

Selective hydrogenation of alkynes for vitamin production in a three-phase structured reactor

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Highlights

- A structured reactor is presented to conduct three-phase hydrogenations of alkynes
- A kinetic model is developed to describe the process over a wide range of conditions
- An overall mass transfer coefficient is estimated from the results in continuous mode

1. Introduction

The semi-hydrogenations of alkynes to alkenes are key transformations in the fine chemical industry to produce vitamins and aroma compounds. In industry, these three-phase reactions are usually carried out using palladium-based catalysts in slurry reactors. These catalysts, mostly in the form of fine powders to avoid mass transfer limitations, require filtration after the reaction [1]. Furthermore, these discontinuous processes involve a number of steps with the intermediate products being collected, stored and often transported to other facilities. To overcome these problems considerable efforts are directed to the conversion of traditional batch processes into discontinuous operations. This paper presents a novel combination of catalyst support and reactor design for the semi-hydrogenation of alkynes in prospect of process intensification. The solvent-free hydrogenation of 2-methyl-3-butyn-2-ol (MBY) to 2-methyl-3-buten-2-ol (MBE) was chosen as test reaction. MBE represents an important intermediate in the industrial synthesis of vitamin E. The selectivity of this process concerns the possibility of hydrogenating MBY to MBE while preventing its further hydrogenation to 2-methyl-2-butanol (MBA). The advantages of this structured reactor are high surface area, good mixing qualities and low pressure drops. Furthermore, it is characterized by a regular geometry easily reproducible and suitable for computational simulations.

2. Methods

This paper is divided into three sections: i) Development of a kinetic model to describe the selective hydrogenation of MBY. ii) Application of the structured reactor in a semi-batch hydrogenation plant with identification of the kinetic regime. iii) Continuous operation of the structured reactor and estimation of the external mass transfer resistance.

The kinetic model was developed using the experimental results collected in a stirred slurry reactor over a wide range of operating conditions. The structured reactor was manufactured with a regular structure by selective laser sintering [2]. The internal packing represents the negative pattern of tetrahedrally arranged overlapping spheres (Figure 1). The metal support was coated with an Al₂O₃/ZnO base layer, impregnated with palladium and characterized by SEM analysis. The reactor was implemented into a hydrogenation plant and operated in both semi-batch and continuous mode.



Figure 1. Structured reactor used during the experimental activity. A part of the outer wall was removed for visualization purposes.

In the first case the liquid phase was continuously circulated through the system and pure hydrogen was continuously supplied. Liquid and gas phase passed through the structured reactor in co-current up-flow. A high liquid flowrate was selected to minimize the external liquid-solid concentration gradient. Liquid samples were withdrawn at defined intervals of time and analyzed by gas-chromatography.

3. Results and discussion

A Langmuir-Hinshelwood mechanism based on the noncompetitive adsorption between hydrogen and organics and dissociative adsorption of hydrogen on the catalyst surface was found to describe the experimental behavior of the system with good accuracy (total percentage standard deviation < 6 %). A first order reaction with respect to hydrogen pressure was applied to simulate the intrinsic kinetics of the process [3]. The knowledge acquired during this preliminary study was transferred to the structured reactor operated in semi-batch mode. Figure 2 presents the initial rate of MBY hydrogenation at various hydrogen flowrates in the investigated range of temperatures. The initial reaction rate was found to increase significantly with hydrogen flowrate at low velocities indicating a non-negligible mass transfer effect [4].

The experimental results obtained at higher flowrates were simultaneously used in a single optimization procedure to estimate the kinetic and adsorption parameters governing the process. In a second stage these best-estimated parameters allowed the modeling of the experimental results collected in the mass transfer limited regime with the estimation of an overall mass transfer coefficient. The occurrence of mass transfer limitations under specific operating conditions was verified by using an empirical criterion. The results of the experimental runs conducted in continuous mode, in terms of overall mass transfer coefficient, were modeled using a predictive Sherwood number correlation. The proposed model predicts the experimental values with maximum deviations of 15 %.

The validation of the model was conducted by using the estimated kinetic parameters and mass transfer coefficients to simulate the experimental results of additional runs not included in the pool used during the optimization procedure. The model allows to predict the concentration profiles of the species involved in the system, conversion and selectivity profiles in a range of temperature and pressure typical of the industrial processes and at various gas and liquid flowrates.

4. Conclusions

The goal of the work was to develop and validate a mathematical model able to simulate both intrinsic kinetics and mass transfer phenomena of the hydrogenation of MBY in design structured reactors. These devices were found to be a viable alternative to transform batch processes with industrial relevance into sustainable and more efficient continuous processes.

References

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Keywords

Hydrogenation; Alkynes; Structured Reactor; Kinetics.

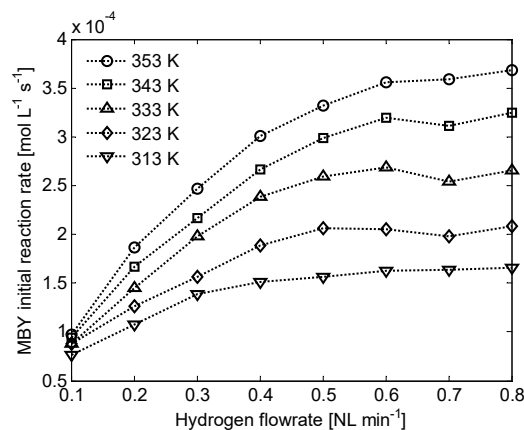


Figure 2. Effect of hydrogen flowrate on the initial rate of MBY hydrogenation. Pressure: 4.0 bar, Liquid flowrate: 70 kg h⁻¹.