COMPARATIVE EFFICIENCY ASSESSMENTS FOR A RANGE OF HYDROGEN PRODUCTION PROCESSES

M. A. ROSEN† and D. S. SCOTT‡

†Department of Mechanical Engineering, Ryerson Polytechnic University, Toronto, Ont., Canada M5B 2K3
‡Institute for Integrated Energy Systems. University of Victoria, Victoria, B.C., Canada V8W 2Y2

Abstract—Efficiencies, based on energy and exergy, are comparatively assessed for a wide range of hydrogen production processes, including processes which are

- hydrocarbon-based (steam–methane reforming and coal gasification),
- non-hydrocarbon-based (water electrolysis and thermochemical water decomposition), and
- integrated (steam–methane reforming linked to the non-hydrocarbon-based processes).

A process simulation and analysis computer code is used throughout. Overall efficiencies, based on primary resource inputs, are determined to range widely, from 21% to 86% for energy efficiencies, and from 19% to 78% for exergy efficiencies. Reductions in efficiencies from 100% are found to be attributable only to emissions for energy analysis, and mainly to internal consumptions for exergy analysis. Exergy losses associated with emissions account for a small portion of the total exergy losses. © 1998 International Association for Hydrogen Energy

INTRODUCTION AND MOTIVATION

Hydrogen is used as a fuel, and as a feed for producing other fuels and commodities. In the future, the role of hydrogen may become more important, as some researchers suggest that the world's energy systems may undergo a transition to an era in which the main energy carriers are hydrogen and electricity [1, 2]. The production of hydrogen has been identified as in need of substantial research [3].

The work reported here is based on the results of many of the authors' previous investigations [4–9] of the energy- and exergy-based performance for various hydrogen production processes. The purpose of this work is to develop a better understanding of the efficiencies of hydrogen production processes, thereby aiding in optimization and improvement efforts, and to provide information that assists in decision-making regarding alternative hydrogen-production processes. This paper is a direct extension of two previous papers that analyze the hydrogen production processes considered herein, one which is concise [9] and another which is more comprehensive [8]. The extension involves assessing and comparing the efficiencies for several categories of input energy forms.

Energy and exergy analyses [10, 11] are used in the assessments of efficiencies. Exergy is the maximum amount of work which can be produced by a stream or system as it is brought into equilibrium with a reference environment, and can be thought of as a measure of the usefulness or quality of energy. Exergy is consumed during real processes, and conserved during ideal processes. The exergy consumption during a process is proportional to the entropy created due to process irreversibilities. Energy analysis is concerned with the conservation of energy, while exergy analysis is a form of Second Law analysis that permits efficiencies to be more rationally evaluated than energy analysis. Many researchers (e.g. [10, 11]) propose that the thermodynamic performance of a process is best evaluated using exergy analysis.

The main processes for hydrogen production include steam–methane reforming (SMR), catalytic decomposition of natural gas, partial oxidation of heavy oil, coal gasification, water electrolysis, thermochemical water decomposition, and photo-chemical, -electrochemical and -biological processes [3]. The first four processes are based on fossil fuels. SMR, coal gasification and water electrolysis are the most important industrial processes for hydrogen production today. The hydrogen production processes considered here (see Table 1) include (i) processes that are significant and well understood and documented; (ii) current and advanced technologies for water electrolysis; and (iii) integrated processes that use by-product oxygen from water electrolysis or thermochemical water decomposition to enhance combustion in the SMR furnace. Detailed process diagrams for the production processes selected for analysis are presented

Table 1. Hydrogen production processes considered, by category, and their efficiencies considering fuel and/or a hypothetical heat source as the external energy inputs

Category	Process	Efficiency (%)	
		Energy	Exergy
Hydrocarbon-based	Steam–methane reforming (SMR)	86	78
	Coal gasification	59	49
Non-hydrocarbon-based	Current-technology water electrolysis	30	26
	Advanced-technology water electrolysis	49	41
	Thermochemical water decomposition	21	19
Integrated	SMR/current-technology water electrolysis	55	48
	SMR/advanced-technology water electrolysis	70	62
	SMR/thermochemical water decomposition	45	40

in Fig. 1. The thermochemical water decomposition process in Fig. 1(e) refers to the Ispra Mark-10 cycle. Corresponding process data and descriptions, based on information in [12–15], are summarized elsewhere [4–9] for each process according to the individual process sections shown in Fig. 1.

ANALYSIS APPROACH AND METHODOLOGY

Analyses and comparisons are performed using a computer code developed by enhancing a state-of-the-art process simulator, Aspen Plus, for exergy analysis [4]. To simplify the simulations and comparisons, (i) combustion is assumed to occur in 40% excess air; (ii) hydrocarbons are considered sulphur free; and (iii) natural gas is modelled as pure methane, coal as pure carbon, and air on a volume basis as 79% nitrogen and 21% oxygen. It is noted that the ensuing results are not significantly sensitive to the simplifications used in modelling fossil fuels here, with efficiencies affected by up to only about 2% compared to the efficiencies when exact fuel models are employed.

For processes in which high-temperature heat is an input (i.e. water electrolysis, thermochemical water decomposition and the integrated processes), the analyses could consider three main inputs: (i) electrical power and process heat, (ii) heat and (iii) a hypothetical heat source. A process includes heat and electricity generation steps in the third case, and an electricity generation step in the second.

The hypothetical heat source, which is intended to be an environmental resource, is considered as the input here so that processes in which some inputs are not environmental resources can be compared with processes

in which all inputs are environmental resources. The exergy of the hypothetical heat source is in all cases considered equal to its energy (an approximately valid assumption for many fossil fuels).

A previously defined reference-environment model [11, 16] is used in the evaluation of energy and exergy quantities, but with a reference-environment temperature (T_0) of 15°C (the approximate mean temperature of the lake cooling water). The reference-environment pressure (P_0) is taken to be 1 atm, and the chemical composition is taken to consist of air saturated with water vapor, and the following condensed phases at 25°C and 1 atm: water (H_2O), gypsum ($CaSO_4 \cdot 2H_2O$) and limestone ($CaCO_3$). In addition to properties in Aspen Plus data banks, which include steam properties based on the 1967 ASME steam tables, base enthalpy and chemical exergy values reported elsewhere [16] are used. The base enthalpy is the enthalpy of a component (at T_0 and P_0) relative to the stable components of the environment (at T_0 and P_0). The base enthalpy of a fuel is equal to the enthalpy change in forming the fuel from the components of the environment (the same environment used in exergy calculations). A compound which exists as a stable component of the reference environment is defined to have an enthalpy of zero at T_0 and P_0.
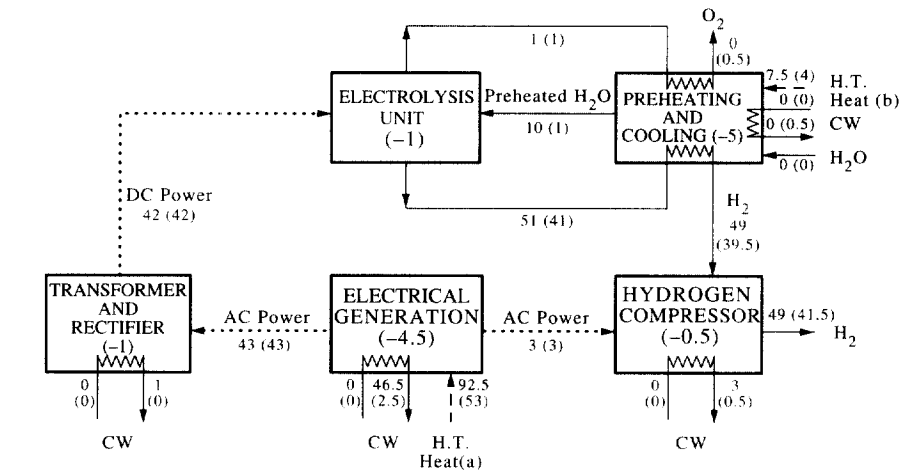
ENERGY AND EXERGY EFFICIENCIES

Overall energy and exergy efficiencies, determined as the ratio of the energy (or exergy) of product(s) to the energy (or exergy) of input(s), are presented in Tables 1–3 for the processes assessed. Three cases of energy efficiencies are presented, depending on the types of

Fig. 1. Simplified process diagrams for hydrogen production indicating flow rates of energy (values not in parentheses) and exergy (positive values in parentheses) for streams, and exergy consumption rates (negative values in parentheses) for devices. The portions of exergy consumption due to the combustion reaction are indicated in small squares in the appropriate sections of Figs. a and b. All values are normalized so that 100 units of energy enter each overall process. Descriptions of input and output streams for the overall process are given in upper case. Throughout, L.T. denotes low-temperature, H.T. denotes high-temperature, CW denotes cooling water, BFW denotes boiler feel water, and P.U. denotes a primary upgrading. a) SMR; b) coal gasification; c) current-technology water electrolysis; d) advanced-technology water electrolysis; e) thermochemical water decomposition; f) SMR/current-technology water electrolysis; g) SMR/advanced-technology water electrolysis; h) SMR/thermochemical water decomposition.
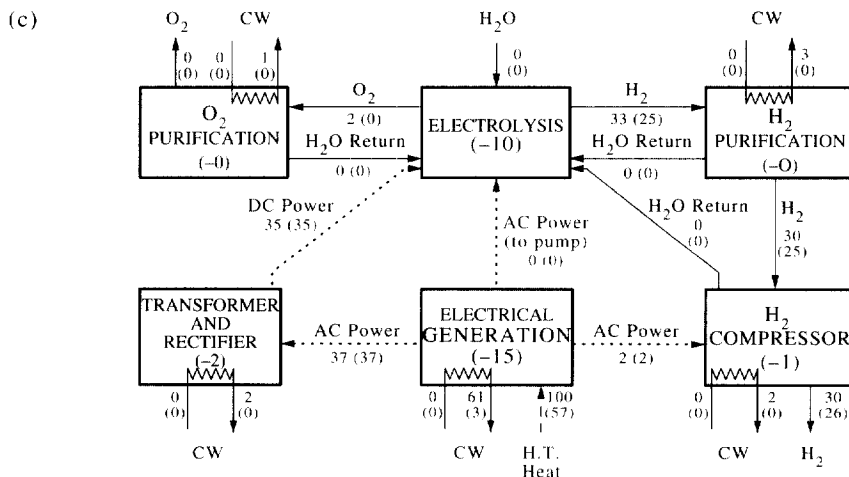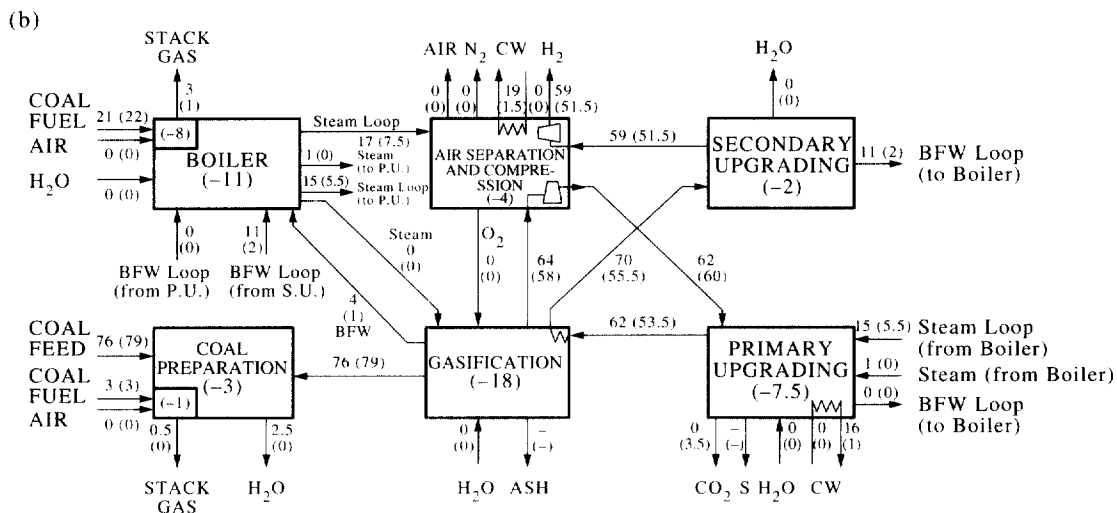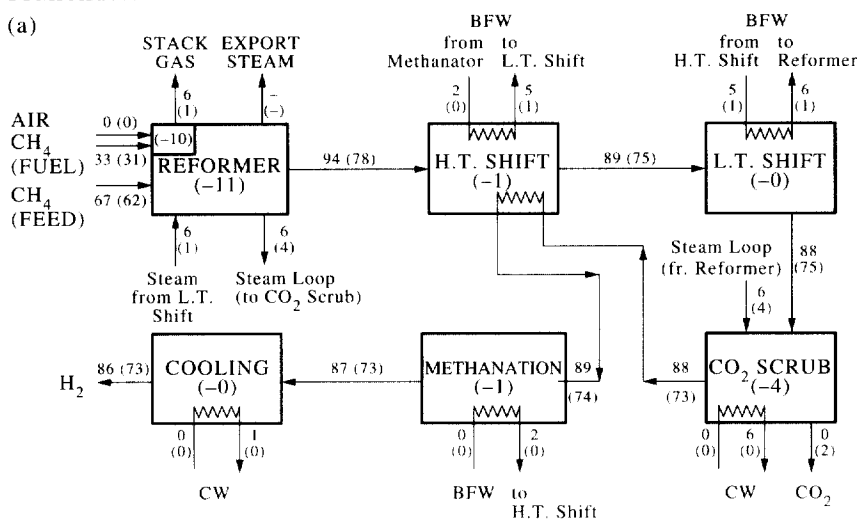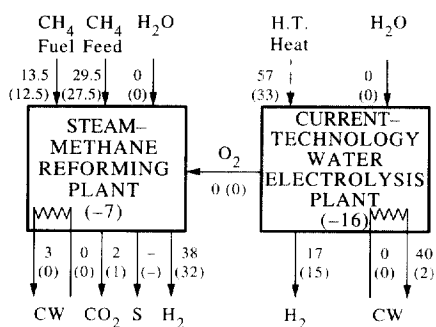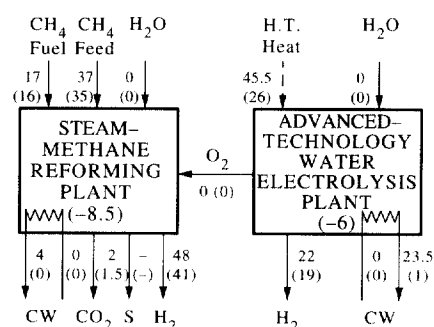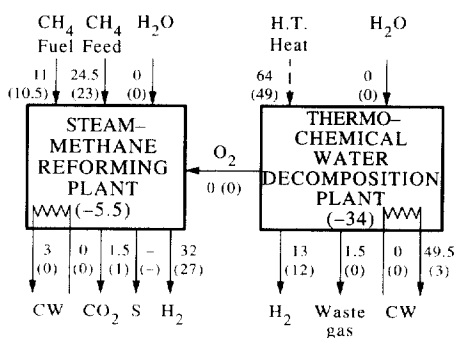
(d)

(e)
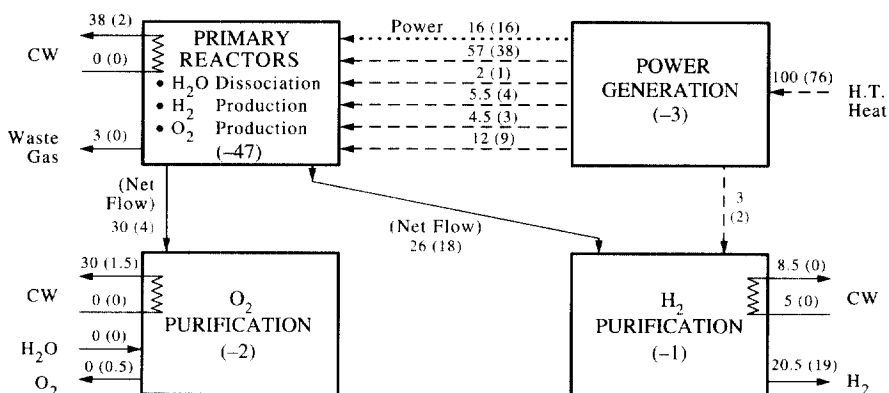
(f)

(g)

(h)

Fig. 1—continued.

Table 2. Hydrogen production processes considered and their efficiencies considering fuel and/or heat as the external energy inputs

Process	Efficiency (%)	
	Energy	Exergy
Steam-methane reforming (SMR)	86	78
Coal gasification	59	49
Current-technology water electrolysis	30	46
Advanced-technology water electrolysis	49	73
Thermochemical water decomposition	21	25
SMR/current-technology water electrolysis	55	64
SMR/advanced-technology water electrolysis	70	78
SMR/thermochemical water decomposition	45	47

Table 3. Hydrogen production processes considered and their efficiencies considering fuel and/or heat and/or electricity as the external energy inputs

Process	Efficiency (%)	
	Energy	Exergy
Steam–methane reforming (SMR)	86	78
Coal gasification	59	49
Current-technology water electrolysis	77	67
Advanced-technology water electrolysis	92	83
Thermochemical water decomposition	21	16
SMR/current-technology water electrolysis	85	76
SMR/advanced-technology water electrolysis	89	81
SMR/thermochemical water decomposition	45	49

energy inputs considered. For the non-hydrocarbon-based processes and the portions of the integrated processes that are non-hydrocarbon-based, the external energy input is considered to be:

- a hypothetical heat source for the efficiencies in Table 1,
- high-temperature heat for the efficiencies in Table 2, and
- electricity and high-temperature heat for the efficiencies in Table 3.

For all energy-input cases considered in Tables 1–3, a fossil fuel is considered as the external energy input for the hydrocarbon-based processes and the parts of the integrated processes that are hydrocarbon-based. By-product credits are not allowed in all cases, although no significant change is observed in the efficiencies if by-product credits are allowed. The overall efficiencies range widely, from 21% to 86% for energy efficiencies, and from 19% to 78% for exergy efficiencies (based on primary resource inputs, e.g., fossil fuels and/or a hypo-

thetical heat source). Similarly, the energy efficiencies range from 21% to 86% and the exergy efficiencies from 25% to 78% when the energy input is high-temperature heat, and the energy efficiencies range from 21% to 86% and the exergy efficiencies from 26% to 78% when the energy inputs are electricity and high-temperature heat.

The efficiencies are evaluated based on the energy and exergy data presented in Fig. 1 for each process. However, it is noted that the diagrams in Fig. 1 correlate directly to the efficiencies in Table 2, in that high-temperature heat is the external energy input for the portions of all processes that are non-hydrocarbon-based, while a fossil fuel is considered as the external energy input for the portion of all processes that are hydrocarbon-based. In determining the efficiencies in Table 1 using the diagrams in Fig. 1, a process step involving the conversion of a hypothetical heat source to heat is added to all processes that are non-hydrocarbon-based (Fig. 1c–e) and all processes that are partly non-hydrocarbon-based (Fig. 1f–h). Similarly, in determining the efficiencies in Table 3 using the diagrams in Fig. 1, the process steps involving the conversion of high-temperature heat to electricity are omitted.

For the same process and efficiency type (energy or exergy), the efficiencies in Table 3 are greater than or equal to those in Table 2, which in turn are greater than or equal to those in Table 1. The efficiencies in Table 1 a–c are accurate, but address different questions. Specifically, the values report how efficiently hydrogen could be produced from electricity, high-temperature heat and fossil fuels in Table 3, from high-temperature heat and fossil fuels in Table 2, and from a hypothetical heat source and fossil fuels in Table 1. Fair comparisons using the different processes are best performed using the data in Table 1; the efficiencies in Tables 2 and 3 are nonetheless useful for understanding the process.

The efficiencies, based on primary resource inputs, for the processes involving hydrogen production from hydrocarbons (SMR and coal gasification) are relatively high, ranging (based on energy or exergy) approximately from 50% for coal gasification to 80% for SMR. Since the hydrogen-to-carbon atomic ratios for methane (4) and coal (0.8) bracket the range covered by most of the hydrocarbons used in hydrogen production, the efficiencies for hydrogen production from hydrocarbons having intermediate ratios can be expected to lie between those determined here for SMR and coal gasification. For each hydrocarbon-based process (and most of the other processes considered in this paper), the overall energy and exergy efficiencies in Table 1 are similar. However, these efficiencies differ for many plant devices. That is, the main energy and exergy losses are associated with different devices. Based on primary resource inputs, all energy losses are associated with waste emissions, while most (over 90% for all processes) of the exergy losses are associated with internal consumptions. Specifically, cooling water and stack gas account for almost 100% of the energy losses and less than 10% of the exergy losses, while internal consumptions, mainly in the gasifier and

combustor for coal gasification and in the combustor for SMR, are responsible for most of the exergy losses.

The efficiencies (based on energy or exergy) for the processes involving hydrogen production from non-hydrocarbons (current- and advanced-technology water electrolysis and thermochemical water decomposition) range from 21% for thermochemical water decomposition to almost 50% for water electrolysis, based on primary resource inputs. The water-electrolysis efficiencies for the advanced-technology case exceed those for the current-technology case. Cooling water accounts for nearly 100% of the energy losses, but less than 10% of the exergy losses, based on primary resource inputs. The remaining exergy losses are associated with internal consumptions, mainly in the conversion of a hypothetical heat source to heat for all processes; and in (i) the electrolysis unit and electrical generation plant for current-technology water electrolysis, (ii) the feedwater preheater and electrical generation plant for advanced-technology water electrolysis, and (iii) the primary reactors (where high-temperature heat is degraded to low-temperature heat) for thermochemical water decomposition.

For the integrated processes for hydrogen production, each efficiency is bracketed by the efficiencies for the separate processes comprising the integrated process. But each integrated-process efficiency is greater than the efficiency of the combined process in which the two separate processes are included but not integrated. For example, the energy and exergy efficiencies in Table 1 of 55% and 48%, respectively, for the integrated SMR/current-technology water electrolysis process are greater than the corresponding energy and exergy efficiencies that would exist for a system that contains two non-integrated processes (SMR and current-technology water electrolysis process) that are each supplied with the same energy inputs as the integrated processes. The energy losses are primarily associated with waste outputs, and the exergy losses with internal consumptions. The integrated processes reduce exergy losses for the non-integrated water electrolysis and thermochemical water decomposition processes by using the oxygen emitted by them. Advantages of the integrated processes over the non-integrated ones include (i) reduced requirements for methane fuel because the oxygen is not accompanied by nitrogen, which requires heating; (ii) increased overall efficiency; (iii) production of an additional by-product since, if the methane fuel is relatively pure, the stack gases are composed of relatively pure CO_2; and (iv) cleaner operation, since stack gas emissions are eliminated if the stack gas is contained as a by-product.

GENERAL TRENDS AND CLOSING REMARKS

Overall efficiencies for the hydrogen production processes considered, based on primary resource inputs, range widely (approximately 20–80%) but, for any given process, the energy and exergy efficiency values are usually similar. This similarity occurs because input energy and exergy magnitudes are similar, and product energy

and exergy magnitudes are similar. For other processes, where these conditions do not hold, values of energy and exergy efficiencies are different. Also, different devices are usually responsible for significant energy and exergy losses (e.g. typical efficiencies for boilers are 30% based on exergy and 85% based on energy).

All energy losses in a process are associated with waste emissions (mainly with output cooling water), and most exergy losses with internal consumptions (mainly due to combustion and heat transfer across large temperature differences). Further, products of fuel production processes often have high energy and exergy contents, and wastes high energy and low exergy contents. Thus, energy analyses often indicate that wastes are valuable, and, to increase efficiency, quantities of waste effluents must be reduced, while exergy analyses indicate that wastes are not valuable and internal consumptions must be reduced to increase efficiency significantly.

REFERENCES

1. Scott, D. S., Hydrogen in the evolving energy system, *International Journal of Hydrogen Energy*, 1993, **18**, 197–204.
2. Barbir, F., Plass, H. J. Jr. and Veziroğlu, T. N., Modelling of hydrogen penetration in the energy market, *International Journal of Hydrogen Energy*, 1993, **18**, 187–195.
3. Hassmann, K. and Kuhne, H.-M., Primary energy sources for hydrogen production, *International Journal of Hydrogen Energy*, 1993, **18**, 635–640.
4. Rosen, M. A. and Scott, D. S., An energy–exergy analysis of the Koppers-Totzek process for producing hydrogen from coal, *International Journal of Hydrogen Energy*, 1987, **12**, 837–845.
5. Rosen, M. A., Thermodynamic investigation of hydrogen production by steam–methane reforming, *International Journal of Hydrogen Energy*, 1991, **16**, 207–217.
6. Rosen, M. A. and Scott, D. S., Exergy analysis of hydrogen production from heat and water by electrolysis, *International Journal of Hydrogen Energy*, 1992, **17**, 199–204.
7. Rosen, M. A., Energy and exergy analyses of electrolytic hydrogen production, *International Journal of Hydrogen Energy*, 1995, **20**, 547–553.
8. Rosen, M. A., Thermodynamic comparison of hydrogen production processes, *International Journal of Hydrogen Energy*, 1996, **21**, 349–365.
9. Rosen, M. A. and Scott, D. S., Analysis of the efficiencies of several hydrogen production processes. *Proceedings of the 11th World Hydrogen Energy Conference*, Stuttgart, 1996, pp. 479–488.
10. Moran, M. J., *Availability Analysis: A Guide to Efficient Energy Use*. American Society of Mechanical Engineers, New York, 1989.
11. Gaggioli, R. A. and Petit, P. J., Use the second law first, *Chemtech*, 1977, **7**, 496–506.
12. Cox, K. E. and Williamson, K. D. Jr, *Hydrogen: Its Technology and Implications*. CRC Press, Boca Raton, FL, 1979.
13. Casper, M. S., *Hydrogen Manufacture by Electrolysis, Thermal Decomposition and Unusual Techniques*. Noyes Data Corp., Park Ridge, NJ, 1978.

14. Kent, J. A., *Riegel's Handbook of Industrial Chemistry*, 8th edn. Van Nostrand Reinhold, Toronto, 1983.

15. Smith, W. N. and Santangelo, J. G., *Hydrogen Production and Marketing*. ACS Symposium Series, Vol. 116. American Chemical Society, Washington, DC, 1980.

16. Rodriguez, L. S. J., Calculation of available-energy quantities. In *Thermodynamics: Second Law Analysis, ACS Symposium Series*, Vol. 122, ed. R. A. Gaggioli. American Chemical Society, Washington, DC, 1980, pp. 39–60.