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

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ABSTRACT

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 batch reactor. The effects of Mo concentration, type of catalyst (liquid or solid), and reaction time were examined to evaluate the sulfur removal and hydrocracking performance. The results indicate that the conventional solid catalyst achieves a higher hydrodesulfurization degree compared to the liquid catalyst across various Mo concentrations. Increasing Mo concentration has a beneficial effect on sulfur removal using both liquid and solid Mo-based catalysts. Regarding hydrocracking, the composition of residue, diesel, and gasoline fractions remains constant independent of catalyst type and Mo loading, indicating that cracking mainly occurs thermally. The analysis of the solid product, produced by the liquid Mo-based catalyst, confirms the formation of MoS_2 nanoparticles. To validate the feasibility of continuous operation in the slurry hydrocracking process, hydrotreating tests using the liquid Mo-based catalyst were additionally conducted in a continuous, high-pressure pilot scale unit, equipped with a continuous stirred-tank reactor (CSTR). The continuous test ran for over 60 hours time-on-stream without any operational issues, highlighting the potential of the slurry hydrocracking process for upgrading difficult feedstocks.

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

INTRODUCTION

In recent years, there has been a notable surge in the demand for greener fuels, leading to an increased interest in refining technologies for low-value industrial by–products like vacuum residue (VR) and unconventional heavy oils from bio-, waste-, and fossil origin [1]. Heavy oils typically contain high levels of metals, heteroatoms, and impurities, yielding relatively low amounts of liquid products. Among all the available processes, slurry phase hydrocracking can successfully upgrade such difficult feedstocks to valuable products and can overcome the coking and plugging issues often encountered in fixed-bed reactors [2]. Utilizing nanodispersed catalysts in slurry phase, hydrocracking proves to be an efficient process for obtaining valuable products, achieving flexibility in product selectivity and yields, and high asphaltene conversion, while minimizing gas and coke production [2, 3]. Solid supported and unsupported dispersed catalysts are commonly used for slurry phase hydrocracking, providing a double functionality (cracking and hydrogenation) [3]. In literature, Mo-based precursors have mainly been used due to low coke formation and high conversion of feed [4]. Kim *et al.* studied the effects of Ni, Co, and Mo precursors on the hydrocracking of vacuum residue, by using Ni-acetylacetonate, Co-octoate, and Mo-octoate, respectively. They focused on the oil dispersibility of the precursors and found, that MoS_2 appears as the most active catalytic phase, following the order $MoS_2 > Co_9S_8 >> Ni_3S_2$. Additionally, other oil-soluble Mo precursors were studied, such as Mo-hexacarbonyl, and Mo-naphthenate. Among them, Mo-octoate demonstrated the best activity in hydrocracking, due to the formation of the smallest catalyst particles during its intermediate oxidation state [5].

In this study, we examine the hydrotreatment of heavy oil in the presence of Mo-based dispersed and conventional solid catalysts in slurry-type batch and continuous reactors. The effects of Mo concentration, type of catalyst, reaction time and process mode were investigated. Detailed analysis was conducted on the raw feedstock and the upgraded products, including both liquids and solids, to shed light on the hydrodesulfurization/hydrocracking performance and the formation of MoS_2 nanoparticles.

METHODOLOGY

Experimental set-ups and testing procedure: The slurry phase hydrocracking of Vacuum Gas Oil (VGO), chosen as model feedstock, was first investigated in a stirred semi-batch autoclave reactor operating at a temperature of 400 °C and a constant pressure of H_2 (100 bar) for 4 h reaction time. Tests, both non-catalytic and catalytic, were carried out using oil-soluble Mo-octoate (15 wt.% Mo) and a commercial NiMo-based solid hydrocracking catalyst that was ex-situ presulfided. Various Mo concentrations (ranging from 250 to 6000 wppm Mo) were employed. The effect of reaction time was examined, and tests were performed for 1, 2, 4 and 6 hours. Hydrotreating tests with the oil-soluble catalyst were also conducted in a continuous high-pressure unit equipped with a 500 mL CSTR reactor, under constant pressure 100 bar, temperature 400 °C and H_2/oil volumetric ratio 940 NL/L. The oil-soluble catalyst was pre-mixed with the feed at 1000 ppmw Mo concentration and was continuously fed to the reactor with a flow corresponding to space time of 6 h (LHSV 0.17 h^{-1}) in the reactor. The reactor outlet is led to a separator, where the gas and liquid parts are separated. The liquid product is collected in a product vessel located on a scale. The gas exit passes through a pressure control valve which maintains the required reactor pressure. The outlet vent is connected to a Wet Test Meter to measure the outlet flow of the system.

Product characterization: After reaction, the resulting products were separated into gas, liquid, and solid phases. The gaseous products underwent GC analysis, while the solid fractions underwent washing with toluene, subsequent drying, and analysis, including elemental analysis, X-ray diffraction, and transmission electron microscopy (TEM). Extensive analysis of the liquid product, including elemental analysis, density measurement and simulation distillation (SimDis), was conducted to determine the fuel properties.

RESULTS AND DISCUSSION

Hydrocracking tests in semi-batch reactor

1. Effect of Mo concentration and catalyst type

Figure 1 shows the hydrodesulfurization (HDS) degree achieved in thermal and catalytic tests using liquid and solid Mo-based catalysts, at Mo concentrations ranging from 250 to 6000 wppm Mo. The increasing Mo concentration leads, in both cases, to increased sulfur reduction. The HDS degree increases exponentially up to a Mo concentration of 1000 wppm and tends to stabilize at higher loadings. The liquid catalyst demonstrates a consistently lower hydrodesulfurization degree, compared to the solid catalyst that achieves 95 % removal of sulfur at 6000 ppm Mo. This was partly expected, considering that the solid catalyst contains besides Mo, also metals such as Co and Ni that promote both hydrodesulfurization and hydrogenation [6]. It has been also reported in literature that certain large sulfur-containing molecules present in the VGO, such as dimethyldibenzothiophene-type compounds, limit the degree of HDS as their removal by hydrogenolysis with MoS_2 alone is inhibited by steric hindrance [7]. It should be noted that in the absence of catalyst (thermal test), the HDS degree removal is ~ 15 %, lower than that achieved with the use of either solid or liquid catalyst. This sulfur removal probably originates from the aliphatic sulfur compounds in the feed that are relatively easily decomposed by thermolysis.

In terms of product yields, high organic liquid recovery (in the range of 90 wt. %) is achieved, with no significant differences observed with catalyst type or Mo concentration. The residue conversion to gasoline and diesel fractions, calculated from the Simulation Distillation analysis results, is shown in **Figure 2** as a function of the Mo loading for both types of catalyst. The corresponding value achieved in the thermal test is also included for comparison. Although a weak increase of residue conversion from 30 - 55% with increasing Mo concentration can be observed, the values achieved in the presence and absence of catalyst are comparable. This suggests that cracking mainly occurs thermally in agreement with literature [2].
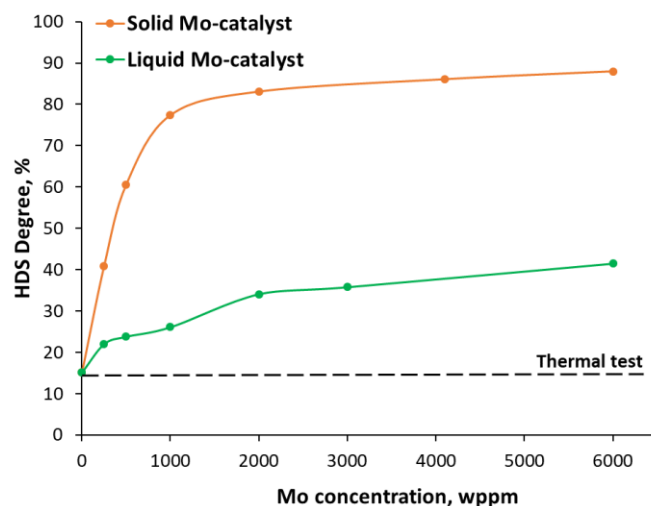
Figure 1. *Effect of Mo concentration and catalyst type on the hydrodesulfurization degree*
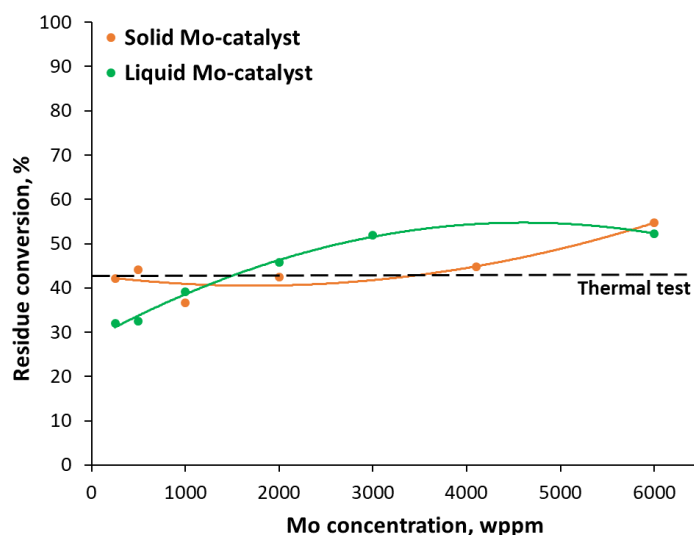

Figure 2. *Effect of Mo concentration and catalyst type on residue conversion*

The residue, diesel, and gasoline fractions of the feedstock and the upgraded products exhibit similarity in all cases (**Figure 3**), confirming that hydrocracking is dominated by thermal reactions.
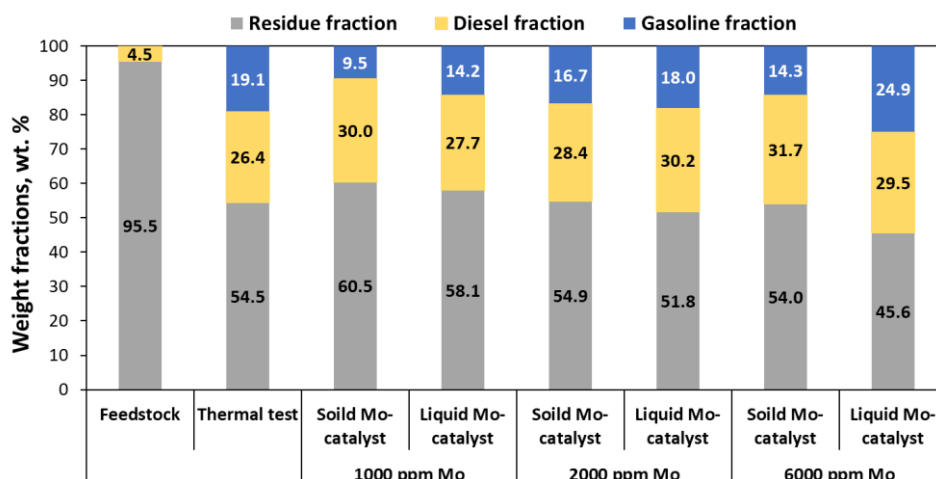
Figure 3. *Gasoline-range (cut-off point 216 °C), diesel-range (cut-off 343 °C) and residue (> 343 °C) fractions in feedstock and liquid products with solid and liquid-type catalyst at different Mo concentrations*

2. Effect of reaction time

The effect of reaction time on the process performance was investigated for the hydrotreating of VGO with dispersed Mo-catalyst at 500 wppm Mo at 400 °C and 100 bar H_2. **Figure 4a** displays the hydrodesulfurization degree achieved as a function of reaction time. As the time increases from 1 to 4 hours, there is a gradual rise in the HDS degree from 7 % to 25 %. At longer reaction time, there is no further change in the sulfur removal, suggesting that the reaction has reached equilibrium at these conditions. **Figure 4b** presents the residue, diesel, and gasoline fractions of the feedstock and the upgraded products obtained at different reaction times. With increasing reaction time, the residue fraction slowly decreases, reaching its minimum value (and thus the higher hydrocracking extent) at 6 h. Considering both the hydrocracking extent and the hydrodesulfurization degree, it can be concluded that the optimal reaction time is 4 h.
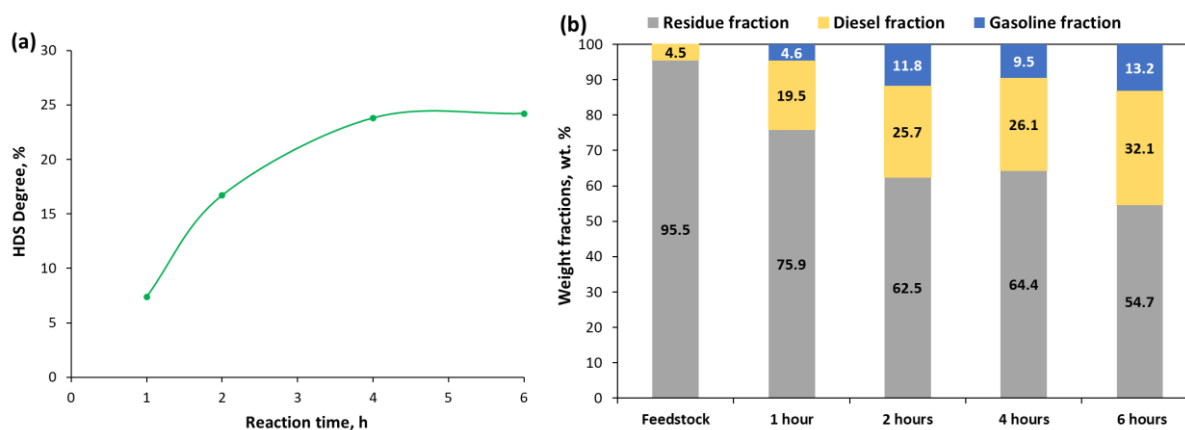

Figure 4. *Effect of reaction time on (a) hydrodesulfurization degree and (b) gasoline, diesel and residue fractions in feedstock and liquid products*

3. Catalyst characterization

Figure 5 shows the XRD diffraction pattern of MoS_2 particles synthesized during the hydrotreatment of VGO using the liquid Μο catalyst. The XRD pattern exhibits strong diffraction peaks at 2θ 14.5º, 33º, 39.3º, 58.5º and 69.7º. These peaks correspond to the hexagonal MoS_2 phase, as identified by the JCPDS card no. 371492 [8].
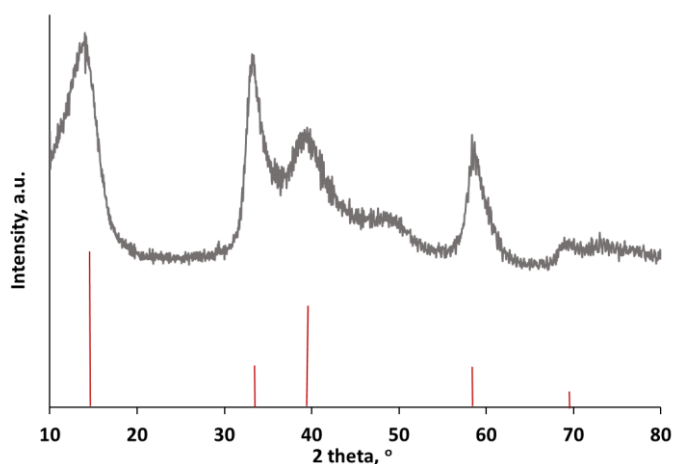
Figure 5. *XRD pattern of MoS₂ nanoparticles*

The structure of the MoS₂ particles was also examined using transmission electron microscopy (TEM). The TEM image (**Figure 6a**) of the MoS₂ particles reveals a laminar morphology, confirming the formation of MoS₂ nanoparticles, in agreement with the literature [5]. The layers exhibit a d-spacing of 0.53 nm, corresponding to the MoS₂ structure. In **Figure 6b**, the electron diffraction pattern indicates the presence of highly crystalline formations, corresponding to (11$\bar{2}$0), (10$\bar{1}$3), and (10$\bar{1}$0) layers.

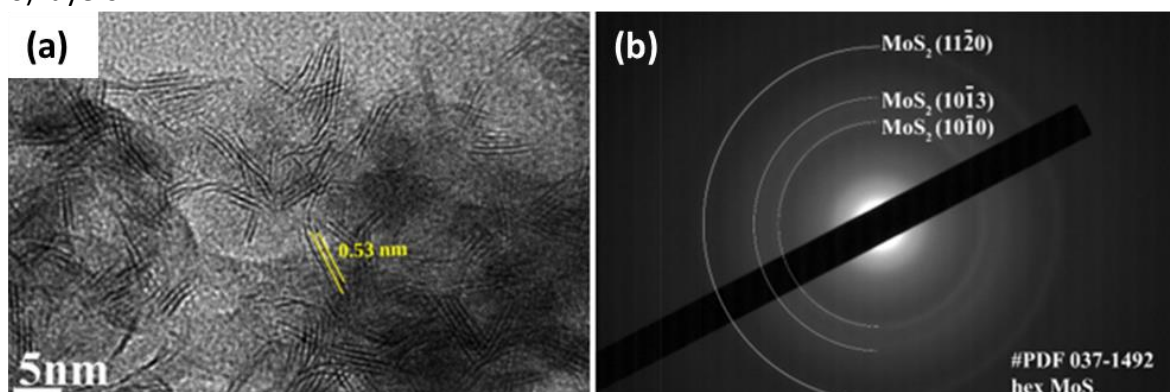***Figure 6.*** *(a) TEM image, (b) Electron diffraction pattern of MoS₂ nanoparticles*

Hydrocracking tests in continuous slurry reactor

To demonstrate the operability of the slurry hydrocracking process in continuous operation, a hydrotreating test with the liquid Mo-catalyst was additionally performed in a continuous, high-pressure pilot-scale testing unit, equipped with a continuous stirred-tank reactor (CSTR). The operating conditions were adjusted to remain close to those applied in the batch scale tests, i.e. temperature of 400 °C, pressure of 100 bar, H_2/oil volumetric ratio 940 NL/L and space time 6 h (LHSV 0.17 h^{-1}) in the reactor. The continuous test was run for more than 60 h time-on-stream, without encountering any operability issues. **Figure 7a** shows the hydrodesulfurization (HDS) degree achieved with the liquid Mo-based catalyst at a Mo concentration of 1000 wppm as a function of time-on-stream. The corresponding value achieved in the batch reactor for 4 h reaction time is included for comparison reasons. With increasing time-on-stream, the sulfur removal exhibits a gradual rise, from ~ 45 % to 60 %. This can probably be attributed to accumulation of the catalytically active MoS₂ phase in the reactor during the continuous operation, as the liquid catalyst is mixed with the VGO feed and is fed continuously to the reactor. This could also explain the much higher HDS degree achieved in the continuous process, compared to the results of the batch test. The

residue conversion to gasoline and diesel fractions is shown in **Figure 7b** as a function of the time-on-stream. The residue conversion initially declines from 30 % to 20 % and stabilizes to this value after ~ 30 hours-on-stream, lower than the conversion achieved in batch mode.
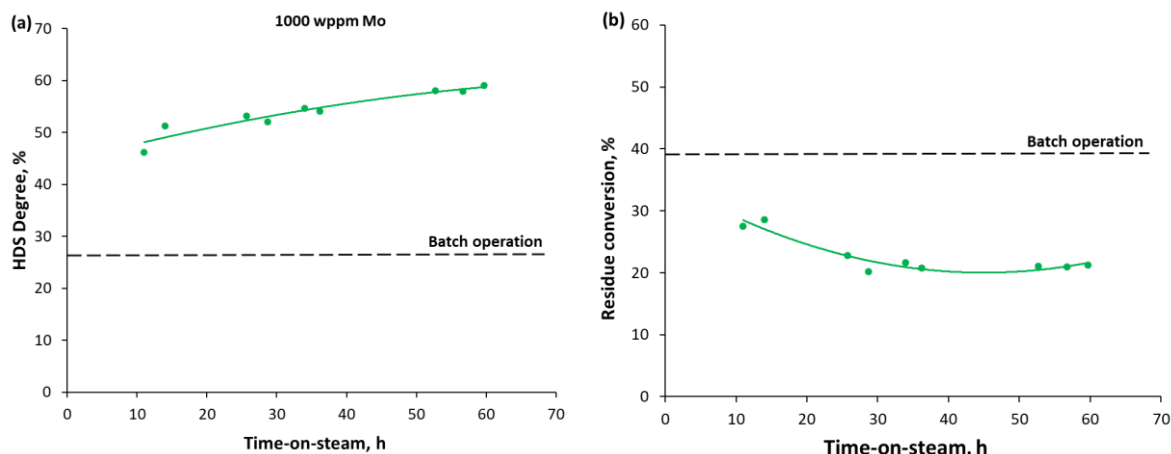

Figure 7. *Effect of process mode on (a) hydrodesulfurization degree and (b) residue conversion*

CONCLUSIONS

The results of this work show that slurry phase hydrotreating can successfully upgrade heavy oils, such as Vacuum Gas Oil, to valuable products, employing both liquid and solid Mo-based catalysts. Tests in a semi-batch reactor show that hydrocracking occurs mainly thermally, although a weak decrease in residue fractions can be achieved in the presence of catalysts. The hydrodesulfurization degree rises sharply up to a Mo concentration of 1000 wppm and stabilizes at higher loadings in both liquid and solid Mo-based catalysts. Characterization of the solid product of the experiments with the liquid catalyst confirms the successful decomposition of the Mo-octoate precursor to catalytically active MoS_2 nanoparticles. To demonstrate the operability of the continuous operation, tests with the liquid Mo-catalyst were additionally performed in a continuous CSTR reactor. The continuous test was run for more than 60 hours time-on-stream without operability issues, demonstrating the high promise of the slurry hydrocracking process for the upgrading of difficult feedstocks. Experiments are on-going to optimize the catalyst and conditions in continuous slurry hydrocracking operation.

ACKNOWLEDGMENTS

REFERENCES

[1] Castello D, Haider MS, Rosendahl LA. (2019). *Renew. Energy*, 141, 420-430.
[2] Nguygen NT et al. (2021). *J. Ind. Eng. Chem*., 102, 112-121.
[3] Liu Y, Gao L, Wen L, Zong B. (2009). *Recent Patents Chem. Eng*., 2, 22-36.
[4] Kang K H et al. (2019). *J. Ind. Eng. Chem.* , 76, 1–16.
[5] Kim S H, Kim K D, Lee D, Lee Y K. (2018). *J. Catal.*, 364, 131–140.
[6] Nadeina K A et al. (2021). *Fuel.* 306, 121672
[7] Kang K H et al. (2020). *J. Catal.*, 384, 106–121.
[8] Nagarajan T et al. (2022). *Sci Rep*, 12.