

## Direct, tandem catalysis synthesis of higher alcohols from syngas: the influence of water on reaction rates and alcohol (regio)selectivity

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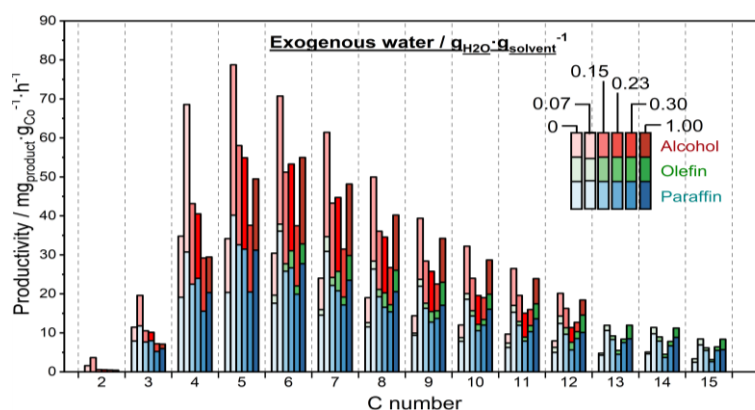
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### Abstract

Synthetic, high-energy-density, liquid e-fuels are expected to play a central role in the reduction of GHG emissions from hard-to-electrify, heavy-duty and long-haul transport, such as waterborne transport. Various liquid e-fuels have been proposed to replace fossil-derived diesel-type fuels, commonly produced through syngas conversion pathways such as Fischer-Tropsch synthesis, methanol synthesis, or direct dimethyl ether (DME) synthesis. The E-TANDEM project aims to enable the efficient and direct production of a new higher-oxygenate diesel-like e-fuel (HOEF) from carbon dioxide, water and renewable energy as the only inputs. The new HOEF formulation, based on heavy aliphatic alcohols and ethers (C<sub>5+</sub>), is expected to combine the combustion advantages and engine/infrastructure-compatibility of paraffinic compounds with the soot reduction potential of oxygenated fuels. The tandem production of higher alcohols combines solid catalyzed, higher olefin-selective Fischer-Tropsch synthesis (FTS) with a molecular complex-catalyzed reductive hydroformylation (RHF) of FTS 1-olefins to higher alcohols in a slurry-phase with a high-boiling-point solvent (squalane). This approach contributes to overcome the operational limitations of alternative routes for the direct and selective conversion of syngas into higher alcohols [1]. Water, a major side-product of the FTS, may have multiple effects on catalytic performance, affecting the syngas conversion rate, selectivity as well as the stability of both the solid and molecular catalysts under the developed hydrothermal conditions (T=200 °C, P>150 bar). In this work, kinetic and selectivity effects of water are systematically studied by incorporating different amounts of exogenous water to the reaction medium, at the onset of batch-wise syngas conversion tests. The addition of exogenous water led to a remarkable increase of both higher alcohol selectivity and productivity, reaching 38 C% and 212 mg·g<sub>Co</sub><sup>-1</sup>·h<sup>-1</sup>, respectively (Figure 1). Furthermore, surface hydrophobization of the FTS catalyst (via grafting with silylating agents) results in a further increase in alcohol selectivity to ca. 45 C%. Remarkably, the presence of water enhanced the linear-to-branched ratio in the higher alcohol products to 4-5, facilitating further alcohol dehydration to synthetic aliphatic ether (e)fuels.



**Figure 1:** Evolution of the liquid product distribution for the tandem FTS-RHF syngas conversion to higher alcohols, as a function of the carbon chain length and the initial content of exogenous water.

[1] Direct Conversion of Syngas to Higher Alcohols via Tandem Integration of Fischer-Tropsch Synthesis and Reductive Hydroformylation, K. Jeske, T. Rösler et al., *Angew. Chem. Int. Ed.* 2022, 61.