

Supporting Information

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SUPPORTING INFORMATION

Continuous-flow asymmetric hydrogenation of the β -keto ester methyl propionylacetate in ionic liquid – supercritical carbon dioxide biphasic systems

Jens Theuerkauf, a Giancarlo Franciò a and Walter Leitner a,b*

- ^a Institut für Technische und Makromolekulare Chemie (ITMC), RWTH Aachen University, Worringerweg 1, D-52074 Aachen (Germany)
 - Fax: (+49 241 80 22177) E-mail: leitner@itmc.rwth-aachen.de or francio@itmc.rwth-aachen.de
- Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, D-45470 Mülheim an der Ruhr (Germany)

- 1. Materials
- 2. Reactor setup for continuous flow hydrogenation: construction details

1. Materials

The gases H₂ (99.999%) and CO₂ (99.995%) were purchased by Praxair. Methyl propionylacetate (Alfa Aesar, 99%) was dried over 3 Å molecular sieves, decanted, distilled and degassed via three freeze-pump-thaw cycles prior to use. (S)-BINAP (99%), HBF₄·Et₂O, pTsOH (≥98.5%), [Bu₄N]Cl (≥97.0%) and dry Methanol (99.99%, H₂O < 50 ppm) were purchased by Sigma Aldrich. [EMIm][BTA] (99%), [EMIm][FAP] (99%), and [Me₃BuN][BTA] (99%) were purchased by Solvent Innovation (now Merck). [OMim]Cl (99%) was purchased by ABCR. [dMEIm][BTA] was prepared via a halide free route according to literature. [1] [HO-EMIm][BTA] and [HSO₃BBIm][BTA][3] were prepared according to a described procedures. Prior to use, the ionic liquids were dried and degassed under vacuum (<10⁻³ mbar) at 60°C for 48 h. Water content could by reduced to a minimum of 5 ppm except for the case of [H-EMIm][BTA] (340 ppm). Water content was determined by a Metrohm KF 756 as average from two independent measurements.

2. Reactor setup for continuous flow hydrogenation: construction details



Figure S1: Photograph of the reactor setup for continuous flow hydrogenation

The new reactor set-up was built according to our previous experience (Figure S1).^[4] The program LabView[™] (National Instruments) was used to record all data, control flows and pressures, and to monitor safety parameters for automatic shutdown procedure.

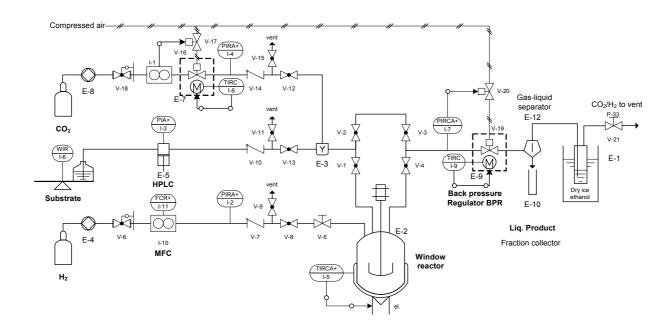


Figure S2: Flow-scheme of the reactor setup for continuous flow hydrogenation

The dosing unit for CO_2 comprises the flow meter I–1, (Bronkhorst, type LiquiFlow), the proportional valve V17 (Festo, type VPPM), and the pneumatic valve V16 (SiTec, $k_v = 0.01$). Hydrogen was delivered through the mass flow controller V-6 (Brooks Instruments, type 5800). The liquid substrate is introduced through a double-piston HPLC pump (Knauer, smartline 100) and monitored by recording the weight loss of the substrate container (I-6). The reactor (E-2) consists of stainless steel autoclave (10 mL) equipped with two thick-glass windows and a magnetic stirring bar. The reactor was heated via two 100 W heating sleeves (Horst) and controlled through a PID-controller (Eurotherm, type 91e). Capillaries for incoming and outcoming flow were connected to the upper part of the autoclave. The total pressure in the system was controlled via a back pressure regulator consisting of a compressed air regulated and heated needle membrane valve (E-9).

The product was separated from the effluent CO_2 flow by customised gas-liquid separator E-12 (Figure S3). The use of the separator allowed for continuous time-resolved sampling of the product mixture in a fraction collector (E-10). The outgoing gas stream from the separator was then passed through a cooling trap containing toluene at $-80^{\circ}C$ (E-1).

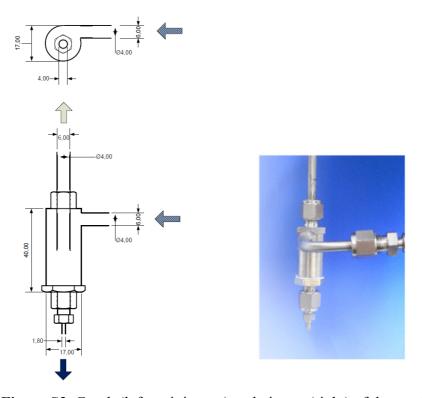


Figure S3. Graph (left, unit in mm) and picture (right) of the gas-liquid separator E-12

Reference:

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