Maximizing utilization of reactivated and left-over catalysts in heavy gas oil hydrotreater: A Case study of ADNOC Refining.

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Abstract: Based on the refinery inventory, several catalyst configurations composed of different amounts of reactivated and fresh CoMo catalyst, including a full reactivated configuration having a stacked CoMo/NiMo/CoMo combination, (50/25/25) have been tested in a pilot-plant reactor under commercially-relevant conditions. Experimental results in term of weight average bed temperature (WABT), H2 consumption, aromatics and diesel yields have been analyzed and compared to the current commercial hydrotreater load and catalyst supplier forecasts. Results show excellent performances of reactivated catalysts and a strong effect of the NiMo layer in the case of the stacked configuration, without compromising cycle length or product quality.

Keywords: Hydrodesulphurization, Catalysts rejuvenation, Pilot-plant catalyst evaluation.

1. Introduction

Commercial HDS catalysts are sulfided molybdenum promoted by cobalt (CoMoS) or nickel (NiMoS) supported on γ-Al2O3. "Type II" active phase, obtained by advanced preparation methods, present significantly superior activity thanks to a higher dispersion of promoters at MoS_2 edges [1]. During the course of the process, catalysts are slowly deactivated by coke accumulation, active phase sintering and metal poisoning. Coke can be removed by a simple combustion process. Rejuvenation process has been developed specifically for "Type II" catalysts to address deactivation by sintering and to re-disperse the active phase [2]. Recently, ADNOC Refining Research Center has studied the possibility to reuse reactivated (regenerated + rejuvenated) CoMo and NiMo catalysts in one of the refinery hydrotreater producing 10ppm diesel without compromising on cycle length and products quality compare to a load of fresh catalyst. Several catalysts configurations have been tested under refinery conditions using pilot-plant reactor. Experimental results have been compared to catalyst supplier commercial forecasts and detailed analysis of the products has been performed to assess the effect of reactivated catalysts on yields, aromatic content and H_2 consumption.

2. Experimental

All the catalysts studied belong to Albemarle's STARS® portfolio. The regeneration and rejuvenation processes have been carried out by Al Bilad Catalyst Company (Saudi Arabia). Four catalysts combinations with different amounts of reactivated and fresh catalysts (Figure 1) have been tested using a pilot-plant operating with conditions similar to the commercial hydrotreater in the refinery (LHSV = 0.64h-1@100% capacity, $Pp(H_2)$ = 55.7 bars, H_2/Oil = 300). The test feed was a heavy gas oil (HGO) obtained from the refinery. Detailed product analyses, including total sulfur and nitrogens analysis, density, simulated distillation, H-NMR and aromatic distribution, have been performed following ASTM standard methods.

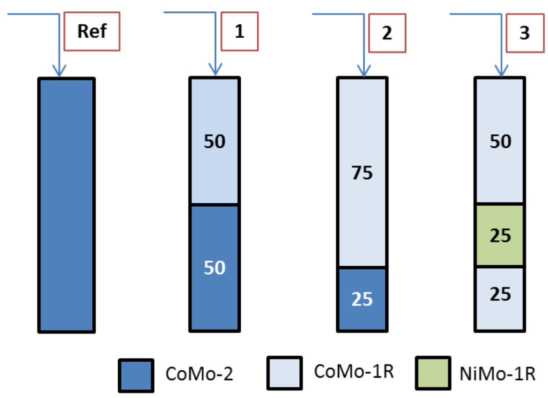

Figure 1. Scheme showing the different catalyst configuration studied. Values in the colored boxes indicate the volume % of the reactor.

3. Results and discussion

Experimental results show excellent catalytic performances of reactivated CoMo. No WABT difference could be observed when having 50% reactivated catalyst in combination with fresh catalyst (configuration #1). The full reactivated stacked CoMo/NiMo/CoMo configuration (#3) performs 2°C better than the full fresh CoMo reference, showing the strong effect of the NiMo layer on the overall reactor performances. In the middle of the reactor, the NiMo layer acts mostly on accelerating organic nitrogen removal which are in the same concentration range than the remaining sulfurs [3]. This alleviates the competition with organic sulfurs, and consequently facilitates the removal of more bulky sulfurs compounds at the end of the reactor. When comparing the pilot-plant experimental results with the catalyst supplier forecasts for the commercial unit very similar trend can be observed, supporting the quality of the pilot-plant test and related results and discussion. Globally, all the analyses tend to show that reactivated catalysts do not have unbalance desulfurization/hydrogenation selectivity and that the ULSD products have very similar properties and quality whatever the quantity of reactivated catalyst used. However, it should be noted that the catalyst supplier forecasts +1.5% and +3% consumption increases, respectively for configuration #2 and #3, compared to the reference configuration. Increase in hydrogenation reaction could be attributed to a partial re-dispersion of the active phase to "Type II" structure during the rejuvenation process, altering the DDS/HYD active sites balance [4].

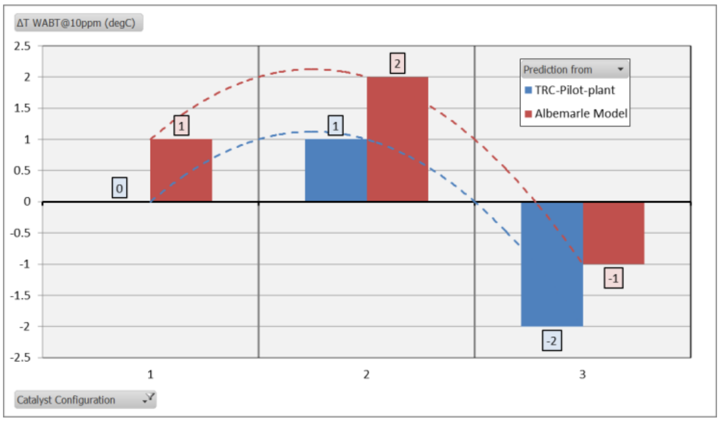

Figure 2. TRC pilot plant results and Albemarle forecast for the different catalyst configuration in term of WABT differences compared to the reference (current commercial unit load)

4. Conclusions

According to the pilot plant study large quantity of reactivated catalyst could be reutilized in the commercial unit without impacting the cycle length or the product quality. Considering the price of a reactivated catalysts being 50% of the fresh one, these scenarios could potentially lead to 30-55% savings on the catalyst cost for the next hydrotreater load.

References

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