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Review Article

On efficiencies, emissions, and the colors of hydrogen—An update

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ABSTRACT: Compared with electricity, more precisely electric energy, hydrogen as a secondary form of energy, an energy carrier, an energy storage material, and a chemical reagent are of growing importance. This change is driven mostly by ecological reasons, with hydrogen replacing fossil fuels and materials and finally reducing the emission of greenhouse gases. It is also relevant because of its conceivable use as an energy carrier in transportation. This update starts with a brief collection of common definitions and terminology and moves across a critical assessment of common misunderstandings towards current and future uses of hydrogen to future perspectives with a particular focus on efficiency.

KEYWORDS: hydrogen economy; energy efficiency; energy carrier; electromobility; fuel cells; energy storage

1. Introduction

Certainly, it is well known that hydrogen is a gas under standard conditions without any color, and even in liquefied form, it hardly has any pronounced coloration. Nevertheless, it is quite common to talk about a growing bundle of hydrogen colors. Find more details and some other aspects of the discussion in reports by Ajanovic et al.[1], Kusoglu[2] and Wu and Holze[3].

Green hydrogen is produced by the electrolysis of water using electric energy from renewable sources without any emission of greenhouse gases.

Yellow hydrogen is produced by the electrolysis of water using electric energy from solar energy alone, without any emission of greenhouse gases. Another definition assumes yellow hydrogen is produced using electric energy from the grid, with its typical mix of electric energy from various sources.

Blue hydrogen is produced from fossil fuels (at the time of writing, mostly natural gas) with carbon dioxide sequestration and storage or utilization in further processes. When run correctly, this process does not create emissions of greenhouse gases. Because CO_2 and not carbon (this difference is overlooked in the report by Ajanovic[1]) are collected and stored, this type of hydrogen should be distinguished from turquoise hydrogen.

Gray hydrogen is produced once again from fossil fuels (at the time of writing, mostly natural gas) without carbon dioxide sequestration. This process, which is currently the dominant one for hydrogen production, is produced from coal in its various forms, mostly bituminous coal, without sequestration of the carbon dioxide formed as a byproduct. The process is also known as coal gasification.

Black hydrogen is produced from coal in its various forms, mostly bituminous coal, without sequestration of the carbon dioxide formed as a byproduct. The process is also known as coal gasification.

Brown hydrogen is produced from lignite, also called brown or soft coal, similar to black hydrogen.

Turquoise hydrogen is produced by the thermal splitting of methane (from, e.g., natural gas) via a pyrolytic process, leaving solid carbon as a byproduct. The process is still in its infancy, but it would avoid the complications associated with carbon dioxide sequestration.

Purple hydrogen is produced using heat and electric energy from a nuclear power plant using electrolysis at elevated temperatures or combined chemical-electrolytic processes.

Pink hydrogen is produced using electric energy from a nuclear power plant.

Red hydrogen is produced using heat from nuclear power in a catalytic water-splitting process at high temperatures.

White hydrogen is a designation suggested for naturally occurring hydrogen. As chemists presumably know for centuries that hydrogen does not occur in nature and the environment in elemental form this assignment is a very special one. Elsewhere this color has been suggested for hydrogen generated as a byproduct in various chemical processes[1].

The preceding collection aims at reasonable completeness without discussing obvious overlaps, contradictions, or almost duplications. In current research and publications, further colors in most cases highly specific in terms of hydrogen production mode are proposed[1]. Details of the various processes have been reported and reviewed elsewhere[4–8], and some of the reports should be considered with care because of substantial misunderstandings[1].

Already at this stage, it becomes obvious that the assignment of a particular "type and color of hydrogen" is based solely on the actual mode of hydrogen production. Any further aspects, like the production of greenhouse gases during the production and installation of the hydrogen-producing facility and its components, are left out. This approach closely resembles the concept of zero-emission vehicles (ZEVs) popular since the 1980s in California, where again only the vehicle and its emissions during operation are considered without taking into account the emission of greenhouse gases during, e.g., the generation of electric energy needed to charge the batteries of said vehicles or during their production. But a careful consideration of greenhouse gas emissions related to the operation of a ZEV should take into account even those gas emissions released during production and setup of the wind turbine and the photovoltaic device later used for charging the batteries in this ZEV; opposite claims denying such emissions as reported sometimes are presumably erroneous[9]. Basically, the same considerations should be applied in a comprehensive consideration of hydrogen and its use.

Hydrogen as an energy carrier (also an "energy vector") has been a discussion topic for a few decades. Whether the term "hydrogen economy" was coined by Bockris[10] in 1972 or whether Beckmann's remark[11], that hydrogen as an energy carrier has been considered since the 1950s remains a question possibly more of interest to historians. Actually, Bockris hinted in a review of the history of the hydrogen economy that F. Lawaczek had written about hydrogen as an option for energy transport in the 1930s[10,12]. Certainly, lower losses during the transmission of hydrogen instead of electric energy have been the focus of the considerations discussed by Bockris[13]. Unfortunately, even at this stage, consideration and calculation were limited just to the transport (or transmission) of electric energy, not taking into account at least the components at the start of the chain (hydrogen production and its energetic efficiency) and at the end of the chain (energetic use of hydrogen and efficiencies of typical processes like fuel cells or internal combustion engines). The use of hydrogen as a chemical reactant in industrial processes, wherein currently coal or natural gas are used as reducing agents (e.g., in the steel industry), has not been the focus of these earlier studies and considerations. On the other hand, given the rapid development of high-power electronics enabling conversion of AC to DC and DC to AC useful for high-voltage DC transmission of electric energy, the use of hydrogen as an energy carrier for transmission is of minor importance only.

This wider perception of hydrogen as an energy carrier, a chemical reactant beyond established uses in common hydrogenation reactions, in particular as a reductant in many chemical processes, and as a storage medium has shifted the general discussion about this chemical element into an almost euphoric mode. Sound and scientific discussion of its use in rational terms, taking into account physicochemical facts and an efficiency-oriented planning of hydrogen production, transportation, and finally application, is sometimes hard to find. Common misperceptions and excessive hopes and speculations differ widely from place to place, depending on the economic and ecological situation. As an example, the current state of discussion in Germany is considered in more detail, taking representative examples. Arguments and economic as well as technological facts are valid beyond this location; nevertheless, extrapolations or predictions beyond this place are left to the interested reader.

2. Hydrogen production

Hydrogen is a chemical commodity with significant amounts generated and consumed by various processes and applications.

2.1. Current hydrogen production

At the time of writing most of the hydrogen production is based on fossil fuels, in particular on reforming natural gas[5]. Further methods like coal gasification are of relatively minor importance[14]. Electrochemical water splitting, i.e. electrolysis, has been around for decades[15–17] with localized applications deployed for specific reasons[5,7]. During electrolysis of water isotope enrichment processes can be run, production of heavy water D_2O is thus connected with electrolyzers. At places with a stable, continuous supply of electric energy mostly from hydropower in a few places, electrolyzers have been set up. All of these installations run with alkaline (30% wt. KOH) water electrolysis at ambient or slightly (because of Joule heating, 60 °C–90 °C) elevated temperatures. A practical weakness of this type of electrolyzer is the need for continuous operation because at an open circuit, i.e. in idle mode, and even at strongly variable electricity supply some of its construction and electrode materials may become unstable and even corrode[18]. The integration of renewable energies with alkaline electrolyzers has been considered in the studies of Brauns and Turek[19] and Xia et al.[20]. Overall efficiencies range from 51% to 88% with respect to electric energy fed into the process and heat retrieved by burning the generated hydrogen (higher heating value). Pressures may go up to 50 bar. Electrolyzer cell stacks in the megawatt range are commercially available.

Replacing the liquid electrolyte solution of the alkaline electrolysis with a solid ionically conducting membrane as an electrolyte yields the polymer electrolyte membrane electrolyzer PEMEL, basically the polymer electrolyte membrane fuel cell running in reverse mode[21–23]. For a comprehensive review see Carmo et al.[24]. Somewhat confusingly this concept has resulted in the acronym RHFC (regenerative hydrogen fuel cell) in Pellow et al.[25]. Such a device has been examined and discussed in detail by Ahn and Holze[22,23], finally, a combination of an electrolyzer and a PEM fuel cell was recommended for both technical and economic reasons when hydrogen is used as a storage medium. This combination and not a fuel cell is actually studied by Pellow et al.[25].

Because of the still costly cation exchange membranes specific expenses for cells are larger than with alkaline electrolysis. Electrolyzers of this type can be scaled up and down economically more easily and in a wider range than alkaline electrolyzers. They are less sensitive to changes in electricity supply. This makes PEMEL particularly attractive as a recipient of fluctuating excess electric energy from existing renewable systems and grid operators (flexible market) as well as a reliable user (firm market) for new renewable systems. The membrane of currently available types acts like an acidic electrolyte, most electrode materials well-established and stable within alkaline electrolyzers cannot be used. Unfortunately, most of the promising electrode materials (electrocatalysts) or PEMEL seem to depend on the use of expensive noble metals. Overall efficiencies of PEMEL are about the same as those of alkaline electrolyzers. Cell stacks (assemblies of single cells mounted electrically in series) with up to 1.5 MW electric power are available. A comparison of the two technologies described above is available[26]. With an optimized separator (or membrane) alkaline electrolyzers are slightly more efficient than acidic ones.

Electrolyzers using solid oxides as electrolytes (actually the reverse version of the solid oxide fuel cell) have been studied intensely when waste heat at an elevated level from nuclear power plants appeared to be available. There are various technological options using heat as an added energy input aiming at reduced cell voltages and thus lower input of electric energy these options appear to be of decreasing relevance because the assumed sources of heat were mostly nuclear power plants which have been phased out in Germany already. Elsewhere plans may differ. A look at extremely long construction times, exploding expenses, vastly delayed time of going online, and further unwelcome events cast at least some doubts on the future of nuclear power plants as an energy source and thus conceivable uses of waste heat for electrolysis of water at elevated temperatures. Accordingly, research activities fluctuate; currently, they appear to be a rather limited research and development focus. Energy efficiencies for this process appear slightly higher than for both previously mentioned processes because the thermal energy needed for operation is not factored into efficiency calculations.

Ohmic resistances in the electrolyzer cause corresponding voltage drops, and in addition, non-ideally slow electrode kinetics show some hindrances. An increase in current density j (i.e., current per area with $j = I/A$) results in an increase in needed cell voltage. As a result, the efficiency of the cell and the process will decrease with growing j and the corresponding electric input. Reducing current densities is no solution since it may increase overall production costs because of lower utilization of the installed hardware.

Because of the fluctuating supply of electric energy, electrolyzers capable of handling variable energy inputs and even temporary shut-downs are welcome, particularly in areas where the electric energy from these sources is fed into a national or even international, continent-wide electric grid with electrolyzers operating to some extent as buffers receiving electric energy not useful elsewhere in the grid and with other users. This buffering function is welcome and actually required for grid stability and to avoid economically as well as ecologically unwelcome shut-downs of windmills and photovoltaics on all grid levels; it is also welcome in small and even micro-grids.

2.2. Future hydrogen production

Green hydrogen production based on renewable energies means electrolysis, i.e., electrochemical decomposition of water. The processes briefly reviewed in the preceding section are still subject to optimization[27,28]. In the case of PEMEL substitution of the still rather expensive membranes, in particular the cation exchange membrane, is an intensely pursued path. Replacement of the noble metals used as catalysts on both electrodes is another subject. Even at reduced use of e.g., iridium the conceivable metal supplies are completely insufficient for a scaled-up hydrogen production. The state of the art of electrocatalysts for water electrolysis has been reviewed[29]. Although some concepts for electrolyzers may be not entirely new, their application towards more efficient water splitting as with capillary designs may provide incremental improvements or even more[30].

A promising alternative to the chemically speaking acidic cation exchange membrane (a proton conductor) is substitution with an anion-conducting membrane (i.e., an alkaline membrane)[31]. When successful, the catalysts and construction materials known from alkaline electrolysis may be employed again. The chemical stability of the available membranes is still disappointing. In addition to improvements regarding this performance detail, further alternative membrane concepts (e.g., filled polymers) are studied[15].

A lack of sources of heat at the temperature level needed for water electrolysis with solid oxide electrolytes makes this option rather unlikely. Attempts to use solid proton-conducting membrane ceramic materials instead with sufficient ionic conductivity at significantly lower temperatures (500 °C to 600 °C) appear to be a relief at first sight, but again, the question of suitable heat sources may be the major barrier.

Further electrochemical options, e.g., co-electrolysis of water and CO_2 are still in the research stage[15]. This also applies to other processes, basically always including steps for carbon capture and storage. Further processes, like solar thermochemical ones, are still in the laboratory stage, according to Steinfeld[32].

3. Uses of hydrogen with a focus on efficiency

In addition to consideration of actual uses of hydrogen as a chemical reactant at the time of writing, its use as an energy carrier and storage option is in its developmental or pilot installation stage, with considerable variations from country to country. Safety aspects, infrastructure, public opinion, and further topics related to hydrogen and its use need further discussion and study; for reviews, see, e.g., Kovač et al.[33].

Because in many current (mostly chemical) uses of hydrogen as a reactant, efficiency considerations and comparisons with further options are not relevant in the following text, particular attention will be paid to its use, in particular non-chemical use, in the upcoming future.

3.1. Current uses of hydrogen

When looking at the broader picture from the viewpoint of greenhouse gas emissions and their mitigation, even at current energy mixes (in terms of energies from various primary energy sources), electrification of transport and heating will result in a reduction of said emissions[34]. An earlier study focused just on vehicles and was less optimistic for countries with a high fraction of electric energy produced using fossil fuels[35].

3.2. Future uses of hydrogen

The current situation wherein there is a surplus of electric energy from renewable sources because of poor grid infrastructure and lacking storage facilities sometimes encountered, e.g., in Germany, will be a thing of the past once these obviously and deeply deplored shortcomings are corrected. The time of surplus electric energy, which sometimes has been considered "for free" and has been included in wide-ranging comparisons[36] will soon be over, everywhere. Because most—if not all—hydrogen will be green hydrogen produced by electrolysis, there will be no surplus of hydrogen either. Actually, in highly industrialized and densely populated countries, e.g., in central Europe, there will be a larger demand than supply. Accordingly, hydrogen use should be planned with careful attention to efficiency, with the term used in a broader sense going beyond the narrow thermodynamic meaning. **Table 1** summarizes essentials without taking into account further details like using e-fuels instead of hydrogen (based on a suggestion, see the report by Energiewende et al.[37]).

Table 1. Efficiencies of uses of hydrogen.

	Area of application			
Efficiency	**Industry**	**Transport**	**Energy grid**	**Residential and buildings**
High	Reducing agent, chemical reagent	Long-range aviation and shipping	-	Support of district heating
Questionable	high-temperature heating	Trucks, buses, trains, short-range aviation and shipping	Storage medium for grid support	-
Bad	Low-temperature heating	Cars and light vehicles	-	Residential heating

Although the use of hydrogen and fuel cells as energy sources in vehicles appears less attractive in terms of overall energetic efficiency their use in trucks seems to be reasonable because of the limitations of using batteries as storage devices in such vehicles and because the overall energy consumption of this class of vehicles amounts to about 4.1% only of overall energy consumption for vehicles[38].

The euphorically touted use of E-fuels certainly gives advantages like the possibility of keeping the current fleet of vehicles and the established fuel distribution infrastructure[39] will most likely not be matched by the availability of enough E-fuels. The high energy demand in its production will restrict its synthesis to places where all ingredients (beyond cheap electric energy) are abundantly available. As of today, their use should be limited to those cases where direct use of electric energy via batteries and supercapacitors or at least via hydrogen and fuel cells, both showing much higher efficiencies, is impossible e.g., in long-range aviation.

When considering emissions from vehicles with internal combustion engines beyond CO_2, further greenhouse effect-relevant emissions, in particular of N_2O and methane, must be considered when overall contributions and effects should be compared[40]. The calculation of CO_2-emission based simply on the chemical reaction equation of the combustion process is not wrong, but with respect to the effects of emitted combustion products, it is incomplete. The consideration gets even more complicated when, beyond efficiency and CO_2-emission per run kilometer, further emissions and consumption of resources are considered. In so-called ecological assessments or environmental footprints, this is tried; it will not be pursued further in this report. Beyond the obvious considerations of efficiencies, the various uses of hydrogen might get out of focus—such approaches have been frequently used to provide tilted criticism. e.g., the high "water consumption" during lithium production may just be water evaporation during brine treatment within the process, and the numbers almost disappear anyway when compared with current numbers reported for agriculture and textile production[41]. Most regrettably, in the latter report on current energy use in mobility, surprisingly small energy consumption is attributed to BEVs and an equally surprisingly large one to vehicles operated with fuel cells. This trivial but somewhat disturbing observation and its confusing consequences have been addressed in a report by Buchal et al.[36]. Therein two midsize cars with a diesel internal combustion engine (ICV) and a battery-fed electric engine (BEV) are compared with respect to CO_2 emissions during operation. For the BEV, two boundary cases are considered: Electricity from the German mix of 2018 and electricity exclusively from renewables. CO_2 emissions during battery production are at least addressed. Finally, an ICV fed with methane is compared. The latter example is connected to renewable energies by assuming that methane produced with hydrogen from electrolysis with renewable energies is used. In conclusion, Buchal et al. report that for a BEV, in the best case, CO_2 emissions per kilometer are 10% higher than those of a diesel-fueled car; in the worst case, this grows to 25%. At this point, the authors refer to CO_2 emissions from the transport sector as being stagnant in Germany for years already. The causes are well known (the rapidly growing fraction of heavy cars, in particular SUVs, with high specific emissions), but too nasty to address them[42]. Knobloch et al.[34] arrive at a slightly different conclusion: Even with the electricity mix of 2020 in 53 world regions covering 95% of worldwide energy and heating demand, the CO_2-emissions per kilometer, including the battery, and assuming a lifetime of 150,000 km, just as done by Buchal et al.[36] of a BEV are smaller than those of a vehicle with ICE. In countries with a large fraction of renewable or nuclear energy (e.g., Island, Sweden, or Switzerland), it may be lower by 70%, whereas in countries with, e.g., a large fraction of oil shale in the mix, it may be 40% higher. The contradiction to Buchal et al. is obvious, but because Knobloch et al. don't quote this report, the reader is left alone in gentle confusion. The interested reader will find out quickly that the reports are hardly comparable because Buchal et al. compared only two relatively big cars, whereas Knobloch et al. took into account the actual mix of cars in a given region. This problem has been noted before by Woo and Choi[35]. Consequently, the results reported by Knobloch et al. without their limitation to a specific class of cars are of much wider validity. This finding is further supported by the fact that these authors refrain from any speculation about technologies and their future, as done by Buchal et al. and one of the coauthors before[43]. Both studies ignore the possibilities and effects of e-fuels[9,39,44,45] whether of the 1.[46], 2.[46], 3.[47], or 4. generation[48]. Given the large number of process steps of the synthetic pathways towards e-fuels proposed so far, energetic efficiency will be small, most likely[49–51] and may be acceptable only when taking into account further arguments like the possibly long distance between production and usage or the absence of any other viable option (as in air transport). Definitely, the consumer will enjoy them; certainly, they merit consideration, at least for a transitional time[44].

This interpretation of the observed difference between the conclusions of Buchal et al.[36] and Knobloch et al.[34] is supported by a much wider consideration with more details in a book edited by Klell et al.[51]. **Figure 1** shows the energy consumption per driven kilometer of vehicles with various engines.

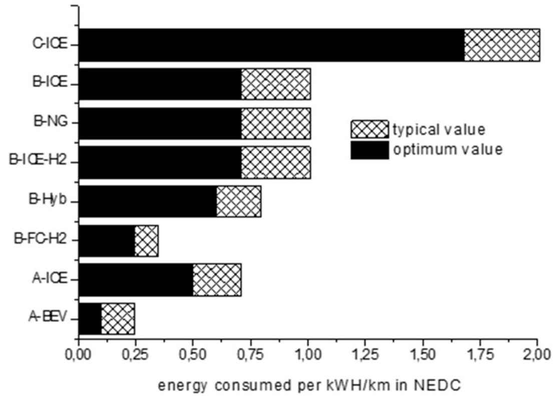

Figure 1. Energy consumed per driven kilometer for A: compact car; B: medium class car; C: luxury car. Operated with: ICE: internal combustion engine with gasoline/Diesel; NG: natural gas with internal combustion engine; ICE-H2: internal combustion engine with hydrogen; Hyb: hybrid; FC-H2: fuel cell with hydrogen; BEV: battery; NEDC: new European driving cycle[51].

Unfortunately, there are no details in the report by Knobloch et al.[34] enabling the assignment of the two selected cars to the categories used in **Figure 1** and the collection edited by Klell et al.[51], the present author refrains from any speculation. Taking in the next step a plain combustion reaction and assuming (as usual) only tailpipe emissions **Figure 2** can be obtained.

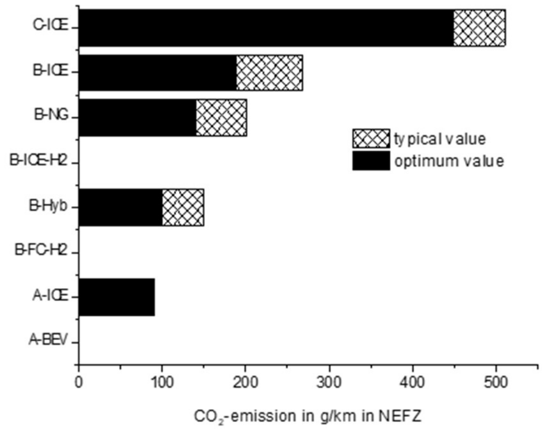

Figure 2. CO_2-emissions per driven kilometer für A: compact car; B: medium class car; C: luxury car. Operated with: ICE: internal combustion engine with gasoline/Diesel; NG: internal combustion engine with natural gas; ICE-H2: internal combustion engine with hydrogen; Hyb: hybrid; FC-H2: fuel cell with hydrogen; BEV: Battery; NEDC: new European driving cycle[51].

The authors obtain overall efficiencies containing the chain from the energy content of the primary energy carrier up to moving the vehicle yielding **Figure 3**[51].

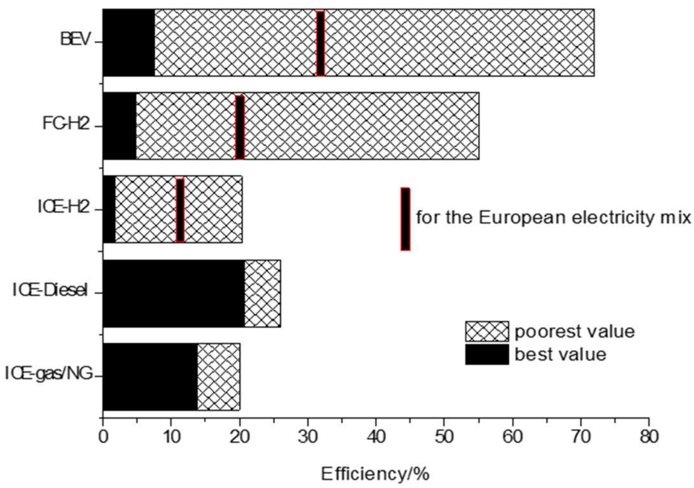

Figure 3. Efficiencies for different driving systems BEV: battery; FC-H2: fuel cell with hydrogen; ICE-H2: internal combustion engine with hydrogen; ICE-Diesel: internal combustion engine Diesel; ICE-gas/NG: internal combustion engine with gasoline or natural gas[51].

The lowest efficiency of a BEV results from using electricity from a lignite-fired power station; the best results from using hydroelectricity. Using hydrogen in the car results in the highest efficiency when using hydrogen from a methane reformer and a fuel cell; the poorest efficiency follows from using an electrolyzer fed from a lignite-fired power station and an internal combustion engine.

Inclusion of the European electricity mix provides an even more realistic picture of efficiency. Already before considering CO_2-emissions obviously electricity from renewable sources and hydrogen produced with these sources is desirable. An answer to the initially addressed question for CO_2-emissions during operation of a vehicle is finally obtained[51], results are displayed in **Figure 4**.

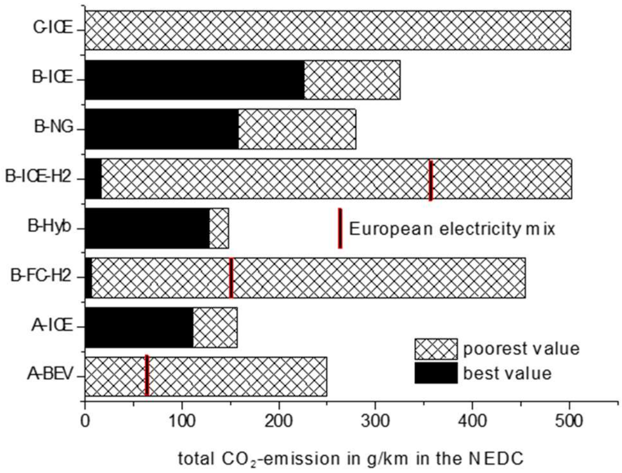

Figure 4. CO_2 emissions per driven kilometer for A: compact car; B: medium class car; C: luxury car. Operated with: ICE: internal combustion engine with gasoline/Diesel; NG: Internal combustion engine with natural gas; ICE-H2: internal combustion engine with hydrogen; Hyb: hybrid; FC-H2: Fuel cell with hydrogen; BEV: Battery; NEDC: new European driving cycle[51].

Once again electric vehicles display their advantage of low CO_2 emissions in particular when electricity from renewable sources is used directly with a BEV or indirectly with hydrogen for storage. Taking instead for a BEV the worst case CO_2 emissions are indeed larger than with the best case with an ICE. This might be taken at first glance as a confirmation of the conclusions by Buchal et al.[36], but already after a look at the more realistic European electricity mix, this apparent confirmation evaporates.

Energetic efficiencies and CO_2 emissions as addressed above are only two of several criteria applied when assessing options. They have their merits and their limitations. Further options are the consideration of energy put into setting up a system vs. the energy stored and released to the grid over the lifetime (net energy analysis) or energy return on investment as demonstrated by Pellow et al.[25].

4. Outlook and perspectives

The scientist's perspective based on thinking in yields and efficiencies will turn out to be insufficient when a topic with far-reaching social and economic implications is considered. As demonstrated above just taking the use of hydrogen in transportation inclusion of more criteria and dimensions tend to result in less clear-cut outcomes and rather relative recommendations. These in addition will be exposed to a critical discussion by non-experts in society and must turn out to be both comprehensible and convincing for the non-scientist. If insufficient care is exercised and the perspective of the non-expert is not taken into account adequately, decisions may be made which most likely will not help to avoid catastrophic developments.

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Conflict of interest

The author declares no conflict of interest.

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