

Catalytic hydrogenation of Fumaric acid to 1,4-butanediol in supercritical CO₂ by ruthenium, palladium and iridium

Camila G. Pereira^{1*}, Adolfo L. Figueredo¹, Liane M. Rossi², Pedro Vidinha², Reinaldo Bazito²

1 - Laboratory of Separation Processes in Food, Department of Chemical Engineering, Federal University of Rio Grande do Norte, Natal, Brazil.

2-Department of Fundamental Chemistry, Institute of Chemistry, University of São Paulo, Av. Prof. Lineu Prestes, 748, 05508-000 São Paulo, SP, Brazil.

*camila@eq.ufrn.br

1,4-Butanediol (BDO) is an important industry compound with wide applicability as an organic solvent for the production of adhesives, fibers and polyurethanes. The recent interest for production of thermoplastics using BDO, caused its demand to increase rapidly. The industrial means used today for its production involve severe operating conditions and keeps a dependence on products derived from fossil fuels. In this way, the production of BDO through the catalytic hydrogenation of biomass has been one of the studied routes to minimize the environmental impact. The use of supercritical carbon dioxide (SC-CO₂) as solvent promotes not only a better conversion but also gives greater safety to the process, taking place under the mild operating conditions. In this context, the present work reports a high selectivity for conversion of fumaric acid to BDO by hydrogenation in SC-CO₂ at 280 bar and 313.15 K, using different catalysts based on ruthenium (Ru), palladium (Pd) and iridium (Ir). The hydrogenation of fumaric acid occurred in at high pressure reactor of variable volume, where the reaction took place in biphasic medium (H₂O + C₄H₄O₄/CO₂ + H₂). The results showed that among the catalysts, Ru presented the best result by completely converting the fumaric acid to succinic acid and BDO. The H₂ concentration increase has a positive effect on conversion. The best operating conditions were 15 bar of H₂ + 265 bar of CO₂ and 313.15 K, obtaining 100% conversion of fumaric acid to BDO, using Fe₃O₄.SiO₂.NH₂@Ru as catalyst. It is worth pointing out that it was not found in literature this process at temperatures lower than 313.15 K and with high selectivity for BDO formation, i.e., absence of tetrahydrofuran in the products, as well as in SC-CO₂.