

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

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ABSTRACT

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 H₂, as fuel or chemical, or syngas. After designing the process and the implementation of kinetic expressions based on experimental data collected in our lab or 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.

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When downscaling the hydrogen production and purification unit to feed a 5 kW fuel cell, the most undetermined item was the fuel cell cost, since no accurate market price is still available.

Finally, ethylene market is steadily increasing by ca. 4% each year due to economic growth. 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 from renewable biomass, bioethanol-to-bioethylene processes have been recently designed, finding economic sustainability, at the moment, in Brazil.

Keywords: Ethanol; Hydrogen; Ethylene; Heat and power cogeneration; Economic assessment.

1. Introduction

Renewables-derived bioethanol is becoming increasingly available as feedstock, produced from different substrates [1]. Consequently, bioethanol has been proposed as a feedstock for various processes, predominantly hydrogen or ethylene production [2–4], which may be considered the most mature ethanol exploitation technologies in the energy field, together with combustion. Indeed, sustainable hydrogen production is interesting for its use as chemical (pure hydrogen for be sold to the market) [5,6] and one of the promising routes is the bio-ethanol steam reforming (BESR) [7–12], which leads to syngas, to be used as such e.g. for methanol or Fischer Tropsch synthesis, or to be purified according to well established routes, such as the water-gas-shift process, possibly followed by methanation or preferential oxidation. The hydrogen-based economy is a matter of deep study and includes the full value chain, from hydrogen production to its storage and distribution [13].

The economic evaluation of hydrogen production from renewable sources is insufficiently addressed in the literature, with limited attention to scale up of production units [14–17] and only few records on economic issues [18–20]. If large scale hydrogen production has been marginally considered from an economic viability point of view, the residential scale, which has prompted the research interest for the development of innovative heat and power cogeneration (CHP) units is even less investigated. This mainly relates to the aleatory costs of non-standard equipment such as the fuel cells.

On the other hand, ethylene is a bulk chemical mainly used for the production of polymers, e.g. polyethylene, polystyrene (through the production of ethylbenzene) and polyvinylchloride. It is also used for the production of ethylene oxide, then of ethylene glycol by its hydrolysis, and of ethanol by hydration, depending of the price of the raw materials. These applications account for *ca.* 90% of its production. The world production in 2014 has been assessed as more than 130 million tons, equally distributed for *ca.* 20-25 Mtons for USA, Europe and Middle East (mainly from Saudi Arabia, with *ca.* 17 Mtons/year and a giant plant with 2 Mtons/year) and roughly double capacity in Asia. In 2016 it overcame 150 Mtons [21]. Its demand is growing with a yearly rate of *ca.* 3.5-4%.

To definitely assess the feasibility and readiness to market of new technologies from renewables, economic assessment is needed to understand the investments needed and the final production costs. Investigations of this kind are rare in the literature. Therefore, to fill this gap, in this work we have considered different possible applications of bioethanol as renewable raw material for the chemical industry, focusing on two main transformation routes: *i)* hydrogen production through steam reforming, either on a large or small scale and *ii)* bioethylene production. The attention is focused on the economic sustainability of the proposed processes, comparing the proper economic performance indexes with conventional production routes.

2. Methods and models

2.1 – Process design

Process simulation was carried out with the AspenONE Engineering Suite® (v. 8.6), in particular with the Aspen Plus® process simulator, and with the Aspen Process Economic Analysis® tool.

The layout of the hydrogen production process has been optimized in previous works [22–27]. 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_{electrical} + 5 kW_{thermal} [28–30]. The system was constituted by several reactors in series for hydrogen production (BESR), purification through High-Temperature Water Gas Shift (HT-WGS) + Low-Temperature Water Gas Shift (LT-WGS) + Methanation (Met) and by a fuel cell with the given power capacity [31]. We have preliminarily investigated, both experimentally and by process simulation, the use of diluted bioethanol feeds [14,25,32–37] for hydrogen and ethylene productions.

In the case of centralized hydrogen production plant the feed was based on 40,000 ton/year of bioethanol, the capacity of a semi-commercial unit providing second generation bioethanol [38]. By contrast, the size of the reformate-based cogeneration unit was set on the need of a mono-familiar unit (5 kW_{electrical} + 5 kW_{thermal}) through a polymer electrolyte membrane fuel cell (PEMFC) system. The CO-purification steps are commonly simulated as Gibbs or equilibrium reactors, whereas here we have set appropriate kinetic models to simulate the WGS and Met units as fixed-bed reactors, based on commercial catalysts. Ethanol steam reforming simulation was instead accomplished by using a home developed kinetic model, based either on commercial or proprietary catalysts [22–24,27].

In the case of the CHP apparatus, the BESR steam reformer was designed as a multitubular shell and tube reactor containing 100 tubes, 1 m long. The reforming reaction is planned inside the tubes, on a coating of catalyst operating at 650°C. The tube wall is heated by the

hot combustion gases coming from a furnace. The kinetic model used [32] includes 14 elementary steps, 4 of which were proposed as rate determining ones: ethanol decomposition (ED), ethanol steam reforming (SRE), methane steam reforming (SRM) and water gas shift (WGS). The kinetic equations were based on a Langmuir Hinshelwood approach, applied to a Ni-based catalyst, where all the species concurring for adsorption over the active sites appear in the denominator of the rate expressions and are included in the overall balance on the active sites [10,33,39,40]. This configuration has been modified in case of the centralized hydrogen production unit since the coated tubes are currently unproven on a large scale. Therefore, the large scale reactor was sized based on the industrial terrace wall steam reforming reactor [41].

The HT-WGS operates as a fixed-bed reactor at 350°C with a commercial $\text{Fe}_2\text{O}_3/\text{Cr}_2\text{O}_3/\text{CuO}$ catalyst following a power-law kinetics [42]. The LT-WGS is carried out at 280°C over a commercial $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ catalyst, also in this case with a power law kinetics [43]. A final methanation unit (210°C) (doubled as a safe guard in the cogeneration unit) lowers the CO concentration below 20 ppm, suitable to feed the PEMFC. A commercial $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst, following a Langmuir-Hinshelwood-Hougen-Watson kinetic expression (LHHW) was employed [44].

Fig. 1 sketches the flowsheet of the CHP plant, which is modified just by substituting the FC with a Pressure Swing Adsorption (PSA) unit in case of the centralised hydrogen production plant.

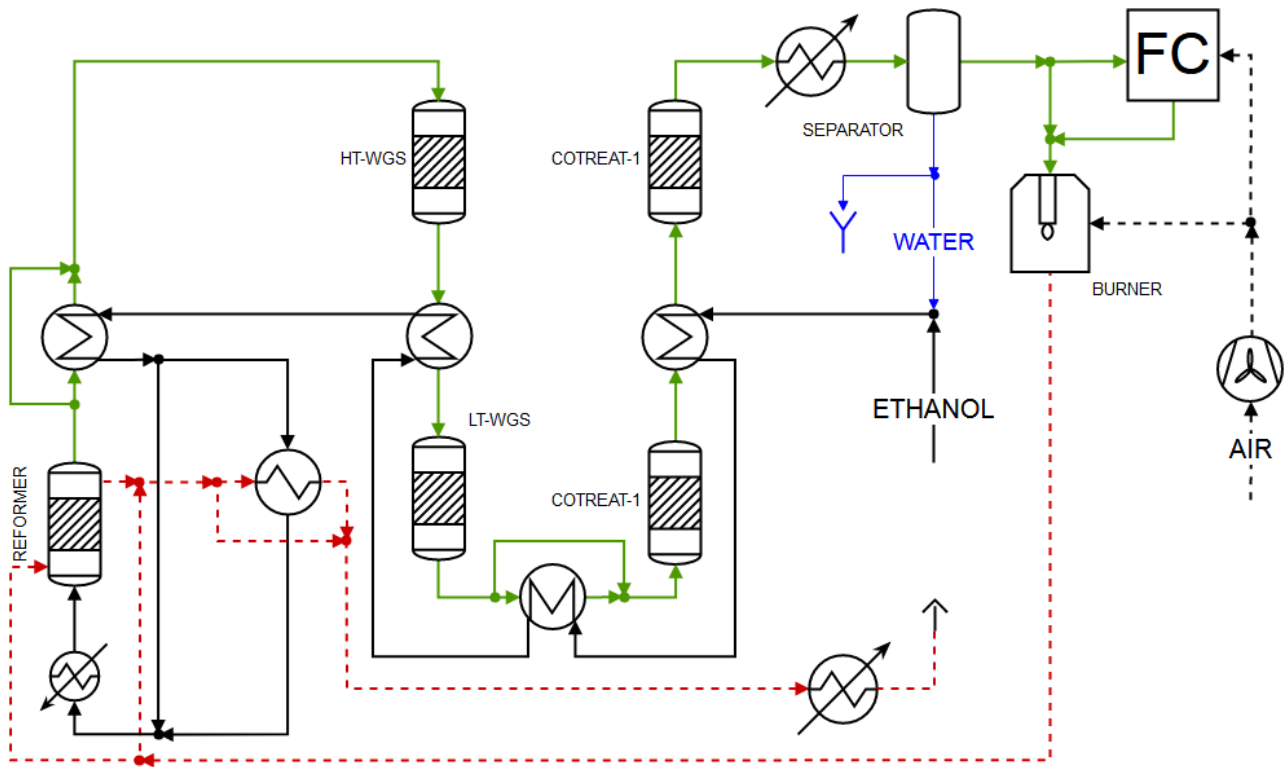


Fig. 1: Flowsheet of the CHP plant.

Details on the kinetic and transport parameters used to size these reactors can be found elsewhere [20,36].

The centralized plant was operated at high pressure due to economic reasons, whereas an almost ambient pressure was selected for the CHP unit. The effect of pressure is controversial, since thermodynamics prescribes operation at low pressure, given the increase of the number of moles during the gas phase reaction. Nevertheless, large centralized plants are often coupled with high pressure downstream processing (e.g. ammonia or methanol synthesis, hydrocracking, storage). Furthermore, volumetric efficiency can be improved at high pressure. Therefore, for the centralized hydrogen production plant we selected an intermediate 20 bar pressure, whereas 1.8 bar was sufficient for the CHP unit to overcome pressure drops. A steam-to-ethanol = 5 mol/mol was selected (40 vol% Ethanol, 60 vol% Water) based on preliminary optimization [45]. This feed

corresponds in principle to a mixture that can be easily achieved through flash separation, a quite inexpensive standard procedure [46,47].

The heat exchanger network was optimized according to the pinch technology, also making use of the Aspen Energy Analyzer[®] tool. A final pressure swing adsorption (PSA) system [48] was added in the centralized plant to eliminate CO₂, obtaining pure hydrogen. By contrast, the whole reformat is intended as a feed for the PEMFC.

After simulation and optimization, we performed an economic analysis to determine for each configuration the Total Capital Investment (TCI) and the OPERating EXpenditures (OPEX). We based our analysis on the following assumptions: *a)* a rate of return of 10 was chosen as profitability factor; *b)* 30 years plant life [18,49]; *c)* working capital = 15% of TCI [50]; *d)* salvage value as a fraction of the initial capital cost; *e)* straight-line depreciation method; *f)* escalation value = 5 for reactants and products; *g)* 8406 operating hours per year.

The price of bioethanol was based on market values [38], in case halved when using the 40% diluted stream [32,33,47,51].

3. Results and discussion

3.1 - Centralised hydrogen production plant

The scheme of the process and the flowsheet used is reported in Fig. 1.

The flowrate of pure hydrogen at the outlet of PSA in the base case plant was 889 kg/h, obtained by feeding 4,567 kg/h of ethanol.

We have first considered different hypotheses for heating BESR reactor. On such a large scale, the only economically viable solutions are the heat supply through a furnace using methane as fuel, or, in case, pure ethanol (azeotropic). However, the latter option decreased considerably the remuneration indexes of the plant. Indeed, the capital costs were similar for ethanol and methane as fuel for the furnace (except some more complex injection of the liquid fuel), but the operating costs were *ca.* 15-20% lower for methane than for ethanol. The

possibility to drive the furnace with part of the reformat produced, which proved viable on a small scale [23,36], leads to unprofitable investment for large scale plants.

The process showed severely OPEX sensitive, relying mainly on the hydrogen selling price and, second, on the bioethanol purchasing/production price. The calculated minimum hydrogen selling price is reported in Table 1, to be compared with a present standard value from methane steam reforming of 1.80 USD/kg [52].

The other key-point is the availability of bioethanol at the cheapest price. The price of bioethanol was chosen considering the commercial selling price of 1st and 2nd generation bioethanol (1G and 2G, respectively) [53] diminished by a certain factor depending on the purity degree, due to savings in separation duties and investments [54]. The costs adopted are reported in Table 1, where 40, 90 and 100 represent the purity (wt%), achievable through flash, flash + distillation, flash + distillation + dehydration, respectively.

Type of bioethanol	Cost (€/L)	Minimum H ₂ selling price (€/kg)
Bio100 1G	0.47	4.09
Bio90 1G	0.43	3.75
Bio40 1G	0.22	2.39
Bio100 2G	0.84	6.50
Bio40 2G	0.42	3.70

Table 1: Bioethanol costs used for the economic assessment [53].

According to a sensitivity analysis with respect to ethanol price, even if no significant cost saving would derive from the use of diluted ethanol, the system remains profitable, with an internal rate of return after taxes higher than 15%. The corresponding minimum hydrogen selling price has been reported in the same Table 1, obtained assuming an internal rate of

return of 10% (which results in a net present value of the plant nil at the end of the plant life). The results clearly show as best option the diluted 1st generation bioethanol (Bio40 1G). This hydrogen selling price is comparable or better than the estimates from different renewable routes. The investment is also sufficiently profitable to attract possible investors. Second generation bioethanol is still insufficiently competitive unless almost halved price can be reached. Different options for the hydrogen value chain are under investigation. Among these only few data are available as reliable estimates of H₂ selling cost [55,56] and amount to 3.8-5.4 US\$/kg for nuclear-based water splitting and 5.4–7.9 US\$/kg for hydropower electrolysis, 6.7-11.6 US\$/kg for thermochemical water splitting [14]. Accordingly, a different option for bioethanol steam reforming would lead to a hydrogen selling price between 4 and 5 US\$/kg, with a similar value for the steam reforming of methane [18]. As for the process efficiency, this can be calculated comparing the energy output as H₂ (based on LHV) vs. ethanol input (also based on LHV). A comparison between different options revealed 62% thermal efficiency for ethanol steam reforming, increasing to 68% when opting for the sorption enhance solution [57]. The presently discussed ethanol steam reforming process, instead, leads to a thermal efficiency of 87.4% (referred to the ethanol feed, only), decreasing to 75-79% while accounting for the heat supply needs for the reformer furnace according to different thermal integration options.

3.2 - Distributed heat and power cogeneration unit (CHP)

Distributed heat and power cogeneration devices are considered as a mean to spread renewable energy for residential use. If on one hand they miss the economic advantage of large scale plants, they are less invasive, thus more socially acceptable, they require much lower investment to favour the demonstration of the technology and they are suitable for remote locations. Bioethanol is considered a suitable biomass-derived feed for these plants,

since it is liquid and non toxic, allowing safer storage in residential places with respect to other fuels or hydrogen itself.

The conceptual design of such units is based on the same layout above described for centralised hydrogen production (SRE + HT-WGS + LT-WGS + Met), obtaining a reformat with maximum 20 ppm CO. The reformat can then be fed to the fuel cell (FC), typically a Polymer Electrolyte Membrane (PEMFC). Conventional PEMFC operate at temperature around 80°C and require such a careful purification from CO, in order to preserve the Pt-based electrocatalysts. Advanced high temperature PEMFC technologies are also becoming available, operating at *ca.* 160°C, which tolerate a higher amount of CO (*ca.* 1 vol%). In such cases, the last Met reactor can be withdrawn with consequent lower costs. PEMFCs are typically indicated as suitable for small power load (< 100 kW), whereas for higher power phosphoric acid fuel cells (PAFC) are more appropriate.

Despite the considerable attention and many demonstrative projects devoted to fuel cells research in the last 20 years, this technology has not still found solid commercial applications, with only some companies that sell fuel cells operating with pure hydrogen, rather than reformat. Therefore, the market price of this unit is not well assessed as can be the other components of the plant, leading to the biggest uncertainty in the economic evaluation as for CAPital EXpenditures (CAPEX).

Furthermore, the economic estimation algorithms used in the chemical engineering field are determined for large scale plants, thus the extrapolation down to microscale (residential size CHP) adds errors, so that the estimation can be considered affordable within a confidence limit of $\pm 40\%$. Another important aspect is that durability of the system is not yet proven, so that a safe estimation of the investment cannot go beyond 10-15 years, impacting very much on the remuneration of the system.

On the other hand, the investor in this case is the house owner, who is interested in obtaining a cheaper technology with respect to conventional centralised heat and power supply,

characterised also by higher environmental sustainability. Possible government incentives can be added, such as a premium price for energy selling, discounts on the raw materials or discounted quota for the acquisition of the apparatus.

All this considered, we based our preliminary economic analysis on different ground with respect to the centralised hydrogen production unit. Given the absence of a well defined cost for the FC units, we have focused mainly on the most assessed components, considering a fork of estimated price for the FC. We focused on a mono-familiar house system, supplying an average of 13 – 15 kW (with a tuneable electric component of 25 – 30 %), whose features have been well described elsewhere [23,25,26,36].

The CHP system has been located in Lombardy, Northern Italy, to fulfil the electrical and thermal needs of a house with 3 people, energy certification “E”. The electrical power is either considered for direct supply to the grid, upon remuneration, or used in-house + selling excess power to the grid. The minimum price fixed in 2017 for reselling electrical energy to the grid has been here considered as a very conservative estimation, *i.e.* 0.039 €/kWh.

Heat is recovered from the CHP system both for house heating and to produce hot sanitary water. The data on prices of natural gas and electricity have been taken from the National Authority for Energy and compared with the prices on the free market of energy in Italy. The yearly needs of natural gas are estimated as 24,786 kWh, corresponding to 2,364 m³ (Standard conditions), whereas the yearly electricity consumption is 2,490 kWh.

We have considered many operating cases during a sensitivity analysis on the CHP unit, here focusing on three most representative: cases #3 and 6 have slightly different electrical output but different quality of the thermal output. Indeed, case #6 releases heat at higher temperature, so it is suitable for vertical radiators and, while case #3 for heating through the floor. They are coupled with case #15 which accounts for the supply of sanitary hot water [25,26,36]. We have assumed that the heating power available is used for 87.5% of the time

to supply heat to the house and 12.5% to supply hot sanitary water through a heat reservoir better described in [25] for its dynamic behaviour. The cases are described in Table 2.

			Oct.-Apr.	May-Sept.
	Case #		15	
Hot water production (3 h/day)	Available electric power	kW	3.2	3.2
	Available heat (only from FC)	kW	9.6	9.6
	% of time water use	%	12.5	12.5
	Case #		3	
House Heating (21 h/d)	Available electric power	kW	4.7	-
	Available heat	kW	10.0	-
	% of time water use	%	87.5	0
	Case #		6	
	Available electric power	kW	4.0	-
	Available heat	kW	10.2	-
	% of time water use	%	87.5	0

Table 2: CHP output in different operating cases.

The breakdown of electricity that is possible to sell to the grid (total or excess power with respect to consumption) and savings from heating are reported in Table 3. The corresponding ethanol consumption and cost (based on the values of Table 1) are also reported in the same Table 3.

	Case #		Jan	Feb	Mar	Apr	May	June	July	Aug	Spet	Oct	Nov	Dec	Total year
Electric power available for selling to the grid	3	kW	4.23	4.23	4.23	4.23	0	0	0	0	0	4.23	4.23	4.23	
	6	kW	3.57	3.57	3.57	3.57	0	0	0	0	0	3.57	3.57	3.57	
Max electricity sold to the grid	15	kW	2.75	2.75	2.75	2.75	2.69	2.69	2.69	2.69	2.69	2.75	2.75	2.75	
	3 + 15	kWh	3009	2718	3009	2912	250	242	250	250	242	3009	2912	3009	21816
Max earning from electricity selling *	6 + 15	kWh	2580	2330	2580	2497	250	242	250	250	242	2580	2497	2580	18877
	3 + 15	€	117.37	106.01	117.37	113.58	9.76	9.44	9.76	9.76	9.44	117.37	113.58	117.37	850.81
Excess electricity for selling to the grid	6 + 15	€	100.61	90.88	100.61	97.37	9.76	9.44	9.76	9.76	9.44	100.61	97.37	100.61	736.22
	3 + 15	kWh	2729	2508	2789	2732	80	82	70	70	72	2809	2662	2719	
Earning from selling excess electricity *	6 + 15	kWh	2300	2120	2360	2317	80	82	70	70	72	2380	2247	2290	
	3 + 15	€	106.45	97.82	108.79	106.56	3.13	3.20	2.74	2.74	2.81	109.57	103.83	106.06	753.70
Savings on heating	6 + 15	€	89.69	82.69	92.03	90.35	3.13	3.20	2.74	2.74	2.81	92.81	87.62	89.30	639.11
	3	kWh	6534	5902	6534	6323	0	0	0	0	0	6534	6323	6534	44685
Savings on heating		SCM	623	563	623	603	0	0	0	0	0	623	603	623	4261
		€	238.76	215.66	238.76	231.06	0	0	0	0	0	238.76	231.06	238.76	2092.29
	6	kWh	6618	5978	6618	6405	0	0	0	0	0	6618	6405	6618	45259
		SCM	631	570	631	611	0	0	0	0	0	631	611	631	4316
Ethanol consumption	-	L	3050	2755	3050	2952	3050	2952	3050	3050	2952	3050	2952	3050	35916
Ethanol cost Bio40 1G **	€		671	606	671	649	671	649	671	671	649	671	649	671	7902

* minimum electricity selling price = 0.039 €

** Bio40 1G price = 0.22 €

Table 3: Estimation of the electric power that is possible to sell to the grid in different operating cases and the respective remuneration. Savings from heating and total consumption of ethanol.

A preliminary estimate of the installation cost of the unit has been carried out and resulted in a fork from 53,500 € and 64,400 €, depending on the configuration (prototype, not commercial scale). It should be remarked that the biggest unknown is the cost of the fuel cell once conventionally on the market. Based on the former estimate, we have considered two hypotheses of life of the apparatus, *i.e.* 15 or 30 years, another unpredictable issue, and calculated a very preliminary balance of plant to understand the boundaries for economic sustainability (Table 4). At first it is immediately evident that the bioethanol cost represents a huge issue even at the very low ethanol selling price here considered, 0.22 €/L. Furthermore, the revenues from electricity selling are another parameter which varies depending on the selling contract and on the possible government incentives. As a base case (#A) we have considered the worse option, *i.e.* the highest ethanol cost (0.22 €/L) and the lowest electricity revenue, considering the minimum electricity selling price fixed by the Italian National Authority (0.039 €/kWh). Under such conditions, independent from plant life, the investment is not paid out and even by decreasing to zero the installation costs, since the operating costs are not covered over the whole plant life. By keeping the same ethanol cost, we increased the remuneration from electricity sales by a factor *ca.* 9.2 and 11.5 (for 30 or 15 years lifetime, respectively) with respect to the minimum selling price. In this case the investment is paid back at the end of plant life (case #B). The opposite case was considered (#C) by keeping fixed the electricity selling price and decreasing the ethanol cost. A maximum ethanol price of 0.05 €/L allows the sustainability of this option for a plant life of 30 years, which is however unrealistic. For the lowest lifetime of the plant, the sustainability is not reached even for a free ethanol supply, since the revenues and savings

do not cover the installation costs. Finally, for a diluted ethanol cost of 0.10 €/L, which may be envisaged after careful optimisation or incentives, the minimum electricity selling price which makes the process economically sustainable was 0.155 €/kWh or 0.227 €/kWh for 30 or 15 years plant life, respectively. In this preliminary evaluation we have not considered the cost escalation of the raw materials (ethanol, natural gas and electricity) due to less predictable values for small supplies.

Though very simplified and with many uncertainties, this analysis underlines the need to ensure premium price for selling electricity to small producers from renewables. Furthermore, less expensive ways to bioethanol supply are the other key for economic sustainability. Finally, besides the system also in this case resulted OPEX sensitive rather than dependent on installation costs, producers of fuel processors and fuel cells must guarantee the long term reliability of the plant to ensure reasonable boundaries for the sustainability of the investment.

Case #	A	B	C	C
Life 30 years	€	€	€	€
Installation	-53,500	-53,500	-53,500	-53,500
Ethanol (Bio40 1G)	-237,046	-237,046	-50,965	-118,523
Revenue electricity (excess, case # 3+15)	22,611	208,668	22,611	90,150
Savings heating	62,769	62,769	62,769	62,769
Savings electricity	19,109	19,109	19,109	19,109
Balance of plant	-186,056	0	0	0

Case A: Ethanol cost = 0.22 €; electricity selling price = 0.039 €

Case B: Ethanol cost = 0.22 €; electricity selling price = 0.36 €

Case C: Ethanol cost = 0.05 €, electricity selling price as for A

Case D: Ethanol cost = 0.10 €, electricity selling price = 0.155 €

Case #	A	B	C	C
Life 15 years	€	€	€	€
Installation	-53,500	-53,500	-53,500	-53,500
Ethanol (Bio40 1G)	-118,523	-118,523	0	-53,335
Revenue electricity (excess, case # 3+15)	11,306	131,144	11,306	65,855
Savings heating	31,384	31,384	31,384	31,384
Savings electricity	9,555	9,555	9,555	9,555
Balance of plant	-119,778	0	-1,255	0

Case A: Ethanol cost = 0.22 €; electricity selling price = 0.039 €

Case B: Ethanol cost = 0.22 €; electricity selling price = 0.45 €

Case C: Ethanol cost = 0 €, electricity selling price as for A

Case D: Ethanol cost = 0.10 €, electricity selling price = 0.227 €

Table 4: Breakdown of the costs of the CHP unit with minimum installation cost and different cases of electricity selling revenues and ethanol cost. The escalation of natural gas and electricity costs are not computed.

3.3 - Ethylene production

3.3.1 - Ethylene production from fossil raw materials

The main technology for ethylene production is steam cracking, fed with a wide variable choice of feedstocks, such as ethane, propane, butane, naphtha and oil. In Europe and Asia, ethylene is obtained mainly from the cracking of naphtha, gasoil and condensates with the coproduction of propylene, C4 olefins and aromatics (pyrolysis gasoline). The cracking of

ethane and propane is mainly applied in USA, Canada and the Middle East, to produce ethylene and propylene, making the plants cheaper to construct and less complex for operation. The technology is very well consolidated, so efforts are focused on further process optimisation, control and advanced furnace design. Also the improvement of single plant productivity is a key for competitiveness. Another key point is the decrease of coking rate, as well as the energy intensification in this highly energy demanding process. Today, the largest plants from gas feed have a capacity of 235 kton/year, while from liquid feed ca. 185 kton/year [58].

Modern plants achieve very high thermal efficiency of the furnaces, up to 95%, lower steam requirement in the downstream compression section and increased capacity by 20-100% in the case of revamped plants.

Some processes are also based on a MTO (methanol-to-olefins) concept, that converts methanol to ethylene and propylene. This is particularly relevant in China where methanol is produced by coal gasification and then transformed into olefins. This route is particularly interesting, because it is designed and optimised dealing with fossil fuels, but it allows adaptation to any renewable feedstock that can economically be transformed into syngas. The production of renewable olefins from pyrolysis of waste plastics and biomass has also been reported in the literature in the last decade and most of the processes are based on catalytic cracking [59–66]. The oxidative coupling of methane is also studied, but major efforts are at the moment needed to improve catalyst selectivity to olefins.

Product purity is variable depending on use, but it often reaches 99.95% with less than 1 ppm acetylene.

Depending on availability and price in each country: gaseous feeds are preferably used in the USA and Middle East, while liquid feeds are mostly used in Europe.

The thermal (steam) cracking process accounts for 95% of ethylene produced worldwide and 60% of propylene. The process consists of four main sections: the furnace, the quenching section (direct and indirect), the compression block and the separation units [67]. The thermal cracking reactor consists of tubular reactors (45 to 90 m), vertically placed in the radiant section of a specifically designed furnace, allowing heating up to 600-850°C, depending on the feed. A variable number of coils (16 to 128, depending on the plant capacity) are made of special Ni/Cr alloys to cope with the very high temperature. Indeed, the pipe skin temperature can reach 850-1100°C. In order to save energy, feed preheating to 500-600°C is done in the top of the furnace, above the radiant section, through convection by the hot gases flowing towards the stack. In order to dilute the stream and to control coking, steam is co-fed in variable amount depending on the feed nature, typically between 0.2 to 1.0 wt/wt [68].

The product spectrum depends of course on the feed and on operating conditions and include light olefins and aromatics as valuable products. The desired cracking temperature (750-900°C) is controlled by a thermocouple at tube outlet, by tuning the fuel to the burners, which are located on the refractory walls of the furnace, and/or on the roof, and/or on its floor [69]. Higher reaction temperature induces higher coke formation.

After the desired residence time in the hot radiant section, the product is quenched directly or indirectly. In the latter case, heat exchangers are specifically designed, allowing very high pressure steam generation (up to 120 bar). Besides this energy recovery, most of the thermal energy of the flue gases in the furnace is used, first in the radiant section, then in the convection zone by feed preheating and for steam generation. The spent gases are let through the stack at ca. 100-150°C to avoid condensation and corrosion in the chimney.

The furnaces size depends on the capacity, but typical modules have the size 10 x 11 x 2 = 220 m³ [69]. The burners are differently located on the internal surface of the furnace, depending on the selected design, and fed either with gaseous or liquid fuels. The latter

need more complex atomization, e.g. through swirling injectors. In every case overstoichiometric air is fed (typically 10-15% excess) to avoid partially combusted products or smoky flames.

The tube coils are located inside the furnace with proprietary arrangement to optimise product yield and energy efficiency. Tubes may have a constant or variable diameter, depending on the feed and on the desired residence time. Lower diameter allows lower residence time, which is typically between 0.08 and 0.25 s in modern reactors.

The draft in the furnace may be natural (based on the density differences due to heating), forced (a fan forces air to the burners), induced (a fan is placed on the stack) or balanced (both the last two options, to avoid dependence on wind conditions).

Current optimisation involves a better definition of the kinetic scheme, coupled with fluid dynamics, in order to optimise process conditions, ethylene yield and save fuel.

An excellent comparison of the production cost of base chemicals (ammonia, methanol, ethylene and propylene) in various countries has been recently published by Boulamanti and Moya [70]. The steam cracking process is analysed depending on different feeds, which have variable price depending on the country considered, and lead to different ethylene yield and valued co-products (Table 5). Ethylene yield hugely varies between 24 and 55% [70] and consumption of materials depends on the feed used (Table 6).

The basis for the production cost calculation did not include depreciation and transportation costs, but accounted for the feedstock, the value of by-products, electricity, thermal energy, catalysts and other chemicals and labour correlated costs (salaries, overheads, taxes, maintenance).

		Units	Ukraine	Russia	Saudi Arabia	USA	EU
Feedstocks	Natural gas	EUR/t	425.42	114.10	29.70	148.96	442.99
	n-Butane	EUR/t	564.83	546.01	475.40	470.39	638.80
	Ethane	EUR/t	549.67	296.54	46.28	145.96	612.44
	Distillate fuel oil	EUR/t	620.65	620.65	698.50	667.46	698.12
	Naphtha	EUR/t	613.42	564.64	708.56	669.58	671.67
	Propane	EUR/t	560.91	549.61	480.49	394.34	612.16
	Refinery gas	EUR/t	488.66	391.92	111.96	244.57	409.74
Co-products	C1 fuel	EUR/t	304.56	182.58	49.51	143.46	525.86
	C3s crude	EUR/t	962.37	831.80	495.78	966.37	1007.55
	C4s crude	EUR/t	786.02	468.99	720.01	835.58	885.02
	Residual fuel oil	EUR/t	426.96	217.71	454.99	474.60	468.42
	Hydrogen	EUR/t	778.13	466.47	126.48	366.52	1343.51
	Pygas	EUR/t	743.72	679.45	804.61	773.89	789.01
Utilities	Electricity	EUR/kWh	0.059	0.039	0.024	0.035	0.085 ^a
	Cooling water	EUR/t	0.019	0.014	0.010	0.013	0.025
	Process water	EUR/t	0.025	0.019	0.015	0.018	0.031
Labour	Hourly rate	EUR/h	3.57	4.79	15.09	20.86	18.01

^a This average refers to Band IE according to Eurostat, but in the actual analysis the price per country and per consumption band for each facility was used.

Table 5: Feedstock, co-products, utilities and labour prices depending on plant location. Reproduced under the Creative Commons Licence Agreement from [70].

		Units	High severity naphtha	Light naphtha	Distillate fuel oil	n-Butane	Propane	Ethane	Refinery gas
Feedstock	Naphtha	t/t	3.30						
	Light naphtha	t/t		3.25					
	Distillate fuel oil	t/t			4.67				
	n-Butane	t/t				2.51			
	Propane	t/t					2.38		
	Ethane	t/t						1.29	
	Refinery gas	t/t							2.18
Co-products	C1 fuel ^a	t/t	0.50	0.62	0.48	0.56	0.65	0.11	0.89
	C3s crude ^b	t/t						0.04	
	C4s crude ^c	t/t	0.34	0.30	0.43	0.26	0.10	0.04	0.13
	Residual fuel oil	t/t	0.13	0.13	1.15	0.04	0.1		
	Hydrogen	t/t	0.05	0.05	0.05	0.04	0.05	0.08	
	Propylene	t/t	0.53	0.53	0.69	0.43	0.40		0.14
	Pygas	t/t	0.75	0.63	0.88	0.18	0.16	0.02	0.03
Utilities	Electricity	kWh/t	44	250	300	180	180	140	148
	Cooling water	t/t	400	206	206	206	206	206	206
	Fuel ^d	GJ/t	22.3	28.4	31.3	24.8	24.6	21.0	21.8
Other materials	Catalyst	EUR/t	5.49	0.71	0.72	0.50	0.51	0.16	0.16
	Chemicals	EUR/t		4.06	4.89	3.92	3.65	3.16	3.16

^a It is usually methane-rich gas.

^b It is the production fraction that can be further processed to propylene of chemical or polymer grade, additional to the propylene produced directly from steam cracking.

^c It is the production fraction that will give butadiene after processing.

^d This fuel consumption represents additional fuel required to support the process generally for heat generation.

Table 6: Feedstock consumption and co-products yields in the case of different (fossil) raw materials. Data given per ton of ethylene produced. Reproduced under the Creative Commons Licence Agreement from [70].

The feedstock most used in USA and Saudi Arabia for steam crackers is domestic natural gas, since naphtha is traditionally more expensive in both countries. By contrast, liquid feeds are preferred in EU. This represents the key for the economic sustainability. Indeed, on one hand most of the cost topics are by far higher in the EU than in the comparative countries computed by Baoulamanti and Moya [70], leading to much higher ethylene production costs. However, when using naphtha a greater spectrum of co-products is available, that allows substantial credits thanks to their higher value in the EU, which make the ethylene production cost sufficiently sustainable. It should be also considered that ethylene import involves the additional costs of transport and depressurization from compressed tanks, which do not suggest import as supply strategy for this commodity.

Overall, the steam cracking costs were calculated as 748 Euro/ton when ethylene was the only product, or 816 Euro/ton for combined ethylene + propylene units. The breakdown is reported in Fig. 2.

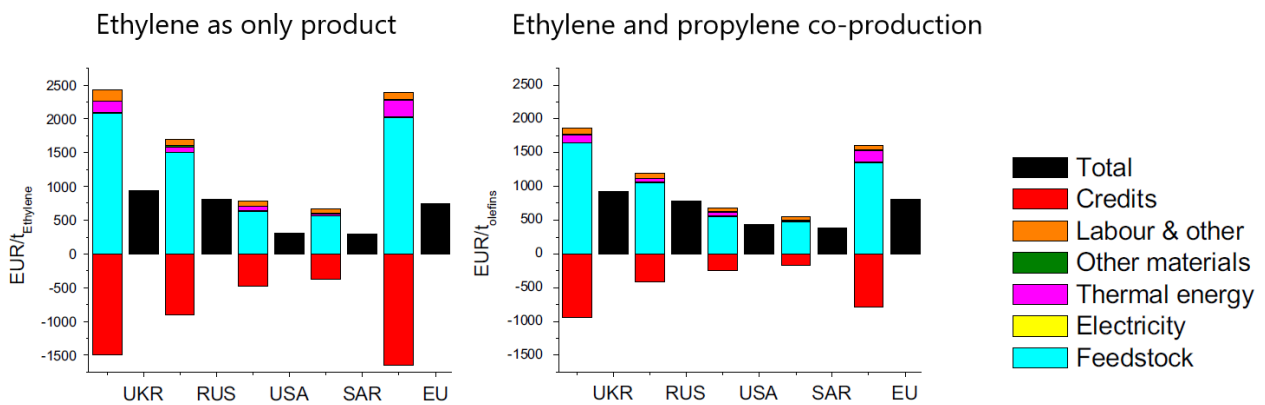


Figure 2: Partition of production costs for various plant locations. Credits include the valorisation of co-products. Reproduced under the Creative Commons Licence Agreement from [70].

3.3.2 - Ethylene production from renewable sources

An increasing attention to renewable feedstocks is due to different reasons. On one hand, there is an increasing demand for improved sustainability in bulk chemical processes. So, if decreasing CO₂ footprint can be achieved by stringent process intensification and optimisation, the use of biomass-derived feeds may further help to improve the CO₂ balance. Indeed, the emission of this greenhouse gas occurring during the transformation of biomass can be, at least partially, consumed during biomass growth.

The easiest route to ethylene, with highest atom efficiency, is ethanol dehydration, typically occurring over acidic catalysts. This process is gaining increasing attention due to the spreading availability of renewable bioethanol. For instance, Braskem started in 2010 the first ethylene production plant fully based on renewable sources, with a capacity of 200 kton/year and a consumption of 462 million litres of ethanol [71,72]. Coupling this plant to polyethylene production allows saving of 2.5 ton CO₂ per ton of plastic produced.

The biobased polymers market has grown at a 35% rate in the period 2006-2011, with a potential demand of ca. 10% of the market, while the current supply is lower than 1% [73]. An interesting economic assessment of a bioethylene production plant has been recently published [73], suggesting the need of a premium price for renewable feedstock to move towards the economic sustainability of the process. The sugar cane to ethanol and to ethylene production route is already in progress in Brazil, with different companies involved such as the above mentioned Braskem and Dow [74].

This production route cannot be applied to the European market due to unavailable and uneconomic availability of sugar cane. Different supplies may be thought depending on the local supply. A case study for the production of ethylene from ethanol has been quantified supposing different scenarios and comparing them with a base case of a steam cracker from naphtha, with 30% ethylene yield.

A first keypoint to be accounted for is the size of the ethanol dehydration plant to have a minimum, critical ethylene productivity. This should be compared with the availability of the needed biomass. Althoff et al. [73] selected 200 kton/year, locating the production plant in the Netherlands and selecting sugar beet as raw biomass. This plant size accounts for ca. 10% of a local ethylene plant productivity and matches the size of a full scale sugar mill.

A first case considers the import of ethanol, both with fuel grade purity (>99%) or diluted (50%), which is suitable for ethylene production. Indeed, in spite of the fact that ethylene is produced by dehydration of ethanol, so cofeeding of water unfavors the reaction thermodynamically, steam addition is often used to prevent catalyst deactivation by coking. Suitable energy integration and a proof of concept of the use of diluted ethanol solutions for this application are available in the literature, together with a preliminary economic assessment [4,19,20,35,37,75].

The overall integration of the ethylene production unit with the upstream ethanol production is also considered as comparative situation [73].

As a raw mass balance, the production of 200 kton/year of ethylene requires 720 kton/year of ethanol 50%. The latter is produced from 1,080 kton/year of thick juice, containing 760 kton/year of sugar. The amount of sugar beets needed for this purpose is 4,320 kton/year. Starting from the sugar beets induced considerable saving for feedstock cost, but an increase of the energy cost is due to sugar processing. All the considered scenarios were non sustainable from the economic point of view, even taking into account premium value for renewable ethylene.

The concluding remarks on the feasibility and economic sustainability issues are reported in Table 7.

Table 7: Comparison of different options for the valorisation of bioethanol.

Process	Centralised H ₂ production	Distributed heat and power cogeneration	Ethylene production
Feasibility on a large scale	✓	✗	✓
Feasibility with diluted (cheaper) bioethanol	✓	✓	✓
Minimum selling price (H ₂ , US\$/kg)	2.39-6.50	-	-
Sensitivity	OPEX sensitive (Bioethanol, H ₂)	CAPEX (Fuel Cell)	OPEX sensitive (Bioethanol)
Issues for market penetration	Bioethanol price and availability	Fuel Cell cost, reliability and durability; Bioethanol price	Bioethanol price and availability

4 - CONCLUSIONS

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.

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