Novel kinetic model for the ethyl acetate synthesis by direct addition on a silicotungstic acid catalyst

Bram Van Wettere[1], Joris W. Thybaut[1,*], Erhin de Werd[1], Saleh Aghakhani[1], Jeroen Lauwaert[2,*]

[1]*Laboratory for Chemical Technology (LCT), Department of Materials, Textiles, and Chemical Engineering, Ghent University, Technologiepark 125, 9052 Ghent, Belgium*

[2]*Industrial Catalysis and Adsorption Technology (INCAT), Department of Materials, Textiles, and Chemical Engineering, Ghent University, Valentin Vaerwyckweg 1, 9000 Ghent, Belgium*

[*]*Corresponding author: Jeroen.Lauwaert@ugent.be & Joris.Thybaut@UGent.be*

Ethyl acetate (EtAc) is an important organic chemical used in glues, surface coatings, thinners, paints, inks, nail polisher removal products and as solvent in physical and chemical processes [1, 2]. Among other processes, the gas phase direct addition of ethylene (C_2H_4) and acetic acid (AcOH) catalyzed by a solid acid such as silicotungstic acid (STA) is the EtAc synthesis route that was commercialized by BP Chemicals and Showa Denko in the '90s [3, 4]. Due to the acidic nature of the catalyst and presence of water (H_2O) in the AcOH feedstock, a variety of by-products, mainly ethanol (EtOH) and diethyl ether (DEE), other esters, alcohols, ethers, aldehydes, ketones and hydrocarbons are formed as well [5].

A kinetic model for the direct addition reaction focusing on the main products has been developed based on a simple mechanism (See Figure 1) in which six reacting components, i.e. C_2H_4, AcOH, H_2O, EtAc, EtOH and DEE, are converted into each other via five reactions, denoted by r_1 to r_5. r_1 to r_3 are direct additions of AcOH, H_2O and EtOH to C_2H_4 yielding EtAc, EtOH and DEE respectively, where r_2 is also referred to as the C_2H_4 hydration, r_4 is the EtOH-AcOH esterification and r_5 is the EtOH condensation or dehydration to DEE.

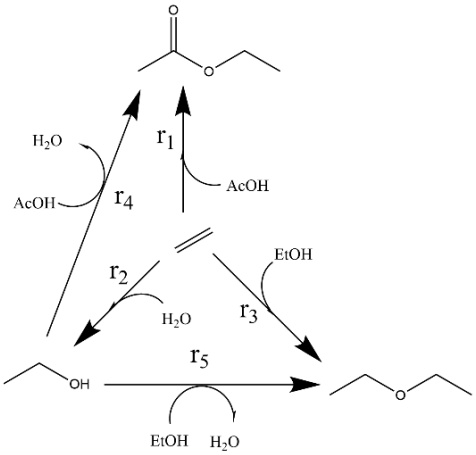

Figure 1: Proposed reaction mechanism for the EtAc synthesis by direct addition.

The non-idealities of the gas phase, due to presence of AcOH, were captured by the Hayden and O'Connell equation of state for which the necessary parameters were retrieved from Aspen databases. Several kinetic models, based on different assumptions with respect to the adsorption of species, have been constructed for which the activation energies and adsorption enthalpies as adjustable parameters, were determined by regression to the experimental data with the aid of Athena Visual Studio. This software package was also used for statistical evaluation of the model and parameter estimates. In the optimized kinetic model, the rates of r_1, r_2 and r_4 are described according to a Langmuir-Hinshelwood mechanism and the rates of r_3 and r_5 according to an Eley-Rideal type mechanism, in which the

adsorption of C_2H_4, AcOH, H_2O, EtAc and EtOH are included. The model has been improved by accounting for the dehydration of STA by H_2O and clustering of the STA protons with EtOH.

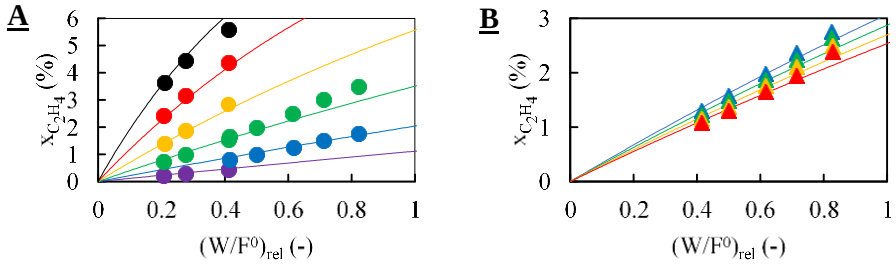

Figure 2: Effect of (**A**) T at 1.2 MPa and (**B**) P at 442 K and space time on $x_{C_2H_4}$ at C_2H_4:AcOH:H_2O:N_2 inlet molar flow ratio equal to 78.2:6.5:5.3:10.0. (●) T = 433 K, (●) T = 439 K, (●) T = 445 K, (●) T = 451 K, (●) T = 457 K, (●) T = 463 K, (▲) P = 0.8 MPa, (▲) P = 1.0 MPa, (▲) P = 1.2 MPa &(▲) P = 1.4 MPa. Symbols and lines represent experimental data points and model predictions respectively.

The kinetic model can accurately describe the effects of operating conditions, where the increase in C_2H_4 conversion ($x_{C_2H_4}$) with space time (W/F^0), temperature (T) and C_2H_4 concentration in the feed ($y_{C_2H_4}{}^0$) and decrease with pressure (P), AcOH ($y_{AcOH}{}^0$) and H_2O feed concentration ($y_{H_2O}{}^0$) are shown in Figure 2 and 3. Moreover, the model is capable to qualitatively predict the effects on selectivity to EtAc, EtOH and DEE. Furthermore, the kinetic model provides insights in how reaction rates are affected by the operating conditions and, hence, explains the observed trends in conversions and selectivities.

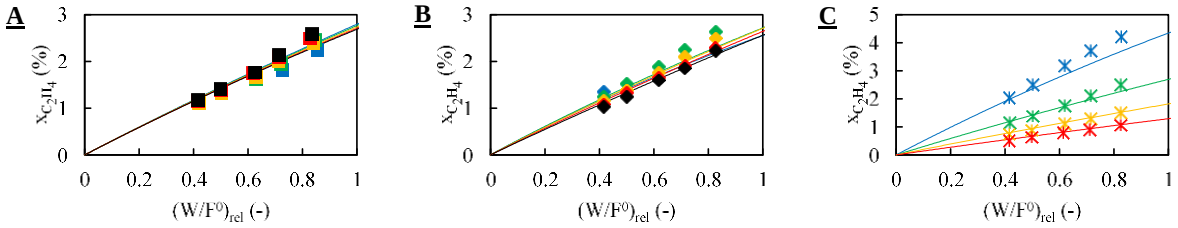

Figure 3: Effect of (**A**) $y_{C_2H_4}{}^0$ with 6.5 mol% AcOH and 5.3 mol% H_2O in the feed, (**B**) $y_{AcOH}{}^0$ with 78.2 mol% C_2H_4 and 5.3 mol% H_2O in the feed) and (**C**) $y_{H_2O}{}^0$ with 78.2 mol% C_2H_4 and 6.5 mol% AcOH in the feed and space time on $x_{C_2H_4}$ at T = 442 K and P = 1.2 MPa. (■) $y_{C_2H_4}{}^0$ = 48.2 mol%, (■) $y_{C_2H_4}{}^0$ = 58.2 mol%, (■) $y_{C_2H_4}{}^0$ = 68.2 mol% ,(■) $y_{C_2H_4}{}^0$ = 78.2 mol%, (■) $y_{C_2H_4}{}^0$ = 85.2 mol%, (◆) $y_{AcOH}{}^0$ = 2.5 mol%, %, (◆) $y_{AcOH}{}^0$ = 4.5 mol%, %, (◆) $y_{AcOH}{}^0$ = 6.5 mol%, %, (◆) $y_{AcOH}{}^0$ = 8.5 mol%, %, (◆) $y_{AcOH}{}^0$ = 10.5 mol%, (✱) $y_{H_2O}{}^0$ = 3.3 mol%, (✱) $y_{H_2O}{}^0$ = 5.3 mol%, (✱) $y_{H_2O}{}^0$ = 7.3 mol% & (✱) $y_{H_2O}{}^0$ = 9.3 mol%. Symbols and lines represent experimental data points and model predictions respectively.

The kinetic model that can simulate the effect of operating conditions on kinetics well, which is essential to consider predictions trustworthy. The model can be implemented in state-of-the-art process simulation software packages, such as Aspen Plus, to simulate the performance and identify better operating points for EtAc production plants that apply the direct addition technology. Hence, the kinetic model is a viable tool to optimize the performance of the production plants.

Keywords: ethyl acetate, direct addition, kinetic model, mechanism

References:

1. Monconduit, M., et al., *Alkyl Acetates (C1-C4)*. Chemical Economics Handbook. 2020: IHS Markit.
2. Pattanaik, B.N. and H.C. Mandalia, *Ethyl acetate: properties, production processes and applications-A review*. IJCRR, 2011. **3**: p. 23-40.
3. Yamamoto, Y., et al., *Direct addition of acetic acid to ethylene to form ethyl acetate in the presence of H4SiW12O40/SiO2*. Applied Catalysis A: General, 2008. **344**(1): p. 55-60.
4. Kozhevnikov, I.V., *Heterogeneous acid catalysis by heteropoly acids: Approaches to catalyst deactivation.* Journal of Molecular Catalysis A: Chemical, 2009. **305**(1): p. 104-111.
5. Howard, M.J., et al., *New acetyls techonologies from BP chemicals*, in *Studies in Surface Science and Catalysis*, H. Hattori and K. Otsuka, Editors. 1999, Elsevier. p. 61-68.