Hydrotreating of shale oil

Xun Tang, Shuyuan Li, Hang Yu

China university of petroleum,Beijing, China

Shale oil hydrogenation was carried out in a fixed-bed reactor over a wide range of operating conditions, using various feeds and hydrotreating catalysts. Three kinds of feedstock were investigated, including whole crude shale oil of Longkou, diesel distillates from Fushun and Huadian shale oils. Hydrogenation catalysts, such as Co-Mo/Al_2O_3, Ni-W/Al_2O_3, and Ni-Mo-W/Al_2O_3, were used to hydrogenate diesel distillate of shale oil, and a commercial catalyst was used to process whole crude shale oil from Longkou. The effects of several factors on the properties of hydrogenated products were evaluated, including temperature (320-420°C), hydrogen pressure (3-9 MPa), liquid hourly space velocity (LHSV) (0.2-2h^{-1}) and of hydrogen-oil ratio (200-1200). Meanwhile, lumped kinetic models were developed for predicting the concentrations of sulfur and nitrogen in production. The results of shale oil hydrogenation indicate that the hydrotreating conditions of diesel are easier than whole crude shale oil. The experimental results of diesel hydrogenation show that the concentrations of sulfur and nitrogen in product are rapidly decreased with increasing temperature, hydrogen pressure and residence time (reciprocal LHSV), while the influence of hydrogen/oil ratio is smaller. The catalyst, Ni-Mo-W/Al_2O_3, has the highest hydrogenation activity for hydrodesulfurization (HDS) and hydrodenitrogenation (HDN). The mostly economical and optimum conditions are as follows: 360°C, 6.0 MPa, 600:1, LHSV 1h^{-1}, and the qualities of product meet domestic diesel standard. The kinetic parameters were determined using lumped kinetic models. The HDS reaction is reasonably well described by a three-lumping kinetic model, and a four-lumping kinetic model can also be used to describe the HDN reaction. The results of whole crude shale oil hydrogenation demonstrate that temperature, hydrogen pressure and LHSV are the main influential factors of HDS and HDN. Under typical reaction conditions (420°C, 7.0 MPa, 1000:1, LHSV 0.5 h^{-1}), HDS conversion is 98.86%, while HDN conversion is 99.39%. Comparing with feedstock, the initial boiling point (IBP) of the product is reduced by 46.6°C corresponding to 156.8°C, and the fraction of light oil is increased from 50.4% to 71.4%, and the colour of oil was changed from dark brown to transparent and slightly yellow.