

The cooperation of MoS₂/Al₂O₃ and NiMoS₂/Al₂O₃ catalysts in the hydrotreating of straight-run gas oil and rapeseed oil mixture

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- 1. Introduction** – Triglyceride-based feedstocks (TG) are the renewable sources for the production of alkanes, valuable components of motor fuels using the hydrodeoxygenation (HDO) over sulfide Co(Ni)Mo/Al₂O₃ catalysts. The co-processing of TG with petroleum feeds is a promising approach - so, S-containing compounds of oil keep the catalysts in sulfide state without sulfiding agents. The HDO of TG can proceed via H₂O or through the CO/CO₂ (HDeCO_x) removal routes. Non-promoted MoS₂/Al₂O₃ catalyst provides TG conversion without CO_x formation, enhancing the yield of liquid hydrocarbons and avoiding the need of H₂ feed cleaning from CO_x. In the current work the behavior of systems, containing Mo/Al₂O₃ and NiMo/Al₂O₃ catalysts is studied in the hydrotreating of straight-run gas oil (SRGO) and rapeseed oil (RSO) in the one unit with the focus on the comparison of two-component systems with the inverse sequence of catalyst's loading in the 2 connected in series reactors (Mo/NiMo vs NiMo/Mo).
- 2. Experimental** – Mo/Al₂O₃ and NiMo/Al₂O₃ catalysts were prepared by impregnation of alumina granules with a solution of active metals precursors, phosphoric and citric acids. The experiments were performed in a trickle-bed down-flow reactors connected in series at 340°C, 4,0 MPa and H₂/feed ratio 600 Nm³/m³, varying LHSV and RSO content (0, 15 or 30 wt.%) in SRGO. In the case of Mo/Al₂O₃ (first reactor) and NiMo/Al₂O₃ (second reactor) configuration the mixture of RSO-SRGO was fed in the first reactor; in the inverse case HDS of SRGO was performed over NiMo/Al₂O₃ catalyst in the first reactor and RSO was added in the second reactor containing Mo/Al₂O₃ catalyst.
- 3. Results and Discussion** - The results obtained using Mo/Al₂O₃-NiMo/Al₂O₃ sequence for the HDT of SRGO-RSO blends confirm that the use of a Mo/Al₂O₃ sulfide catalyst in the front bed of the reactor ensures the complete HDO of RSO via the H₂O removal avoiding the formation of CO_x. The LHSV was determined allowing the ULSD production from SRGO and it was shown, that the RSO addition has no effect on the HDS degree. The use of above configuration was shown to increase the diesel yield (in comparison with NiMo/Al₂O₃), decrease the formation of greenhouse gases (CO_x and CH₄, produced due to CO_x hydrogenation), allows avoiding a problems associated with the purification of recycled hydrogen. But there are at least two drawbacks: NiMo/Al₂O₃ catalyst in second layer can suffer from the contact with water produced in HDO of TG; Mo/Al₂O₃ catalyst in first layer can accumulate the metal impurities that can turn the selectivity of TG conversion to the HDeCO_x route. The use of inverse modification (NiMo/Al₂O₃ - Mo/Al₂O₃ sequence) avoids the above drawbacks without loss of productivity. The effects of RSO content and reactor configuration on the product quality are evaluated.
- 4. Conclusions** – The use of two-component systems allowed avoiding the CO_x formation in the production of ULSD from the SRGO-RSO feeds. The use of NiMo/Al₂O₃ - Mo/Al₂O₃ configuration avoids some technological issues but has no benefit in the productivity of unit. The properties of the products are more dependent on RSO content than on the configuration of catalytic system.

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