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HYBRID TANDEM CATALYTIC CONVERSION PROCESS TOWARDS HIGHER OXYGENATE EFUELS

E-TANDEM - Deliverable report

D2.1 Report on surrogate HOEF production

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Author(s)	Alberto Rodríguez Gómez (CSIC), Laura Latorre Valverde (CSIC), Gonzalo Prieto (CSIC) Jeongmin Ji (MPG), Andreas J. Vorholt (MPG)	2024-07-20
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V1.0	10/07/2024	Laura Latorre Valverde (CSIC), Alberto Rodríguez Gómez (CSIC), Gonzalo Prieto (CSIC)	First draft produced and delivered to MPG for additions
V2.0	20/07/2024	Jeongmin Ji (MPG) Andreas J. Vorholt (MPG)	MPG reviews first draft and implements editions and additions with data on ether surrogate production upscaling
V3.0	22/07/2024	Gonzalo Prieto (Coord)	Coordinator reviews and edits consolidated draft prior to internal review by UCT
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Project summary

E-TANDEM's ambition is to unlock an efficient and direct production of a new higher-oxygenate diesel-like e-fuel for the marine and heavy-duty transport sectors. This oxygenated fuel is directly produced from water, CO_2, as the sole carbon source, and renewable power as the sole energy input, in a once-through hybrid catalytic conversion process integrating three major catalysis branches: (1) high-pressure electrocatalysis *syngas* production coupled to a tandem catalytic e-syngas conversion, encompassing (2) thermocatalysis with solid catalysts and (3) chemocatalysis with molecular complexes. The project will demonstrate the new e-fuel production process at bench-scale, and assess its capacity to cope with fluctuating energy inputs.

Publishable executive summary

Central to the objectives of E-TANDEM is a thorough evaluation of the physicochemical characteristics of the proposed higher-oxygenate e-fuel (HOEF). This includes analysis of its blendability with fossil benchmark fuels, such as marine gasoil (MGO), as well as evaluation of the e-fuel, in neat form and blends thereof, as to their compatibility with existing regulations for diesel fuels and materials which are relevant for those encountered in the current fleet of internal combustion engines (ICE) and fuel storage and distribution infrastructures. Aging properties are also to be evaluated. These tasks consume greater amounts of fuel than those to be eventually produced once the e-fuel production concept is experimentally demonstrated at benchtop scale (with cumulative productivities in the sub-L range). Therefore, fuel formulation and characterization tasks are conducted with surrogate synthetic fuels, which are prepared at multi-Liter scale, with chemical compositions resembling closely those which are relevant for the HOEF in its two considered realizations:

(i) A mixture of synthetic aliphatic higher (C_{6-10}) alcohols.
(ii) A mixture of synthetic aliphatic higher (C_{8-20}) ether compounds.

This report outlines experimental results associated to the production of the two surrogate mixtures. First, the formulation of a mixture of higher alcohols is described, blending preset amounts of commercially available *n*-alcohols and 2-methylalkyl alcohols, as well as *ad hoc*-synthesized 2-methylalkyl alcohols in those cases where there is no commercial availability. Next, the report discusses lab-scale development and optimization of an experimental recipe for the catalytic dehydration of the mixture of synthetic higher alcohols into their higher derivatives, as well as the upscaling of said recipe from a few mL/batch lab scale to a 10 L/batch benchtop scale. The role of type (Lewis vs Brønsted) and density of surface acid sites on the solid catalyst, and process conditions for the selectivity and yield of the alcohol dehydration reaction is analyzed. Using model alcohol reactants in neat, solventless form as well as dissolved in suitable inert solvents, the influence of operational parameters such as the linear-to-branched (L/B) molar ratio and the hydrocarbon chain length of the alcohol reactants, as well the concentration of water (major side product) on the alcohol dehydration kinetics are analyzed at lab scale. The selection of a solid dehydration catalyst as well as reaction conditions are found to be crucial to optimize the selectivity and yield to synthetic ethers (the product of the bimolecular dehydration of alcohols), while avoiding the side production of olefins (side-products as a result of monomolecular alcohol dehydration pathways). Under conditions considered preferred for the upscaling of the process to bench scale, a selectivity to synthetic ethers >85% could be attained for the recovered liquid products (ca. 60% overall yield). The alcohol dehydration process was upscaled stepwise to a 10 L/batch level, enabling the production of relevant volumes of the higher ether surrogate e-fuel. The resulting ether mixture is going to be applied in fuel formulation and characterization tasks.