Air Carbon Recycling for Aviation Fuel Technology

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v0.2	2023-01-15	V.Gil, Aragon Hydrogen Foundation ALL	Final draft of the report, consolidated version
v0.3	2023-01-31	V.Gil, Aragon Hydrogen Foundation	Consolidated version. Final document after Quality Assurance submitted to the EC

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Executive Summary

This report includes a summary of the work performed during the first period of 4AirCRAFT, from 1st May 2021 to 31st October 2022.

During the first half of the project, we have developed a novel catalyst for CO_2 conversion that contains only non-precious elements.

Currently, the selectivity and efficiency of the conversion of the novel catalyst is being improved by chemical modification and exploring the combination of supports and catalyst to reach the target value.

We have also performed the synthesis of several inorganic nanocatalysts for the conversion of CO to hydrocarbons. After the synthesis and initial characterization, catalytic testing and screening have been performed. Our results show moderate conversion rates for CO in agreement with reported catalysts. However, further investigations are focused on reaching milder synthesis conditions than current ones. Selectivity to aviation fuels has not been achieved yet, which indicates that further optimization of the catalysts is required.

X-ray diffraction (XRD), thermogravimetric analysis (TGA), volumetry and in situ infrared (IR) spectroscopy were employed to gain a deeper understanding into the catalytic properties of the different catalysts.

High-resolution transmission electron microscopy (HRTEM), Energy Dispersive X-ray Spectroscopy (EDX) and electron diffraction gave a view of the microstructure of the layered double hydroxides (LDH) (basal spacing, homogeneity, defects).

Various types of biocatalysts and biomimetic catalysts were screened for the organic-synthetic dehydration target reaction, and most promising catalysts have been prioritized. Biomimetic catalysts have been included in the screening study since an enzymatic dehydration of primary alcohols was not observed. We could demonstrate that with the most suitable catalytic systems, dehydration can be conducted under mild reaction conditions and furnish the desired alkene products in good yields of more than 70 %. As a primary alcohol raw material, hexan-1-ol was used. Process optimization of this key step, for which *in situ*-product removal through distillation is essential, is currently ongoing.

HRTEM, EDX and electron diffraction gave a view of the microstructure of Metal Organic Frameworks (MOF) (morphology and preliminary enzyme distribution).

Regarding the biocatalysts´ encapsulation the activity of the enzyme once immobilized is partially affected in comparison to the one of the free biocatalysts. Alternative biomimetic systems are being developed as a mitigation plan to obtain a system able to work efficiently at mild conditions.

In case of inorganic supports manufacturing, supports for functionalization with MOF`s and supports with lamellar porosity features for electrocatalysts have been developed.

Structural components for the cascade reactor have been preliminary designed and are subject to optimization through the findings from their performance.

A plan for Communication, Dissemination and Awareness and a plan for Exploitation were developed. A project website has been developed (www.4aircraft-project.eu). The External

Advisory Board has been engaged representing some of the world's leading industries on sustainable fuels production for transport and petrochemical use as well as sustainable feedstock for specialty chemicals and other purposes.

1. 4AirCRAFT concept and objectives

The aviation sector has the second-highest energy demand in the transportation industry after the road sector and it is highly dependent on energy-dense fuels. Although aviation carriers, manufacturers, and governments have all aimed to increase energy efficiency through significant technological advances over recent decades, this transport mode has struggled to find alternatives to fossil-based fuels and nowadays it is responsible for a high share of the 13% of the greenhouse transport sector emissions.

Unfortunately, **conventional technologies to produce aviation fuels are based on the use of fossil sources and** often suffer from **low selectivity** and **conversion** while **lacking energy efficiency**.

Therefore, **new technology** solutions are required, in which the **rational design of catalytic materials** able to reduce the energy barriers of the key steps within the reaction chain is a must.

4AirCRAFT aims to develop a game-changer technology for the direct conversion of CO_2 to ≥ C_8. By the cooperative development, validation and exploitation of the rational design of each material, their synergetic combination, and the fine-tunning of each “catalytic environment” in a holistic manner more energy efficient processes as compared to conventional synthesis routes will be investigated.

4AirCRAFT aims at producing alternative high-density fuels at mild conditions, which thanks to a cascade reactor based on process intensification, use of CO_2 as carbon source and renewable energies ultimately lead aviation industry to a sustainable future.

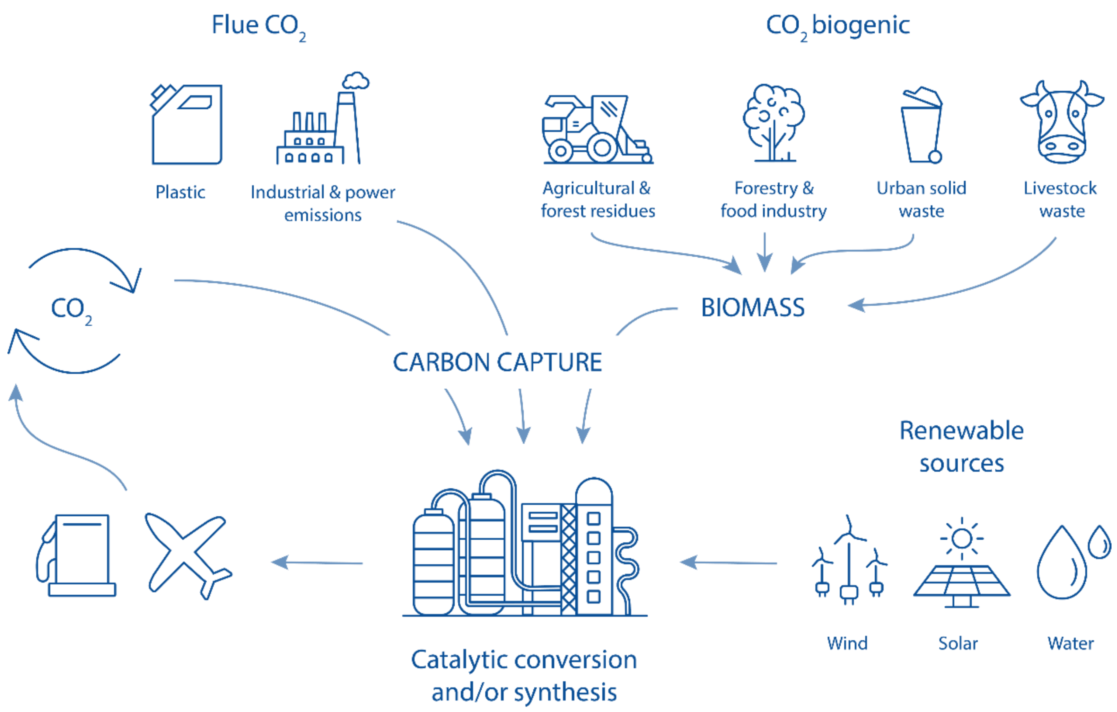

Figure 1. 4AirCRAFT concept.

The project integrates and exploits a novel multi-catalyst reactor technology that might combine electro-, chemo- and bio- & biomimetic catalysts. 4AirCRAFT investigates their controlled spatial distribution within application tuned catalyst carrier structures that are based on metal-organic frameworks and engineered inorganic scaffolds with hierarchical porosity distribution. In terms of inorganic catalysts, size and shape of metal nanoparticles, metal clusters, and single atoms at the surface of catalyst carrier structures will be developed, and precise structure-performance-selectivity relationships will be established. In terms of bio-& biomimetic catalyst, special emphasis will be given to assure the long-term stability of deployed enzymes through programmed anchoring and shielding from detrimental reaction conditions.

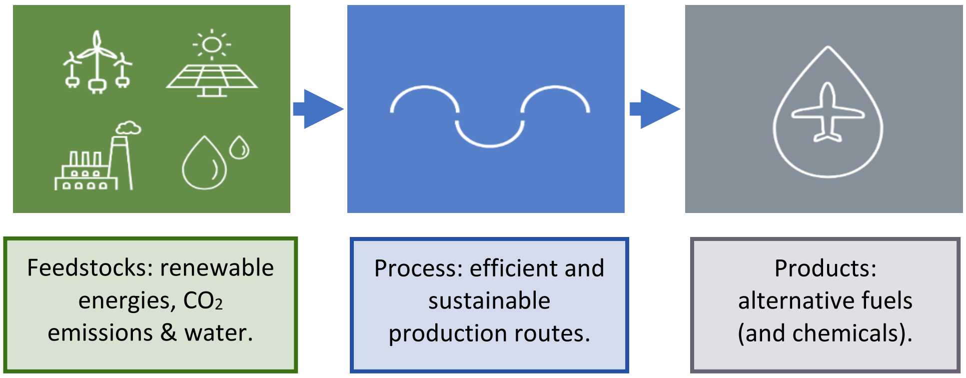

Figure 2. 4AirCRAFT approach.

Table 1. 4AirCRAFT objectives.

Objective	Research activity	Description
O1	Electrocatalysts	Development of novel catalyst formulations for CO_2 reduction reaction.
O2	Bio- & biomimetic catalysts	Tailor-made design of biocatalyst for key steps in air fuel production.
O3	Bifunctional nanocatalysts	Development of novel bifunctional catalysts for advanced olefins synthesis.
O4	Catalysts carriers	Optimisation of catalytic properties by the development of novel porous catalyst carriers for selective catalyst stabilisation.
O5	Advanced characterization	Structural and mechanistic investigations.
O6	Reactor	Cascade reactor design and development.
O7	Proof of the concept	4AirCRAFT proof of concept, determination of its environmental life cycle aspects.
O8	Impact	Networking activities with ongoing projects and other initiatives.
O9	Impact	Awareness, communication and dissemination activities, carrying out key actions to engage stakeholders.

2. Summary of activities carried out: Month 1-Month 18

The status by month 18 of 4AirCRAFT objectives listed in section 1.1. are shown in subsections below. This progress is organised by work package following the work plan structure in Figure 3.

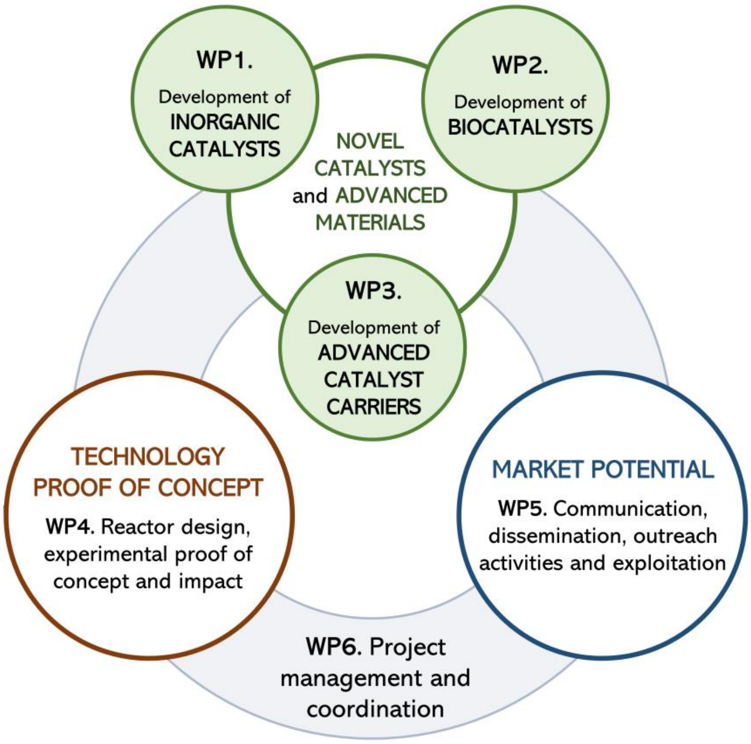

Figure 3. Work plan structure of 4AirCRAFT project.

The objective of WP1 is to investigate advanced electro-catalysts with carbon dioxide affinity along nano-catalyst for simultaneous CO and short hydrocarbons conversion to long chain hydrocarbons.

During the first half of the project, it has been developed a novel catalyst for CO_2 conversion that contains only non-precious elements. The electrocatalytic activity using different electrochemical cells and catalytic activity for Fischer-Tropsch reactions were intensively investigated as well as the structural and morphology characterization of the most promising materials.

The selectivity and efficiency of the conversion of the catalyst is not only being improved by chemical modification and exploring the combination of supports and catalyst but also by performing the synthesis of several inorganic nano-catalysts for the conversion of CO to hydrocarbons.

Results of catalytic testing and screening show CO conversion. However, further investigations are focused on reaching milder synthesis conditions than current ones.

In parallel, research efforts are focused on the understanding of the nature of the interaction of electrocatalyst and CO_2 and the mechanisms involved in the formation of the products of the reactions.

Inorganic Zn-based electrocatalysts resulted to be the most efficient and selective materials for the CO_2 reduction reaction with a 67% of selectivity for CO evolution and 94% selectivity for CO and H_2. Bifunctional catalysts based on Fe species and zeolite H-ZSM-5 support were prepared by different chemical routes in which dry impregnation procedure resulted to be most efficient to catalytic activity with a reaction selectivity for C2-C5 hydrocarbons of 53.5 %. The acid properties have also a positive effect on the selectivity. Currently, the selectivity of both, electrocatalysts and nanocatalysts materials, are investigated to achieve superior values. Chemical composition, physicochemical properties (particle size, morphology, etc.) and of the porosity and acidic properties of the zeolites using in the nanocatalysts are some of the strategies considered. In parallel, research efforts are focus on the understanding of the nature of the interaction of electrocatalyst and CO_2 and the mechanisms involved in the formation of the products of the reactions.

WP2 focuses on the design of suitable biocatalyst for dehydration of alcohols being of relevance as intermediates for alternative jet fuels. Bio-&biomimetic catalyst immobilization in unique structures such as ceramic membranes and MOFs is also explored. WP2 objective is to transfer the developed chemo-/enzymatic cascade into the whole reactor concept and related process development and optimisation towards obtaining process data fulfilling the requirements for industrial bulk chemicals production.

So far insights into the scope and limitation of biocatalytic dehydration of primary alcohols to form alkenes from renewable feedstocks have been addressed. As alternative catalysts to enzymes, alternative biomimetic systems are being developed to obtain a system able to work efficiently at mild conditions. For this purpose, various bio- and biomimetic catalysts were screened and prioritized.

This working package already revealed an efficient process for the dehydration of these primary alcohols, which gives high product yield under mild reaction conditions for such a transformation. Accordingly, activities in terms of patent protection are being investigated.

The objective of WP3 is the fabrication and optimisation of advanced catalyst carriers based on metal organic frameworks (MOFs) and hierarchical scaffolds with highly favourable microstructures for diverse catalyst hosting and reactions.

The crystallization conditions of tetravalent metal-based MOFs have been softened down to room temperature during this period. For the first time, the efficient encapsulation of a model enzyme into the material during its crystallization has been achieved. In parallel, the integration of the MOFs into hierarchical scaffolds has been performed, to later on integrate the bio-/biomimetic catalysts in the system during the second period of the project. As alternative catalysts to enzymes, new acidic and super-acidic MOFs have been crystallized, and post-synthetically oxidized and sulphated. Additionally, hierarchical supports with lamellar porosity features have been also successfully developed as catalyst carriers for electro- and nanocatalysts functionalization.

Performance assessment of supported catalysts and computer simulation of functionalized catalyst carriers have been initiated.

The main objective of WP4 is the development of the cascade reactor for evaluation performance and proof of the concept.

The following activities of WP4 were defined:

- Design adjustment and assembly of cascade reactor structures.
- Design and commissioning of the test bench.
- Experimental proof-of-concept.
- Perform an impact assessment concerning environmental life cycle aspects.

Structural components with corresponding functional parts as advanced catalyst carriers for cascade reactor have been preliminary designed and are subject to optimization through the findings from their performance. Advanced catalyst carriers had to be designed and functionalized with the most promising catalysts in terms of efficiency and catalytic performance (feedback from WP1, WP2 and WP3). The reactor module focused on the electrochemical reduction of CO_2 to CO is currently being developed.

In WP5 a plan for Communication, Dissemination and Awareness as well as a plan for Exploitation has been developed. The project identity has been addressed through the Project Logo, colour patterns and templates for Documents and presentations. Further communication material has been developed such as fact sheets and the 4AirCRAFT press kit which will be kept up to date throughout the project live span. As the center for all public communication of all project related information a project website has been developed (www.4aircraft-project.eu) where the latest developments around 4AirCRAFT are publicly available. Advisory Board Members and stakeholders from the industry have been engaged to maximized the project impact.

3. Progress beyond state of the art and Next steps

At the core of 4AirCRAFT innovation is the synergetic combination of tailor-made electro-, chemo- and bioinspired catalysts and their controlled spatial distribution within application tuned catalysts carrier structures. This will enhance the activity of catalytic phases and materials allowing high CO_2 conversion rates and selectivity towards long-chain hydrocarbons.

The conversion of CO into aviation fuels under mild reaction conditions, such as below 250 °C would already represent an achievement beyond the state-of-the-art. This would already represent massive economic and environmental impacts in the aviation industry and thus on society.

A promising catalytic dehydration methodology leading to the desired alkene products (which serves as key intermediates for the envisaged jet fuels) has been developed in the first phase of this project. Based on this progress, we will now further focus on optimization and process intensification of this technology, which is expected to be a “ready-to-use”-technology for technical purpose at the end of the project. In case of success, this technology will be also usable for other related industrial alkene products, thus then representing a “technology platform” with applications also in the other segments of the chemical industry, in particular for the fields of bulk and specialty chemicals.

This is the first time that an enzyme encapsulation is achieved in chemically robust MOFs. Further optimization of the process can give rise to a robust biocatalyst-based system able to work under non-conventional conditions usually employed for enzymes. If this point is reached, the techno-economic impact of the result could gain the interests of petrochemical and pharmaceutical industries.

Regarding the status of the project objectives, we are close to reach our selectivity target for CO formation. The present results suggest that there is enough potential for the achievement of the final target (more than 90% of selectivity or Faradaic efficiency for CO formation), by adjusting compositions of materials and experimental conditions.
About the overpotentials, only small current density for the CO formation has been observed. The overpotentials might be reduced with the combination of catalyst support and cell configurations. About the catalyst durability, we have shown that the CO-forming activity was maintained in at least 6 h as a first assessment. After a catalyst showing high enough Faraday efficiency has been developed, the catalyst durability should be evaluated.

Further research activities on the second half of the project are focused on improvement of electro-, nano- and bio-/biomimetic catalysts and advanced catalysts carriers along module reactors assembling for final testing and proof of the concept. Impact of the novel technology and potential of the key results will be also explored.

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