Esterification of small molecules in a combined-catalyzed biphasic system

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Novel sustainable feedstocks are required for the development of future production processes that can replace fossil production methods. One possible feedstock is CO_2, which causes global warming and climate change and is available in high amounts in the atmosphere [1]. To utilize excess CO_2 it can be integrated into production processes as carbon source, or be converted into other, more reactive C1-molecules, for example, formic acid or formaldehyde, by biological, electrochemical or chemical techniques. C1-molecules can be used as substrates from different catalyst types, whereby each catalyst has its advantages. By combining chemical catalysts with biocatalysts and microbes in one process, best features of each catalyst can be combined to more sustainable and efficient processes. In the optimal case, even no downstream processing is required [2]. Within the Fuel Science Center, a cluster of excellence at RWTH Aachen University, our colleagues have already developed a combined microbial and chemo-catalytic one-pot process for the production of formic acid and bioethanol including a CO_2 integration step and using renewable resources [3]. Now, we extend the process to produce ethyl formate in the same vessel (see Figure 1) by addition of an enzymatic step.

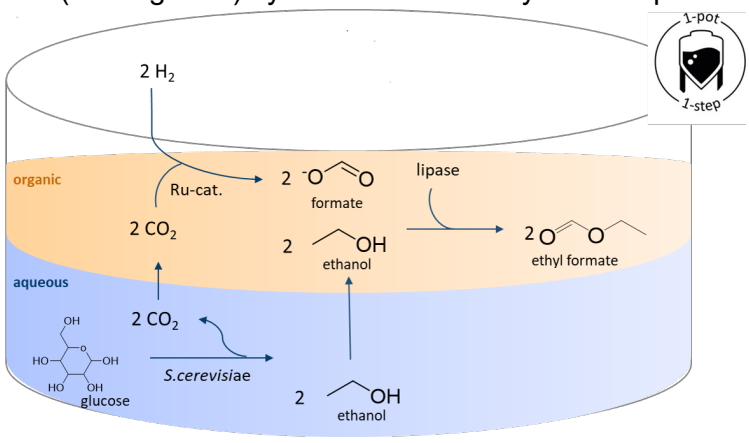

Figure 1: One-pot, one-step process with three different catalyst types.

We showed, that ethyl formate can be enzymatically synthesized in the aqueous phase with carboxylic acid reductases A-domains (CAR-As). However, we identified that ethyl formate is prone to hydrolysis under aqueous conditions. A synthesis directly in the organic phase, in which ethyl formate is stable, is advantageous and is possible with the commercially available, immobilized *Candida antarctica* lipase B. We tested various solvents in a biphasic synthesis system, where CPME showed best results. CPME is a green solvent, not miscible with water, and possesses an appropriate cross-solubility of formic acid and ethanol.

[1] Satanowski, *EMBO Reports*, **2020**, 21, 4, e50273.

[2] Mengers, H.G., Guntermann N., von Westarp W.G, Jupke, A., Klankermayer J., Blank L.M., Leitner W., Rother D., *Chemie Ingenieur Technik*, **2022**, 95, 485-490.

[3] Guntermann N, Mengers H.G., Franciò G., Blank L.M., Leitner W., *Green chemistry*, **2021**, 23, 9660–64.