Abstract

The global energy demand is on rise due to factors like population growth, urbanization, industrialization, and technological advancements, and a significant portion of the demands are met by oil. However, the depletion of conventional oil reserves and the high concentration of sulfur- and nitrogen-containing compounds in oils derived from unconventional sources poses several challenges. As the detrimental effects of these compounds extend to environmental issues, human health, and refinery processes, it is essential to reduce the sulfur and nitrogen concentration of oil and bring it within the permissible limits. Refineries have traditionally used hydrotreatment, but oxidative, adsorptive, extractive, and biological methods have emerged as suitable alternatives, each with its challenges. This work focuses on oxidative desulfurization and denitrogenation of petroleum fuel with geopolymers, which are environment friendly and economically efficient materials possessing a porous structure, ion-exchange capability, mechanical strength, and resilience to high temperatures, which makes them suitable for use as catalysts and catalyst supports. The geopolymer catalysts were prepared via three-staged sequential treatments targeted to introduce hierarchical porosity and improve the surface area and acidity of the material. The modified geopolymer catalysts were used for the oxidative desulfurization, oxidative denitrogenation, and ultrasound-assisted oxidative desulfurization and denitrogenation of fuel oil. The studies systematically assessed parameters affecting the oxidation of sulfur- and nitrogen-containing compounds, and noticed a total oxidation of 85 and 89% of sulfur and nitrogen in individual system, and a total conversion of 93.7 and 100% of sulfur and nitrogen upon two stage oxidation in simultaneous system was observed. Possible reaction mechanisms, and pseudo-homogenous and heterogenous kinetic models were proposed for the oxidative desulfurization and denitrogenation processes. The simultaneous oxidation process was optimized through multi-objective optimization of six variables with response surface methodology. The oxidation efficiency of geopolymers was further enhanced by impregnating them with highly oxidative silver dichromate via direct impregnation, sonochemical, and surfactant-assisted routes. The resulting composite catalysts showed improved physicochemical characteristics, and their activity towards oxidative desulfurization, denitrogenation, and simultaneous oxidative desulfurization-denitrogenation of fuel oil was assessed and the best process among the three demonstrated 100 and 85% reduction in the total sulfur and nitrogen contained in the oil. In summary, the study successfully demonstrated the application of geopolymer-based catalysts for the oxidative desulfurization and denitrogenation of fuel oil, showcasing their effectiveness and potential in addressing environmental concerns.

Keywords: *Oxidative desulfurization, Oxidative denitrogenation, Ultrasound-assisted oxidation, Simultaneous oxidative desulfurization and denitrogenation, Sulfated geopolymer, Silver dichromate-geopolymer composite, Heterogenous kinetics*