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Upcycling of CO2 to ethyl formate in a hybrid process

AUTHORS

Nina KLOS / FORSCHUNGSZENTRUM JÜLICH, IBG-1, WILHELM-JOHNEN-STRASSE, JÜLICH
Lars M. BLANK / INSTITUTE OF APPLIED MICROBIOLOGY, WORRINGER WEG 1, AACHEN
Walter LEITNER / MAX PLANCK INSTITUTE FOR CHEMICAL ENERGY CONVERSION, KAISER-WILHELM-PLATZ 1, MÜHLHEIM AN DER RUHR
Dörte ROTHER / FORSCHUNGSZENTRUM IBG-1 BIOKATALYSE, WILHELM-JOHNEN-STRASSE, JÜLICH

PURPOSE OF THE ABSTRACT

In recent years, greenhouse gas emissions have increased and therefore the integration of CO2 in the production of chemicals or fuels is beneficial. When using CO2 as a substrate, small molecules are synthesized in the first step, such as formic acid from an electrochemical conversion. The further valorization of small molecules with well established, traditional chemistry methods have often high energy demands and do not completely fit into the concept of green chemistry. A biocatalyic conversion using enzymes in various formulations provides an alternative. This bears the advantages that enzymes work e.g. under mild conditions and have high selectivity, which could increase the process sustainability and the value of gained products simultaneously [1].

Within the Fuel Science Center, an cluster of excellence at RWTH Aachen University, our colleagues have already developed a combined microbial and chemo-catalytical one-pot synthese process for the production of formic acid and bioethanol from renewable resources [2]. In this biphasic process an aqueous yeast fermentation is used for the production of bioethanol and CO2. The CO2 is captured together with H2 using a ruthenium catalyst in an organic phase above the fermentation broth in the same vessel to synthesize formic acid. This process should now be extended with a biocatalytic step to increase the product spectrum again in the same vessel. In detail we want to upgrade the product to ethyl formate, which is industrially applicable in the food industry [3]. The biocatalytic esterification reaction from ethanol and formic acid to ethyl formate should be performed by using carboxylic acid reductases (CARs) (E.C.1.2.1.30) (see Figure 1).

Carboxylic acid reductases (CARs), work under aqueous conditions and are a highly potent class of enzymes identified in recent years. Recently, we established methods for the expression of high titers of actively und solubly produced CARs for the reduction of aromatic carboxylic acids to aldehydes [4,5]. Apart from the physiologically known reaction, they catalyzed the reduction from carboxylic acid to aldehydes, amidation, thioesterification and esterification reactions [6-8]. Pongpamorn et al. have already described esterification reactions using CARs (only A-domain) with aromatic carboxylic acids as substrates, however short-chain aliphatic acids, such as formic acid, have not yet been used [8].
We expect that the overall process concept will combine the advantages of chemocatalysis, microbial catalysis, and biocatalysis with the goal of developing a simple, sustainable process that can compete with existing fossil resource-based processes.

FIGURES

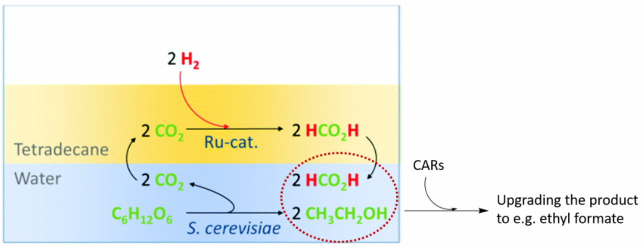

FIGURE 1

Figure 1. One-pot, one-step process from glucose and CO2 to formic acid and bioethanol [2].

By adding CARs the product spectrum can be increased.

FIGURE 2

KEYWORDS

#biocatalysis | #hybrid process | #CARs | #CO2 usage

BIBLIOGRAPHY

[1] Alcántara, Biocatalysis as Key to Sustainable Industrial Chemistry, ChemSusChem, 15, 9, e202102709 (2022).

[2] Guntermann, Bio-energy conversion with carbon capture and utilization (BECCU): integrated biomass fermentation and chemo-catalytic CO2 hydrogenation for bioethanol and formic acid co-production, Green chemistry, 23, 9680 - 9864 (2021).

[3] Simpson, Effects of ethyl formate on fruit quality and target pest mortality for harvested strawberries, Postharvest Biology and Technology, 34, 3, 313-319, (2004).

[4] Weber, Production of the Carboxylate Reductase from Nocardia otitidiscaviarum in a Soluble, Active Form for in vitro Applications, ChemBioChem, 22, 10, 1823 - 1832, (2021).

[5] Weber, Multi-enzyme catalysed processes using purified and whole-cell biocatalysts towards a 1,3,4-substituted tetrahydroisoquinoline, RSC Adv., 13, 10097-10109 (2023).

[6] Wood, Adenylation Activity of Carboxylic Acid Reductases Enables the Synthesis of Amides, Angew. Chem. Int. Ed., 56, 46, 14498 - 14501 (2017).

[7] Schnepel, Thioester-mediated biocatalytic amide bond synthesis with in situ thiol recycling, Nature Catalysis, 6, 89-99 (2023).

[8] Pongpamorn, Carboxylic Acid Reductase Can Catalyze Ester Synthesis in Aqueous Environments, Agric. Angew. Chem. Int. Ed., 60, 11, 5749 - 5753 (2021).