THERMODYNAMIC FOUNDATIONS OF BIOSYNTHETIC FUEL TECHNOLOGIES: OVERCOMING CHALLENGES IN BIOMASS HYDROGENATION AND HYDRODEOXYGENATION

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As fossil resources deplete, chemical thermodynamics becomes a critical engine for designing efficient biosynthetic fuel processes. This study presents a hybrid thermodynamic framework (combining high-precision experiments with quantum chemistry) to bypass kinetic bottlenecks and guide catalyst design for the hydrogenation and hydrodeoxygenation (HDO) of biomass.

Three key systems were investigated to validate this approach:

1. Lignin Models (Eugenol): Thermochemical properties (enthalpies of formation, vaporization, and phase transitions) for an 18-reaction HDO network were determined via transpiration, calorimetry, and G4 calculations. We demonstrate that while no thermodynamic barriers exist, product distribution is governed by support acidity. Ru/HNT catalysts showed a shift from 79% selectivity for methoxy-propylphenol to 42% for propylcyclohexane upon acid-etching, aligning with our predictions.
2. Terpenoid Conversion (Carvone): Gibbs energies and entropies were quantified for 15 pathways. The results explain observed chemoselectivity (exo > endo > C=O) and provide a quantitative basis for selective production of dihydrocarvone or carvacrol.
3. Hydrogen Storage (Limonene & LOHC): Thermodynamic assessment of direct and transfer hydrogenation confirms high equilibrium constants and near-complete conversions, proving these systems viable for hydrogen-carrier technologies.

The developed "centerpiece" approach offers a rapid, low-cost toolkit for screening renewable molecules and scaling industrial processes. These results support green chemistry priorities, providing a rigorous thermodynamic route to sustainable aviation and diesel fuels.

Keywords: chemical thermodynamics, biosynthetic fuels, hydrodeoxygenation, LOHC, quantum chemistry, catalyst optimization.

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