



Selective removal of nitrogen compounds from gas oil using functionalized polymeric adsorbents: Efficient approach towards improving denitrogenation of petroleum feedstock



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HIGHLIGHTS

- Synthesis of polymeric adsorbents for the removal of nitrogen impurities from gas oil.
- Effect of polymer supports on the denitrogenation efficiency of polymeric adsorbents.
- Role of monomer composition and porogenic solvents in textural properties of polymers.
- Regeneration and reusability studies of the complexing agents.

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ABSTRACT

A major challenge in achieving deep hydrodesulfurization with the conventional hydrotreating technology is the inhibition and deactivation of the catalyst caused by heterocyclic nitrogen compounds. In this research, novel polymeric adsorbents were introduced for the selective removal of nitrogen compounds from bitumen-derived light gas oil. Synthesis of polymers with high internal phase emulsion (polyHIPEs) was carried out using a monomeric mixture of unsaturated polyester resin, glycidyl methacrylate and divinylbenzene. To facilitate the selective removal of nitrogen compounds, reactive epoxy groups present in glycidyl methacrylate were used to functionalize the polyHIPEs with a fluorenone based π -acceptor, 2,4,5,7-tetranitro-9-fluorenone (TENF). Successful application of the synthesized polymers was found in the batch adsorption experiments at ambient temperature. Functionalized polyHIPEs were capable of selectively adsorbing nitrogen species from light gas oil. The optimum ratio of monomers was found to be one of the key factors in determining the polymer performance. Particles with high glycidyl methacrylate content with toluene as the porogenic solvent were capable of removing 14.6% of nitrogen compounds. Reusability studies were performed successfully by regenerating the used polymers with toluene; which aids the separation of complexing agent and the adsorbed nitrogen species.

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1. Introduction

Recent developments in the petroleum refinery processes are focused on the production of ultra-low sulfur fuels due to the stringent environmental regulations [1]. Presently, hydrotreating is the most efficient technique used for the removal of these sulfur and nitrogen impurities found in gas oil. It is a group of technologies which involves HDS (hydrodesulfurization – removal of sulfur compounds), HDN (hydrodenitrogenation – removal of nitrogen compounds), HDM (hydrodemetallization – removal of metals)

and HDA (hydrodearomatization – saturation of the aromatics) in the presence of hydrogen at high temperature and pressure. Alumina supported Ni and Mo based catalysts are widely used in industries for hydrotreating of gas oil [2–4]. From decades, rigorous efforts are being made by researchers to enhance the catalyst activity. It is quite challenging to achieve deep HDS with the conventional hydrotreating technology under typical operating conditions. One of the major reasons for the loss of catalyst activity is the presence of heterocyclic nitrogen compounds in the feed [5]. These compounds adsorb onto the catalyst active sites leading to the inhibition and deactivation of the hydrotreating catalyst [6–8]. Another approach to achieve deep HDS is the non-catalytic treatment of feed. The principle behind using non-catalytic processes

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is the selective adsorption of nitrogen and sulfur impurities without using H_2 at ambient temperature. Non-complex designs, easy operational requirements and comparatively low cost are some of the advantages responsible for their worldwide popularity among researchers. Porous adsorbents such as activated carbon derived from wood, coke, coconut husk and coal have been studied for the removal of sulfur and nitrogen compounds from liquid hydrocarbon feed [9–11]. Various zeolites [12–14], Ionic liquids [15,16] and metal-organic frameworks [17,18] have also been utilized in the field of denitrogenation and desulfurization of fuels.

Moreover, hydroprocessing catalyst inhibiting nitrogen species such as indole, carbazole and alkyl substituted carbazoles can be removed by using functionalized polymers capable of adsorbing these compounds prior to hydrotreatment [19,20]. These compounds are often referred to as the non-basic nitrogen compounds because the lone pair of electrons on the nitrogen atom is delocalized within the aromatic system, in contrast to the basic nitrogen compounds where the lone pair of electrons is localized on the nitrogen atom. Due to the formation of π -electron cloud, these compounds are electron rich and can act as electron donors. However, fluorenone derived compounds like 2,4,7-trinitro-9-fluorenone (TriNF) and 2,4,5,7-tetranitro-9-fluorenone (TENF) are electron poor due to the presence of electron withdrawing nitro groups and can act as electron acceptors. As shown in Fig. 1, these electron donor and acceptor compounds are capable of forming charge transfer complexes (CTC), resulting in the removal of inhibiting nitrogen compounds from gas oil [21–23]. The π -acceptors can be easily immobilized on porous polymer supports to enhance the adsorption process and also to prevent leaching of the π -acceptors in gas oil. Sévignon et al. [24] studied the desulfurization of Straight Run oil (SR) using 4,5-dicyano-2,7-dinitrofluorenone immobilized on poly(styrene) via hydrazone linker and successfully eliminated 23% of the total sulfur present in the diesel feed. Selective removal of non-basic nitrogen compounds from diesel feed via charge transfer complex mechanism was investigated by Macaud et al. [21]. A total of 60 wt% of nitrogen compounds were removed from Straight Run oil using π -acceptor immobilized on a hydrophilic support whereas only 30 wt% of nitrogen removal was obtained from the immobilized polymer with lipophilic support. Milenkovic et al. [25] successfully removed alkyl dibenzothiophenes which constitute a major portion of sulfur containing molecules present in gas oil. Selective formation of charge transfer complexes was observed between dibenzothiophene derivatives present in the model feed and the π -acceptor

(TENF). 16% and 14% decrease in sulfur impurities was observed from gas oil containing 860 ppm and 11,300 ppm of total sulfur, respectively.

Recently, researchers have been synthesizing highly functionalized polymers which can be modified for a variety of applications. Glycidyl methacrylate (GMA) containing emulsion-templated porous polymers were functionalized by Kimmins et al. [26] for biocatalysis. Ruckenstein and Hong [27] synthesized polymer-supported biocatalysts for their application in vinylation reaction. Mert et al. [28] prepared polyester-glycidyl methacrylate based polyHIPEs (polymers with high internal phase emulsion) for heavy metal removal. In their study, heavy metal ions such as Silver, Copper and Chromium were successfully adsorbed on the polyHIPE monoliths. Jungbauer and Hahn [29] have extensively mentioned about the removal of large biomolecules using polymethacrylate monoliths. Hence, polyHIPEs have demonstrated their great potential as separation media. However, these polyHIPEs were never used in the petroleum related research.

This work focuses on the synthesis, functionalization and characterization of polymers with high internal phase emulsion for the removal of refractory sulfur and nitrogen compounds from bitumen-derived light gas oil (LGO). The polymer monoliths were prepared using unsaturated polyester resin (UPR), glycidyl methacrylate (GMA) and divinylbenzene (DVB) as monomers in the continuous phase, hereafter referred to as polyHIPEs. Reactive epoxy groups were used to functionalize the polyHIPEs with π -acceptor, TENF. All functionalized polyHIPEs have characteristic textural properties which ease the adsorption of different types of heterocyclic nitrogen and sulfur compounds from refinery feed.

2. Experimental

2.1. Materials

The functional monomer; glycidyl methacrylate ($\geq 97.0\%$), the diluent monomer; divinyl benzene (80%), triethanolamine ($\geq 99.0\%$), Anhydrous N,N-dimethylformamide (99.8%), acetone oxime ($\geq 98.0\%$), 9-fluorenone (98%), fuming nitric acid (90%), tetrahydrofuran (99.9%), and p-toluene sulfonic acid monohydrate ($\geq 98.5\%$) were purchased from Sigma Aldrich. Unsaturated polyester resin was purchased from Viking Plastics Ltd., Edmonton, Canada. Concentrated sulfuric acid (95–98%) and toluene (99.9%) were purchased from Fisher Scientific. The radical initiator

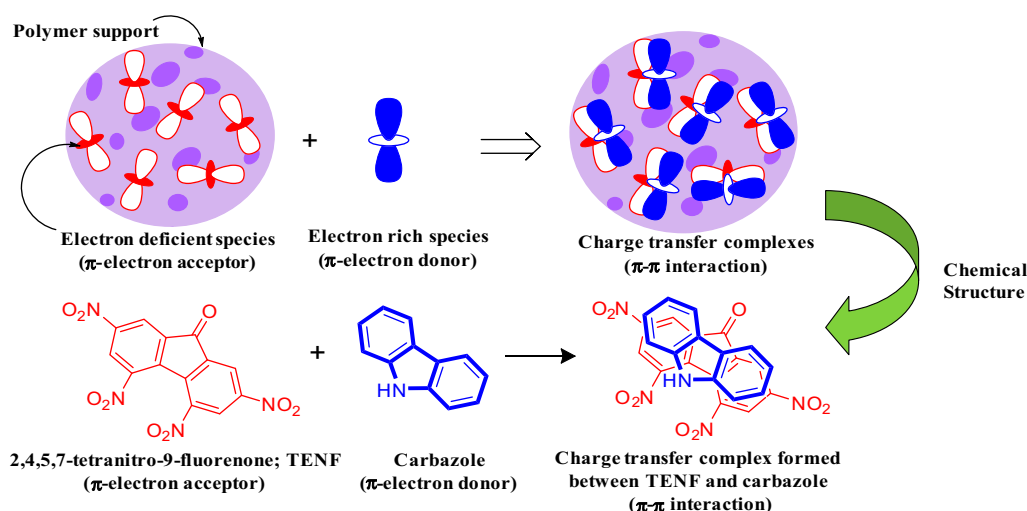


Fig. 1. Visual representation of the formation of charge transfer complex between electron donor and electron acceptor.

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