# Hydrogen, ethylene and power production from bioethanol: are we ready for the renewable market?

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## Introduction

The economic sustainability of renewable based sources is a matter of debate and the technology is changing very fast. We here considered three examples of exploitation of bioethanol as renewable source: a) centralised hydrogen production; b) heat and power cogeneration (residential scale); c) ethylene production. Bioethanol can be a suitable starting material for the production of H<sub>2</sub>, as fuel or chemical, or syngas for its conventional uses. After designing the process and the implementation of kinetic expressions based on experimental data collected in our lab and derived from the literature, an economic evaluation and sensitivity analysis allowed to assess the economic sustainability of hydrogen production and purification by the steam reforming of bioethanol. The attention was mainly put on diluted bioethanol solutions, easy to purify and cost effective. The centralised hydrogen production from bioethanol was considered cost effective at least starting from diluted bioethanol from first generation crops. The main items affecting the exploitation potential were the market hydrogen price and bioethanol cost, the process being OPEX (OPerating EXpenditures) sensitive. On the other hand, when dowscaling the hydrogen production and purification unit to feed a 5 kW fuel cell, the most undetermined item was the fuel cell cost, since no fixed market price is still available. Therefore, the sustainability of the process strictly depends on the possibility to build cheap equipment and to guarantee long time reliability for the plant life. Also in this case, however, the system was OPEX-sensitive, the economic sustainability mainly depending on the bioethanol cost and the electricity selling price.

Finally, ethylene market is steadily increasing by *ca.* 4% each year due to economic growth. The current production technologies rely on very well established processes form fossil sources, such as ethane and propane, refinery gas, light naphtha and fuel oil feedstocks. Different technologies are adapted to the main feeds or versatile plants are designed to cope with different raw materials depending on their availability and price. Reliable technologies are optimised, leading to giant plants with overall yearly production capacity over 150 million ton/year. Nevertheless, the demand for renewable ethylene, as well as the increasing oil price experienced in the recent past, suggested the development of alternative routes to ethylene. Based on the increasing availability of ethanol form renewable biomass, bioethanol-to-bioethylene processes have been recently designed, finding economic sustainability, at the moment, in Brazil.

### Materials and Methods

Process simulation was carried out with the AspenONE Engineering Suite  $^{\otimes}$  (v. 8.6), in particular with the Aspen Plus  $^{\otimes}$  process simulator, and with the Aspen Process Economic Analysis  $^{\otimes}$  tool.

## Results and Discussion

The layout of the hydrogen production process has been optimized on a large scale to convert 40,000 ton/year of bioethanol. The small scale cogeneration unit (ca. 7 Nm³/h H₂) was designed according to experimental testing of an apparatus for the combined heat and power cogeneration (CHP) with output 5 kW<sub>electrical</sub> + 5 kW<sub>thermal</sub>. Both systems were constituted by several reactors in series for hydrogen production (Reformer), purification through High-Temperature Water Gas Shift (HT-WGS) + Low-Temperature Water Gas Shift (LT-WGS) + Methanation (CO-treat) and, in case, by a fuel cell (FC).

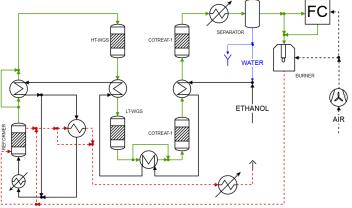


Figure 1: Flowsheet of the CHP plant.

#### Significance

Hydrogen production by steam reforming of ethanol has been investigated both on a large centralised scale and to small domestic applications. Centralised hydrogen production plants turned out sufficiently remunerative, with a minimum hydrogen selling price higher than the current from methane steam reforming, but comparable or better than other renewable routes to hydrogen. Larger uncertainties characterise the economic assessment of smaller plants for residential size CHP. In both cases the system showed OPEX sensitive, depending especially on the bioethanol feed cost and to the selling price of the products (hydrogen or electricity). The boundaries for the economic sustainability of the process have been preliminarily set.

Ethylene production is continuously growing worldwide and is mainly based on the steam cracking of fossil based feedstocks. Production costs and yield widely vary depending on the feed selected and on the location of the plant. Europe shows the highest production costs, thus representing a viable location to propose alternative processes. However, at the moment many efforts are needed towards the economic sustainability of the process. An integrated route should be searched to produce bioethylene from renewables. Currently, imported ethanol may offer the main margin for improvement, so that accurate process integration and the use of intensified technologies may represent a short term solution. For instance, the use of less purified ethanol solutions can induce important cost and energy savings.