



Comparison of thermodynamic and environmental indexes of natural gas, syngas and hydrogen production processes

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Abstract

The thermodynamic efficiency and the environmental sustainability of selected processes that deliver gaseous energy carriers (natural gas, syngas from coal gasification, and hydrogen from steam reforming of natural gas and alkaline electrolysis) is explored by means of a multi-criteria, multi-scale approach based on four methods: material flow accounting, energy analysis, exergy analysis, and emergy synthesis.

The average energy and exergy conversion efficiencies of syngas (76% and 75%, respectively) are found to be higher than those for hydrogen (64% and 55%). However, coal-to-syngas conversion generates a significant amount of solid waste, which should be dealt with carefully. In addition, the material intensity is much higher for syngas (e.g. abiotic MI = 768 g/g) than for natural gas and hydrogen (21 and 39 g/g, respectively), indicating a higher load on the environment. On the other hand, the emergy intensity (transformity) for syngas (5.25×10^4 seJ/J) is shown to be lower than for hydrogen (9.66×10^4 seJ/J), indicating a lower demand for global environmental support. Therefore, material intensities and transformities offer two complementary pieces of information: transformities account for the “memory” of the environmental resources that were used up in the past for the production of the inputs, whereas MIs are strictly calculated within the time frame of the life cycle of the investigated process. The higher transformity values calculated for pure hydrogen suggest careful and appropriate use of such an energy vector. © 2004 Elsevier Ltd. All rights reserved.

1. Introduction

1.1. Investigated gaseous energy carriers

This paper focuses on the three most promising gaseous energy carriers that are readily available using well-established technology. This choice stems from the realisation that, although

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desirable, the exploitation of the truly renewable energy sources is still often hampered by the intrinsic localisation of their availability (e.g. geothermal and hydroelectric power), and will not be easily up-scalable in the foreseeable future. On the contrary, despite their well-known economic and environmental problems, fossil fuels continue to be employed as the main energy source on the global scale, and it seems unlikely that there should be a significant drop in their use in the near term.

Thus, the most urgent problem to be addressed is how to make a more efficient and environmentally friendly use of fossil fuels through feasible technological improvements. Among these, steam reforming of natural gas and coal gasification seem to be interesting alternatives. These reforming processes and their products (hydrogen and syngas) can then be compared to the direct use of the parent fossil fuels in order to evaluate the possible technical and environmental advantages that they provide.

In this first stage of the assessment, we look into the production/energy conversion processes, delegating the investigation of the possible uses of the different energy carriers to a subsequent stage. It is, however, important to realise that a complete life cycle analysis of the different options is needed to be able to compare them from a larger perspective. For example, there are some energy losses associated with the production of hydrogen from natural gas. However, the whole picture may look rosier if these losses are compensated for by its highly efficient use in dedicated fuel cells to produce electricity, together with a low level of local air pollution in urban centres.

1.2. The approach

Although this is certainly not the first time that this topic is dealt with, most previous works have been characterised by a single approach, which may easily lead to misleading conclusions. Our assessment is carried out by means of a careful comparison of several different methods, each with its own scale of applicability. This results in a comprehensive analysis which is able to highlight the differences between the investigated processes from several points of view. The adopted scheme is illustrated in Fig. 1.

First of all, to ensure that all significant input and output flows have been accounted for, a preliminary mass balance is set up on the local scale of the investigated process, which requires that the law of conservation of mass be fulfilled, i.e. that input mass equal output mass.

- For each flow of matter supplied to a process, a larger amount of matter must be previously processed elsewhere. The latter can be classified in the following environmental compartments: abiotic matter (e.g. minerals and metals that are extracted, purified and processed), water (any kind of water flow that is diverted from its natural pathway, e.g. for floatation, cooling, etc.), and biotic matter (e.g. standing biomass and soil biota that is killed and/or removed from its natural ecosystem). The total amount of matter from each compartment that is processed on the global scale to provide a given material input to the analysed process is then referred to as the (*abiotic, water or biotic*) *Material Intensity (MI)* of that input [1]. The resulting total MIs of the product that constitutes the process output are calculated as the sum of the MIs of the inputs, and are interpretable as a quantitative measure of the present ecosystem disturbance associated with the withdrawal and use of natural resources.

- An exergy analysis is performed on the local scale, with the aim of calculating the Second Law efficiency of the investigated process with reference to the surrounding environment [3].
- Lastly, an *emergy* synthesis is performed as a valuable tool for evaluating the past environmental support that was directly and indirectly required to provide the output product. Energy is defined as the amount of exergy of one form that is directly or indirectly required to provide a given flow or storage of exergy or matter; thus, all inputs to a process are measured in common units of equivalent joules (eJ) [4]. When solar radiation is chosen as the reference form of exergy, inputs are measured in units of solar equivalent joules (seJ). Solar energy (from now on simply referred to as *emergy*) can thus be interpreted as the “memory” of the total exergy previously used up to provide a product or service, and is used when the global support from the biosphere to the process is investigated (“ecological footprint”). Converting flows of different nature into flows of one kind requires conversion coefficients called specific emergies (seJ/unit) or *transformities* (seJ/J). It is worth noting that if different exergy flows were only summed into a total without accounting for the convergence of environmental work supporting them, their donor-side quality would not be accounted for, and useful information on the relationship of the process with the biosphere dynamics would be lost. Moreover, *emergy* synthesis also accounts for free environmental inputs such as sunlight, wind, rain, as well as the indirect environmental support embodied in labour and services, which are not usually included in traditional energy and exergy analyses.

1.3. System boundaries

The local scale of each of the investigated case studies coincides with the physical boundaries of the plant (or chain of processes, in the case of natural gas) where the energy conversion processes take place. Assets (e.g. building materials) are not included in the analysis, as their contribution to the process is negligible if distributed over their operational life span.

The expansion to the life cycle scale is performed consistently for the four analysed processes, but in ways that are dependent on the specific evaluation approach. For the material intensity analysis, the life cycle scale is expanded spatially and back in time up to the inclusion of the extraction of all the primary resources directly or indirectly required for the analysed process, while for the embodied energy analysis, the expansion is limited to the inclusion of all direct and indirect commercial energy inputs. Lastly, in the case of the *emergy* synthesis, the time expansion goes back to the formation of the resources themselves, since it accounts for the “memory” of all the exergy cumulatively used up by the biosphere to produce the analysed output.

All the stages of the LCA are performed according to the international environmental management norms ISO 14040/1997 to ISO 14043/2000 [5].

2. Description of processes

The energy conversion processes analysed in this paper are: (A) natural gas refining, (B) syngas production via coal gasification (Koppers–Totzek process using five different kinds of

feedstock coal), (C) hydrogen production via steam reforming of natural gas (four different plants), and (D) hydrogen production via alkaline electrolysis of water (with in-situ electricity production from diesel oil and natural gas).

(A) Natural gas extraction from North Sea off-shore platforms and its refining and transport to the final user are investigated.

The main source of data [6] is compared to other authors [7–10]), in order to get an average world picture.

(B) In the Koppers–Totzek coal gasification process, pulverised coal is rapidly partially oxidised with oxygen and steam at essentially atmospheric pressure, and at a temperature of 1750 K, according to the reactions:



The gaseous mixture in output from the gasifier, rich in CO (~50% w/w) and H₂ (~30% w/w), is called raw synthesis gas or “syngas”, which can be used as it is, as a medium-heating-value gaseous mixture (this is the case considered in this paper). Alternatively, the syngas can be purified to H₂ through additional shift reactions, if required. A block diagram of the process is provided in Fig. 2.

The process under examination here is a typical Koppers–Totzek reactor, for which the main source of input data is Fan et al. [11], compared to and integrated with Rosen and Scott [12]. In fact, the scope of the present paper is not to investigate one specific industrial plant, but rather to shed new light on an average representative of a well-established technology, by means of a novel multi-criteria approach, as well as to compare it to other competing processes producing gaseous energy carriers.

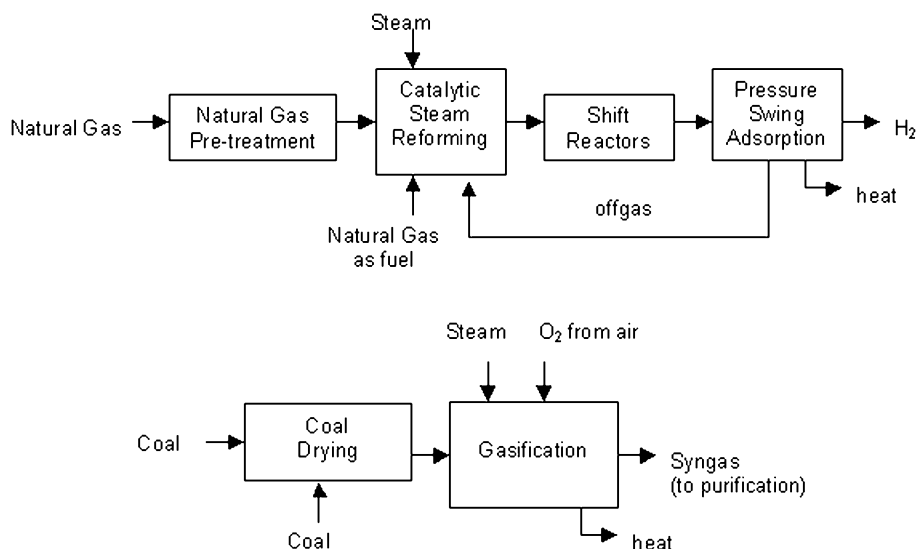


Fig. 2. Block diagrams for natural gas steam reforming and coal gasification.

(C) The steam reforming process basically consists of three main steps: synthesis gas generation, water–gas shift and gas purification. The feedstock natural gas is mixed with process steam and made to react over a Ni-based catalyst. To protect the catalyst, natural gas has to be desulfurised before being fed to the reformer. The following reactions take place in the reformer, at a temperature of 1000 K:



The reforming reaction is strongly endothermic and energy is supplied by combustion of additional natural gas. The synthesis gas leaving the reformer (a mixture of CO, H₂, CO₂ and CH₄) is cooled and fed to a series of shift reactors to produce more hydrogen. Lastly, hydrogen is separated and purified to over 99% purity in a pressure swing adsorption unit. A block diagram of the process is provided in Fig. 2.

Input and operational data for three of the four investigated steam reforming plants were provided directly by the manufacturer [13], the main differences among them lying in their different project optimisation goals. The fourth system is a larger plant originally analysed by Spath and Mann [14] for the US National Renewable Energy Laboratory (NREL). Results are integrated with Rosen [15].

To all the investigated steam reforming and coal gasification processes, we applied the same basic assumption that the only products of interest be, respectively, hydrogen and syngas, thus neither including the necessary amount of cooling water in the computation of the material intensities, nor counting the resulting output steam as an additional energy output (instead, it is assumed to be re-condensed and discharged as liquid water).

(D) Alkaline water electrolysis is a well-established industrial process in which electricity is used to split water into its component elements, generating hydrogen in a 1:1 molar ratio, with cell efficiencies in the order of 80–90%. The needed electricity can be purchased from the grid (an interesting option in the case of excess electricity production from hydroelectric plants, for example), or produced in situ. In this paper, a typical industrial alkaline water electrolysis plant is considered (data from Rosen [15]), with a local electricity generator powered by diesel oil. As an alternative, the same plant is also analysed with the generator virtually replaced with a different one running on natural gas (this work).

3. Results and discussion

The complete mass and energy balances of natural gas extraction and processing are shown in Tables 1–3, in order to clearly illustrate the way in which each accounting is performed. The exergy and emergy accounting of natural gas, as well as all the other evaluations for the remaining energy carriers are performed in a similar way and generate the required set of performance indicators.

All the main indicators resulting from our integrated assessment are reported in Figs. 3–5. All efficiencies are calculated from published data ([3,6–9,11–18]), integrated with standard thermodynamic data. Due to the need of comparing processes and results from different sources, stan-

Table 1
Mass inventory on the local and global scale (Inputs) in Norwegian Natural Gas production (data are per 1 g of natural gas delivered)

Mass inventory on the local scale		Mass inventory on the global scale (based on material flow accounting procedure)									
Description of flow	Units	Mass (local scale) (g)	MIF abiotic (g/g) ^a	Ref. abiotic (global scale) (g) ^b	MIF water (g/g) ^a	Ref. water (global scale) (g) ^b	MIF air (g/g) ^a	Ref. air (global scale) (g) ^b	MIF biotic (g/g) ^a	Ref. biotic (global scale) (g) ^b	
<i>Renewable inputs</i>											
O ₂ from air	g	2.38×10^{-1}	0.00	[a]	0	[a]	2.38×10^{-1}	0.00	[a]	0	
N ₂ from air	g	2.45×10^{-4}	0.00	[a]	0	[a]	2.45×10^{-4}	0.00	[a]	0	
<i>Non-renewable inputs</i>											
Main resource											
Raw natural gas	g	1.02×10^0	1.00	[b]	1.02×10^0	[b]	0	0.00	[b]	0	
<i>Additional materials</i>											
Steel	g	1.70×10^{-3}	6.60	[c]	1.12×10^{-2}	[c]	1.83×10^{-2}	2.19	[c]	3.73×10^{-3}	
Concrete	g	3.14×10^{-3}	3.05	[d]	9.59×10^{-3}	[d]	8.87×10^{-3}	4.34	[d]	1.36×10^{-2}	
Water	g	2.00×10^{-1}	0.00	[a]	0	[a]	2.00×10^{-1}	0.00	[a]	0	
Food and beverages	g	4.53×10^{-4}	1.00	[e]	4.53×10^{-4}	[e]	0	0.00	[e]	0	
Chemicals	g	1.93×10^{-3}	1.00	[e]	1.93×10^{-3}	[e]	0	0.00	[e]	0	
<i>Fuels and electricity</i>											
Fuel gas	g	4.80×10^{-2}	1.11	[c]	5.31×10^{-2}	[c]	1.43×10^{-2}	0.29	[c]	1.38×10^{-2}	
Diesel and marine fuel	g	5.12×10^{-3}	1.44	[f]	7.38×10^{-3}	[f]	5.74×10^{-2}	3.40	[f]	1.74×10^{-2}	
Jet fuel	g	2.10×10^{-4}	1.44	[f]	3.03×10^{-4}	[f]	2.35×10^{-3}	3.40	[f]	7.15×10^{-4}	
Total direct inputs	g	1.524	1.11	[g]	1.11	[g]	3.01×10^{-1}	0.29	[g]	2.87×10^{-1}	
										0.00004	
										4.44×10^{-5}	

Data source: Bakkane [6].

[a], By definition; [b], due to its raw nature natural gas is accounted only for its mass contribution to the corresponding MI category; [c], Ulgiati et al. [16]; [d], Meriten et al. [21]; [e], Due to the strong aggregation of these input flows, it is impossible to assign them a reliable set of material intensities. Therefore, only a very conservative contribution equal to those for heavy oil; [g], final result of the analysis.

^a MIF (material intensity factor) is the amount of matter that has been or needs to be processed to make and deliver one unit of input.

^b Total matter processed at larger scale to make and deliver the input flow.

Table 2

Mass inventory on the local scale (outputs) in Norwegian Natural Gas production (data are per 1 g of natural gas delivered).

Mass Inventory on the local scale outputs		
Description of flow	Units	Mass (local scale)
<i>Product</i>		
Natural gas for final users	g	1.00
Injection gas	g	
<i>Waste generation (solid emissions)</i>		
Classified waste	g	4.04×10^{-4}
Household waste	g	4.53×10^{-4}
Sewage	g	1.15×10^{-2}
Industrial waste (steel and concrete)	g	4.94×10^{-3}
<i>Emissions to air (airborne emissions)</i>		
CO ₂	g	1.69×10^{-1}
CO	g	1.85×10^{-4}
NO ₂	g	7.99×10^{-4}
N ₂ O	g	2.51×10^{-6}
SO ₂	g	1.28×10^{-5}
H ₂ O vapor	g	1.29×10^{-1}
CH ₄ losses	g	2.49×10^{-2}
VOC (in diesel combustion)	g	8.97×10^{-5}
Halon	g	2.05×10^{-7}
<i>Discharges to sea (liquid emissions)</i>		
Drilling chemicals	g	3.41×10^{-4}
Weighting chemicals	g	1.17×10^{-3}
Production chemicals	g	1.54×10^{-5}
Pipeline chemicals	g	5.13×10^{-8}
Waste water	g	1.89×10^{-1}
Total Outputs	g	1.531
Unbalance I/O		-0.5%

Data source: Bakkane [6].

dard higher heating values and specific exergies were used throughout; our results may therefore be slightly different from those of the cited literature.

Fig. 3 summarises the results for syngas production from the various kinds of feedstock coal (Table 4). One first interesting finding is that both the life cycle energy efficiency and the local-scale exergy efficiency of the gasification process do not vary significantly with the type of coal used.

As opposed to the relatively constant efficiencies, the material intensities and the transformities of syngas exhibit a marked dependence on the type of feedstock coal used. Even more interestingly, the trends of the two indicators are opposite: while MIs become larger and larger as the carbon content of the feedstock coal decreases, indicating a higher load on the environment, transformities seem to favour the use of lower grade coals. In order to correctly interpret these results, it must be kept in mind that transformity accounts for the “memory” of the

Table 3
Energy flows in Norwegian Natural Gas production (data are per 1 g of natural gas delivered)

Description of flows	Units	Mass (local scale)	Oil equivalent per unit (g oil/unit)	Ref.	Global oil demand (g Oil Eq.)	Global energy demand ^[a] (J)
<i>Non-renewable inputs</i>						
<i>Main resource</i>						
Raw natural gas	g	1.02	1.26	[b]	1.29	5.40×10^4
<i>Additional materials</i>						
Steel	g	1.70×10^{-3}	0.98	[c]	1.66×10^{-3}	6.95×10^1
Concrete	g	3.14×10^{-3}	0.06	[d]	1.88×10^{-4}	7.86
Water	g	2.00×10^{-1}	1.43×10^{-4}	[e]	2.87×10^{-5}	1.20
Food and beverages	g	4.53×10^{-4}	–	[d]	0	0
Chemicals ^a	g	1.93×10^{-3}	3.46	[f]	6.68×10^{-3}	2.80×10^2
<i>Fuels and electricity</i>						
Fuel gas	g	4.80×10^{-2}	1.37	[h]	6.43×10^{-2}	2.69×10^3
Diesel and marine fuel	g	5.12×10^{-3}	1.23	[g]	6.30×10^{-3}	2.64×10^2
Jet fuel	g	2.10×10^{-4}	1.32	[g]	2.78×10^{-4}	1.16×10^1
Natural gas delivered	g	1.00	1.37	[h]	1.37	5.74×10^4

[a], Oil flows multiplied by 41860 J/g; [b], energy content ratio of crude oil to natural gas; [c], Bargigli and Ulgiati [20]; [d] Boustead and Hancock [7] p. 328. (reinforced concrete); [e], Smil [18]; [f], SimaPro 4.0 Database; [g], Biondi et al. [22]; [h], final result of the analysis.

^a Chemicals include drilling chemicals, weighting chemicals, production chemicals, pipeline chemicals and miscellaneous chemicals. Due to the high aggregation of the flow of input chemicals and the impossibility to assign a suitable energy production cost to each of them, a chemical product has been selected—among those available in SimaPro 4.0, a database of materials and processes dedicated to LCA—with the highest energy requirement for the production process, 145 MJ/kg (toluene diisocyanate). This value was assigned to the sum of all chemicals used in the process, likely overestimating the energy cost for their production. Notwithstanding this overestimation, the contribution of chemicals to the total cost of natural gas extraction and processing is negligible. SimaPro 4.0 Database. PRE Consultants BV, Amersfoort, The Netherlands.

environmental resources that were used up in the past for the production of the inputs, which in the case of coal goes back to millions of years, whereas MIs are strictly calculated within the time frame of the life cycle of the investigated process. Thus, the two indicators give different answers to different questions: MIs are a measure of present ecosystem disturbance associated with resource extraction and use, and transformities are a measure of global environmental support, as well as renewability.

The different efficiency values computed for hydrogen produced via steam reforming of natural gas (Fig. 4) essentially mirror the different characteristics of the individual investigated plants. In the case of the small modular plants (24,000 Nm³(H₂)/day) manufactured by HydroChem, the higher efficiencies are those of the “low energy” unit, which is designed and optimised for the lowest energy consumption during the operating phase. On the contrary, the “low capital” unit, designed with the main goal of low building expenses, shows the worst efficiencies. Finally, the comparatively higher efficiencies boasted by the larger plant (1,500,000 Nm³(H₂)/day) from the US NREL study may be at least in part explained by its very size.

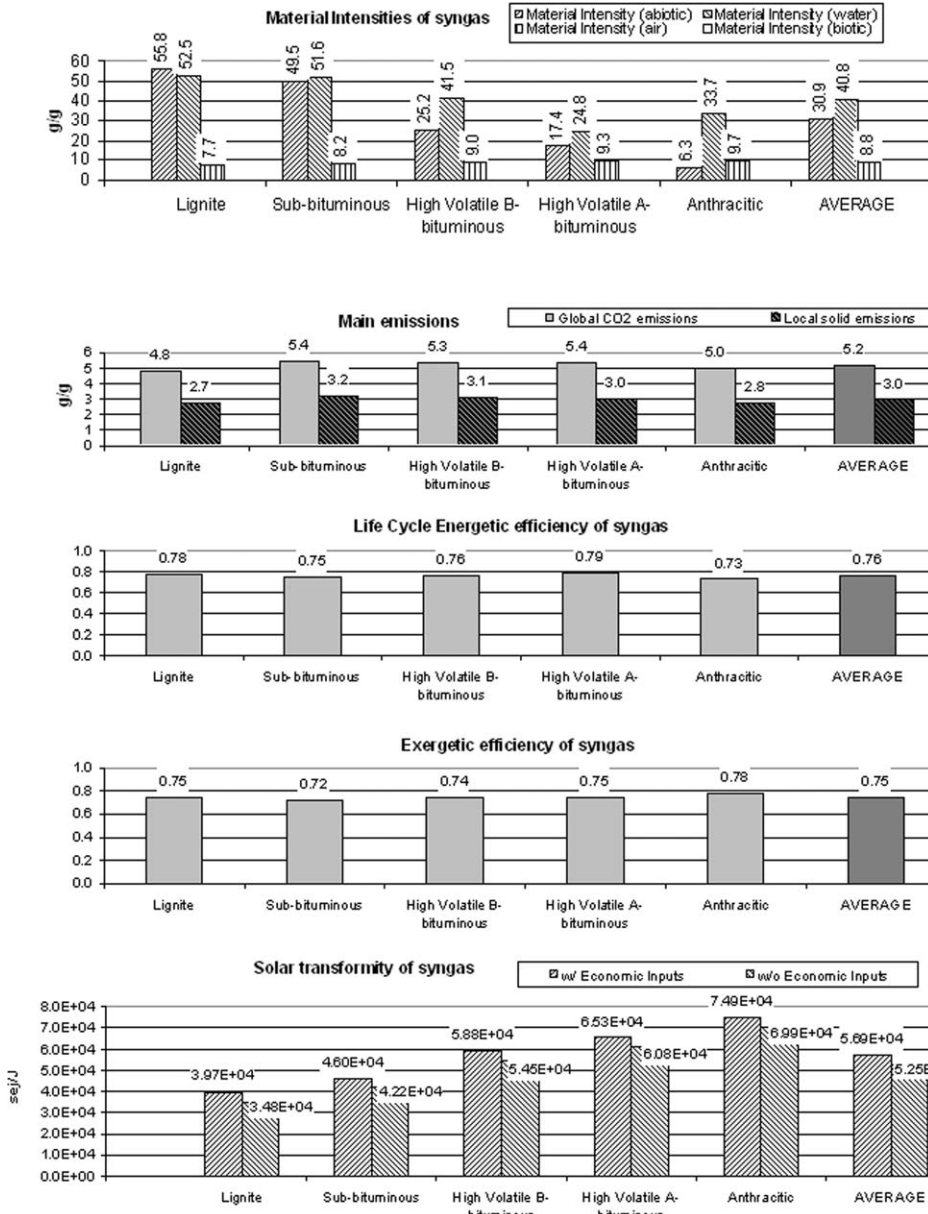


Fig. 3. Performance indicators for syngas for the different kinds of feedstock coal used.

MIs and transformities are also more favourable for the hydrogen produced by this latter plant.

Fig. 5 shows a comprehensive comparison of the mean values of the calculated indicators for all the investigated energy carriers.

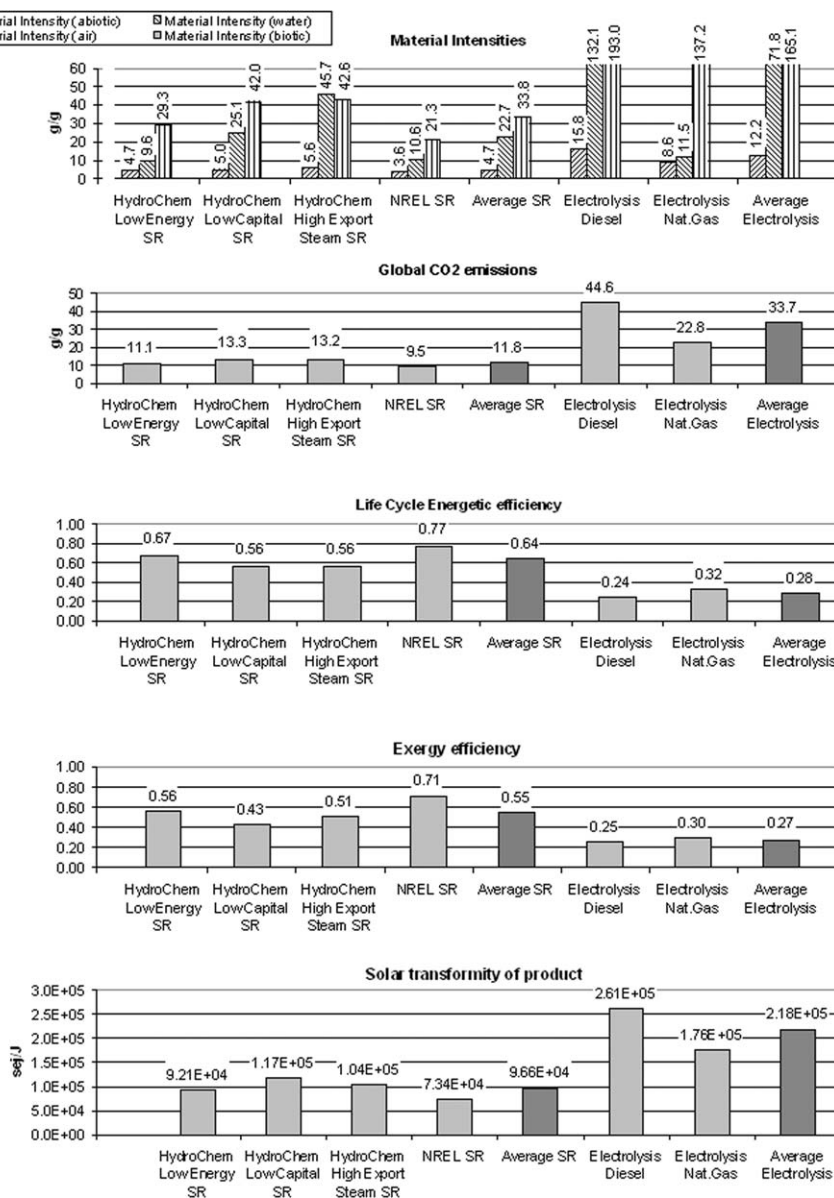


Fig. 4. Performance indicators for hydrogen produced by selected plants.

Syngas production stands out as being characterised by comparatively high life-cycle and process efficiencies, coupled to higher material intensities (in particular regarding the important abiotic compartment) and emissions. It is important to note that the solid emissions are mainly composed of ashes and coal tars, which are rich in carcinogenic polynucleated aromatic hydrocarbons (PAHs), and can cause serious ecotoxicological problems to the environment in the area surrounding the plant if they are simply dumped in a landfill. Thus, even if coal

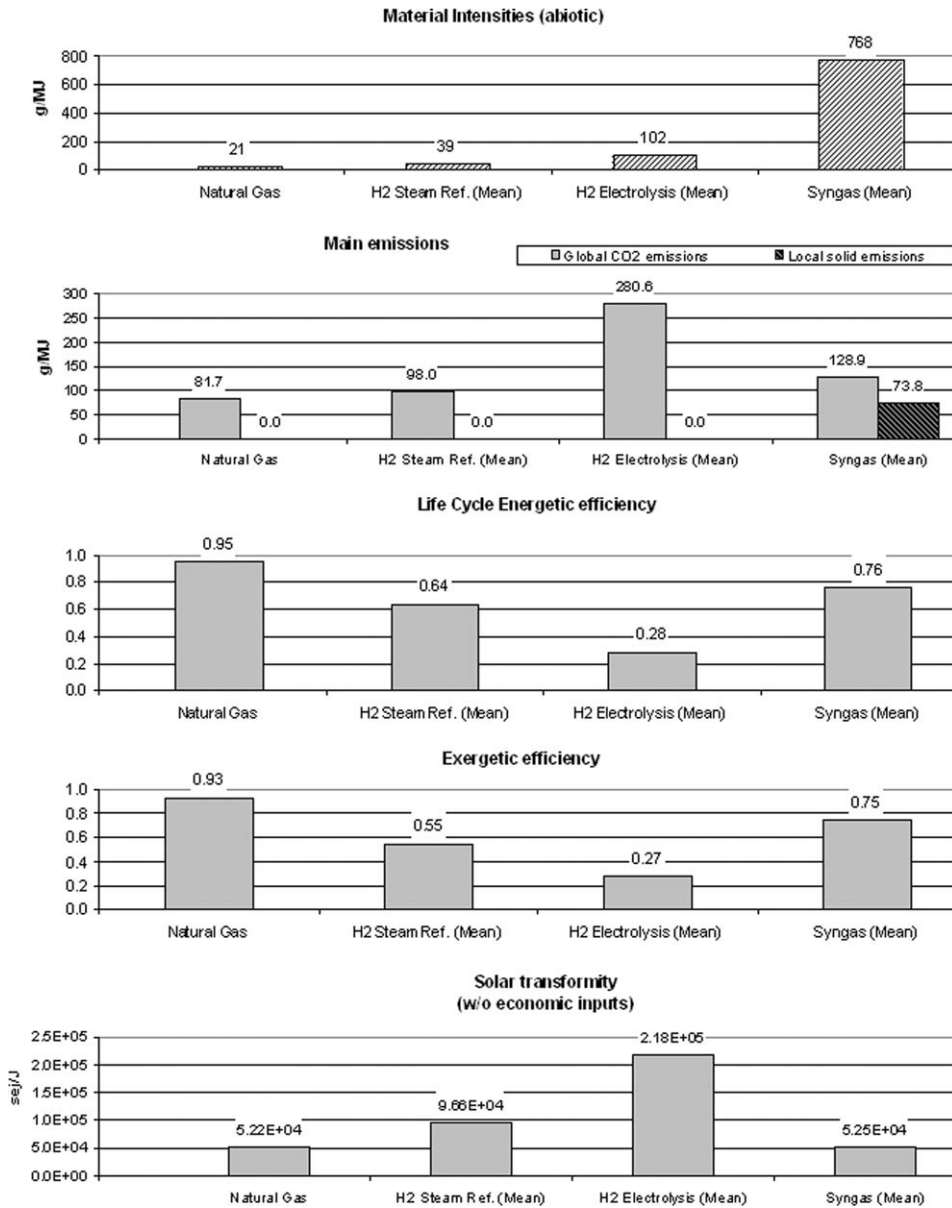


Fig. 5. Comparison of performance indicators for natural gas, syngas and hydrogen.

gasification can be regarded as an efficient and relatively economical way to convert a solid fossil fuel to a more convenient and versatile gaseous energy carrier (syngas), the eventual large-scale application of such technology will require that the problem of the solid emissions be dealt with carefully, reducing the overall conversion efficiency itself. The low transformity of syngas (almost equal to that of natural gas, a primary energy carrier) reflects the fact that coal has the lowest transformity amongst all fossil fuels. It must, however, be noted that the results

Table 4
Types of feedstock coal used for syngas production (average values from literature)

Coal type	C% (w/w)	H ₂ O% (w/w)	Specific exergy (J/g)
Lignite	36	43	14,900
Sub-bituminous	42	28	17,100
High volatile B-bituminous	55	13	23,700
High volatile A-bituminous	62	13	26,100
Anthracite	75	4	30,800

could be significantly different if the emergy cost of the environmental remediation of coal mining and the safe disposal of solid emissions were taken into account (according to the procedure suggested by Ulgiati et al. [19]).

Hydrogen from steam reforming is characterised by favourably low material intensities and emissions (low CO₂ and virtually non-existent solid emissions), albeit at the price of somewhat lower average efficiencies and a higher transformity. This latter parameter embodies an indication of its higher quality, both from the donor side (larger emergy requirement per unit mass) and from the user side (higher specific exergy), and suggests a careful and appropriate use of this valuable energy carrier.

Hydrogen from electrolysis shows the worst indicators of the whole set of investigated energy carriers, essentially due to the low efficiency (35%–45%) of the inevitable extra step of thermal electricity production. The only exception to this general trend are again the MIIs, which are far greater for syngas, because of the huge amounts of inorganic material that is required in the coal mining and processing phases. Thus, this technology only seems to be applicable in specific cases, where a surplus of largely renewable electricity is available (e.g. in conjunction with large hydroelectric plants).

Lastly, all reforming and gasification systems generally produce output heat flows characterised by relatively high temperatures, which are theoretically marketable or usable elsewhere. According to Spath and Mann [14] (H₂ from steam reforming), such heat amounts to about 10% of the energy content of the input fuel; according to Fan et al. [11] (syngas from coal gasification) it is about 15%; finally, according to our estimate (all investigated reforming systems) it ranges between 9% and 13%. The exergy associated with these heat flows is not negligible, but unlikely to be easily usable. Spath and Mann assume the marketability of these waste heat flows, and therefore optimise their energetic balance including them as a useful co-product. Their assumption, however, is not easily generalisable, especially for coal gasification, since it would require a close proximity and a perfect match between heat supply and final user need. We have chosen not to include any waste heat flows in our efficiency calculations, which are therefore slightly lower than others presented in scientific literature.

4. Conclusions

Syngas and hydrogen seem to offer good opportunities for more efficient and appropriate use of the remaining resources of fossil fuels, both in the case of direct combustion and use in fuel

cells (FCs). The increased efficiency of use should help delay the inevitable depletion of fossil fuel stocks.

It is also interesting to note that one of the present bottlenecks of solid oxide and molten carbonate FCs is the very reforming step, the efficiency of which we estimated to be around 45% [16]. The higher efficiencies of stand-alone reforming calculated in this paper suggest the employment of a centralised hydrogen production process for subsequent use in FCs, thus removing a severely limiting factor. Moreover, MCFCs can tolerate input gases with a non-negligible percentage of CO and CO₂, making a coupling of these devices to coal gasifiers viable. This could be an effective way of exploiting low quality coals (e.g. lignite).

As a concluding remark, we would like to underline that evaluating comparable alternative processes, when specific answers regarding different possible uses of resources in the space-time frame of interest are sought, necessarily requires the adoption of a multi-criteria approach. It must be realised that in virtually all cases there is no single “optimal” solution to all problems. Only an analysis based on several complementary approaches can highlight the inevitable trade-offs that reside in alternative scenarios, and thus enable a wiser selection of the option embodying the best compromise in the light of the existing economic, process and environmental conditions.

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