

MODELING OF LIMONENE HYDROGEN REACTION IN SUPERCRITICAL DIOXIDE CARBON

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Catalytic hydrogenation is one of the key processes in the chemical industry. The performances of hydrogenation and distribution of its products are strongly influenced by activity, selectivity and interaction between reaction and mass transfer kinetics. Catalytic hydrogenation is usually performed in a triphasic medium: liquid, gas and solid catalyst. The mass transfer at the interfaces is generally the limiting step. Then supercritical CO₂ offers a very interesting reactional medium which may help to overcome such limitations. We propose in this paper a dynamic model for the hydrogenation reaction of limonene in supercritical dioxide carbon. The hydrogenation reaction occurs in a tubular reactor; the reactor outlet stream feeds an vaporliquid equilibrium cell; then the liquid phase is returned to the reactor; total pressure is maintained constant using a pure CO₂ feed stream. The composition of the reactor outlet is measured during the experiment time. The hydrogenation has been studied for different values of the operating parameters (liquid flow rate of the reactor inlet, hydrogen initial pressure). Constitutive (thermodynamic and kinetic models) and governing (balances) equations are described. The resulting Differential and Algebraic model (DAE) is solved using the Gear Algorithm, according to an Oriented Equation solution strategy. Key points, such as initial conditions, are discussed. We chose the Peng Robinson equation of state to describe the phase behavior. Mixing rules are conventional: quadratic for a and linear for b with one binary interaction coefficient. The kinetic model of limonene hydrogenation is not well known. A general LangmuirHinshelwood model has been selected. Then a sensitivity analysis is performed in order to select the relevant parameters. Finally, the selected parameters are fitted using a modified LevenbergMarquardt algorithm.