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Chemistry and energy beyond fossil fuels. A perspective view on the role of syngas from waste sources☆

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ABSTRACT

After briefly introducing the future scenario for energy and chemical production to remark the need to develop new catalytic routes to use C-sources alternative to fossil resources, this perspective paper discusses two key technologies in this direction to move beyond fossil fuels: i) waste-to-chemical, with a discussion of the techno-economic aspects to convert municipal solid wastes to base chemicals (urea, methanol, olefins), and ii) power-to-X, with focus on CO_2 methanation. Attention is on the role of syngas in the future scenario, evidencing some of the open questions for catalysis on these technologies. For CO_2 methanation, it is highlighted that the crucial aspects of catalysts development are often not properly addressed, in spite of the abundant literature.

1. Introduction

Syngas (synthesis gas, i.e. a mixture of H_2, CO, and CO_2 in variable proportions) is one of the pillars of production of chemicals and energy vectors. Fig. 1 shows, in a simplified scheme, how syngas is at the interface of chemistry and energy, being involved in current production of many relevant chemicals or energy products. The syngas market size in year 2016, by end uses, was about 180 Mtons/y for ammonia, 85 Mtons/y for methanol, 40 Mtons/y for H_2, 21 Mtons/y for Fischer-Tropsch liquids, 25 Mtons/y for syngas to power (IGCC), 8 Mtons/y for substituted natural gas (SNG). The projected Compound Annual Growth Rate (CGGR) in the 2016–2024 period is about 8–9%, with an overall production increasing from 116,600.0 MWth in 2014 projected to reach 213,100.0 MWth by 2020 [1]. There are thus large market expectations driven by high demand for industrial chemicals, fuels, agriculture products, and electricity worldwide.

Syngas can be produced from different carbon sources. Today, fossil fuels are still the dominant feedstock (> 96–97%), with syngas produced by coal gasification accounting for about 70% of the production followed by a nearly equal share (˜15%) of syngas production from natural gas and petroleum & byproducts. Syngas from biomass or waste gasification accounts for only a few percentages of the worldwide syngas production. Forecasts appear thus positive for syngas market, but there are also a series of issues. The first regards the high dependence from the fossil fuel cost, which shows high fluctuations and large unpredictability. Syngas production is a highly energy-intensive process requiring large plants (to be energy-efficient) with massive capital investments and long amortization and construction times. The negative combination of unpredictability in the long-term of the main cost element and the requirement of long-term investments represent thus a relevant issue. These aspects deters investors. In parallel, the use of renewable energies is progressively becoming economic with respect to the use of fossil fuels in many applications (see, for example, IRENA – International Renewable Energy Agency – recent report [2]). This will cause a relevant impact also on petrochemistry and in general on the raw materials and energy sources for chemical production [3]. Thus, in addition to environmental motivations, including the social pressure for climate change mitigation, the substitution of fossil fuels with alternative cleaner and renewable energy sources is a theme of increasing relevance and motivated by both economic and geopolitical (security and diversification of resources) reasons. Thus, the possibility of making chemistry and energy without fossil fuels is of increasing relevance [3], even if still a large debate exists about timing [4–6]. We should note, however, that i) the declining profitability of oil extraction is a fact, and ii) there are clear megatrends in mobility and sustainable energy which will impact the use and added-value of some refinery fractions, with a consequent increase on the overall costs. In fact, the fossil fuel market, due to its structure largely dominated from few producers, is not driven from production costs, but from the need to use oil revenues to sustain the country economies of oil producers, which

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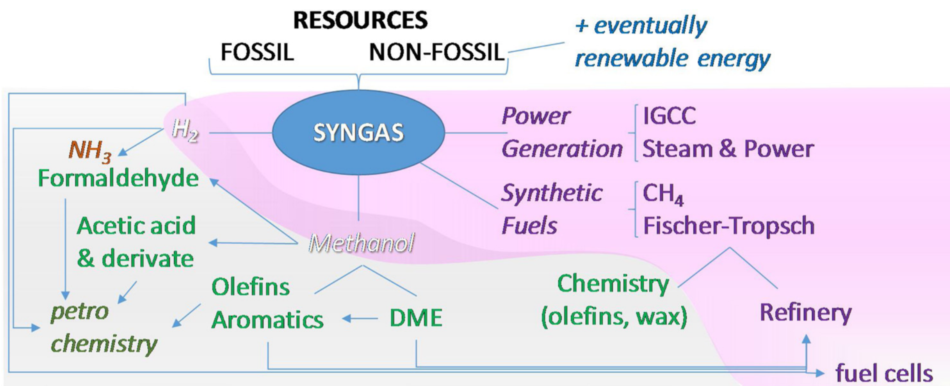

Fig. 1. Schematic presentations of the different typologies of products obtained from syngas and the possibility to produce it by fossil and non-fossil resources, the latter eventually by using renewable energy. In violet are indicated energy products and in green petrochemical products, while in white products at the interface between chemistry and energy. *Note:* IGCC: Integrated Coal Gasification Combined Cycle; DME: dimethyl ether. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

are independent drivers for oil prices. This cost structure will induce a rise of fossil raw materials, being the entire economy of producers too much depending on these incomings. This megatrend scenario, that was indicated from some economists and also remarked by us for chemical production a decade ago [5], indicates that the common idea that fossil fuels will continue to be the backbone for energy and chemistry, will be soon no longer valid.

Transitions in chemistry and energy require several years to be completed, but history shows that transitions, when started, can be faster than expected [5]. The rate in market introduction of low-investment (distributed) technologies is faster than that which is often supposed, because new technologies less depending on fast fluctuating markets have competitiveness incentives and these introduce new competitors on a blocked market, where few operators act in a quasi-monopoly situation as that for energy based on fossil raw materials. Therefore, the proper question is not whether this happens before or after a peak in the production of fossil fuels, but rather when the investment in the old technology (based on fossil fuels) will be no longer convenient. In chemistry/energy this is a critical decision factor, due to the long amortization times and trends in fossil raw materials costs. Sustainability and social pressure are main elements for industrial decisions and market dynamic is a crucial element for evaluation. The Energy Return On Investment (EROI) [7], i.e. the ratio of energy delivered to energy costs, that was often used to demonstrate that fossil fuels are needed to support modern industrial societies (the famous net energy cliff), do not more demonstrate the advantages of using fossil resources with respect to alternatives, particularly when all the factors, i.e. economics, energy efficiency dynamics and energy costs (environmental), are accounted for [8].

Thus, it is an ensemble of factors (just few indicated above for conciseness) driving the change, which is not linear and for which the usual methodologies to make predictions, based on i) linear extrapolation of present trends, ii) advantage of scale economy, iii) market and country economies separation, etc. are not able to catch correctly the evolving scenario. Although the complexity of these predictions makes still difficult to find a common agreement, particularly on timing for the transition, we should remark that the transition is on-going and faster than expected, as perhaps confirmed from the increasing general perception in the last decade about this fast-changing scenario. Even traditionally conservative companies, strongly oriented to fossil fuels markets, are now paying attention on these aspects on energy transition and related impact on (petro)chemistry.

Chemical production should thus consider how to make base chemicals from alternative sources, waste materials being clearly an obvious choice also in consideration of a circular economy [9]. This requires to develop a strategy based on short-, and medium-long term objectives, to enable an effective and smooth transition.

The use of bio-resources is part of this change, but is not discussed here for conciseness. It was addressed in refs. [10–14] among others.

On a short-term, municipal solid wastes (MSW) are a main source of carbon that should be addressed between the various usable C-based wastes for the production of bio-based products. Incineration/thermo-valorization of MSW, however, is still the major solution adopted on a worldwide basis [15–18]. A first part of this perspective will be thus dedicated to the analysis of the feasibility using MSW to produce chemicals, the so called waste-to-chemicals (WtC) approach, with emphasis on the role of syngas played on these technologies and questions they open for catalysis research. WtC is also part of the alternative concept of waste bio-refineries [19]. To remark that it is out of the scope to present a general discussion of the possibilities to convert biomass and MSW to syngas and further to chemicals. The analysis for conciseness is limited to selected examples showing the potential of the WtC approach, and the roles of syngas and catalysis in this strategy.

On a medium-term perspective, the use of waste CO_2, in combination with renewable energy sources to provide the energy for the conversion, is another valuable source of carbon to produce fuels or chemicals for a sustainable energy or chemical production. The use of these wastes (CO_2 and MSW) is an important element of the general strategy towards a transition to a circular economy, a sustainable/low carbon economy and an improved waste management [20]. CO_2 use is also a crucial element to move to a renewable energy-driven economy [3,21], with the expected benefits in terms of contribution to reduction of fossil raw materials and climate change mitigation. Different products and many strategies, from thermal to photo- and electro-catalysis, are possible in CO_2 valorisation [21–23]. We will not discuss here the different possibilities, but just analyse the specific case of CO_2 conversion to methane, as an example of the possibilities, open problems, and challenges given for catalysis. Various reviews have been published on this topic recently [24–27]. We will thus not discuss here the state-of-the-art in this reaction, but just present specific examples, mainly from personal activities, to evidence better the questions and perspectives of developing catalysts for this reaction.

2. Municipal solid waste as C-source for chemistry

Municipal Solid Waste (MSW), in particular the organic fraction these contain and which is indicated often with different names (we will use here the term of Refuse Derived Fuels – RDF) is a waste C-source widely available and in growing amount. It is not utilized for producing chemicals today, although the base techno-economic conditions for the implementation of these technologies exist, as shown later here. It is thus surprising how limited attention has been given to this technology up to now, and related discussion on the role of syngas and catalysis on pushing forward this solution.

It is evident, in fact, that a major issue to substitute fossil resources with alternative C-sources for chemical production is represented by the cost of the raw materials, which determines, on the average, up to 60–70% of the production costs in the case of base chemicals. However, as shortly commented before, there are also a series of additional motivations pushing the transition to low-carbon alternatives, such as i)