Hydroconversion of alkane/cycloalkane mixture – SEMK modeling study

Nebojša Korica, Pedro S.F. Mendes, Jeriffa De Clercq and Joris W. Thybaut

Laboratory for Chemical Technology, Ghent University, Technologiepark 125, Ghent, Belgium
Industrial Adsorption and Catalysis, Ghent University, Valentin Vaerwyckweg 1, Schoonmeersen-gebouw C, Ghent, Belgium

One of the most frequently used ways to convert oil refinery streams and alternative feedstocks into more valuable products, e.g., vacuum gas oil into jet fuel and diesel, is hydroconversion over bifunctional catalysts. The reaction mechanism comprises metal-catalyzed (de)hydrogenation, where yields alkene intermediates, and acid-catalyzed isomerization and cracking reactions of protonated intermediates [1,2]. A maximum isomer yield is achieved if the acid-catalyzed reactions are rate determining, i.e., when *ideal* hydrocracking occurs [1].

Hydrocracking of single component feeds, i.e., alkanes or cycloalkanes, has already been investigated in detail. The kinetic parameters of elementary reactions [1,2], as well as the impact of the operating conditions on transition between ideal and non-ideal hydrocracking regimes have been evaluated [3]. However, realistic industrial feeds are complex mixture of alkanes, cycloalkanes, and aromatics. Co-reactants are expected to impact the conversion, selectivity, and transition from ideal to non-ideal hydrocracking. These effects might be related to differences in physisorption, dehydrogenation, and/or protonation. In order to fully understand the impact of co-reactants, quantifying the relevant phenomena via modeling would be of strategic advantage.

The Single-Event MicroKinetic (SEMK) methodology is ideally suited for this quantification of underlying mixture effects. SEMK has manifested itself as a convenient tool for simulation of hydroconversion, as it accounts for all elementary physico-chemical steps [2]. Thanks to this fundamental character, this methodology can be employed for the simulation of the hydroconversion behavior of alkane/cycloalkane mixtures, the model itself being trained against the behavior of single model components. In mixture behavior, the conversion of the preferentially adsorbed compound is only marginally affected by the presence of a less strongly adsorbed compound, while the conversion of the latter is significantly impeded by the former. The mixture effect was also found to impact on the operating conditions where a transition from ideal to non-ideal hydrocracking occurs.

Experimentally, the hydrocracking of *n*-octane and methyl cyclohexane mixtures over Pt/CBV712 catalyst is evaluated. The experimental data will be simulated with the SEMK model starting from reported parameter values. Some reassessment may be required for the present SEMK model to reliably extrapolate to different ranges of n-alkanes and cycloalkanes, and ideal hydrocracking reaction conditions.

References:
[1] Weitkamp,J., ChemCatChem 4(2012) 292-306
[2] Martens,G.G.,Thybaut,J.W., and Marin,G.B., Ind.Eng.Chem.Res. 40(2001) 1832-1844
[3] Thybaut,J.W.,Laxmi Narasimhan,C.S.,Denayer,J.F.,Baron,G.V.,Jacobs,P.A.,Martens,J.A., and Marin,G.B, Ind.Eng.Chem.Res. 44(2005) 5159-5169

E-mail: Nebojsa.Korica@UGent.be

Website: www.lct.ugent.be