Fuel cell electric vehicles. Investigation of the energy balance for optimal reforming process of bio-ethanol

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Abstract. Hydrogen ecosystem and hydrogen economy are relevant topics for the mobility. This article summarizes the ways of production of “green” hydrogen. The hydrogen storage and transportation are discussed as well. The article presents the concept of electric vehicle with serial range extender to extend the vehicle autonomy. Fuel cell system powered by hydrogen produced through reforming of liquid fuel from renewable resources such as bioethanol is considered as a range extender module. Alkaline fuel cell and solid oxide fuel cell are investigated for the use of a variety of liquid fuels instead of traditionally used hydrogen in others types of fuel cells. This article investigates the energy balance of the different types of fuel cells, powered by bio-ethanol. Three variants for ethanol conversion are investigated: variant 1: reforming of bio-ethanol in external reformer to hydrogen and its conversion in alkaline fuel cell, variant 2: reforming of bio-ethanol in external reformer to hydrogen and its conversion in a solid oxide fuel cell; variant 3: direct reforming of the bio-ethanol in the solid oxide fuel cell. The chemical processes for each variant are proposed and thermodynamic energy balance is calculated. From the results is visible that the most efficient configuration is the variant 3, the direct reforming of the bio-ethanol by the solid oxide fuel cell. The variant 3 delivers 15 MJ of energy output per kilogram of bio-ethanol, used in the fuel cell.

1. Introduction
The automotive industry is challenged by very strict emissions regulation. The CO$_2$ emissions levels tend to be drastically reduced to 50 g/CO$_2$ km in 2030. The hydrogen question and discussion is larger than the automotive industry and the clean mobility energy services and products that the automotive sector in Europe, has to provide. The electrification of the vehicles is currently in progress in Europe, driven by the European CO$_2$ emissions regulation and hydrogen is seen in the energy outlooks to be used as well for vehicular propulsion, and as well as enabler to reach the CO$_2$ emissions targets. The current CO$_2$ regulation considers the emissions from tank-to-wheel perspective and thus the electric and the fuel cell vehicles are accounted as zero emissions vehicles. Introducing electricity and hydrogen as energy vectors for mobility set the questions of the global efficiency of the conversion chain, of the total energy resources to be used and the total CO$_2$ emissions from well-to-wheels perspective. From the hydrogen point of view the well-to-wheels perspective raises multitude of scientific, technological and economic questions.

2. Hydrogen production and storage
Renewable energies increase their part in the energy mixes due to the energy transition needs. The sustainable energy system should become clean but as well reliable and affordable. The renewable
energy production and energy demand are intermittent thus an integrated system approach is required considering energy conversion and storage. The authors propose in [1] a concept for a neighbourhood called Power-to-H3. Locally produced renewable energy is partly converted and stored in the form of heat and hydrogen. Rainwater collection, storage, purification and use is as well implemented. Hydrogen can be obtained from different sources of raw materials including water. Hydrogen production methods are required to be eco-friendly and to deliver high purity of hydrogen. Water electrolysis and especially PEM water electrolysis is considered as most promising technique for high pure efficient hydrogen production from renewable energy sources [2]. Figure 1 shows the hydrogen production methods.

![Figure 1. Hydrogen production methods.](image)

Biomass energy contributes a major portion in global renewable energy. Biomass has ever-growing share in electricity production worldwide. \( H_2 \) is considered as a clean energy fuel having high energy density (122 kJ/g), which is three times higher than hydrocarbon fuels. Heating value of 61,100 Btu/lb of \( H_2 \) is also nearly three times higher than methane (23,879 Btu/lb). When hydrogen is produced by the reformation of fossil fuels (petroleum or coal) this involves large greenhouse-gas footprints. The authors present in [3] promising approaches applied to achieve biomass based hydrogen production by using microbes, called biohydrogen fermentation using crops straws, agri-waste; industrial waste or naturally occurring organic rich biomasses (like molasses). The hydrogen is considered as carbon free fuel. Supply of low-carbon energy for heat, balancing of electricity at national grid and application in transportation sector preferred hydrogen over other carbon based gaseous biofuels. The fertilizers and the petroleum companies are considered to be at the largest users of \( H_2 \) with respectively 50% and 37%. With the demand of the fuel cells the demand of hydrogen is increasing with 6% the last five years.

The major application of \( H_2 \) are:

- Utilization for hydration of substantial oils for fuel production, foods hydration, and alkali hydration for fertilizers production.
- As \( H_2 \) is the perfect electron donor, it is uses for diminishing nitrate, perchlorate, selenite, and a suite of other oxidized water contaminations.

In the present the industrial application of hydrogen is equivalent to only 3% of the total energy consumption. This is expected to grow significantly in the years to come [3].

For the moment the hydrogen market is with low demand. In this case, small-scale water electrolysis based hydrogen production is more cost-efficient than large-scale production. The study in [4] shows that there is a good business for local water electrolysis. The hydrogen has to supply captive fleets of trucks.
The life-cycle environmental performance of hydrogen as a transportation fuel focuses on its production [5]. The steam reforming of natural gas still arises as the key hydrogen production technology in the short term. Water electrolysis is the main technology in the medium and long term. In scenarios with very restrictive carbon footprint limits, biomass gasification also appears as a key hydrogen production technology in the long term.

Metal hydrides are known as option for high-density hydrogen storage [6]. In addition, they give the opportunity to develop a new hydrogen compression technology due to their thermodynamic possibilities.

Calcium carbonate (CaCO₃) and Mg-substituted CaCO₃ were selected as adsorbents for hydrogen with high amount of release after high-pressure hydrogen loading. [7]. Their crystal structures, specific surface areas, hydrogen content at high pressure, and the amount of hydrogen released in water were investigated.

Hydrogen can be considered as balancing and storage grid for intermittent energies [8]. Two onsite storage technologies, i.e., power-to-hydrogen-to-power and lithium battery, are investigated to size the storage system and to estimate its profitability [8].

Among several candidates of hydrogen storage, liquid hydrogen, methylcyclohexane (MCH), and ammonia are considered as potential hydrogen carriers, in terms of their characteristics, application feasibility, and economic performance [9]. Liquid hydrogen faces challenges in huge energy consumption during liquefaction and boil-off during storage. MCH has main obstacles in largely required energy in dehydrogenation. Ammonia encounters high energy demand in both synthesis and decomposition (if required). In terms of energy efficiency, ammonia is predicted to have the highest total energy efficiency (34–37%), followed by liquid hydrogen (30–33%) and MCH (about 25%). In addition, from cost calculation, ammonia with direct utilization (without decomposition) is considered to have the highest feasibility for being massively adopted, as it shows the lowest cost (20–22 JPY/Nm3-H₂ in 2050).

The authors outline in [10] the four biggest measurement challenges that are faced by the hydrogen industry including flow metering, quality assurance, quality control and sampling.

This article [11] presents a detailed breakdown of the energy conversion chains from intermittent electricity to a vehicle. Battery electric vehicles (BEVs) and Fuel cell electric vehicles (FCEVs) are considered. The traditional well-to-wheel analysis is used to study the effective coupling of renewable electricity sources and associated storage needs.

The recent literature review states the art of the hydrogen technologies by giving orders of magnitude of processes, costs, technologies, efficiencies, about the technical and the economic viability of the “hydrogen economy” concept. The main idea is to cover the whole “life cycle” of the hydrogen as energy vector. The main categories are: hydrogen production, hydrogen storage, hydrogen transport and distribution and hydrogen conversion on vehicles or energy grid conversion. From the literature review it comes out that the hydrogen is seen as energy carrier and connector for different energy grids: electricity, natural gas and as a storage medium for renewable energies. The leading spots in term of hydrogen research are in North of Europe and in Japan. Japan has the ambition to demonstrate the progress of hydrogen energy on real scale during the Olympic games of Tokyo in 2021. Recent studies from Nederland and Norway consider the hydrogen with production from renewable energy and highlight the economic benefit of stand-alone installations with small production capacity. The literature review summarizes the ways of hydrogen production and classifies them. The main need is to produce clean, “green” hydrogen. Clean hydrogen is seen to be produced by renewables: water electrolysis powered by renewable electricity and biomass. The current production of hydrogen is coming from the natural gas steam reforming, but water electrolysis and biomass are seen as future ways (technologies) for clean hydrogen production, from 2030. Other question concerning the hydrogen production is the sizing of the capacity of the installations. This question is directly related to the storage of the hydrogen. Hydrogen is very reactive molecule and its storage in pure state is a complex process. The literature review describes the compressions levels for the compressed gas hydrogen. The compression process presents important operating costs. The
classification of the hydrogen storage ways is proposed. According to the classification, hydrogen can be stored in physical, adsorption or chemical forms. The physical forms of storage are the compressed gas and the liquefied hydrogen. They deliver pure hydrogen but present high operating costs related to the high-energy consumption to maintain them is their respective physical state. The chemical storage concerns the metal hydrides and the chemical hydrides. Metal hydrides present different opportunities for storage of hydrogen in a solid state. They need to be investigated to improve efficiency, storage capacity, to reduce cost and energy demand. The adsorption of hydrogen is done in porous materials: MOFs or carbon based materials (calcite). This way of storage is as well under scientific investigation. Japan has the leading position with the hydrogen storage in calcite. The chemical hydrides are the most promising way of hydrogen storage and transportation in liquid form, in the future. Ammonia is the best chemical hydride candidate, presenting the highest hydrogen content. A research direction related to the ammonia is how to convert it directly in adapted converters (fuel cells) without dehydrogenation process, which is costly, and need purification. Japan is as well leading in the ammonia research area. The literature review points out lack of regulation and difficulties by the distribution of the hydrogen at the tank stations to the customers. Main challenges are the measures of the quantities, the control of the quality and the sampling of the hydrogen for purity control. These difficulties are related to the lack of measure instruments for large utilization, calibrated to work at 700-900 bar pressure and the purity control capacity available locally. Hydrogen is clearly seen as an energy carrier for extended energy grids, as stocker for renewable electricity and depending of the installation size can be competitive to Li-Ion stationary battery for local grid storage. Hydrogen production from renewables and Li-Ion stationary batteries demonstrate benefit to balance the global electricity grid and to reduce losses related to intermittence of the renewables.

3. Fuel cell range extender concept

Several solutions have been developed in order to improve the competitiveness of the electric vehicles. The range extender concept (serial hybrid) is one of the concepts proposing an additional range for the electric vehicles. A second advantage is the reforming of a liquid fuel on board what avoiding the storage of hydrogen under elevated pressure. This proposal suggests the use of fuel cell system powered by hydrogen produced through reforming of liquid fuel from renewable resources such as bioethanol. The fuel cell installation has an integrated fuel reformer. This article considers alkaline fuel cell and solid oxide fuel cell (SOFC). The SOFC is a fuel cell operating at high temperature range 800°C to 1000°C. Figure 2 presents the overall layout system based on SOFC. This kind of fuel cell can use a variety of fuels instead of traditionally used hydrogen in others types of fuel cells. It can be powered by CH₄, C₂H₅OH, CO or others fossil fuels what is very advantageous from the application point of view of such fuel cells on board of automobiles. In this case we have not any problems with the purity of the produced hydrogen which is strongly required to power PEMC stack system. That is why we need high active and selective catalytic system exhibited 100% of fuel conversion, which will be applied in the micro reactor directly before the SOFC fuel cells stack system (figure 2).

Figure 2. Vehicle propulsion system with an innovative range extender system [12].
During the research tasks the most suitable liquid fuel will be selected and will be used as a substrate for hydrogen generation and finally to produce electricity using a SOFC or alkaline fuel cell. One of the best candidates for fuel is the bio-ethanol, which can be obtained from sugar beet, sugar cane and other plants. Ethanol and especially bio-ethanol is convenient for reforming in the reactor before the fuel cell and has the advantage to be a renewable fuel, produced from biomass, as illustrated from figure 3. The main advantage of the concept is to obtain a long range, with easily supply of liquid fuel that has a carbon neutral life cycle.

![Concept of e-Bio Fuel Cell](image)

**Figure 3.** Carbon neutral cycle of the e-Bio Fuel Cell vehicle [12].

4. **Energy balance of the fuel cell system, production and conversion of hydrogen**

The choice of bio-ethanol is favorable by the fact that this non-toxic compared to methanol. It is easily available. It is easily converted under atmospheric pressure and it is a large possibility to obtain it from biomass. Bioethanol has the property to be stored on easy way under liquid form, and to be used on a safety way. Bio ethanol is as well a renewable energy source.

It is possible to obtain different configurations of energy vectors (fuels) and types of fuel cell. According of the type of fuel, the processes that the fuels pass through are different (figure 4).

One can observe from Figure that to use the fuels for the alkaline fuel cell the fuels have to pass through different steps in order to reduce the content of CO after the reforming stage. The alkaline fuel cell needs pure hydrogen, because of risk of contamination of the electrodes by CO.

The following processes are applied:

**Variant 1:**

**Reforming (Steam reforming)** – A process in which reacts steam at high temperature with the fossil fuel, as noted in equation (1) and in equation (2):

\[
\text{CH}_3\text{CH}_2\text{OH} + 3\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 6\text{H}_2 \quad \Delta H = 347 \text{ kJ mol}^{-1} \tag{1}
\]

\[
\text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{O} \rightarrow 2\text{CO} + 4\text{H}_2 \quad \Delta H = 298 \text{ kJ mol}^{-1} \tag{2}
\]
**WGS (Water-gas shift reaction WGSR)** – describes the reaction of carbon monoxide and water vapour to form carbon dioxide and hydrogen. It is one of the most important reactions used to balance the $\text{H}_2/\text{CO}$ ratio, as given in equation (3):

\[
\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \quad \Delta H = -41.16 \text{ kJ mol}^{-1} \quad (3)
\]

**PROX (Preferential Oxidation)** – the catalyst preferentially oxidises CO. The PROX process allows for the reaction of CO with oxygen, reducing CO concentration from approximately 0.5–1.5% in the feed gas to less than 10 ppm, as given in equation (4):

\[
2\text{CO} + \text{O}_2 \rightarrow \text{CO}_2 \quad \Delta H = -172.35 \text{ kJ mol}^{-1} \quad \text{neglected} \quad (4)
\]

**Drying.** The drying process serves to evaporate water.

**PSA (Pressure Switching Adsorption)** is a technology used to separate CO$_2$ species from a mixture.

Gibbs free energy of formation $\Delta G_f$ is the energy that accompanies the formation of 1 mole of a substance from its constituent elements.

Standard Gibbs free energy of formation $\Delta G_0$ is the energy that accompanies the formation of 1 mole of a substance in its standard state (absolute pressure $p = 1$ atm (101.3kPa) and temperature $T=273.15+25$ K) from its constituent elements in their standard state. The values of $\Delta G_0$ (and $\Delta H_0$) are given in tables of thermodynamic properties.

Gibbs free energy of formation $\Delta G_f = 0$ or $\Delta G_f \geq 0$ for chemical elements (C, H, O, etc.) is expressed by equation (5).
The following definition is applied:
\[ \Delta G_{\text{reaction}}^0 = \left( \sum v_i \Delta G_i^0 \right)_{\text{products}} - \left( \sum v_j \Delta G_j^0 \right)_{\text{reactants}} \]  \hspace{1cm} (5)

The SOFC fuel cell has the advantage to accept the hydrogen from after the reforming of different fuels or to be directly power by the different fuels, without any transformation of the fuels.

**Variant 2:**
This variant considers SOFC fuel cell with external reformer, where the liquid fuel is decomposed to hydrogen and other substances. The hydrogen is thus injected to the SOFC. This variant is as well illustrated in figure 2.

**Variant 3:**
Variant 3 considers the case where the liquid fuel is injected directly to the SOFC, without external reforming. The bio-ethanol is reformed in internally integrated reformer.

Figure presents the working principle of the e-Bio Fuel Cell system. The system produces hydrogen from ethanol-blended water through reformer. The main reaction is 
\[ \text{C}_2\text{H}_5\text{OH} + 3\text{H}_2\text{O} \rightarrow 6\text{H}_2 + 2\text{CO}_2. \]

The \( \text{H}_2 \) produced in the reformer reacts with the oxygen from the air in the SOFC and the produced electricity and heat. The electricity is used to charge the high voltage battery of the vehicle. The heat is reused in the reformer to help the reforming of bio-ethanol to water. Thus, the system has a high efficiency of 55%.

![Figure 5. Working principle of the e-Bio Fuel Cell system.](image)

Figure defines three different energy systems between fuels and converters. The energy balance of these three systems will be investigated to understand and to compare the efficiency of conversion and the global energy efficiency of the three scenarios. For the energy balance the thermodynamics based on the enthalpies of the reactions is used.

Table 1 presents the comparisons of the values of the energy balance for the different configurations (variants) presented in Figure. From the results is the visible that the most efficient configuration is Variant 3, the direct reforming of the bio-ethanol by the SOFC Fuel Cell. The energy consumption of the different processes are presented in Table 1. The criteria to be observed is to output power of the fuel cell for the same quantity of bio-ethanol injected in the fuel converter. Variant 3 presents 15.15 MJ/kg of injected ethanol in the system.
Table 1. Comparison of the values of the energy balance for the different configurations.

| Configuration | Vaporiser kJ/mol | Reformer kJ/mol | Dryer kJ/mol | PSA (CO₂ separation) kJ/mol | Process of H₂ generation MJ/kgₜₐₜ | Fuel Cell output MJₑₜ₁ₑᵢₜ /kgₑ₉ₒ₁₉ |
|---------------|------------------|----------------|-------------|-----------------------------|---------------------------------|----------------------------------|
| Variant 1 (EtOH+H₂O) | -466.45          | -337.98        | 39.31       | -21.85                      | -7.78                           | 11.04 (PEM)                      |
| Variant 2 (EtOH+H₂O) | -466.45          | -342.10        | –           | –                           | -8.08                           | 12.61 (SOFC)                     |
| Variant 3 (EtOH)   | –                | –              | –           | –                           | 0.00                            | 15.15 (SOFC)                     |

Error! Reference source not found. summarizes the advantages and the disadvantages of the different conversion configuration, presented in Figure .

Table 2. Advantages and disadvantages of the different configurations (variants).

| Advantages                           | Disadvantages                                                                 |
|--------------------------------------|-------------------------------------------------------------------------------|
| Variant 1 Low cost fuel cell.        | The lowest overall system efficiency.                                        |
|                                      | Compatible to all types of FC.                                               |
|                                      | Multiple chemical processes.                                                 |
|                                      | Three catalytic converters (at least one of them contain Pt catalyst).       |
|                                      | System load can not be adjusted on-line.                                    |
|                                      | Overall large dimensions difficult to use in a small size vehicles.          |
| Variant 2 Overall system efficiency  | Only SOFC cell could be used.                                               |
| is slightly higher in comparison to | Limited number of start/stop cycles.                                        |
| multistep process.                  | Limited lifetime of SOFC system.                                            |
| System load can be adjusted on-line |                                                                                |
| in the limited range.               |                                                                                |
| It is not necessary to remove CO from |                                                                                |
| the H₂ stream.                      |                                                                                |
| Only one catalytic reactor is used.  |                                                                                |
| Low requirements on the type of fuel. |                                                                                |
| Variant 3 The highest overall system | Only SOFC cell could be used.                                               |
| efficiency. The most compact        | Limited number of start/stop cycles.                                        |
| configuration. System load can be    | Limited lifetime of SOFC system.                                            |
| adjusted on-line in the limited      |                                                                                |
| range. It is not necessary to remove |                                                                                |
| CO from the H₂ stream. Only one     |                                                                                |
| catalytic reactor is used. Low       |                                                                                |
| requirements on the type of fuel.    |                                                                                |

5. Conclusion
The variant 3 presenting direct reforming of bio-ethanol is the most efficient combination. In conclusion, is proposed the working principle of the bio ethanol fuel cell for range extender unit for vehicle application with 15.15 MJ of electric energy per kilogram of converted bio-ethanol. SOFC with integrated reformer of the bioethanol is the best fuel cell for the concept for a range extender unit. It presents the best energetic balance, from energy conversion point of view.
It presents the following advantages to be used to power electric vehicles:

- Long lifetime.
- Low - costs of the electrodes.
- Gases produced in SRE process can directly be used to power fuel cell stack.
- High fuel efficiency.
- Various compounds could be used to power fuel stack even natural gas.
- Chemical stable of the solid electrolyte.
- Low cost of raw materials for the electrolyte production.

Disadvantages of using SOFC to power electric vehicles:

- High operating temperature.
- Long start-up.
- Mechanical and chemical compatibility issues.

Next research will be the investigation for the best catalyst system to integrate to the reformer to maximize the hydrogen yield and the stability of the conversion reaction from bioethanol to hydrogen.

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