting in coke formation and decrease of gasoline yield. Depending on reaction conditions, nitrogen compounds may adsorb reversibly or irreversibly on catalyst sites [5]. Even though the adsorption of nitrogen compounds is higher than that of polyaromatic sulfur compounds, the reactivity of nitrogen compounds is much lower [15]. According to Beltramone et al. [16], the inhibition effect of nitrogen compounds over $NiMo/Al_2O_3$ catalyst in HDS process increases in the

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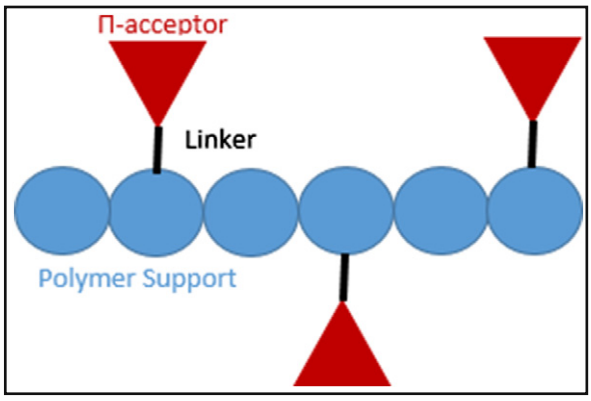

Fig. 1. Functionalized polymer structure.

following order: ammonia > indoline > indole > tetrahydroquinoline > quinolone.

Researchers have found that they can achieve higher sulfur removal efficiency in HDS by eliminating nitrogen content from HGO [5,6,17–19]. Different methods have been developed to remove nitrogen species from liquid fuels in which selective adsorption of nitrogen compounds by solid materials showed promising results for improving the efficiency of HDS processes. Studies have shown that the pretreatment of gas oil with functionalized polymers is a promising method for the removal of nitrogen compounds and refractory sulfur compounds [20,21]. In addition to their removal efficiency, the advantages of using the functionalized polymers are (1) the ease of separation and handling, (2) negligible contamination with gas oil, and (3) their reusability. These polymers are also less toxic, and therefore environmentally friendly, than other methods used for nitrogen and sulfur removal from gas oil, such as ionic liquid. For example, PGMA are used in different medical applications such as drug and gene delivery [22,23]. This method is based on the formation of charge-transfer complexes between the electron rich (Π-donor) and electron poor (Π-acceptor) compounds. Milenkovic et al. [24] have studied the ability of tetranitro-9-fluorenone, (TENT) to form CTC with alkyldibenzothiophene, alkyl(DBT), in order to reduce sulfur content in model gas oil. The capability and selectivity of CTC was correlated to the frontier orbital energies: the highest occupied molecular orbital (HOMO) of the Π-acceptor and the lowest unoccupied molecular orbital (LUMO) values of the Π-donor. In several studies, TENF was chosen as a π-acceptor because of its affinity to form CTC with nitrogen and sulfur compounds in gas oil; however, Macaud et al. [25] found that TENF was non-selective toward nitrogen compounds. Thus combining TENF with a polymer would increase the selectivity of TENF toward nitrogen compounds. Later, Macaud et al. [20] tested different combinations of functionalized polymers and reported that hydrophilic polymers adsorbed less nitrogen than hydrophobic polymers; nevertheless, they were more selective toward non-basic nitrogen compounds than the hydrophobic polymers. Milenkovic et al. [26] extended his earlier study to include more sulfur containing polyaromatic compounds that can form CTC with TENT. Ultra-deep desulfurization of diesel fuel was achieved, leading to less than 10 ppm sulfur, with high selectivity toward DBT by using a new Π-acceptor molecule, 4,5-dicyano-2,7-dinitroflourenone, immobilized on a hydrophobic support, poly (styrene-co-divinylbenzene) [27]. Similarly,

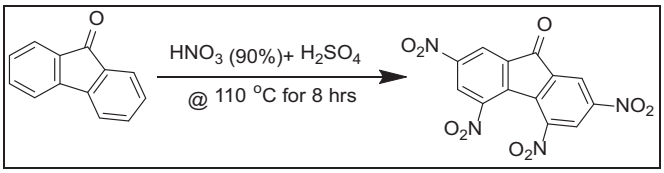

Fig. 2. Synthesis of 2,4,5,7-tetranitro-9-fluorenone (TENF).

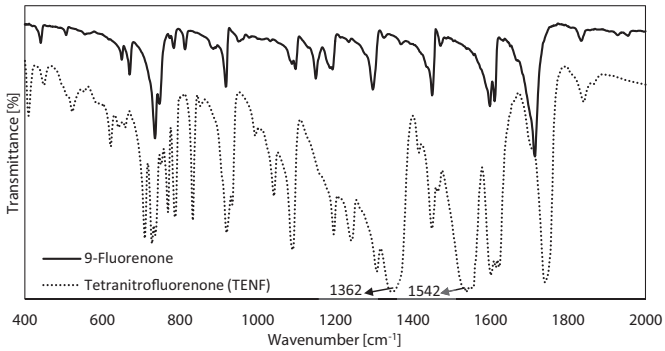

Fig. 3. FTIR spectra of the 9-flourenone and TENF.

TENF was immobilized on poly (styrene-co-divinylbenzene) beads to selectivity adsorb refractory sulfur-compounds from diesel feedstock [28]. Macaud et al. [25] was able to remove 50–90% of nitrogen content and 10% of the sulfur content from a model compound using TENF immobilized on polyglycidylmethacrylate. Furthermore, Favre-Reguillon et al. [29] prepared several complexing agents with different combinations of polymer supports (various type of polystyrene, polyhipe, polyglycidylmethacrylate), linkers (hydrazine, hydroxylamine, amine), and Π-acceptors (tri-and tetranitroflourenone, 4,5-dicyno-2,7-dinitroflourenone, pyromellitic dianhydride) for extraction of sulfur and nitrogen compounds in organic mixtures. In their study, polyhipe, polyglycidylmethacrylate, and different types of polystyrenes were used as a polymer supports. They observed that sulfur and nitrogen removal efficiency varied based on the composition of the complexing agents. A recent study has shown that the pretreatment of bitumen-derivative heavy gas oil with PGMA polymer incorporated with TENT can remove up to 6.7% of the nitrogen species in a single contact using 15:100 polymer to HGO ratio [21]. Even though different functionalized polymers have been used to remove nitrogen and sulfur species, the effect of polymer support on the efficiency of nitrogen and sulfur removal has never been studied. Moreover, most of these polymers have been tested with model compounds or light gas oil. The primary objective of this work was to study the effect of polymer support on the removal efficiency of nitrogen and sulfur compounds from different feeds including model compound, light gas oil, heavy gas oil, and a blend of heavy and light gas oil. Therefore, three functionalized polymers containing the same linker and π-acceptor, but different polymer supports, were synthesized and characterized, before determining their removal efficiency in various feeds.

2. Experimental details

Three polymers were prepared, in which the π-acceptor, 2,4,5,7-tetranitro-9-fluorenone (TENF), and the linker, hydrazine (-NN-), were common among the polymers. The polymers were: (1) polyacrylamide

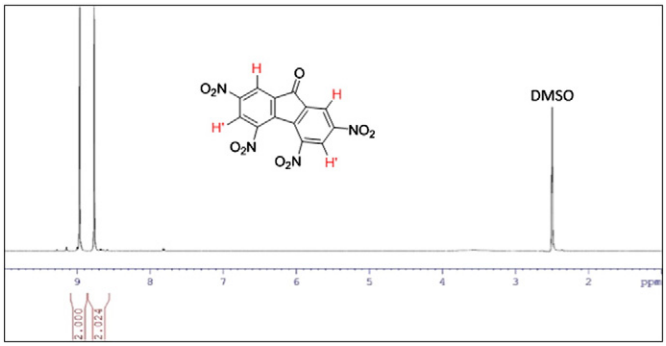

Fig. 4. ^{1}H NMR spectra of the synthesized TENF.