

Développement et optimisation d'un procédé de production de molécules d'intérêt par hydrogénation du CO₂ à partir d'hydrogène renouvelable

Doctorant·e

DURAN MARTINEZ LAURA ELIZABETH

Direction de thèse

POLAERT ISABELLE (Directeur·trice de thèse)

Date de la soutenance

09/10/2024 à 09:00

Lieu de la soutenance

LSPC

Rapporteurs de la thèse

BILLET ANNE-MARIE INP ENSIACET, Toulouse

MONNIER HUBERT INRS, Vandoeuvre lès Nancy

Membres du jury

BILLET ANNE-MARIE, , INP ENSIACET, Toulouse

COMMENGE JEAN-MARC, , Université de Lorraine

LEDOUX ALAIN, , INSA de Rouen Normandie

MONNIER HUBERT, , INRS, Vandoeuvre lès Nancy

PITault ISABELLE, , Université Claude Bernard Lyon 1

POLAERT ISABELLE, , INSA de Rouen Normandie

Abstract

The transition from fossil fuels to renewable energy sources is becoming increasingly urgent due to their significant contribution to global climate change. The rising levels of carbon dioxide in the atmosphere highlight the critical need for sustainable alternatives. Converting CO₂ into value-added molecules (energy carriers) offers a promising solution to reduce reliance on fossil fuels. This thesis explores the potential of the catalytic hydrogenation of CO₂ to produce value-added chemicals such as methane, methanol, and dimethyl ether (DME). These processes not only offer a means to reduce CO₂ emissions but also provide a path toward sustainable fuel production. The research explores various catalytic processes, with a particular emphasis on thermal catalysis due to its higher efficiency and suitability for industrial implementation. The one-step CO₂ hydrogenation to DME is the case of study. Preliminary experiments were conducted into a laboratory fixed bed reactor to better understand catalyst performance. Different catalysts were tested for DME synthesis. Since the reactions that take place into CO₂ hydrogenation to DME comprise the methanol synthesis from CO₂ followed by methanol dehydration, a mixture of catalysts was done for the direct DME synthesis. For the powder mixture, two different CuO/ZnO/Al₂O₃ (CZA) catalysts, one commercial and one developed, were tested for methanol synthesis and two CZA zeolites (HY and HZSM-5) were tested for methanol dehydration. The physical mixture of CZA-C plus HZSM-5 was chosen for further analysis. The effect of temperature, pressure, feed molar ratio (H₂/CO₂) and gas hourly space velocity (GHSV) were assessed for the development of the kinetics of DME synthesis. A Langmuir–Hinshelwood kinetic model for methanol synthesis was proposed, along with a novel relationship for methanol dehydration to DME, since the reaction is not at equilibrium. An Optimal Temperature Profile (OTP) reactor integrating the kinetic model developed was studied for precise temperature control to maximise CO₂ conversion. Simulations and optimisations confirmed that longer residence times by adjusting catalysts mass is more effective for higher CO₂ conversion. A minimal advantage (<1%) was identified in terms of CO₂ conversion for the OTP reactor over an isothermal reactor. However, the combined productivity of DME and methanol had a better performance (>4.4%) over the isothermal reactor. An OTP multi-tubular reactor with variable coolant temperature, comprising 958 tubes, achieved 34.18% CO₂ conversion and a combined methanol and DME production rate of 30.84 mol.h⁻¹ per tube, approaching to thermodynamic equilibrium without recirculation.