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Journal of Power Sources 167 (2007) 461–471
JOURNAL OF POWER SOURCES
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Exergetic life cycle assessment of hydrogen production from renewables

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Received 6 January 2007; received in revised form 14 February 2007; accepted 14 February 2007
Available online 25 February 2007

Abstract

Life cycle assessment is extended to exergetic life cycle assessment and used to evaluate the exergy efficiency, economic effectiveness and environmental impact of producing hydrogen using wind and solar energy in place of fossil fuels. The product hydrogen is considered a fuel for fuel cell vehicles and a substitute for gasoline. Fossil fuel technologies for producing hydrogen from natural gas and gasoline from crude oil are contrasted with options using renewable energy.

Exergy efficiencies and greenhouse gas and air pollution emissions are evaluated for all process steps, including crude oil and natural gas pipeline transportation, crude oil distillation and natural gas reforming, wind and solar electricity generation, hydrogen production through water electrolysis, and gasoline and hydrogen distribution and utilization. The use of wind power to produce hydrogen via electrolysis, and its application in a fuel cell vehicle, exhibits the lowest fossil and mineral resource consumption rate. However, the economic attractiveness, as measured by a "capital investment effectiveness factor," of renewable technologies depends significantly on the ratio of costs for hydrogen and natural gas. At the present cost ratio of about 2 (per unit of lower heating value or exergy), capital investments are about five times lower to produce hydrogen via natural gas rather than wind energy. As a consequence, the cost of wind- and solar-based electricity and hydrogen is substantially higher than that of natural gas.

The implementation of a hydrogen fuel cell instead of an internal combustion engine permits, theoretically, an increase in a vehicle's engine efficiency of about of two times. Depending on the ratio in engine efficiencies, the substitution of gasoline with "renewable" hydrogen leads to (a) greenhouse gas (GHG) emissions reductions of 12–23 times for hydrogen from wind and 5–8 times for hydrogen from solar energy, and (b) air pollution (AP) emissions reductions of 38–76 times for hydrogen from wind and 16–32 times for hydrogen from solar energy. By comparison, substitution of gasoline with hydrogen from natural gas allows reductions in GHG emissions only as a result of the increased efficiency of a fuel cell engine, and a reduction of AP emissions of 2.5–5 times. These data suggest that "renewable" hydrogen represents a potential long-term solution to many environmental problems.

Keywords: Hydrogen; Production; Exergy; Efficiency; Renewables; Fuel cell

1. Introduction

Expansions of modern power generation and transportation systems should account simultaneously for economic growth and environmental impact. The latter corresponds mostly to the combustion of hydrocarbon fuels and the accompanying emissions of large quantities of greenhouse gases and air pollutants (see Fig. 1). Rising concerns about the effects of global warming, air pollution emissions and declining fossil fuel stocks have increased interest in renewable energy sources such as wind and solar energies. An environmentally advantageous scheme for power generation and transportation systems based on renewable technologies and hydrogen is presented in Fig. 2.

The prospects are good for generating electricity, hydrogen or synthetic fuels from only renewable energy sources. In some ways, electricity generation technologies including wind turbines and photovoltaic cells are as developed as hydrogen production via water electrolysis. Pure hydrogen can be used as a fuel for fuel cell vehicles, which are rapidly improving nowadays, or converted into synthetic liquid fuels by means of such processes as Fischer–Tropsch reactions [1].

The use of hydrogen as a fuel for fuel cell vehicles can lead to significant changes in air pollution and greenhouse gas emissions. In a fuel cell stack, electricity (which is converted into mechanical work in electrical motors with efficiencies higher

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doi:10.1016/j.jpowsour.2007.02.031

Nomenclature

AP	air pollution emissions (g)
C	cost (US$)
E	energy (MJ)
EEQ	exergy equivalent of materials and devices (MJ)
EOP	operation exergy (MJ)
Ex	exergy (MJ)
ExLCA	exergetic life cycle assessment
G	Gibbs free energy (kJ mol^{-1})
H	enthalpy (kJ mol^{-1})
LCA	life cycle assessment
LFT	life time
LHV	lower heating value (MJ kg^{-1})
m	mass (g)
NO_x	nitrogen oxides
p	pressure (atm)
Q	heat (kJ)
R	universal gas constant (J mol^{-1} K^{-1})
S	entropy (kJ mol^{-1} K^{-1}, in Eq. (6))
T	temperature (K)
T_0	reference-environment temperature (K)
VOC	volatile organic compound
w	weighting coefficient of air pollutant
W	work

Greek letters

α	ratio in costs of hydrogen and natural gas
ε	ratio in efficiencies
γ	capital investments effectiveness factor
η_e	energy efficiency
η_{ex}	exergy efficiency

Subscripts

atm	atmosphere
AP	air pollution
cmp	compressor
dir	direct
el	electric
ex	exergy
f	fuel
g	gasoline
H	hydrogen
i, j	indexes
ind	indirect
LFC	life cycle
max	maximum
min	minimum
ng	natural gas

Superscripts

cmp	compressor
eng	engine
gt	gas turbine
i	index
LFC	life cycle
ng	natural gas
VCL	vehicle

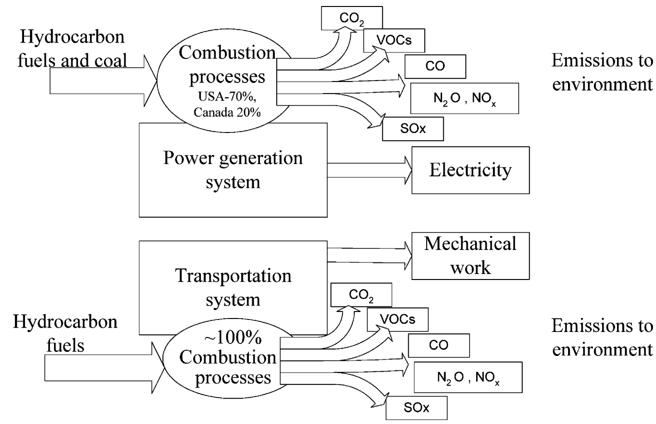

Fig. 1. Environmental impact of modern power generation and transportation systems.

than 90%) is generated via the following electrochemical reactions:

$$\begin{aligned} &\text{Anode}: \quad 2H_2 \rightarrow 4H^+ + 4e^- \\ &\text{Cathode}: \quad O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \end{aligned} \tag{1}$$

These reactions occur in a proton exchange membrane fuel cell stack at low temperature (<100 °C) and involve separation of oxygen from air at the cathode. At these conditions the formation of harmful nitrogen oxides is inhibited and only water is produced during power generation. Thus, the utilization of hydrogen in fuel cell vehicles can be considered as ecologically benign, regarding direct vehicle emissions. Any associated emissions of pollutants and greenhouse gases are associated with hydrogen production.

In internal combustion engine (ICE) vehicles, gasoline (a mixture of hydrocarbons) is combusted in air. The reaction can be represented as

$$C_nH_m + \left(n + \frac{m}{4}\right) O_2 \rightarrow nCO_2 + \frac{m}{2}H_2O + Q \tag{2}$$

where the values of the coefficients m and n depend on the specific fuel characteristics. The heat Q released during this exothermic reaction is in part converted to mechanical work. According to the Carnot principle, the higher is the temperature of fuel combustion the greater is the mechanical work that can be extracted theoretically. The average temperature of

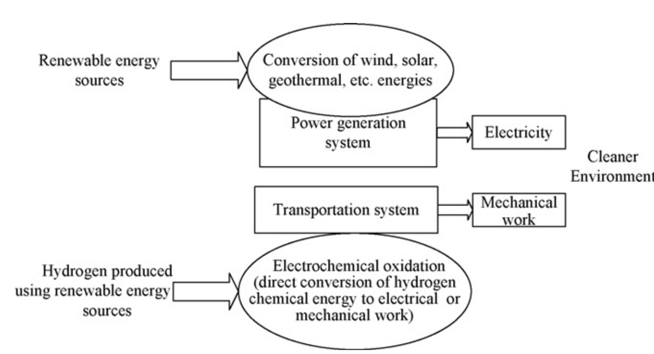

Fig. 2. An environmentally improved scheme for power generation and transportation systems.

the combusting mixture of gasoline and air is about 1300 °C. At such high temperatures the formation of nitrogen oxides is promoted. Evaporation of gasoline and incomplete combustion lead to emissions of volatile organic compounds and carbon monoxide. Thus, air pollution and greenhouse gas emissions are associated with gasoline production and its utilization in ICE vehicles.

Renewable-based hydrogen can lead to the significantly lower environmental impacts, depending on the characteristics of the many steps and chains involved over their lifetimes, from natural resource extraction and plant construction to final product distribution and utilization. Adequate evaluation of environmental impact and energy use throughout the overall production and utilization life cycle ("from cradle to grave") is critical for the proper evaluation of technologies.

Life cycle assessment (LCA) is a methodology for this type of assessment, and represents a systematic set of procedures for compiling and examining the inputs and outputs of materials and energy, and the associated environmental impacts, directly attributable to a product or service throughout its life cycle. A life cycle is the interlinked stages of a product or service system, from the extraction of natural resources to their final disposal [2]. The importance of LCA becomes apparent if one considers industrial processes (metallurgical, chemical, etc.) for products (metals, plastics, glass, etc.) and services, since almost all currently rely on fossil fuels, the consumption of which leads to a range of environmental impacts.

Within a LCA, the mass and energy flows and environmental impacts related to plant construction, operation and dismantling stages are accounted for. The determination of all input and output flows is often very complicated, so some simplifications and assumptions are often made to facilitate an LCA. The challenge is to ensure the assumptions and simplifications (e.g., simplified models of processes) retain the main characteristics of the actual system or process being analyzed.

During the past decade several researchers have tried to enhance LCA methods [3–6] by considering exergy rather than or in conjunction with energy flows. Such an extension of LCA is referred to as exergetic life cycle assessment (ExLCA). As exergy is the mechanical work theoretically obtainable from a flow or system, exergy accounts for both quantity and quality of energy and thus more precisely characterizes the efficiency of fossil and mineral resource consumption [7,8]. The main objective of the present study is to extend our earlier work on the life cycle assessment of hydrogen fuel cell and gasoline vehicles [9] by including exergy and to apply the work to hydrogen production processes from renewables (e.g., solar, wind) and natural gas for PEM fuel cell vehicles and gasoline production for internal combustion engine vehicles. The present study also aims to examine the efficiency, cost effectiveness, environmental impact and sustainability aspects of the processes for comparison purposes.

2. Exergetic life cycle assessment

In a LCA of a system involving several technological steps, the ith technological step is evaluated by its material and energy flows (e.g., fossil fuel consumption) and environmental impacts. The exergy consumption rate corresponding to fossil fuel use can be evaluated with the following expression:

$$\dot{\mathrm{Ex}}^{i}_{\mathrm{LFC}} = \dot{\mathrm{Ex}}^{i}_{\mathrm{dir}} + \Delta\dot{\mathrm{Ex}}^{i}_{\mathrm{dir}} + \Delta\dot{\mathrm{Ex}}^{i}_{\mathrm{ind}} \tag{3}$$

where $\dot{\mathrm{Ex}}^{i}_{\mathrm{LFC}}$ is the life cycle fossil fuel exergy consumption rate, $\dot{\mathrm{Ex}}^{i}_{\mathrm{dir}}$ the rate fuel exergy is directly transformed into final products, $\Delta\dot{\mathrm{Ex}}^{i}_{\mathrm{dir}}$ the rate fuel exergy is consumed to perform the transformation and $\Delta\dot{\mathrm{Ex}}^{i}_{\mathrm{ind}}$ is the rate fuel exergy is consumed through being embodied in construction materials and equipment, and during installation, operation, maintenance, decommissioning, etc. The difference between $\dot{\mathrm{Ex}}^{i}_{\mathrm{dir}}$ and $\Delta\dot{\mathrm{Ex}}^{i}_{\mathrm{dir}}$ can be explained by considering the example of natural gas reforming, which is often the first stage in large-scale manufacturing of ammonia, methanol and other synthetic fuels. The sum of the reactions to produce hydrogen through natural gas reforming is the following endothermic process:

$$CH_4 + 2H_2O \xrightarrow{T \approx 950\,^{\circ}\mathrm{C}} 4H_2 + CO_2; \quad \Delta H = +165\,\mathrm{kJ\,mol^{-1}} \tag{4}$$

As seen in reaction (2), methane is directly converted to hydrogen. The reaction is driven by high-temperature heat, which is typically supplied by another flow of methane being combusted according to

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O; \quad \Delta H = -802.6\,\mathrm{kJ\,mol^{-1}} \tag{5}$$

In this example, $\dot{\mathrm{Ex}}_{\mathrm{dir}}$ includes the exergy of the methane utilized in reaction (4) and $\Delta\dot{\mathrm{Ex}}_{\mathrm{dir}}$ includes the exergy of the methane employed in reaction (5).

The standard exergies of most fuels are similar to their lower heating values (LHVs). The lower heating value is equal to the heat released by the complete burning of all fuel components to CO_2 and H_2O in the form of a vapour. The standard exergy of fuels $\mathrm{Ex}^0_{\mathrm{f}}$ is equal to the maximum work obtainable (or the work obtainable in an ideal fuel cell), and can be evaluated as the negative of the standard Gibbs free energy change ΔG^0 (at $p_0 = 1$ atm, $T_0 = 298$ K) for the fuel combustion reaction:

$$\mathrm{Ex}^0_{\mathrm{f}} = -\Delta G^0 = -(\Delta H^0 - T_0 \Delta S^0) \tag{6}$$

Here, ΔH^0 and ΔS^0 are, respectively, the change of standard enthalpy and entropy in this reaction. For the standard exergy calculation H_2O can be considered a liquid or vapour. The lower heating values [10] and standard chemical exergies, along with the ratios of standard chemical exergy to LHV, are presented for different fuels in Table 1 following Szargut et al. [11]. In this table, the resulting water is a vapour.

When electricity, hydrogen or other manufactured secondary energy carriers are used as the input exergy source, the generally accepted efficiencies are usually applied to evaluate the direct input fossil fuel exergy rates $\dot{\mathrm{Ex}}^{i}_{\mathrm{dir}}$ and $\Delta\dot{\mathrm{Ex}}^{i}_{\mathrm{dir}}$. For use of electricity, for example, which is often generated from fossil fuels,

Table 1
Values of standard exergy and LHV and their ratio for different fuels

Fuel	Lower heating value LHV (MJ kg^{-1})	Standard exergy Ex_f^0 (MJ kg^{-1})	Ex_f^0/LHV
Hydrogen	121.0	118.2	0.977
Natural gas	50.1	52.1	1.04
Conventional gasoline	43.7	46.8	1.07
Conventional diesel	41.8	44.7	1.07
Crude oil	42.8	45.8	1.07

Sources: [10,11].

$\Delta \dot{Ex}_{dir}^{i}$ is expressible as

$$\Delta \dot{Ex}_{dir}^{i} = \frac{\dot{W}_i}{\eta_{ex}} \quad (7)$$

where η_{ex} is the exergy efficiency for electricity generation from a fossil fuel. If the fossil fuel exergy and LHV values are similar, the exergy η_{ex} and energy $\eta_e = \dot{W}_i/\dot{LHV}_i$ efficiencies for the processes of electricity, mechanical work and hydrogen generation do not differ significantly.

The indirect exergy $\Delta \dot{Ex}_{ind}$ cannot be treated as equal to the embodied exergy (i.e., the exergy required to produce a given material or device) or energy. The embodied exergy (energy) adequately reflects the environmental impact of the material extraction and material and device production stages, but it is inconsistent with the economic cost of these products. Note that construction materials are also produced from mineral sources (ores, limestone, etc.) which, like fossil fuels, have value; their exergy (energy) contents are much lower than their real economic values. To account for this, the exergy (energy) equivalent (EEQ) of construction materials and devices [9,12] is calculated by dividing the cost of materials or devices utilized in a given technological stage by the cost of a unit of fossil fuel exergy (energy). Then, the indirect exergy consumption rate is evaluated with the following expression:

$$\Delta \dot{Ex}_{ind} = \frac{\sum EEQ + EOP}{LFT} \quad (8)$$

where $\sum$EEQ is the sum of the exergy equivalents of construction materials and devices related to a given technological operation, EOP the operation exergy, i.e., the fossil fuel exergy required for installation, construction, operation, maintenance, decommissioning, etc., of equipment, and LFT is the lifetime of the unit performing a technological operation. The use of different data, efficiencies, costs, etc., introduces some uncertainties into LCA, but LCA nonetheless is a powerful tool for evaluating and comparing the exergy (energy) efficiencies and environmental impacts of entire technological chains, including their construction and operating stages.

3. Case study: exergetic life cycle analysis

An exergetic life cycle assessment is presented of four technologies (two using fossil fuels and two renewables) for producing gasoline and hydrogen and their use in internal combustion engine (gasoline) or fuel cell (hydrogen) vehicles. Life cycle exergy efficiencies, capital investment effectiveness factors and environmental impacts are examined. Although numerous LCAs of gasoline and hydrogen vehicles have been reported [13–18], the need to consider exergy and energy losses throughout the life cycle of fuels, starting from production and through to utilization in a vehicle, have not been carefully considered. Such comprehensive assessments can help explain why renewable technologies for hydrogen production are economically less attractive than traditional ones. The principal technological steps to produce gasoline from crude oil, and hydrogen from natural gas and solar and wind energies, are presented in Fig. 3.

3.1. Natural gas and crude oil transport

To evaluate and compare the exergy consumption and environmental impact of transporting natural gas and crude oil by pipeline, equal lengths of pipelines (1000 km) are considered. Typical characteristics for transporting crude oil and natural gas via pipeline from several sources [19–21] are listed in Table 2. The energy values embodied in the materials and devices are evaluated and used to obtain exergy values assuming that the only fossil fuel employed in their production is natural gas. The exergies embodied in the pipeline materials, compressors and pumps, and the exergy equivalents, are presented in Table 3. It is assumed that the operation exergy (EOP) to install, maintain and operate the equipment is equal to the embodied exergy to produce it.

The mechanical work or electricity required for pipeline transportation is assumed produced by a gas turbine unit with an average exergy efficiency $\eta_{ex}^{gt} = 0.33$ [19]. This assumption permits evaluation of the direct exergy consumption rate. Table 4 lists the direct and indirect exergy consumption rates to transport

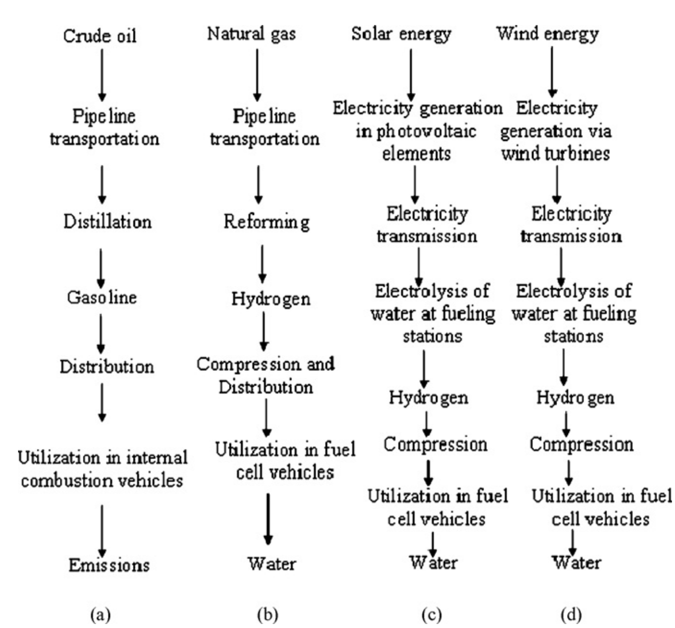

Fig. 3. Principal steps in utilizing in transportation (a) crude oil, (b) natural gas, (c) solar energy, and (d) wind energy.

Table 2
Typical characteristics for crude oil and natural gas pipeline transportation

Characteristic	Natural gas	Crude oil
Velocity in pipeline w (m s^{-1})	7.0	2.0
Diameter of pipeline d (m)	0.8	0.4
Length of pipeline L (m)	1.0×10^6	1.0×10^6
Viscosity of crude oil μ (mPa s)	0.011	60.0
Efficiency of isothermal compressors (natural gas) and pumps (crude oil)	0.65	0.65
Maximum pressure in natural gas pipeline p_{max} (atm)	70.0	–
Minimum pressure in natural gas pipeline p_{min} (atm)	50.0	–
Exergy rate of input flow (MJ s^{-1})	6,914	90,849
Mass of pipeline (tonnes)	126,102	64,739
Embodied exergy in pipeline (GJ)	4,551,428	2,316,103
Lifetime of pipeline (years)	80	80
Embodied exergy in compressors and pumps (GJ)	1,574,277	4,174,729
Lifetime of pumps and compressors (years)	20	20

Sources: [19–21].

Table 3
Embodied exergy, exergy equivalent (EEQ) and operation exergy (EOP) for natural gas and crude oil pipeline transportation

Materials and equipment	Embodied exergy per second of lifetime (MJ s^{-1})	Exergy equivalent per second of lifetime (MJ s^{-1})	Operation exergy per second of lifetime (MJ s^{-1})
Natural gas pipeline	1.79	11.3	n/a
Natural gas compressors	2.50	77.4	n/a
Total	4.29	88.7	4.29
Crude oil pipeline	0.92	5.82	n/a
Crude oil pumps	6.62	205.4	n/a
Total	7.54	211.2	7.54

an amount of natural gas and crude oil with an exergy flow rate $\dot{\text{Ex}}_{dir}$ of 1 MJ s^{-1}.

3.2. Natural gas reforming and crude oil distillation

The exergy losses in natural gas reforming, where methane is the only source of exergy input, comprise approximately 22% of the total exergy input of methane [22]. The exergy efficiency and environmental impact to produce 1 MJ of exergy of gasoline have been estimated according to the energy consumption of all petroleum refineries in the U.S. in 1996 [23]. The overall direct exergy rates in the reforming and transportation stages are presented in Table 6 (column 2).

The indirect exergy for natural gas reforming is based on data of Spath and Mann [24]. In Table 5, the material requirements of a natural gas reforming plant are presented. The values of the energy embodied in materials, from Spath and Mann [24], have been used to obtain the values of embodied exergies assuming that embodied energy relates to the LHV of natural gas. In Table 6 (column 3), the resulting indirect exergy values are presented. It is assumed that the operation exergy to install, maintain and operate the equipment is equal to the embodied exergy consumed to produce it. Comparing the values of direct and indirect exergies reveals that the indirect exergy rate ($\Delta\dot{\text{Ex}}_{ind}$) is more than ten times less than the direct exergy rate ($\Delta\dot{\text{Ex}}_{dir}$). In the following calculations, therefore, the indirect exergy consumption rate is neglected.

Data to calculate the indirect exergy consumption for crude oil refining are not available. However, as shown by Lange and Tijm [25], the capital cost of crude oil distillation is lower than that for natural gas reforming. As in the case of natural gas reforming, the indirect exergy consumption for crude oil refining is negligible compared to the direct exergy consumption.

Table 4
Indirect and direct exergy consumption rate to transport a quantity of natural gas and crude oil with an exergy content of 1 MJ s^{-1}

Transportation	$\Delta\dot{\text{Ex}}_{dir}$ (kJ s^{-1})	$\Delta\dot{\text{Ex}}_{ind}$ (kJ s^{-1})
Natural gas pipeline transportation	95.3	13.0
Crude oil pipeline transportation	16.2	2.2

3.3. Renewable hydrogen production via wind energy

The production of hydrogen using wind energy considered here involves two main systems: a wind turbine that produces electricity which in turn drives a water electrolysis unit that produces hydrogen. The energy of wind is converted to mechanical work by wind turbines and then transformed by an alternator to ac electricity which is transmitted to the power grid (Fig. 3). The efficiency and output of wind turbines depends on location. Applications of wind energy normally make sense only in areas with high wind activity. Data for a 6 MW wind power generation plant [26] are used here. Table 7 presents the material requirements and indirect exergy consumption for this plant.

Based on data of Spath and Mann [27] for electrolysis to produce hydrogen with a 72% efficiency (on an exergy basis), the indirect exergy (energy) are 6.61% of that for a wind power generation plant. Accounting for a 7% electricity loss during transmission, the efficiency of hydrogen production is 66.9%. Thus, a 6 MW wind power plant combined with water electrolysis can produce 3.93 MJ s^{-1} of exergy in the form of hydrogen. Based on these data the indirect energy consumption in a wind power plant coupled with water electrolysis for 1 MJ of exergy in the form of hydrogen is determined (see Table 7, column 7).

3.4. Renewable hydrogen production via solar energy

The production of hydrogen using solar energy considered here involves two main systems: a solar photovoltaic system that produces electricity which in turn drives a water electrolysis

Table 5
Hydrogen plant material requirements (base case)

Material	Quantity required (tonnes)	Embodied exergy (GJ $tonnes^{-1}$)	Embodied exergy consumption per second of lifetime (MJ s^{-1})	Exergy equivalent per second of lifetime (MJ s^{-1})	Operation exergy per second of lifetime (MJ s^{-1})	Indirect exergy rate $\Delta\dot{E}x_{ind}$ (MJ s^{-1})
Concrete	10,242	1.5	0.0236	0.361	n/a	n/a
Steel	3,272	35.8	0.185	1.180	n/a	n/a
Aluminum	27	209.5	0.00896	0.0581	n/a	n/a
Iron	40	24.4	0.00155	0.00986	n/a	n/a
Total	13,581	271.1	0.219	1.600	0.219	1.83

Assumes a 20-year lifetime, a 1.5 million Nm^3 day^{-1} hydrogen production capacity and a hydrogen exergy production rate of 183.810 MJ s^{-1}.

Table 6
Total rate of direct exergy consumption for natural gas and crude oil transportation and reforming (distillation) processes

Fuel	$\Delta\dot{E}x_{dir}$ (MJ s^{-1})	$\Delta\dot{E}x_{ind}$ (MJ s^{-1})
Hydrogen	0.391	0.025
Gasoline	0.168	n/a

Data units are MJ s^{-1} of fuel exergy produced.

unit that produces hydrogen. The photovoltaic elements convert solar energy into direct current (dc) electricity, which is transformed by inverters to alternating current (ac) electricity and transmitted to the power grid. At fuelling stations, ac electricity is used to electrolyze water to produce hydrogen (Fig. 3). Data are considered here for a 1.231-kW building-integrated photovoltaic system in Silverthorne, Colorado [21], which utilizes thin-film amorphous silicon technology and for which indirect exergy consumption has been evaluated. Tables 8 and 9 present the material requirements and indirect exergy consumption for hydrogen production by photovoltaic power generation and water electrolysis. A procedure similar to that used for the wind power plant in the previous section is applied to evaluate the indirect exergy consumption associated with electrolysis. Taking into account the efficiency of electrolysis and transmission losses, the 1.231-kW photovoltaic system combined with water electrolysis can produce 807.3 J s^{-1} of hydrogen exergy.

Table 7
Material requirements and corresponding rate of indirect energy consumption $\Delta\dot{E}x_{ind}$ for a 6 MW wind power generation plant coupled with an electrolyser to produce hydrogen

Materials and processes	Quantity required (tonnes)	Embodied exergy (GJ $tonnes^{-1}$)	Embodied exergy consumption per second of lifetime (MJ s^{-1})	Exergy equivalent per second of lifetime (MJ s^{-1})	Operation exergy per second of lifetime (MJ s^{-1})	Indirect exergy $\Delta\dot{E}x_{ind}$ (MJ s^{-1})
Concrete	7647.3	1.46	0.0141	0.216	n/a	n/a
Copper	5.275	136	0.000911	0.0119	n/a	n/a
Fiberglass	496.6	13.5	0.00851	0.122	n/a	n/a
Steel–carbon/low alloy	1888.0	35.8	0.0857	0.545	n/a	n/a
Steel–stainless	226.2	55.1	0.0158	0.101	n/a	n/a
Total	10263.4	n/a	n/a	0.994	0.136	1.130
Electrolysis	n/a	n/a	n/a	n/a	n/a	0.075
Total	n/a	n/a	n/a	n/a	n/a	1.21
Total for 1 MJ s^{-1} of H_2 exergy	n/a	n/a	n/a	n/a	n/a	0.301

Table 8
Exergy equivalents for thin film photovoltaic solar cell block with 157.2 m^2 of surface area in a thin film 1.231-kW photovoltaic system

Material	Embodied exergy (MJ m^{-2})	Exergy equivalents (MJ m^{-2})	Embodied exergy in manufacturing (MJ m^{-2})	Exergy equivalent (GJ $unit^{-1}$)
Encapsulation	0.220×10^3	3.472×10^3	0.143×10^3	568.12
Substrate	0.0266×10^3	0.170×10^3	0.0587×10^3	35.84
Deposition materials	0.0196×10^3	0.308×10^3	0.0962×10^3	63.53
Busbar	0.00530×10^3	0.0835×10^3	0	13.14
Back reflector	0.000728×10^3	0.0114×10^3	0.0770×10^3	13.90
Grid	n/a	n/a	0.0356×10^3	5.60
Conductive oxide	n/a	n/a	0.101×10^3	15.84
Total for solar cell block	0.272×10^3	4.044×10^3	0.511×10^3	716.0

Table 9
Indirect exergy consumption rate for the units of a 1.231-kW thin film photovoltaic system with a lifetime of 30 years

Unit	Embodied exergy (GJ unit^{-1})	Exergy equivalent (GJ unit^{-1})	Operation exergy per second of lifetime (J s^{-1})	Indirect exergy $\Delta\dot{Ex}_{ind}$ (J s^{-1})
Inverters	41.6	115.9	n/a	n/a
Wiring	3.02	48.6	n/a	n/a
Solar cell block	123.1	716.0	n/a	n/a
Total	167.8	880.4	82.12	1012.7
Electrolysis	n/a	n/a	n/a	67.0
Total per unit	n/a	n/a	n/a	1079.6
Total for 1 MJ s^{-1} of hydrogen exergy	n/a	n/a	n/a	1337.8

Table 10
Direct exergy consumption rates for 1 MJ of chemical exergy of hydrogen and gasoline to compress $\Delta\dot{Ex}_{dir}^{cmp}$ and distribute $\Delta\dot{Ex}_{dir}^{distr}$ these energy carriers to refueling stations

Energy carriers	$\Delta\dot{Ex}_{dir}^{cmp}$ (MJ s^{-1})	$\Delta\dot{Ex}_{dir}^{distr}$ (MJ s^{-1})
Hydrogen from natural gas, $p_{min}=20$ atm, $p_{max}=350$ atm	0.119	0.025
Hydrogen from wind energy, $p_{min}=1$ atm, $p_{max}=350$ atm	0.238	n/a
Hydrogen from solar energy, $p_{min}=1$ atm, $p_{max}=350$ atm	0.238	n/a
Gasoline	n/a	0.0025

Table 11
Life cycle assessment of the exergy efficiency of fossil fuel and mineral resource utilization to produce 1 MJ s^{-1} of chemical exergy of hydrogen and gasoline

Energy carriers	$\dot{Ex}_{dir}$ (MJ s^{-1})	$\sum\Delta\dot{Ex}_{dir}$ (MJ s^{-1})	$\sum\Delta\dot{Ex}_{ind}$ (MJ s^{-1})	Total $\dot{Ex}_{LFC}$ (MJ s^{-1})	η_{ex}^{LFC}
Hydrogen from natural gas, $P=350$ atm	1	0.535	n/a[a]	1.535	0.65
Hydrogen from wind energy, $P=350$ atm	n/a	0.238	0.301	0.539	1.86
Hydrogen from solar energy, $P=350$ atm	n/a	0.238	1.338	1.566	0.64
Gasoline	1	0.171	n/a[a]	1.171	0.85

[a] For fossil fuel technologies, the indirect exergy consumption rate is considered negligible relative to the direct exergy consumption rate.

3.5. Hydrogen compression

The density of hydrogen at standard conditions is low. To assist in storage and utilization as a fuel, the density is often increased via compression. Neglecting the indirect exergy consumption ΔEx_{ind}, the total and direct fossil fuel (natural gas) exergy consumption ΔEx_{dir}^{cmp} to compress isothermally 1 mol of hydrogen can be expressed, assuming ideal gas behavior, as

$$\Delta Ex_{dir}^{cmp} = \frac{RT_0}{\eta^{cmp}\eta_{el}^{ng}} \ln\left(\frac{p_{max}}{p_{min}}\right) \quad (9)$$

where $T_0 = 298$ K is the standard environmental temperature and $R = 8.314$ J mol^{-1} K^{-1} is the universal gas constant. The direct exergy consumed in compressing hydrogen is shown in Table 10 and is evaluated assuming an isothermal compression efficiency η_{cmp} of 0.65 and assuming that electricity is generated from natural gas with an average efficiency of $\eta_{el}^{ng} = 40\%$ (which is reasonable since the efficiency of electricity production from natural gas varies from 33% for gas turbine units to 55% for combined-cycle power plants, with about 7% of the electricity dissipated during transmission). A maximum pressure $p_{max} = 350$ atm in the tank of the fuel cell vehicle is considered [28]. Minimum pressures before compression of $p_{min} = 1$ atm and $p_{min} = 20$ atm are taken for hydrogen production through electrolysis and natural gas reforming [24], respectively.

3.6. Hydrogen and gasoline distribution

Hydrogen distribution is replaced by electricity distribution in cases using wind and solar energy (Fig. 3) and such distribution has been accounted for in hydrogen production. The distribution of compressed hydrogen after its production via natural gas reforming is similar to that for liquid gasoline, but compressed hydrogen is characterized by a lower volumetric energy capacity and higher material requirements for a hydrogen tank. According to the 1997 Vehicle Inventory and Use Survey, the average "heavy-heavy" truck in the U.S. travelled 6.1 miles gal^{-1} of diesel fuel [29]. Neglecting the indirect exergy consumption rate $\Delta\dot{Ex}_{ind}^{distr}$, the total and direct fuel (diesel) exergy consumption rate $\Delta\dot{Ex}_{dir}^{distr}$ is evaluated assuming a distance of 300 km is traveled before refueling for a truck with a 50 m^3 tank (see Table 10).

3.7. Life cycle exergy efficiency of fossil fuel and mineral resource utilization

The overall results of the life cycle assessments are summarized in Table 11. The life cycle exergy efficiency of fossil fuel and mineral resource utilization is defined as follows:

$$\eta_{ex,H_2}^{LFC} = \frac{\dot{Ex}_{H_2}}{\dot{Ex}_{LFC}^{H_2}} \tag{10}$$

for hydrogen production technologies and

$$\eta_{ex,g}^{LFC} = \frac{\dot{Ex}_{g}}{\dot{Ex}_{LFC}^{g}} \tag{11}$$

for gasoline production from crude oil. Here, $\dot{Ex}_{H_2}$ and $\dot{Ex}_{g}$ are the exergies of hydrogen and gasoline, and $\dot{Ex}_{LFC}^{H_2}$ are $\dot{Ex}_{LFC}^{g}$ are the overall life-cycle fossil fuel and mineral exergy consumption rates to produce hydrogen and gasoline, respectively.

The life cycle assessment indicates that the exergy efficiency of fossil fuel and mineral resource utilization to produce compressed hydrogen from wind energy η_{ex}^{LFC} reaches 1.86, meaning that the consumed fossil fuel exergy (embodied in materials, equipment, etc.) is 1.86 times less than the exergy of the hydrogen produced. A value of η_{ex}^{LFC} greater than 1 occurs because the exergy of wind is considered "free" and is not included in the expression for η_{ex}^{LFC}. This value should not be confused with the exergy efficiencies of wind power generation plants, which are about 12–25% and usually calculated as the ratio of electricity produced to the sum of all sources of input exergy (mainly kinetic exergy of wind). The life cycle exergy efficiency to produce hydrogen from solar energy also accounts for solar energy being "free," but in this case η_{ex}^{LFC} is less than 1 because valuable materials are employed in the photovoltaic solar cells and indirect fossil fuel and mineral exergy consumption becomes very high.

The chemical exergies of gasoline and hydrogen are converted to work with different efficiencies in an internal combustion engine (ICE) vehicle and a proton exchange membrane fuel cell (PEMFC) vehicle. The efficiency ranges from 0.2 to 0.3 for an internal combustion engine [19] and from 0.4 to 0.6 for a fuel cell engine [30]. The efficiency of fossil fuel energy consumption in a vehicle η_{ex}^{VCL} can be expressed as the product of the life cycle $\eta_{ex}^{LFC}$and engine η_{ex}^{eng} efficiencies:

$$\eta_{ex}^{VCL} = \eta_{ex}^{LFC}\eta_{ex}^{eng} \tag{12}$$

Fig. 4 shows the mechanical work produced per unit of life cycle fossil fuel exergy consumption as a function of the ratio in efficiencies ε of fuel cell (hydrogen powered) and internal combustion (gasoline powered) vehicles. Note that the curves for hydrogen from natural gas and solar energy coincide in this scale. This figure indicates that the efficiency of a fuel cell vehicle operating on hydrogen from natural gas must be at least 25–30% greater than that for an internal combustion gasoline engine to be competitive. The application of hydrogen from wind energy in a fuel cell vehicle is extremely efficient with respect to fossil and mineral resources utilization.

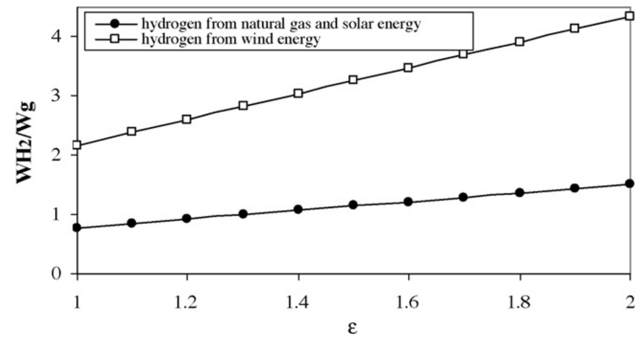

Fig. 4. Mechanical work per exergy of fossil fuels consumed to produce 1 MJ of exergy of gasoline and hydrogen as a function of the ratio in efficiencies ε of fuel cell (hydrogen powered) and internal combustion engine (gasoline powered) vehicles.

4. Economic implications of exergetic life cycle assessment

Fossil fuel and renewable energy technologies for hydrogen production are generally distinguished by (1) source of energy consumed, (2) efficiency of hydrogen production per unit of energy consumed, and (3) capital investments made per unit of hydrogen produced. To account for all of these factors, the authors introduced the capital investment effectiveness factor γ as a measure of economic effectiveness [9,12]. This indicator is proportional to the relationship between gain and investment and is expressible as

$$\gamma = \frac{\dot{Ex}_{H_2}(\alpha - 1/\eta_{ex}^{LFC})}{\Delta\dot{Ex}_{ind}} \tag{13}$$

Here, the numerator is proportional to the gain from the exploitation of a technology and the denominator to the investments made in it. Also, α is the ratio in costs of hydrogen (C_{H_2}) and natural gas (C_{ng}):

$$\alpha = \frac{C_{H_2}}{C_{ng}} \tag{14}$$

Furthermore, $\dot{Ex}_{H_2}$ is the capacity of hydrogen production, expressed in units of exergy of hydrogen per second, $\Delta\dot{Ex}_{ind}$ the indirect exergy rate which is proportional to the capital investments in a technology, and η_{ex}^{LFC} is the life cycle exergy efficiency of fossil fuel and mineral resource utilization (Eq. (10)). The initial solar and wind energies do not have any price, so they are not included in the denominator of Eq. (13) for renewable technologies. As a result, the value of η_{ex}^{LFC} for renewable technologies can exceed 1.

Technology applications for hydrogen production via wind and solar energy, although increasing, are not yet widespread due to their economic challenges. Fig. 5 presents γ as a function of the cost ratio α for hydrogen and natural gas, for life cycle exergy efficiencies of $\eta_{ex}^{LFC} = 0.72$ for hydrogen

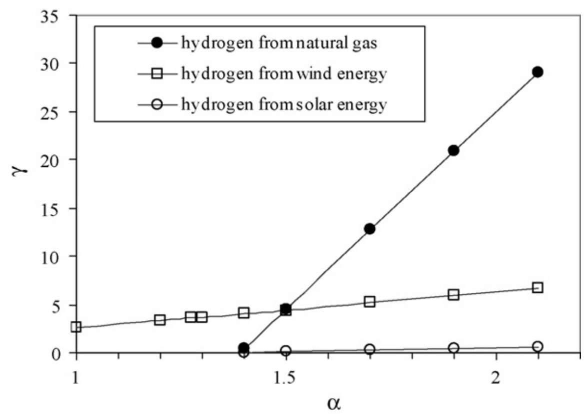

Fig. 5. Capital investment effectiveness factor γ for several hydrogen production technologies as a function of the cost ratio α for hydrogen and natural gas.

via natural gas, of $\eta_{ex}^{LFC} = 3.32$ for hydrogen via wind energy and of $\eta_{ex}^{LFC} = 0.75$ for hydrogen via solar energy. Here, the compression stages are excluded for all technologies, and the distribution stage is excluded for hydrogen via natural gas. Since the cost of 1 MJ of hydrogen exergy is presently about two times more than that of natural gas [31] it follows from Fig. 5 at $\alpha = 2$ that the capital investment effectiveness factor for hydrogen production via natural gas is about five times higher than that to produce hydrogen via wind energy. This situation can be altered by reducing the construction materials requirements of wind per unit of electricity generated. A fair assessment when comparing different renewable technologies requires consideration of both energy efficiency (ability to convert renewable energy to mechanical work or electricity) and efficient use of construction materials and equipment exploitation.

5. Environmental impact reduction by substitution of renewables for fossil fuels

Now, we consider the reduction of environmental impact related to the introduction of wind and solar technologies. The direct and indirect fossil fuel exergy consumptions $\dot{\text{Ex}}_{\text{dir}}$, $\Delta\dot{\text{Ex}}_{\text{dir}}$ and $\Delta\dot{\text{Ex}}_{\text{ind}}$ lead to different kinds of harmful emissions, which are divided in this section into greenhouse gas and air pollution emissions. A greenhouse gas (GHG) indicator can be used to assess greenhouse gases according to the values of their global warming potentials [32]. Airborne pollutants are analogously combined into a generalized indicator of air pollution AP in line with their impact weighting coefficients (relative to NO_x) as follows:

$$\text{AP} = \sum_{1}^{3} m_i w_i \qquad (15)$$

where m_i is the mass of air pollutant i and w_i is the corresponding weighting coefficient. For simplicity, we consider here only three pollutants (CO, NO_x, VOCs). Note that values of weighting coefficients w_i were obtained by the Australian Environment Protection Authority [33] using cost–benefit analyses of health effects. The weighting coefficients for greenhouse gases, based on global warming potentials relative to carbon dioxide which is assigned a value of unity, and air pollutants are listed in Table 12.

Table 12
Weighting coefficients for greenhouse gases and airborne pollutants

Compound	Weighting coefficient
Greenhouse gases	
CO_2	1
CH_4	21
N_2O	310
Airborne pollutants	
CO	0.017
NO_x	1
VOCs	0.64

Although wind and solar energies can be considered "free," the quantity of construction materials consumed per unit of electricity or hydrogen produced for a "renewable" plant is normally much higher than that for more traditional technologies for electricity and hydrogen production from natural gas. Taking into account air pollution emissions from the construction and operation stages of power or hydrogen generation plants, and their lifetimes and capacities, the indirect greenhouse gas and air pollution emissions per unit of produced energy are calculated. For fossil fuel technologies, these indirect life cycle emissions are very small with respect to the direct emissions related to fuel combustion or removing carbon from methane (natural gas) to produce hydrogen.

Assuming that embodied energy is related to the natural gas combustion energy, greenhouse gas and air pollution emissions per megajoule of produced electricity, hydrogen and gasoline from previous LCA studies [9,12,34,35] are presented in Table 13. The GHG and AP emissions from producing a unit of electricity from natural gas are calculated assuming that electricity is generated from natural gas with an average efficiency of 40%, as was done above in the ExLCA.

In order to transmit hydrogen or use it in a fuel cell vehicle, it needs to be substantially compressed to reach an appropriate volumetric energy density. For instance, the pressure of gaseous hydrogen in the tank of Honda's fuel cell car is about 350 atm [28]. Data regarding hydrogen compression in Table 13 have been obtained assuming that electricity for "renewable" hydrogen compression is derived from the same renewable energy sources and electricity for compression of hydrogen from natural gas is generated in a natural gas power generation plant. The electrical energy required E_{el} to compress one mole of hydrogen is calculated according to the formula for isothermal compression with a compressor efficiency coefficient $\eta_{cmp} = 0.65$:

$$E_{el} = \frac{RT_0}{\eta_{cmp}} \ln\left(\frac{p_{max}}{p_{atm}}\right) \qquad (16)$$

where the environment temperature is $T_0 = 298$ K, R the universal gas constant and p_{max} is the required pressure of hydrogen and the atmospheric pressure is $p_{atm} = 1$ atm. As can be seen in Table 13, the environmental impact of hydrogen compression using renewable-based electricity is very small compared to that for the stages of electricity production and electrolysis.

Table 13
Greenhouse gas and air pollution emissions (in g MJ^{-1} of electricity or LHV of hydrogen and gasoline) for various production technologies

Technology	m_{GHG}	m_{CO}	m_{NO_x}	m_{VOCs}	AP
Electricity from natural gas					
Electricity from natural gas with a thermal efficiency $\eta_e = 40\%$	149.9	0.094	0.11	0.72	0.57
Hydrogen from natural gas					
Natural gas pipeline transportation and reforming to produce hydrogen at pressure $p = 20$ atm[a]	75.7	0.022	0.026	0.054	0.061
Hydrogen compression from 20 to 350 atm	6.8	0.0042	0.0050	0.032	0.026
Hydrogen delivery to fueling stations ($p = 350$ atm)	3.1	0.0072	0.045	0.00135	
Total for $p = 350$ atm		0.026	0.031	0.086	0.087
Electricity and hydrogen from wind energy					
Electricity generation	4.34	0.0030	0.0035	0.00027	0.0038
Hydrogen production via electrolysis	2.51	0.0017	0.0020	0.000159	0.0022
Hydrogen compression to $p = 350$ atm	0.40	0.00027	0.00033	2.54×10^{-5}	0.00035
Total for $p = 350$ atm	7.25	0.0050	0.0058	0.00045	0.0063
Electricity and hydrogen from solar energy					
Electricity generation	10.7	0.0073	0.0087	0.00068	0.0092
Hydrogen production via electrolysis	6.18	0.0042	0.0050	0.00039	0.0053
Hydrogen compression to $p = 350$ atm	1.0	0.00067	0.00080	6.23×10^{-5}	0.00085
Total for $p = 350$ atm	17.9	0.012	0.015	0.0011	0.015
Gasoline from crude oil					
Crude oil pipeline transportation and distillation to produce gasoline	12.1	0.012	0.061	0.023	0.015
Gasoline delivery to fuelling stations	0.19	0.00044	0.0028	8.26×10^{-5}	0.11
Gasoline utilization in ICE vehicles[b]	71.7	0.86	0.05	0.15	0.11
Total	84.0	0.87	0.11	0.17	0.24

[a] Hydrogen is produced by natural gas reforming at the typical pressure of 20 atm.
[b] Taken from Walwijk et al. [37].

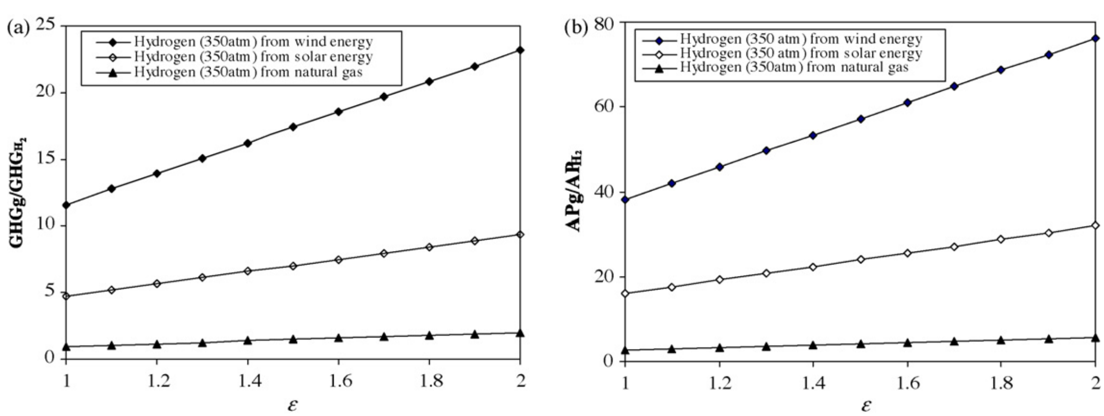

Fig. 6. Reductions of GHG (a) and AP (b) emissions as a result of hydrogen substitution for gasoline, as a function of the ratio in efficiencies ε of fuel cell (hydrogen powered) and internal combustion engine (gasoline powered) vehicles.

The respective reductions of GHG and AP emissions as a result of gasoline substitution with hydrogen (GHG_g/GHG_{H_2} and AP_g/AP_{H_2}) as a function of the ratio in efficiencies ε of fuel cell (hydrogen powered) and internal combustion engine (gasoline powered) vehicles are presented in Fig. 6. "Renewable" hydrogen substitution for gasoline is observed to lead to a reduction in greenhouse gas emissions of more than five times (from 12 to 23 for hydrogen derived from wind and from 5 to 8 derived from solar energy) and air pollution of more than ten times (from 38 to 76 for hydrogen derived from wind and from 16 to 32 derived from solar energy). It can be seen that gasoline substitution with hydrogen from natural gas allows a reduction in GHG emissions only as a result of the increased efficiency of a fuel cell engine, while at the same time yields a reduction of AP emissions from 2.5 to 5 times. Therefore, the data in Fig. 6 suggest that "renewable" hydrogen represents a potential long-term solution to environmentally related transportation problems.

6. Conclusions

Exergetic life cycle assessment has been used to evaluate exergy and economic efficiencies and environmental impacts as a result of substituting wind and solar energy for fossil fuels to produce hydrogen. Fossil fuel technologies for hydrogen production from natural gas and gasoline from crude oil are contrasted with renewable ones. Hydrogen is considered a fuel for fuel cell vehicles and a substitute for gasoline. Exergy efficiencies and greenhouse gas and air pollution emissions have been evaluated during all process steps, including crude oil and natural gas pipeline transportation, crude oil distillation and natural gas reforming, wind and solar electricity generation, hydrogen production through water electrolysis, and gasoline and hydrogen distribution and utilization.

The use of wind power to produce hydrogen via electrolysis, and its application in a fuel cell vehicle, exhibits the lowest fossil fuel consumption rate. However, the economic attractiveness (capital investment effectiveness factor) of renewable technologies depends significantly on the ratio in costs for hydrogen and natural gas. For example, at the present cost ratio of about 2 (per unit of LHV or exergy), capital investments are about five times lower to produce hydrogen via natural gas than to produce hydrogen via wind energy. As a consequence, the costs of wind- and solar-based electricity and hydrogen are substantially higher than the cost of natural gas. It was reported by [36] that the average cost of wind- and solar-based electricity, respectively, exceeds that of natural gas by about 2.25 and 5.25 times.

"Renewable" hydrogen appears to provide a potential long-term solution to environmentally related problems. Depending on the ratio in efficiencies of fuel cell (hydrogen powered) and internal combustion engine (gasoline powered) vehicles, substitution of gasoline with "renewable" hydrogen leads to GHG emissions reductions of up to 23 times for hydrogen from wind and 8 times for hydrogen from solar energy, and air pollution emissions reductions of up to 76 times for hydrogen from wind and 32 times for hydrogen from solar energy.

Acknowledgements

The financial support of an Ontario Premier's Research Excellence Award, the AUTO 21 Network of Centres of Excellence (NCE) and the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

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