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Evolving scenarios for biorefineries and the impact on catalysis☆

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ABSTRACT

The model of future biorefineries is changing driven from many motivations, particularly the need of improving sustainability and integration with the chemical production. This conceptual review discusses this change, with focus on the case of integrated chemical biorefineries, and how the new scenarios for a sustainable chemical production require to develop new related models of biorefineries. Two cases are discussed in detail: (i) olefin biorefineries and (ii) biorefineries for sustainable chemical production. In addition, some elements for an integrated solar biorefinery approach are also given. The status of catalysis research to enable the development of these biorefinery models was discussed, together with an analysis of the industrial developments in the field and some elements of assessment of the different routes. The aim was to provide fundamentals to understand how this area is evolving, and thus identify where research effort has to be focused. It was also commented how the simple economic analysis, with boundary limits to plant gate, although important, is not enough to properly identify the future scenarios.

1. Introduction

The drivers pushing towards a bio-based economy are many: (i) Kyoto and related politics to reduce carbon footprint, (ii) security of supply, (iii) agricultural policies, (iv) sustainability and (v) support of the local economics. There is thus a mix of motivations driving the development of these areas mostly based on social and policy aims rather than purely economic and industrial incentives [1]. For this reason, government policies drive change in energy/chemical production from bio-based materials through a mix of actions such as mandate fuel mix, subsidies, renewable targets and carbon targets. The consequence is that there are different country/regional priorities. This is schematically illustrated in Fig. 1 evidencing the different relevance given to aspects such as greenhouse gas (GHG) emissions, energy and domestic economy by some country/regions, reflecting then in different priorities and targets for the development of a bio-based economy [2]. This is clearly an evolving scenario, because (i) some expectations of few years ago are not more valid or different and (ii) local socio-political pushes determine different priorities conditioning the evolution of the bio-based economy on country/regional level rather than on a global scale.

Even taking into account that priorities could be different depending on the specific country/region, it is necessary to analyze the future scenarios for a bio-based economy, in order to discuss the possible type of biorefineries and related needs of new catalysts. In fact, the macro-trends of research in catalysis in the area of bio-refinery appear not well aligned with the priorities which may be identified for future biorefinery scenarios and briefly discussed in the following sections. This concept may be exemplified using the topics discussed in the most recent review (March 1st, 2014) returned by Scifinder in searching with the keywords "catalysis" and "biorefinery" [3]. The topics discussed for first generation biorefineries are the following: (i) biodiesel production, (ii) conversion of glycerol and (iii) bio-ethanol from starch-rich biomass. For second generation biorefineries: (i) cellulosic ethanol, (ii) lactic acid from glucose, (iii) pyrolysis of ligno-cellulosic biomass, (iv) bio-oil upgrading and (v) gasification of biomass and bio-oil to syngas. The discussion in the next sections about the future scenario for biorefineries evidences that the priorities are probably different and as a consequence the need in terms of catalysis development.

For the specific characteristics briefly outlined before, the field of bio-refinery and -economy is depending largely on external factors to techno-economic aspects. Therefore, it is not possible to leave aside an analysis of these external factors to identify the possible scenario for future biorefineries and as a consequence the priorities and needs for catalysis. This paper is thus organized in two main

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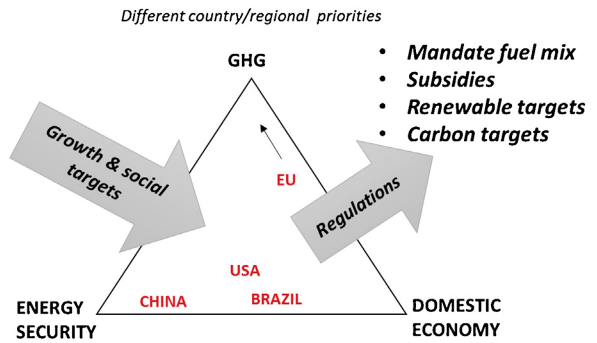

Fig. 1. Different relevance given to aspects such as greenhouse gas (GHG) emissions, energy and domestic economy by some country/regions, reflecting in different priorities and targets for the development of a bio-based economy.
Adapted from Ref. [2].

sections. A first part discusses briefly the drivers and routes for future sustainable biorefineries to identify the possible scenario. A second part analyses more specifically two main concepts of future biorefineries which derive from the preliminary evaluation. The focus in this part is to analyse the current state of development in the discussed routes, in terms of catalytic performances and industrial targets. In fact, other papers and reviews (cited later) have discussed aspects such as the relation between catalyst composition, reaction mechanism and performances, but an analysis of the key priorities for catalyst development necessary is often missing. As remarked before, often the aspects discussed in literature and the objectives for catalyst development are not coincident with the industrial needs.

2. Biorefineries of the future

It must be shortly introduced that in a region such as Europe, sustainability and low carbon economy are two of the key elements strongly influencing biofuel targets and in general bio-economy, through government policies, such as subsidies and mandated use of biofuels. The reason was the need to address concerns related to the environment, energy security and rural development, but the cost-effectiveness of achieving these goals under current subsidy/policy schemes is often low [4]. On the average, the use of bioenergy allows to save about 50% of CO_2 emissions with respect to fossil fuels, although many parameters affect LCA (life cycle assessment) of the use of bioenergy [5]. In addition, some alternatives to biofuels are possible today. Methanol produced from the reuse of CO_2 and renewable energy (RE) has a potentially larger impact in terms of saving CO_2 emissions, as well as in terms of resource and energy efficiency [6]. Solar fuels derived from CO_2 and RE [7–9] could be an economic and more eco-efficient alternative to biofuels. It is thus possible a shift in the government policies on biofuel targets, with a consequent impact on the future of biorefineries [10].

On the other hand, reuse of CO_2 emitted in biorefineries (fermentation processes generate large volumes of carbon dioxide, for example about 1 ton CO_2 per ton of bioethanol produced by glucose fermentation) and the integration of solar energy into the biorefinery scheme are important elements determining the future of biorefinery. They will be shortly discussed in Section 4.2.

2.1. Drivers for future biorefineries

Few years ago, discussing the alternative routes in the catalytic transformation of lignocellulosic materials [11,12], some elements driving the future of biorefineries were analyzed from the perspective of sustainability and low-carbon economy: (i) use of waste biomass and marginal lands, (ii) minimize intensive cultivations and transport, (iii) no food competition and (iv) reduce impact on water. Between the consequences the need of (a) developing efficient technologies of transformation at small-scale, (b) realizing small plants (low investments) with a tight integration with chemical production (common platform molecules) and food (e.g. development of agro-chemical/energy districts), and (c) avoiding high temperature processes (thermochemical treatments are complex, costly particularly for small-scale and show a low energy efficiency, in terms of ratio between final and input energy, when applied on small scale).

Although a detailed discussion is out of the scope, it is necessary to remark that new factors/trends influencing the strategic choices for future biorefinery scenarios are emerging today in response to new options and requests for energy, climate and environmental issues, energy security. We believe that the following aspects are critical from this perspective, and motivate the aspects discussed later, even if it is correct to evidence that there is not a general consensus on the statements reported below:

- Biofuel expectations for 2050 have to decrease from 27% of total transport fuel (IEA Blue Map scenario [13]) to about 15%, due to increased availability of non-conventional fossil fuels (particularly, shale gas in US and coal in China), and also some alternative fuels such as those deriving from CO_2 using renewable energy.
- The transition from 1G (1st generation) to 2G/3G biofuels will be probably less fast than expected; a main reason is that 1G technologies are simpler, and require less investments.
- 2G biofuel routes will be dominated from routes with full use of biomass and which well-integrate within the actual refinery scheme. In this context alternatives such as bio-crude vs. platform molecules, waste biomass vs. dedicated crops have to be analyzed.
- Higher efficient biomass production minimizing land use is necessary. Algae utilization, in particular using seawater, is a required direction to proceed, but technologies to allow their economic processing (besides growing) are crucial.
- Integration with chemical production will be a key factor for platform molecules. Integrated chemical biorefineries is the direction to valorize the higher added value of chemical production.
- Integration of bio- and solar-refineries, in order to exploit and valorize the CO_2 produced in biorefineries as well as to integrate RE sources in biorefinery production (solar biorefineries).

2.2. Routes for sustainable biorefineries

An analysis of the routes for sustainable biorefineries, according to the drivers briefly outlined above, should start from current identification of the potential routes for the development of biorefineries up to 2030 [14]. There are different possible biorefinery schemes identified in this report, although the relative impact on the future scenario is different. They were classified depending on the prevailing type of raw materials:

- *Starch and sugar biorefineries*: processing starch crops, such as cereals (e.g. wheat or maize) and potatoes, or sugar crops, such as sugar beet or sugar cane.
- *Oilseed biorefineries*: currently produce mainly food and feed ingredients, biodiesel and oleochemicals from oilseeds such as rape, sunflower, and soybean.
- *Green biorefineries*: processing wet biomass, such as grass, clover, lucerne or alfalfa. They are pressed to obtain two separate product streams: fibre-rich press juice and nutrient-rich pressed cake.
- *Lignocellulosic biorefineries*: processing a range of lignocellulosic biomass via thermochemical, chemiocatalytic or biochemical routes.