HYDROTREATING OF HEAVY OILS IN SLURRY REACTOR WITH Mo-BASED DISPERSED CATALYSTS: COMPARISON WITH SOLID CATALYSTS

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ABSTRACT

As the demand for greener fuels is growing, the development of refining technologies for low-value industrial by-products, such as vacuum residue (VR) and unconventional heavy oils of bio-, waste-, and fossil-origin, has attracted much research attention [1]. Heavy oils, depending on the feedstock, are characterized by high content of metals, heteroatoms and impurities, as well as low yield to liquid products. The slurry phase hydrocracking is an effective process to obtain valuable products with high asphaltene conversion, minimum production of gas and coke, and flexibility with product selectivity and yield [2]. Solid supported and unsupported dispersed catalysts are commonly used for slurry phase hydrocracking, providing a double functionality (cracking and hydrogenation) [3]. In particular, Mo-based catalysts proved to be suitable for cracking and hydrogenation and have been studied under different reaction conditions [2].

In the present study, we investigate the hydrotreatment of Vacuum Gas Oil (VGO) in the presence of Mo-based dispersed and conventional solid catalysts in slurry-type reactor. A stirred semi-batch autoclave reactor was used at 400 °C under constant H_2 pressure (100 bar). Non-catalytic and catalytic tests were conducted with oil-soluble Mo-octoate (15 wt.% Mo) and commercial ex-situ presulfided NiMo-based solid hydrocracking catalyst, at different Mo concentrations (250 – 6000 wppm Mo). The effect of reaction time was examined, and tests were performed for 1, 2, 4 and 6 hours. After the reaction, the products were separated into gas, liquid, and solid fractions. The liquid product was extensively analyzed (elemental analysis, density, SimDis etc.) The gas products were analyzed with GC. The solid was first washed with toluene, dried, and then analyzed (elemental analysis, X-ray diffraction, transmission electron microscopy - TEM). The results show that the conventional solid catalyst achieves a higher hydrodesulfurization degree (~70%) than the liquid catalyst (~30%) at different Mo concentrations. In terms of hydrocracking, the residue, diesel, and gasoline fractions are similar in all cases, indicating that cracking mainly occurs thermally in agreement with the literature [2]. The analysis of the solid product, produced by the liquid catalyst, demonstrates the formation of MoS_2 nanoparticles, responsible for its catalytic activity.

KEYWORDS: Dispersed Catalyst, Mo-octoate, Heavy Oils, Slurry Reactor, Hydrotreating

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