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Hydrocracking of Vacuum Residual Oil (Part 3) Combination of Hydrothermal Cracking and Hydrocracking

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An integrated hydrocracking process using a combination of hydrothermal cracking and hydrocracking was proposed and tested using a micro-autoclave. In the first hydrothermal cracking stage, Arab heavy residue was cracked under hydrogen at 8 MPa (cold charge) and 430°C for 2 h. In the second stage of hydrocracking, an alumina-supported nickel molybdenum catalyst was added to the first stage product and hydrocracked under hydrogen at 8 MPa (cold charge) and 410°C for 2 h. Two series of reactions were tested in three cycles. In the first series, fresh catalyst was used in every cycle whereas, in the second series, the same catalyst was used in successive cycles.
Relatively high yields of distillable fraction (VD) were obtained by this integrated hydrocracking process, although 60 wt% was the maximum yield of VD in the hydrothermal cracking process and hydrocracking process. In the first series, the yields of VD and vacuum residue (VR) in the first cycle were 85.7 wt% and 6.7 wt%, respectively. The yields of VD in the second and third cycles were 86.9 wt% and 87.8 wt%, respectively, which indicates that the yield of VD increased with recycling and that the cracking of the hexane-soluble fraction in VR proceeded by recycling. In the second series, the yield of VD in the first, second and third cycles were 86, 86 and 69 wt%, respectively, which suggests that the catalyst activity decreased in the third cycle.
The basic catalytic activities of the fresh catalyst (catal. A), spent catalyst used in the hydrocracking of VR directly (catal. C) and spent catalyst used in the hydrocracking of VR after hydrothermal cracking (catal. B) were measured for hydrogenation,

hydrodesulfurization and hydrodenitrogenation using 1-methylnaphthalene, dibenzothiophene and carbazole, respectively. Catal. A was most active followed by catal. B for all reactions. Two major explanations are possible why higher VD yield was obtained in this integrated hydrocracking process. First, unstable components in VR were stabilized in the hydrothermal cracking process, so deactivation of catalyst was less compared to catalyst exposed to untreated VR. Second, hydrogenation of unsaturated bonds in VR proceeded during hydrocracking process, so the hydrogenated VR was cracked more easily compared to untreated VR in the hydrothermal cracking process.

Keywords: Hydrocracking, Hydrothermal cracking, Vacuum residue, Bottom cycle, Spent catalyst, Nickel molybdenum alumina catalyst

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