FROM SYNGAS TO FUELS AND CHEMICALS: CHEMICAL AND BIOTECHNOLOGICAL ROUTES

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Marco Ricci graduated in Chemistry *cum laude* at the Università "La Sapienza" in Roma in 1979. In the same year, he joined the Istituto eni Donegani where he is currently the head of the Sustainable Chemistry unit.
In 1984 he was Research Associate at the Laboratoire de Chimie de Coordination in Toulouse (France) with dr. Bernard Meunier, working on the use of manganese porphinates as biomimetic catalysts for the oxidation of saturated hydrocarbons.
His research interests focus on selective oxidation, synthetic models of redox enzymes, homogeneous catalysis and, more recently, on energy from renewables and CO_2 biofixation.
He has been awarded of the Oscar Masi prize for the industrial innovation (1991, for selective catalytic oxidations with hydrogen peroxide), the eni Innovation Award, and the National Innovation Prize (both 2011, for the production of fuel oil from solid urban waste).
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Abstract
Chemical and energy uses of syngas is shortly reviewed, focusing the attention on the CO/H_2 mixtures obtained from biomass gasification (bio-syngas).

Introduction
Humankind can not probably avoid a transition from a fossil fuels-based economy to another one based on different energy sources. In the long term, only Sun can provide enough energy to satisfy the increasing world's need, but most of the technologies for the exploitation of its energy are still not economical, nor can be scaled up to the necessary scale. In the meantime, a relatively simple way to exploit solar energy is the use of fuels derived from biomass, including CO/H_2 mixtures obtained from biomass gasification, or fuels produced from them.

Discussion
Current uses of syngas can be arranged into three main classes:
- as a chemical feedstock for producing a number of chemical intermediates;
- as a fuel by itself (and as a biofuel if bio-syngas is concerned);
- as a raw material for other fuels or biofuels.

Syngas is the obvious key-intermediate in the industrial production of hydrogen. Other major chemicals produced from it include methanol and ammonia. Several other uses of syngas or of carbon monoxide can be found in intermediates production and in fine chemistry.

As a fuel, syngas has approximately half of the energy density of natural gas and can be used for its heat value in steam cycles, in gas engines, in fuel cells or in turbines to generate power with co-production of heat.

Alternatively, syngas can be used to prepare top-quality fuels via the Fischer-Tropsch (FT) reaction, affording complex mixtures of hydrocarbons, or even via fermentation by anaerobic micro-organisms able to transform it into ethanol.
The use of bio-syngas, however, presents some specific problems, particularly in the case of FT processes.
Syngas produced from biomass gasification has a low H_2/CO ratio, usually close to 1, very far from the value of 2 required by the FT stoichiometry. Furthermore, bio-syngas usually has several specific impurities: hydrogen sulphide, COS, nitrogen compounds (mainly ammonia and hydrogen cyanide), and hydrogen chloride. So, the ideal FT catalyst to be used on bio-syngas must be able to perform also water gas shift reaction, producing some more H_2 at the expenses of CO. At the same time, the catalyst should be as tolerant as possible towards the impurities or, alternatively, an expensive purification train must be included in the process design. As the result, when syngas produced by biomass gasification is concerned, iron-based catalysts are probably to be preferred to the cobalt-based ones which are more active but, at the same time, are also more sensitive to the impurities (particularly, H_2S and COS) and, being poor catalysts for the water gas shift reaction, require higher H_2/CO ratios.
A quick assessment, which takes into account theoretic (thermodynamic) and practical limits of biomass production, shows that farming of giant reed (*Arundo donax*) on a production area with a radius of 20 km would allow to produce ca. 11.000 bpd (barrels per day) of liquid fuels (ca. 550 kt/y), a figure not so different from those accepted as economically appealing. For the calculation, the following assumptions have been made: dry biomass productivity, 40 t/ha x y; harvesting efficiency, 0.8; dry biomass heat value, 17.4 GJ/t; energy efficiency of the process, 0.3; diesel fuel heat value, 37,8 GJ/t.
Interestingly, FT reaction can also exploit CO_2/H_2 mixtures, rather than the more traditional CO/H_2 ones.

References

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