**DEVELOPPING A KINETIC MODEL FOR THE CONVERSION OF BIOETHANOL INTO 1,3-BUTADIENE OVER A ONE-STEP HFZN/SIO2 CATALYST.**

G.M. Cabello González1\*, J.R. López Beltrán, A. L. Villanueva Perales1, M. Campoy Naranjo1, F. Vidal Barrero1, A. Martínez2, P. Ollero1

*1Departamento de Ingeniería Química y Ambiental - Universidad de Sevilla (España)*

*2Instituto de Tecnología Química - Universidad Politécnica de Valencia (España)*

*\*Corresponding author: gcabello3@us.es*

**Highlights**

* A kinetic model was developed for the one-step ethanol to butadiene process.
* The kinetic model includes the effect of co-feeding water.
* The experimental observations were explained through the model parameters.

**1. Introduction**

1,3-Butadiene is an important building block for the manufacture of synthetic rubber, resins, and elastomers. In the last years, the increasing use of ethane as steam cracking feedstock instead of heavier fractions has decreased the production of 1,3-butadiene, but its demand continues growing, so 1,3-butadiene short-term demand is not expected to be satisfied by the current capacity of oil refineries. In that context, the production of 1,3-butadiene from renewable sources, such as bioethanol, rises as an environmentally friendly alternative that may help solving demand issues.

In spite of the potential relevance of this process, very few studies have attempted to propose a kinetic model of the ethanol to 1,3-butadiene conversion, and none of these studies considered the most supported ethanol to 1,3-butadiene pathway, which includes ethanol dehydrogenation into acetaldehyde and its posterior aldo-condensation to crotonaldehyde, crotyl alcohol production from ethanol and crotonaldehyde MPVO reduction, and crotyl alcohol dehydration into 1,3-butadiene. That way, we aim to generate a formal kinetic model describing the main reaction pathway that can predict the catalyst performance in a range of operating conditions around the optimum. Besides, this kinetic model includes the effect of co-feeding water among with the ethanol feedstock, what has never been reported so far for this process.

**2. Methods**

 The catalyst was prepared following the methodology reported in the work of De Baerdemaeker et al. [1]. Catalytic tests were carried out in a continuous flow fixed-bed reactor at 340-380 ºC, 1.12-9.8 h-1, 0-15% w/w water in the feedstock, ethanol partial pressure of 0.21 bar and atmospheric pressure. The bed was divided into three sections. The top section was a SiC bed, the middle one comprised a bed of catalyst (0.3-0.5 mm) diluted in the necessary amount of SiC to obtain a bed length of 13 cm, and the bottom section was also a SiC bed. All sections were separated by a glass wool plug. The ethanol was fed with an HPLC-pump and N2 was used as carrier gas. The reactor output line was electrically traced and insulated to avoid product condensations before analysis by an Agilent 7890A on-line gas chromatograph (GC) equipped with two flame ionization detectors (FID) and a thermal conductivity detector (TCD).

**3. Results and discussion**

Making use of the tests carried out in the laboratory-scale reactor, a power-law model was developed, and the statistically significant variables in the rate expression for the generation of each product were found. The reaction scheme considered for the calculation of the balance is a simplification of the one proposed in our previous work [2]. The considered reaction rates are based on exponential rate equations or Langmuir-Hinshelwood kinetic.

The differential mole balance equations were solved obtaining an initial guess of the kinetic parameters assuming constant molar flow along the reactor and solving the algebraic system. These rough parameters were used as initial guess values for solving the differential mole balance along the reactor.

* Main reactions: C2H5OH 🡪 C2H4O +H2

 C2H5OH +C2H4O 🡪 C4H6 + 2H2O

* Ethanol dehydration: 2C2H5OH 🡪 (C2H5)2O + H2O

 C2H5OH 🡪 C2H4 +H2O

* Butanol formation: 2C2H5OH 🡪 C4H9OH + H2O
* Butenes formation: C4H9OH 🡪 C4H8 + H2O
* Heavy compounds formation (diphenylketone) : 6.5 C2H4O 🡪 C13H10O + 5.5H2O + 2.5H2

 **4. Conclusions**

The formation of 1,3-butadiene over a Hf-Zn catalyst was evaluated. The main products observed were acetaldehyde, butadiene, ethene, diethyl ether, butanol, butenes and heavy compounds. A Langmuir−Hinshelwood type of kinetic model was developed for the equations involving acetaldehyde production and consumption. The model can be used to predict the rates of formation of the products and the predictions agree with the experimental data, as well as to design an industrial facility.

**References**

1. T. De Baerdemaeker, M. Feyen, U. Müller, B. Yilmaz, F.S. Xiao, W. Zhang, T. Yokoi, X. Bao, H. Gies, D.E. De Vos, ACS Catal. 5 (2015) 3393–3397.
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