



# How Hybrid Catalysis Can Support the Deployment of the "Carbon Cyclic Economy-CCE"

## **Michele Aresta\***

Innovative Catalysis for Carbon Recycling-IC2R Ltd, Tecnopolis, Valenzano, Italy

#### Abstract

The Carbon Cyclic Economy is at the heart of the Circular Economy that will characterize the future of our Society. Cycling Carbon will mimic Nature that has developed the Carbon Cycle over million years and uses such tool for stabilizing the atmospheric content of  $CO_2$ , the most easy-to-reach and abundant form of carbon. A Man-Made Carbon Cycle will complement the natural one and will contribute to mitigate climate change. The use of sources of carbon as an alternative to fossil-carbon (waste biomass, waste plastics and  $CO_2$ ) is the way to cycle GtC/y, using perennial energy sources (Solar, Wind, Hydro, Geo-Power, SWHG). The role of hybrid catalysis has a fundamental importance for the deployment of such renewable sources of carbon.

# Opinion

Cycling Carbon for feeding the Chemical Industry (but also the Energy Sector) is one of the key aspects of the Circular Economy-CE. Waste biomass used plastics and  $CO_2$  are the sources of renewable carbon that may substitute fossil C, progressively reducing the extraction of carbon from ground and its transfer to the atmosphere. The Carbon Cyclic Economy-CCE will greatly reduce the environmental impact of anthropic activities and produce economic benefits in the medium-long term [1]. All alternative sources listed above raise issues for their full deployment, even depending on the kind of products one plans to produce. In particular  $CO_2$ , that is the most abundant among them, has quite peculiar requirements whether it must be used for making chemicals or energy products. In fact, in the latter case it needs both energy and hydrogen that must be provided by non-fossil-C sources, a quite stringent demand. Recycling of carbon requires catalysis (chemo-, electro-, bio-catalysis) for overcoming energy barriers, speeding-up reactions, driving the selectivity towards target products. Hybrid systems may represent the best options, as "one can do what other(s) cannot". Bio-catalysis can be carried out by using either enzymes or full microorganisms. Enzyme-catalyzed processes have been used for centuries to make wine, beer, bread and cheese.

In general, enzymatic processes are faster, cleaner and easier to operate than microbial processes, which occur under strictly controlled conditions and require careful separation and purification steps of the final products [2]. Waste biomass (municipal solid waste, water treatment plants sludge, manure, residues from agriculture, wood industry and food industry) can be recycled by using integrated chemo-electro-bio applications in the frame of exploitation of the concept of Biorefinery, avoiding the energy-consuming gasification to Syngas and making a direct use of the rich complexity of biomass [3]. Electro-chemical systems can be integrated with biotechnology (to produce Bio-electrochemical systems-BES) to afford powerful tools for speeding recycling processes. Photo Bio Electrochemical Systems (PBES) are also interesting new options for waste, capital costs-CAPEX and operational cost-OPEX reduction and increasing the conversion yield and selectivity towards a target product. Supposed that chemo-catalysts and enzymes do not deactivate each-other, such combination, a quite complex and new matter that deserves careful investigation for highlighting its

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\*Corresponding author: Michele Aresta, Innovative Catalysis for Carbon Recycling-IC2R Ltd, Tecnopolis, Valenzano, Italy

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potential, may represent a solution for several problems that have not been solved so far by applying a single technology.

Waste plastics are quite a new topic as so far little has been done for their effective recycling. In fact, only 9% of the over 360 Mt of plastics produced each year are recycled, using a variety of technologies from mechanical recycling, to chemical and biorecycling. However, all recycling options face challenges in dealing with economic viability, legal status, technical performance, environmental concerns and supporting infrastructure. Here the nature of the polymers plays a key role for the application of catalytic technologies. The production of bioplastics may represent a route to implementing an effective recycling process driven by hybrid catalysis. As a matter of fact, fossil-C derived polymers such as polyethene and polypropene are scarcely recyclable by catalytic processes and better recycling using mechanical or thermal technologies [4]. Hybrid catalysis could find useful application in the recycling of polymers of bio-origin, such as cellulosic materials or polyesters applying the Biorefinery strategy [5]. The attack of ether or ester linkages is the preferential site for chemo-catalysts, microorganisms, or enzymes. Designing new bio-based polymers may favor high-rate recycling. This field needs deep investment in R&I to improve the deployment of the recycling strategy [6].

Recycling carbon in the form of  $CO_2$  is the field where hybrid catalysis will have a key role in maximizing the use of renewable carbon and pushing the CCE. The utilization of  $CO_2$  must be considered a strategic technology for the future and is attracting considerable attention for its upscale from fundamental research to industrial application. The efficient conversion of (renewable)  $CO_2$  using enzymes could complement the thermal, electro chemical, photochemical and photoelectrochemical processes for its effective utilization, [7] eventually reducing the impact on climate change while producing useful chemicals or fuels. Heterogeneous catalysis,

electrocatalysis and photocatalysis are presently the three predominant technologies for converting  $CO_2$  into useful chemicals, such as methanol, formic acid, acrylic acid and carbonates, among others [8]. The integration with the enzymatic approach to convert  $CO_2$  brings-in several advantages [9] such as high selectivity under mild reaction conditions without any significant impact on the environment [10].

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