NATO Science for Peace and Security Series - C:
Environmental Security

Assessment of Hydrogen Energy for Sustainable Development

Edited by
John W. Sheffield
Çiğdem Sheffield

Springer

This publication is supported by: The NATO Science for Peace and Security Programme

Assessment of Hydrogen Energy for Sustainable Development

NATO Science for Peace and Security Series

This Series presents the results of scientific meetings supported under the NATO Programme: Science for Peace and Security (SPS).

The NATO SPS Programme supports meetings in the following Key Priority areas: (1) Defence Against Terrorism; (2) Countering other Threats to Security and (3) NATO, Partner and Mediterranean Dialogue Country Priorities. The types of meeting supported are generally "Advanced Study Institutes" and "Advanced Research Workshops". The NATO SPS Series collects together the results of these meetings. The meetings are co-organized by scientists from NATO countries and scientists from NATO's "Partner" or "Mediterranean Dialogue" countries. The observations and recommendations made at the meetings, as well as the contents of the volumes in the Series, reflect those of participants and contributors only; they should not necessarily be regarded as reflecting NATO views or policy.

Advanced Study Institutes (ASI) are high-level tutorial courses intended to convey the latest developments in a subject to an advanced-level audience

Advanced Research Workshops (ARW) are expert meetings where an intense but informal exchange of views at the frontiers of a subject aims at identifying directions for future action

Following a transformation of the programme in 2006 the Series has been re-named and re-organised. Recent volumes on topics not related to security, which result from meetings supported under the programme earlier, may be found in the NATO Science Series.

The Series is published by IOS Press, Amsterdam, and Springer, Dordrecht, in conjunction with the NATO Public Diplomacy Division.

Sub-Series

A.	Chemistry and Biology	Springer
B.	Physics and Biophysics	Springer
C.	Environmental Security	Springer
D.	Information and Communication Security	IOS Press
E.	Human and Societal Dynamics	IOS Press

http://www.nato.int/science
http://www.springer.com
http://www.iospress.nl

Series C: Environmental Security

Assessment of Hydrogen Energy for Sustainable Development

edited by

John W. Sheffield
University of Missouri-Rolla,
Rolla, MO, U.S.A.

and

Çiğdem Sheffield
United Nations Industrial Development
Organization – International Centre
for Hydrogen Energy Technologies,
Istanbul, Turkey

Springer

Published in cooperation with NATO Public Diplomacy Division

Proceedings of the NATO Advanced Study Institute on
Assessment of Hydrogen Energy for Sustainable Development:
Energy & Environmental Security
Istanbul, Turkey
7–10 August 2006

A C.I.P. Catalogue record for this book is available from the Library of Congress.

ISBN 978-1-4020-6441-8 (PB)
ISBN 978-1-4020-6440-1 (HB)
ISBN 978-1-4020-6442-5 (e-book)

Published by Springer,
P.O. Box 17, 3300 AA Dordrecht, The Netherlands.

www.springer.com

Printed on acid-free paper

CONTENTS

PREFACE

The NATO Advanced Research Workshop (ARW) entitled "Assessment of Hydrogen Energy for Sustainable Development: Energy & Environmental Security" was held during the four-day period, 7–10 August 2006, in Istanbul, Turkey. This NATO-ARW was organized to discuss the issues concerning environmental security and sustainable development of hydrogen energy technologies using advanced renewable energies sources, such as wind, solar, biomass, wave, geothermal, and hydro energy. In addition, an assessment of the difficult problems of environmental security and development of hydrogen energy technologies was needed to review the technological, financial, legal, and institutional barriers to a cost-competitive, standardized, widely accessible, safe, and environmentally benign hydrogen economy.

Energy and environmental security are truly major problems facing our global economy. Fossil fuels, particularly crude oil, are confined to a few regions of the world and the continuity of supply is governed by dynamic political, economic, and ecological factors. These factors conspire to force volatile, often high fossil fuel prices while, at the same time, our environmental policies are demanding a reduction in greenhouse gases and toxic emissions. Thus a coherent energy strategy is required, addressing both energy supply and demand, taking account of the whole energy life cycle including fuel production, transmission and distribution, and energy conversion, and the impact on energy equipment manufacturers and the end-users of energy systems. In the short term, our aim should be to achieve higher energy efficiency and increased energy supply from local energy sources, in particular renewable energy sources. In the long term, a hydrogen-based economy will have an impact on all these sectors. In view of technological developments, vehicle and component manufacturers, transport providers, the energy industry, and even householders are seriously looking at alternative energy sources and fuels and more efficient and cleaner technologies – especially hydrogen and hydrogen-powered fuel cells.

The aim of this NATO-ARW was thus to bring together legal experts, engineering specialists, policy analysts, and scientists to focus on hydrogen energy for sustainable development; to discuss policy and technical issues essential for the development and deployment of hydrogen energy technologies; to discuss how to foster large-scale, long-term public–private cooperation to advance hydrogen energy technologies and infrastructure development; to analyze and set priorities for research, development, and deployment and ensuring support for the most promising and beneficial activities.

The NATO-ARW format consisted of invited lectures, oral, and poster contributions. By attending this workshop, all of the participants gained an insight into the current status of hydrogen systems and had the opportunity to develop collaborations between participants.

This Proceedings brings together the papers of invited and contributed participants. We hope that they will serve as both a useful reference and a resource material for all the participants and for those whose interest in the subject matter may develop after the event.

This NATO Advanced Research Workshop, “Assessment of Hydrogen Energy for Sustainable Development: Energy & Environmental Security” (Ref. No. CBP.EAP. ARW 982094) was supported by the North Atlantic Treaty Organisation (NATO) Security through Science Programme. Their contribution is gratefully acknowledged.

Finally, this workshop was also carried out in cooperation with the United Nations Industrial Development Organisation – International Centre for Hydrogen Energy Technologies (UNIDO-ICHET). Based in Istanbul, UNIDO-ICHET acts as a conduit for knowledge and technology flow between developed and developing countries by providing support, facilities, and expertise concerning all aspects of energy conversion technologies involving hydrogen.

John W. Sheffield
Çiğdem Sheffield

ENERGY SECURITY THROUGH HYDROGEN

JOHN W. SHEFFIELD[*]
Department of Mechanical and Aerospace Engineering,
University of Missouri-Rolla
Rolla, Missouri 65409-0050, USA

Abstract: Energy and environmental security are major problems facing our global economy. Fossil fuels, particularly crude oil, are confined to a few regions of the world and the continuity of supply is governed by dynamic political, economic, and ecological factors. These factors conspire to force volatile, often high fuel prices while, at the same time, environmental policy is demanding a reduction in greenhouse gases and toxic emissions. A coherent energy strategy is required, addressing both energy supply and demand, taking account of the whole energy life cycle including fuel production, transmission and distribution, and energy conversion, and the impact on energy equipment manufacturers and the end-users of energy systems. In the short term, the aim should be to achieve higher energy efficiency and increased supply from local energy sources, in particular renewable energy sources. In the long term, a hydrogen-based economy will have an impact on all these sectors. In view of technological developments, vehicle and component manufacturers, transport providers, the energy industry, and even householders are seriously looking at alternative energy sources and fuels and more efficient and cleaner technologies – especially hydrogen and hydrogen-powered fuel cells. The Hydrogen Energy System has the best potential of becoming the energy system of the future. Hydrogen can be produced from sustainable, renewable sources and may contribute to meet the growth in world energy demand. For example, hydrogen is a carbon-free energy carrier. When hydrogen is used in fuel cells, there are no harmful emissions. The current production of hydrogen is estimated to be approximately 500 billion m^3/year, equivalent to 3.3 million barrels of oil per day. This is equivalent to approximately 10% of the energy currently used in the transportation sector. Today, hydrogen is mostly made by partial oxidation

---

[*] John W. Sheffield, Professor of Mechanical and Aerospace Engineering, University of Missouri-Rolla, Rolla, MO 65409-0050, U.S.A.; e-mail: sheffld@umr.edu

J.W. Sheffield and Ç. Sheffield (eds.), Assessment of Hydrogen Energy for Sustainable Development, 1–8.

or steam reforming of oil, natural gas steam reforming, methanol reforming, and water electrolysis. But the production possibilities are diverse, even modified algae can produce hydrogen. The production of hydrogen is relatively simple compared to processes to make conventional fuels. As a consequence, nobody will be able to control the supply of hydrogen. Hydrogen is an energy carrier, which means it can store energy. Thus hydrogen is particular suitable for renewable energy systems. For example, surplus wind energy or solar energy produced under good conditions can be used to produce hydrogen via electricity.

1. Background

The NATO Advanced Research Workshop (ARW) entitled "Assessment of Hydrogen Energy for Sustainable Development: Energy & Environmental Security" was organized to discuss the issues concerning environmental security and sustainable development of hydrogen energy technologies using advanced renewable energies sources, such as wind, solar, biomass, wave, geothermal, and hydro energy. In addition, an assessment of the difficult problems of environmental security and development of hydrogen energy technologies will review the technological, financial, legal, and institutional barriers to a cost-competitive, standardized, widely accessible, safe, and environmentally benign hydrogen economy. The goal will be to bring together legal experts, engineering specialists, policy analysts, and scientists to focus on hydrogen energy for sustainable development; to discuss policy and technical issues essential for the development and deployment of hydrogen energy technologies; to discuss how to foster large-scale, long-term public–private cooperation to advance hydrogen energy technologies and infrastructure development; to analyze and set priorities for research, development, and deployment and ensuring support for the most promising and beneficial activities.

It should be noted that the use of hydrogen as an energy carrier entails a number of challenges for the developers of hydrogen energy technologies. International rules and regulations, laws, and technical standards need to be adjusted to the transition of fuels. One example of an international development is the European Integrated Hydrogen Project, which is developing common international standards and regulations in this area. The lack of proper international standards is regarded as a barrier for the introduction of hydrogen as an energy carrier.

An important issue with respect to handling of hydrogen is the safety of hydrogen storage, fueling, and transportation. Extensive safety assessments are necessary in order to have a sufficient basis for rules and regulations to be accepted by each country. For example, the maintenance of a hydrogen fueling station is an area that needs international standards. One of the challenges for the hydrogen energy system is obtaining a consensus between European, North American, and Japanese, who are the main players in the field of hydrogen energy technologies.

On October 10, 2002 the European Commission launched a high level group with representatives from 19 different organizations involved in the development of hydrogen and fuel cells. In her speech to the European delegates EU commissioner Loyola de Palacio disclosed the energy political setting:

> The challenges for the European Union's energy policy are huge: reconciling security of supply with a reduced environmental impact of energy use and in the same time keeping our economies competitive and growing. Hydrogen can contribute to meet these challenges, and so we should support its quick, efficient and effective penetration into the market.

While North America and Japan are increasing their investment in hydrogen-related research and development and actively coordinating with private industrial partners, European public financial support from the European Union and Member States remains at a significantly lower and fragmented level. To stay competitive, financial resources from the European Union and Member States must be increased and efforts well coordinated to achieve critical mass and increase efficiency in the development of these key future hydrogen energy technologies essential for sustainable economic development and environmental security.

2. Situation in Europe

Europe has serious energy security concerns driven by soaring petroleum prices, persistent instability in the Middle East, Russia's politically driven energy policies for Europe, the fragmented European energy market, dwindling European energy production, Europe's inability to project military force beyond the continent, and rising economic nationalism within Europe.

Europe has increasingly become dependent upon a narrow band of supplier. For example roughly half of the natural gas that is now consumed in Europe comes from Russia, Norway, and Algeria. Europe currently imports 45% of their petroleum from the Middle East and 40% of their natural gas from Russia. In addition, Russia is the second largest exporter of crude oil to Europe.

Of concern to many energy experts is the fact that Russia controls the world's largest reserves of natural gas and is also the world's largest natural gas producer. For example, in 2004 natural gas from or transported through Russia accounted for 70% of European imports. The Russian state controlled company, Gazprom, produces for 85% of Russian output and manages 100% of Russian exports. Gazprom provides about 20% of earnings to Russia's federal budget and supplies gas to generate around 50% of electricity in Russia. Gazprom has more natural gas than any other natural gas company in the world, with 16.9% of the world's proven natural gas reserves, and over 60% of Russia's reserves. Gazprom's proven natural gas reserves are estimated at around 29.1 trillion m^3. Gazprom controls the Russian pipeline network and is thus able to limit competition from other producers. Gazprom has been buying upstream assets in central Asia and downstream European utilities and other energy consumers. The long-term strategy of Gazprom is to be a worldwide energy company which continues to open up new promising markets. The greatest potential demand for Russian natural gas exists in China. In March 2006, executives of Gazprom signed a protocol with their counterparts from the Chinese National Company of Oil and Gas. The "Protocol on Deliveries of Natural Gas from Russia to the People's Republic of China" was signed in the scope of the official visit of the Russian President V. Putin to the People's Republic of China. This protocol determined the terms, the volumes, and the routes of natural gas deliveries together with the basis of the price formation formula. The first deliveries of the Russian "blue fuel" are expected in China in 2011. However, such investments have done little to increase Russia's real natural gas production capacity. According to the International Energy Agency, Russia should make an annual minimum investment of $11 billion in the natural gas sector to meet it future domestic and international supply commitments. To make matters worse, Russia continues to consume its own energy assets in a highly inefficient manner, partly because the energy market is subsidized in Russia. Thus energy policy changes are also needed if Russia is to best develop its natural resources and meet its supply commitments to Europe. In defense of Gazprom, it should be noted that the published mission of Gazprom is to meet the gas needs of Russian consumers in the best possible and most balanced way, as well as to meticulously comply with its long-term contractual commitments and intergovernmental agreements on gas export. However, the real message is clear when one examines the changes in share capital structure within Gazprom. These significant changes are noted Table 1.

TABLE 1. Recent changes in Gazprom share capital structure

Shareholder %	2000	2001	2002	2003	2004	2005
The Russian federation	38.37	38.37	38.37	38.37	38.37	50.002
Russian companies	33.64	34.06	35.07	36.10	36.81	29.482
Individual Russian citizens	17.68	16.07	15.06	14.03	13.32	13.068
Non-Russian companies	10.31	11.50	11.50	11.50	11.50	7.448
Total:	**100.00**	**100.00**	**100.00**	**100.00**	**100.00**	**100.00**

http://eng.gazpromquestions.ru/page4.shtml

3. Situation in USA

The USA has less than 5% of the world's population but currently consumes 25% of the world's oil. During the Arab oil embargo of the 1970s, 36% of US oil was imported. That figure rose to 56% by 2001 and will likely reach 64% over the next 15 years. The situation has become so serious that even President George W. Bush, to the surprise of many who have long known him as closely linked to the Texas oil industry, conveyed in the State of the Union Address that "America is addicted to oil", implying, of course, that it was time for Americans to begin to kick the habit.

In regards to natural gas, it should be noted that the Russian company Gazprom is weighing its options of going international with its new product: liquefied natural gas (LNG). Russia's Arctic continental shelf is viewed as the resource base for a project to export Russian LNG. The USA is viewed as the best export destination for Russian LNG since the US Department of Energy predicts that demand for natural gas will be increasing at a rate of 1.5% annually in the USA until 2025. The USA has already offered to join Russia in its LNG projects, and to market Russian natural gas in the USA. In 2005, Gazprom started using tankers to deliver liquefied natural gas to the USA. Gazprom sent its first LNG shipment to Great Britain in 2006. And in 2006, Gazprom plans to send three to five tankers with LNG to the USA. LNG shipments will continue under medium-term contracts with USA companies until 2009. After 2010, direct shipments of the Russian LNG to the USA are planned to start under long-term contracts.

4. Energy policies

The fundamental objectives of many national energy policies are to ensure that the economy of each nation has access to sufficient, affordable, and reliable energy supplies on terms and conditions that support that nation's economic growth and prosperity. However, due to the global nature of the energy markets and the increasingly integrated energy markets, events that impact the energy security of any country can affect the energy security of another country, and vice versa. For a pipeline attack in Africa, tensions over nuclear enrichment programs, burgeoning economic growth in China and India, and natural disasters are issues that have direct impacts on the global energy security. Thus, both global and local energy policies are important.

Since current energy technologies do not meet the challenge of sustainable energy and environmental security, a transition to a new sustainable energy system is inevitable. Affordable, stable energy prices are essential for economic growth, thus the new energy technologies need to be effective, predictable, and flexible. Thus, the sustainable energy system should include both energy-efficient end-use technologies and sustainable renewable energy sources.

An error in energy policy would be to view sustainable energy as a choice between the outright replacement of fossil fuels or having nothing at all. In reality, however, it is the partial implementation of new renewable energies that can provide a transition until a permanent energy solution can be obtained. This being the case, it matters little if renewable energy production will at first be dwarfed by more traditional fossil supplies. The energy base of the future will have to be created using the energy base existing now, just as the fossil fuel-based economy was built using previously existing sources. A potential question of concern for environmental security relates to the current practice of hydrogen production from natural gas or other fossil fuels feed stocks. However, hydrogen can be produced directly from water through photoelectrochemical processes or electrolysis, which could be powered from wind and solar energy sources. The challenge for the transition to hydrogen energy technologies is one of economic constraints imposed under the current global energy markets and numerous energy policies. Perhaps the following statements by Nader Elhefnawy in his paper "Towards a Long-Range Energy Security Policy" published on Sunday, March 5, 2006 by Parameters (US Army War College) should serve as a clear warning.

> Even without taking into account related problems like the greenhouse effect, the security problems posed by the exhaustion of supplies of

easily accessible cheap oil and gas are highly varied and daunting. The likely result would be the exacerbation of familiar problems like resource conflict, weapons proliferation, and state failure. However, other problems are more novel, not least of all the potential for changes in the international balance of power based not only on which countries control the lion's share of the world's fossil fuel supplies, but which are most dependent on those supplies.

The most obvious concern is a reinvigoration of resource conflict. As the oil deposits believed to lie under a disputed piece of ground or sea floor become more valuable economically, governments might be more prepared to fight for them. Since the War on Terrorism began in 2001, China, seeing itself in a more vulnerable strategic position, has been more willing to negotiate its claims over the South China Sea. However, the issue has yet to be resolved, and an oil-hungry China can yet take a harder line, especially if this becomes more profitable. China also has behaved provocatively elsewhere, sending naval vessels into Japanese claims around the Senkaku Islands. Similar conflicts remain unresolved in other regions, including sub-Saharan Africa and Latin America. Moreover, even states unlikely to go to war over territory would face greater prospects of involvement in an armed conflict, and find a powerful incentive to develop and deploy long-range power-projection capabilities. Resource wars also can be a cause of internal conflicts or unrest. The war in the Indonesian region of Aceh is partly driven by the government's determination to hold onto an oil-rich region, and the resentment of the inhabitants has been partly a response to the damage oil production has done to local communities. Oil also was at stake in the fight over East Timor, which on the first day of its independence concluded a deal with Australia regarding its oil-rich offshore claims.

The problem may in fact be exacerbated by certain solutions to the world's energy problems. To give one example, the development of new technologies which permit cost-effective drilling for oil in deeper waters could create new flash-points. Cheaper deep-water drilling, for instance, would make the oil under the South China Sea a more valuable prize. As certain kinds of alternative energy technologies are developed, the value of certain resources is also likely to become more strategically important (like platinum for hydrogen fuel cells), with similar results.

The resistance to planning that left the United States without an Industrial policy has resulted in a $700 billion annual trade deficit, caused in large part by American imports of manufactured products once made

> at home. With the beginning of the end of the oil age possibly around the corner, the United States cannot afford to be without an energy policy. A logical starting point is a program to nurture renewable sources and conserve fossil fuels on a scale far more ambitious than anything previously attempted or currently being considered.

5. Conclusions

New policies for energy and environmental security in Europe are clearly needed. The proposed hydrogen energy economy based on the rational use of renewable energy is sustainable and provides enhanced energy and environmental security.

References

1. Nader Elhefnawy, “Towards a Long-Range Energy Security Policy”, from Parameters – US Army War College Quarterly, Vol. XXXVI, No. 1, pp. 101–114, Spring 2006.
2. International Energy Outlook 2006, US DOE EIA Report DOE/EIA-0484 (2006), available at http://www.eia.doe.gov/oiaf/ieo/index.html.
3. Renewable Energy - Market & Policy Trends in IEA Countries, IEA Study Book, 2004, part 1 available at http://www.iea.org/textbase/nppdf/free/2004/renewable1.pdf and part 2 available at http://www.iea.org/textbase/nppdf/free/2004/renewable2.pdf.
4. Gazprom, information available at http://www.gazprom.ru/eng/.

21ST CENTURY'S ENERGY: HYDROGEN ENERGY SYSTEM

T. NEJAT VEZIROĞLU*
Director, Clean Energy Research Institute,
University of Miami
President, International Association for Hydrogen Energy
Miami, FL, USA.

Abstract: Fossil fuels (i.e., petroleum, natural gas, and coal), which meet most of the world's energy demand today, are being depleted fast. Also, their combustion products are causing the global problems, such as the greenhouse effect, ozone layer depletion, acid rains, and pollution, which are posing great danger for our environment and eventually for the life in our planet. Many engineers and scientists agree that the solution to these global problems would be to replace the existing fossil fuel system by the Hydrogen Energy System. Hydrogen is a very efficient and dean fuel. Its combustion will produce no greenhouse gases, no ozone layer depleting chemicals, little or no acid rain ingredients, and pollution. Hydrogen, produced from renewable energy (e.g., solar) sources, would result in a permanent energy system, which we would never have to change. However, there are other energy systems proposed for the post-petroleum era, such as a synthetic fossil fuel system. In this system, synthetic gasoline and synthetic natural gas will be produced using abundant deposits of coal. In a way, this will ensure the continuation of the present fossil fuel system. The two possible energy systems for the post-fossil fuel era (i.e., the solar hydrogen energy system and the synthetic fossil fuel system) are compared with the present fossil fuel system by taking into consideration production costs, environmental damages, and utilization efficiencies. The results indicate that the solar hydrogen energy system is the best energy system to ascertain a sustainable future, and it should replace the fossil fuel system before the end of the 21st century.

Keywords: hydrogen, fossil fuel consumption, solar-hydrogen energy system

---

* To whom correspondence should be addressed. T. Nejat Veziroğlu, Room 219, Engineering Bldg., Clean Energy Research Institute, University of Miami, 1251 Memorial Drive, Coral Gables, FL 33124, U.S.A., e-mail: Veziroglu@miami.edu

J.W. Sheffield and Ç. Sheffield (eds.), Assessment of Hydrogen Energy for Sustainable Development, 9–31.

1. Energy-related global problems

Soon after the invention of the steam engine in the 1860's, when the Industrial Revolution started to replace humans' and beasts' toil with nature's energy sources, a bright future seemed to be certain for humankind. More and more of nature's energy, initially in the form of wood and coal, later as oil and natural gas, were being harnessed for the benefit of humans. This resulted in mass production of goods, with corresponding reduction in prices and rising living standards.

Communities asked for factories, railroads, highways, seaports, and airports. These meant more jobs, more income, more goods, and more services. The world's standard of living was rising. When the Industrial Revolution started, the annual gross world product per capita was in some tens of dollars; today, it is $6,600 and rising exponentially.

Fossil fuels, which fed this amazing economic growth, were the medicine to cure deprivation. But it was an untested medicine, at that. As the planet Earth consumed more and more fossil fuels, two important predicaments started to emerge: (1) the fossil fuels would be depleted in a foreseeable future, and (2) the fossil fuels and their combustion products were causing global environmental problems.

1.1. DEPLETION OF FOSSIL FUELS

The demand for energy continues to rise because of two main reasons: (a) the continuing increase in world population, and (b) the growing demand by the developing countries in order to improve their living standards. At the present time, a large portion (about 65%) of the world energy demand is met by the fluid fossil fuels (i.e., petroleum and natural gas), because of their availability and convenient use. However, it is expected that the world fossil fuel production will soon peak, and thereafter begin to decrease [1–4][†]. Figure 1 shows estimates of the production rates of the fossil fuels and the world demand. It can be seen that the fluid fossil fuel production worldwide will continue to rise for the next 15 years, and then will start to decrease. The coal production – because of the environmental reasons – is expected to remain nearly constant for the next decade and then start to decrease.

Meantime, as a result of the growing world population and the desires of the peoples to better their living standards, the world demand for fluid fuels is rising (Figure 1). It is expected that the world population (which is about 6 billion at the moment and rising at 1.5% per year) growth will slow

---

[†] Numbers m square brackets refer to references listed at the end of the paper.

down and reach about 10–12 billions by the end of the next century [5]. Consequently, the world demand for fluid fuels will slow down and reach around 1.6 × 10^{12} GJ‡ per year. There will be a growing gap, starting within the next ten years, between the demand and production of fluid fuels.

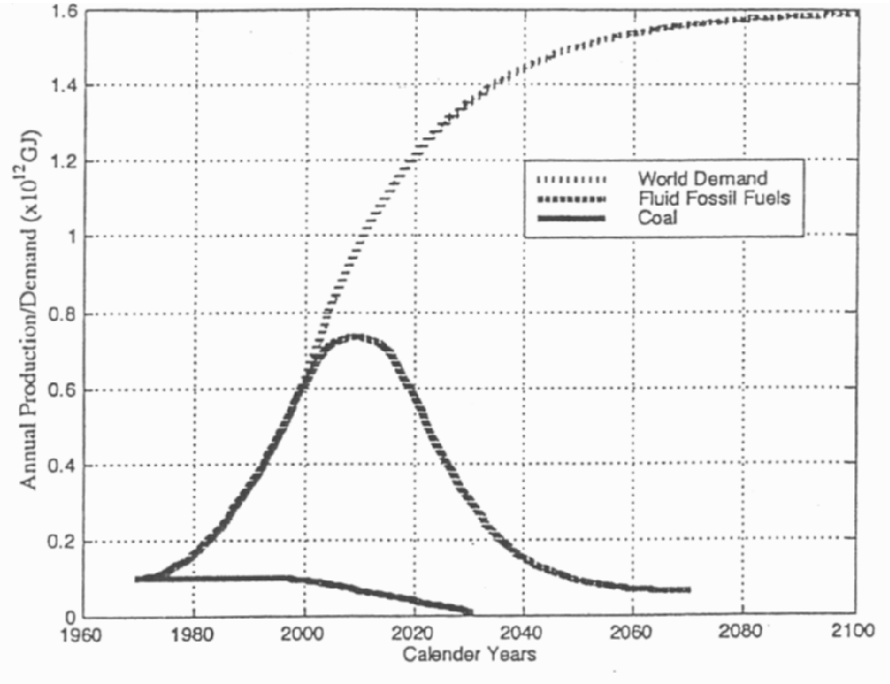


Figure 1. Estimates of world fossil fuel production

1.2. ENVIRONMENTAL DAMAGE

The second predicament involving the fossil fuels is the environmental damage being caused by the fossil fuels and by their combustion products. Technologies for fossil fuel extraction, transportation, processing, and particularly their end use (combustion), have harmful impacts on the environment, which cause direct and indirect negative effects on the economy. Excavation of coal devastates the land, which has to be reclaimed and is out of use for several years. During the extraction, transportation, and storage of oil and gas, spills and leakages occur, which cause water and air pollution. Refining processes also have an environmental impact. However, most of the fossil fuel environmental damage occurs during the end use. The end us of all fossil fuels is combustion, irrespective of the final purpose (i.e.,

---

‡ 1 GJ of energy is approximately equal to the energy contained m 3.4 gallons of petroleum.

heating, electricity production, or motive power for transportation). The main constituents of fossil fuels are carbon and hydrogen, but also some other ingredients, which are originally in the fuel (e.g., sulfur), or are added during refining (e.g., lead, alcohols). Combustion of the fossil fuels produces various gases (CO_x, SO_x, NO_x, CH), soot and ash, droplets of tar, and other organic compounds, which are all released into the atmosphere and cause air pollution. Air pollution may be defined as the presence of some gases and particulates which are not a natural constituent of the atmosphere, or even presence of the natural constituents in an abnormal concentration. Air pollution causes damage to human health, animals, crops, structures, reduces visibility, and so on.

Once in the atmosphere, triggered by sunlight or by mixing with water and other atmospheric compounds, the above stated primary pollutants may undergo chemical reaction, change their form, and become secondary pollutants, like ozone, aerosols, peroxyacyl nitrates, various acids, etc. Precipitation of sulfur and nitrogen oxides, which have dissolved in clouds and in rain droplets to form sulfuric and nitric acids is called acid rain; but also acid dew, acid fog, and acid snow have been recorded. Carbon dioxide in equilibrium with water produces weak carbonic acid. Acid deposition (wet or dry) causes soil and water acidification, resulting in damages to the aquatic and terrestrial ecosystems, affecting humans, animals, vegetation, and structures.

The remaining products of combustion in the atmosphere, mainly carbon dioxide, together with other so called greenhouse gases (methane, nitrogen oxides, and chlorofluorocarbons), result in thermal changes by absorbing the infrared energy the Earth radiates into the atmosphere, and by reradiating some back to the Earth, causing global temperatures to increase. The effects of the temperature increase are melting of the ice caps, sea level rise, and climate changes, which include heat waves, droughts, floods, stronger storms, more wildfires, etc.

Using the studies by scores of environmental scientists, the above stated damages have been calculated for each of the fossil fuels [6]. Table 1 presents the results for each type of damage, in 1998 US dollars. It can be seen that the environmental damage for coal is $14.51 per GJ of coal consumed, for petroleum $12.52 per GJ of petroleum consumed, for natural gas $8.26 per GJ of natural gas consumed, and the weighted mean damage in the world is $12.05 per GJ of fossil fuel consumption. These damage costs are not included in the prices of fossil fuels, but they are paid for by the people directly or indirectly through taxes, health expenditures, insurance premiums, and through a reduced quality of life. In other words, today fossil fuels are heavily subsidized. If the respective environmental damages were included in the fossil fuel prices, it would force earlier introduction of cleaner fuels, such as hydrogen, with many benefits to the economy and the environment.

TABLE 1. Environmental damage caused by each of fossil fuels

Type of damage (*n*)	Environmental damage 1998 $ per GJ					
	Coal		Petroleum		Natural gas	
	Itemized damage	Sub-totals	Itemized damage	Sub-totals	Itemized damage	Sub-totals
Effect on humans		5.16		4.19		3.09
Premature deaths	1.75		1.42		1.05	
Medical expenses	1.75		1.42		1.05	
Loss of working efficiency	1.66		1.35		0.99	
Effect on animals		0.75		0.63		0.45
Loss of domestic livestock	0.25		0.21		0.15	
Loss of wildlife	0.50		0.42		0.30	
Effect on plants and forests		1.99		1.61		1.20
Crop yield reduction – ozone	0.25		0.21		0.15	
Crop yield reduction – acid rains	0.13		0.10		0.07	
Effect on wild flora (plants)	0.77		0.62		0.46	
Forest decline (economic value)	0.27		0.22		0.16	
Forest decline (effect on biological diversity)	0.53		0.43		0.33	
Loss of recreational value	0.04		0.03		0.03	
Effect on aquatic ecosystems		0.26		1.55		0.16
Oil spills	–		0.44		–	
Underwater tanks leakages	–		0.90		–	
Liming lakes	0.04		0.03		0.03	
Loss of fish population	0.04		0.03		0.03	
Effect on biological diversity	0.18		0.15		0.10	
Effect on man-made structures		1.66		1.34		0.98
Historical buildings and monuments degradation	0.18		0.15		0.10	
Buildings and houses' detriment	0.37		0.30		0.22	
Steel constructions corrosion	0.99		0.80		0.59	
Soiling of clothes, cars, etc.	0.12		0.09		0.07	
Other air pollution costs		1.45		1.16		0.88
Visibility reduction	0.30		0.23		0.18	
Air pollution abatement costs	1.15		0.93		0.70	
Effect of strip mining		0.73		–		–
Effect of climactic changes		2.04		1.66		1.22
Heat waves – effects on humans	0.27		0.22		0.16	
Droughts –agricultural losses	0.16		0.13		0.10	
Livestock losses	0.13		0.10		0.07	
Forests losses	0.16		0.13		0.10	

Wild flora and fauna losses	0.93		0.75		0.56	
Water shortage and power production						
Problems	0.25		0.21		0.15	
Floods	0.07		0.06		0.04	
Storms, hurricanes, tornadoes	0.07		0.06		0.04	
Effect of sea level rise		0.47		0.38		0.28
TOTALS		14.51		12.52		8.26

In order to see the worldwide dimensions of the fossil fuel environmental damage, Table 2 has been prepared. It can be seen that 37% of the total damage is caused by coal, while the coal consumption is 31% of the total fossil fuel consumption. On the other hand, only 20% of the damage is caused by natural gas, which has a market share of 29%. It is clear that increasing the natural gas consumption at the expense of coal and petroleum will be environmentally beneficial. This would also prepare the way for greater public acceptance of gaseous fuels, which would result in a smoother change to hydrogen, also a gaseous fuel. It can also be seen from Table 2 that the annual worldwide environmental damage caused by fossil fuels is 1998 $4,345 billion, or equal to 11% of the gross world product. This is a very large figure. Conversion to a cleaner fuel, such as hydrogen, would enable the world to save this enormous sum and perhaps use it to improve the quality of life worldwide.

TABLE 2. Worldwide fossil fuel consumption and environmental damage for 1998

Fossil fuel consumption	(10^{18} J per year)
World coal consumption	112
World petroleum consumption	148
World natural gas consumption	105
World fossil fuel consumption	365
Environmental/damage estimate	(1998 billion $)
Damage due to coal	1,625
Damage due to petroleum	1,853
Damage due to natural gas	867
Total damage	4,345
Demographic and economic data	
World population (in billions)	5.96
Damage per capita ($)	730
World GWP (billion $)	39,340
GWP per capita ($)	6,600
Damage/GWP	0.11

2. Reasons for hydrogen energy system

Because of the foregoing, energy researchers are looking at the possible alternative sources of energy to replace the fossil fuels. There are quite a number of primary energy sources available, such as thermonuclear energy, nuclear breeders, solar energy, wind energy, hydropower, geothermal energy, ocean currents, tides, and waves.

At the consumer end, about one-quarter of the primary energy is used as electricity and three-quarters as fuel. The above mentioned primary energy sources must therefore by converted to these energy carriers needed by the consumer. In contrast with the fossil fuels, none of the new primary energy sources can be directly used as a fuel, e.g., for air transportation, land transportation. Consequently, they must be used to manufacture a fuel or fuels, as well as to generate electricity.

Since we need to manufacture a fuel for the post fossil fuel era, we are in a position to select the best possible fuel. There are many candidates, such as synthetic gasoline, synthetic natural gas (methane), methanol, ethanol, and hydrogen. The fuel of choice must satisfy the following conditions [7]:

- It must be convenient fuel for transportation.
- It must be versatile or convert with ease to other energy forms at the user end.
- It must have high utilization efficiency.
- It must be safe to use.

In addition, the resulting energy system must be environmentally compatible and economical.

2.1. TRANSPORTATION FUEL

Surface vehicles and airplanes must carry their fuel for a certain distance before replenishing their fuel supply. In the case of space transportation, the space vehicles must carry their, fuel, as well as the oxidant, necessary for their scheduled range. Therefore, it is important that the transportation fuel be as light as possible and also take as little space as possible. We can combine these requirements in a dimensionless number, termed the motility factor [8]:

$$\phi_M = \frac{\left(\frac{E}{M}\right)\left(\frac{E}{V}\right)^{2/3}}{\left(\frac{E_h}{M_h}\right)\left(\frac{E_h}{V_h}\right)^{2/3}} \tag{1}$$

where E is the energy generated by the fuel, M the mass of the fuel, V the volume of the fuel, and the subscript h refers to hydrogen. The higher the motivity factor, the better the fuel for transportation. Table 3 lists the pertinent properties of some fuels, as well as the motivity factors calculated using Eq. (1). It can be seen that among the liquid fuels LH_2 has the best motivity factor, while methanol has the lowest motivity factor. Among the gaseous fuels, GHz has the best motivity factor.

TABLE 3. Energy densities (HHV) and motivity factors for liquid and gaseous fuels

Fuel	Chemical formula	Energy per unit mass $\left(\frac{E}{M}\right)$ J/kg	Energy per unit volume $\left(\frac{E}{V}\right)$ J/m	Motivity factor ϕ_M
Liquid fuels				
Fuel oil	$C_{\leq 20}H_{\leq 42}$	45.5	38.65	0.78
Gasoline	$C_{5-10}H_{12-22}$	47.4	34.85	0.76
Jet fuel	$C_{10-15}H_{22-32}$	46.5	35.30	0.75
LPG	$C_{3-4}H_{8-10}$	48.8	24.40	0.62
LNG	$\sim CH_4$	50.0	23.00	0.61
Methanol	CH_3OH	22.3	18.10	0.23
Ethanol	C_2H_5OH	29.9	23.60	0.37
LH_2	H_2	141.9	10.10	1.00
Gaseous fuels				
Natural gas	$\sim CH_4$	50.0	0.040	0.75
GH_2	H_2	141.9	0.013	1.00

Consideration of the utilization efficiency advantage of hydrogen further improves hydrogen's standing as the best transportation fuel. Of course, this is one of the reasons why hydrogen is the fuel of choice for the space programs around the world, even though presently it is more expensive than fossil fuels.

2.2. VERSATILITY

At the user end, all fuels must be converted through a process (such as combustion) to other forms of energy, e.g., thermal energy, mechanical energy, and electrical energy. If a fuel can be converted through more than one process to various forms of energy at the user end, it becomes more versatile and more convenient to utilize. Table 4 lists various fuels and processes by which they can be converted to other forms of energy at the user end. It can be seen that all the fuels, except hydrogen, can be converted through one process only, that of combustion. Hydrogen, however, can be converted to other forms of energy in five different ways; i.e., in addition to flame combustion, it can be converted directly to steam, converted to heat through catalytic combustion, act as a heat source and/or heat sink through chemical reactions, and converted directly to electricity through electrochemical processes [9]. In other words, hydrogen is the most versatile fuel.

TABLE 4. Versatility (convertibility) of fossil fuels

Conversion process	Hydrogen	Fossil fuels
Flame combustion	Yes	Yes
Direct steam production	Yes	No
Catalytic combustion	Yes	No
Chemical conversion (hydriding)	Yes	No
Electrochemical conversion (fuel cells)	Yes	No

2.3. UTILIZATION EFFICIENCY

In comparing the fuels, it is important to take into account the utilization efficiencies at the user end. For utilization by the user, fuels are converted to various energy forms, such as thermal, mechanical, and electrical. Studies show that in almost every instance of utilization, hydrogen can be converted to the desired energy form more efficiently than other fuels [6].

Table 5 presents the utilization efficiency factors, defined as the fossil fuel utilization efficiency divided by the hydrogen utilization efficiency, for various applications. It can be seen that hydrogen is the most efficient fuel. This results in conservation of resources, in addition to conserving energy.

TABLE 5. Utilization efficiency comparisons of fossil fuels and hydrogen

Application	Utilization efficiency factor $\phi_u = {}^{\eta_F}/_{\eta_H}$
Thermal energy	
Flame combustion	1.00
Catalytic combustion	0.80
Steam generation	0.80
Electric power, fuel cells	0.54
Surface transportation	
Internal combustion engines	0.82
Fuel cells/electric motor	0.40
Subsonic jet transportation	0.84
Supersonic jet transportation	0.72
Weighted average	0.72
Hydrogen utilization efficiency factor	1.00
Fossil fuel utilization efficiency factor	0.72

2.4. SAFETY

The safety aspects of fuels involve their toxicity on the one hand and the fire hazard properties on the other. In addition to the toxicity of their combustion products, the fuels themselves can be toxic. The toxicity increases as the carbon to hydrogen ratio increases. Hydrogen and its main combustion product, water or water vapor, are not toxic. However, NO_x, which can be produced through the flame combustion of hydrogen (as well as through the combustion of fossil fuels) displays toxic effects.

Table 6 lists the characteristics of fuels related to fire hazards. Lower density makes a fuel safer, since it increases the buoyancy force for speedy dispersal of the fuel in ease of a leak. For the same reason, higher diffusion coefficients are helpful. Higher specific heat causes a fuel to be safer, since it slows down, the temperature increases for a given heat input. Wider ignition limits, tower ignition energies, and tower ignition temperatures make the fuels less safe, as they increase the limits in which a fire could commence. Higher flame temperature, higher explosion energy, and higher flame emissivity make a fuel less safe as well, since its fire would be more damaging.

TABLE 6. Characteristics related to fire hazard of fuels

Property	Gasoline	Methane	Hydrogen
Density[a] (kg/m^3)	4.40	0.65	0.084
Diffusion coefficient in air[a] (cm^2/sec)	0.05	0.16	0.610
Specific heat at constant pressure[a] (J/gK)	1.20	2.22	14.89
Ignition limits in air (vol%)	1.0–7.6	5.3–15.0	4.0–75.0
Ignition energy in air (mj)	0.24	0.29	0.02
Ignition temperature (°C)	228–471	540	585
Flame temperature in air (°C)	2,197	1,875	2,045
Explosion energy[a] (g TNT/kJ)	0.25	0.19	0.17
Flame emissivity (%)	34–43	25–33	17–25

[a]At normal temperature and pressure. [b]Theoretical maximum; actual 10% of theoretical.

Table 7 compares the safety of fuels. For each of the toxic elements and fire hazard characteristics, it ranks the fuels from 1 to 3, 1 being the safest and 3 the least safe. These rankings have been summed up for each fuel in order to arrive at an overall ranking. The total rankings have been prorated to obtain the *safety factors*, defined as the ratio of the total Tanking for hydrogen to that of a given fuel. It can be seen that hydrogen becomes the safest fuel; white gasoline is the least safe, methane being in between the two.

TABLE 7. Safety ranking of fuels

Characteristic	Fuel ranking[a]		
	Gasoline	Methane	Hydrogen
Toxicity of fuel	3	2	1
Toxicity of combustion (CO, SO_x, NO_x, HC, PM)	3	2	1
Density	3	2	1
Diffusion coefficient	3	2	1
Specific heat	3	2	1
Ignition limit	1	2	3
Ignition energy	2	1	3
Ignition temperature	3	2	1
Flame temperature	3	1	2
Explosion energy	3	2	1
Flame emissivity	3	2	1
TOTALS	30	20	16
Safety Factor ϕ_S	0.53	0.80	1.00

[a] 1, safest; 2, less safe; 3, least safe.

2.5. BEST FUEL

When we look at the fuel options critically under the criteria given above, it becomes clear that hydrogen is the best transportation fuel, the most versatile fuel, the most efficient fuel, and the safest fuel. In summary, hydrogen is the best fuel.

3. Hydrogen energy system

As a result of the above discussion, it becomes clear that it would be expedient to manufacture hydrogen using any and all primary energy sources, in order to make up for their shortcomings. Such an energy system is then called the "Hydrogen Energy System".

Figure 2 presents a schematic diagram of the proposed hydrogen energy system. In this system, hydrogen, (and oxygen) is produced in large industrial plants where the primary energy source (solar, nuclear, and even fossil) and water (H_2O), the raw material, are available. For large-scale storage, hydrogen can be stored underground in ex-mines, caverns and/or aquifers. Hydrogen is then transported, by means of pipelines or supertankers, to energy consumption centers. Subsequently, it is used in electricity, transportation, industrial, residential, and commercial sectors as a fuel and/or an energy carrier. The by-product is water or water vapor. If flame combustion of hydrogen is used, then some NO_x is also produced. Water and water vapor are recycled back, through rain, rivers, lakes, and oceans, to make up for the water used in the first place to manufacture hydrogen.

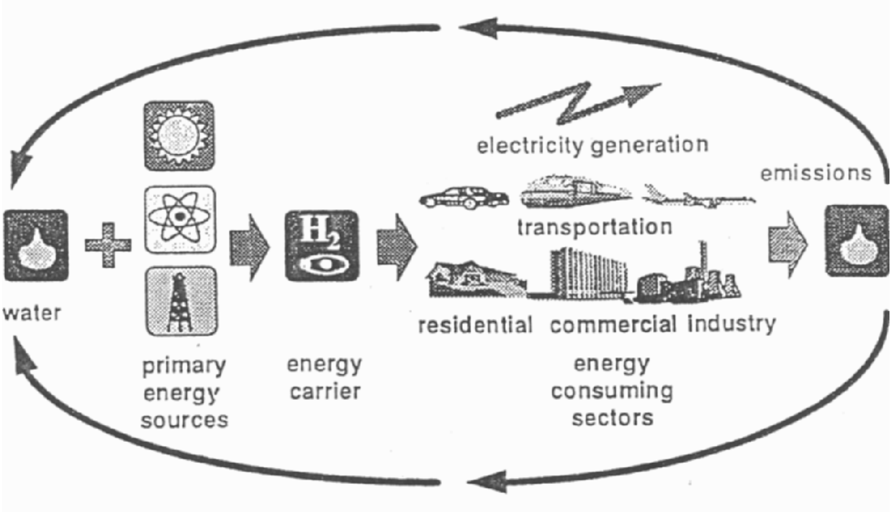


Figure 2. A schematic diagram of hydrogen energy system

The oxygen produced in the industrial plant making hydrogen could either be released into the atmosphere, or could be shipped or piped to industrial and city centers for use in fuel cells (instead of air) for electricity generation. This would have the advantage of increasing the utilization efficiency. The oxygen could be used by industry for nonenergy applications, and also for rejuvenating the polluted rivers and lakes, or speeding up sewage treatment.

It should be noted that in the hydrogen energy system, hydrogen is not a primary source of energy. It is an intermediary or secondary form of energy or an energy carrier. Hydrogen complements the primary energy sources, and presents them to the consumer in a convenient form at the desired locations and time.

Details of the hydrogen energy system, including production, storage, transportation, distribution, utilization, environmental impact and economies, can be found in the proceedings of the THEME and the World Hydrogen Energy Conferences [10–22], and in the books by Bockris, Veziroglu and Smith [23], and Veziroglu and Barbir [24].

4. Competing energy systems

Essentially, there are three contending energy systems: (1) the present fossil fuel system, (2) the coal/synthetic fossil fuel system, and (3) the solar hydrogen energy system, which is a special ease of the hydrogen energy system.

4.1. FOSSIL FUEL SYSTEM

A simplified version of today's energy system is shown in Figure 3. Fossil fuels are used for transportation (mostly petroleum products), for heat generation in residential, commercial, and industrial sectors, and for electric power generation. For transportation, mostly petroleum products are used (gasoline, diesel fuel, jet fuel, etc.). Heat generation includes space heating, domestic water heating, cooking, steam generation, and direct heating and/or drying in various industrial processes. All three forms of fossil fuels are used for these purposes. In electric power generation, coal is used mainly for the base load generation, and natural gas and heating oil are used for peak load. Part of the electric power is produced by hydro and nuclear power.

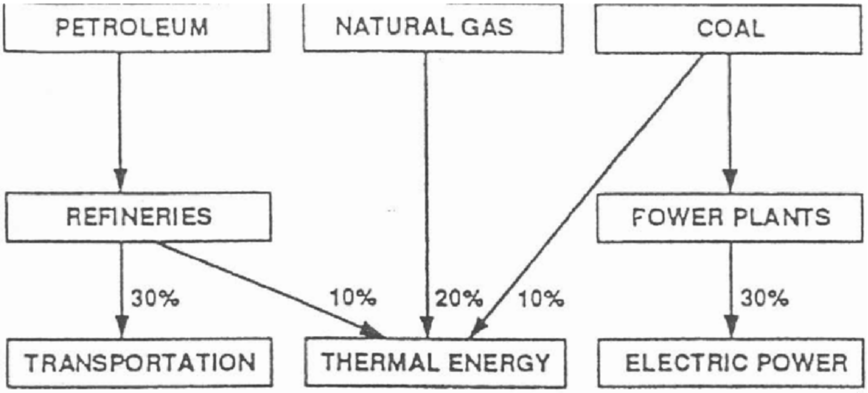


Figure 3. Fossil fuel system

In comparing with other energy systems, it can be assumed that 40% of primary energy (in fossil fuel equivalent units) will be used for thermal energy generation, 30% for electric power generation, and 30% for transportation (two-thirds for surface transportation and one-third for air transportation) [23]. Energy supplied by hydro and nuclear power plants (mostly in the form of electric power) and by other nonfossil fuel sources do not have to be taken into account, since it is assumed that it will be the same for the three systems considered. Actually, it is reasonable to expect that in the future even more electrical energy will be supplied by these sources.

When one considers the early 2000's, it can be expected that about one half of the thermal energy will be supplied by natural gas, and the rest by petroleum fuels (fuel oil and residual oil) and coal. Coal is assumed to be the main energy source for electricity generation, gasoline for surface transportation, and jet fuel for air transportation. This is of course a simplified version of the fossil fuel energy system, but it is close enough to the present patterns of energy consumption, and can be used as the basis for comparisons.

4.2. COAL/SYNTHETIC FOSSIL FUEL SYSTEM

Reserves of fossil fuels are finite, particularly those of oil and natural gas. Known reserves of oil and natural gas are about 8,000 El (1 El = 1018 l), which would be enough for the next 40 years at the current consumption rate [24]. If the exponential population growth and the demand growth are taken into account they would only last about 25 years. Even if the estimated additional undiscovered resources were added, that would satisfy energy needs for fluid fuels an additional 30 years or so. Coal reserves are much larger, known reserves are about 20,000 El, but estimated ultimately recoverable resources add up to 150,000 El. These large amounts of coal could eventually be used to produce synthetic liquid fuels, allowing society to continue employing the present energy system. Such a system is called the coal/synthetic fossil fuel system, since coal is to be used to manufacture synthetic fossil fuels, as well as to be directly used for electricity generation.

In this case, it can be assumed that the present fossil fuel system will be continued by the substitution with synthetic fuels derived from coal wherever convenient and/or necessary. Patterns of energy consumption are also assumed to be unchanged (see Figure 4). Coal will be used extensively for thermal power generation and for electric power generation, because it is much cheaper than synthetic fuels. However, some end uses require fluid fuels. Therefore it has been assumed that synthetic natural gas (SNG) will be used for some thermal energy generation (primarily in the residential sector) and also as fuel for surface transportation, where it will share the market with synthetic gasoline. Synthetic jet fuel will be used in air transportation.

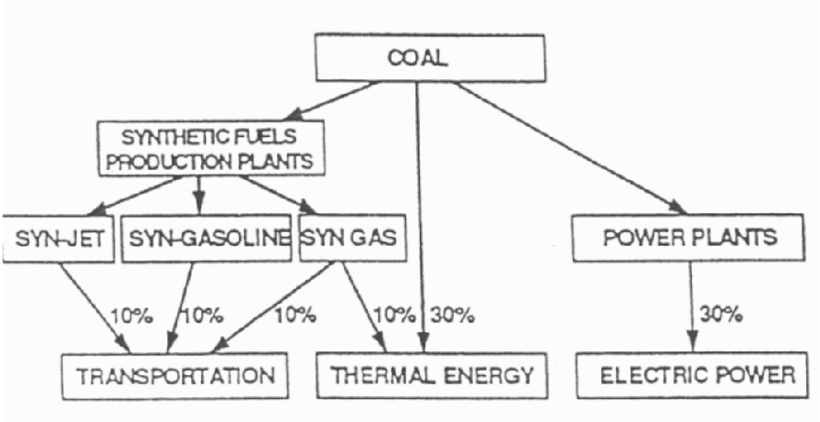


Figure 4. Coal/synthetic fossil fuel system

4.3. SOLAR-HYDROGEN ENERGY SYSTEM

If solar energy, in its direct and/or indirect forms (e.g., hydro, wind, etc.), is used to manufacture hydrogen, then the resulting system is called the “solar hydrogen energy system.” In this system, both the primary and secondary energy sources are renewable and environmentally compatible, resulting in a dean and permanent energy system. Figure 5 presents a schematic of the solar hydrogen energy system.

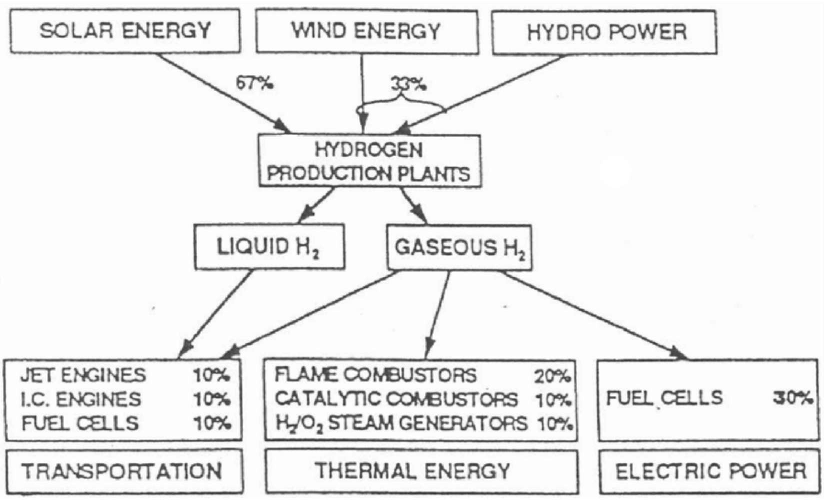


Figure 5. Solar–hydrogen energy system

In this case, it is assumed that the conversion to the hydrogen energy will take place, and one-third of hydrogen needed will be produced from hydropower (and/or wind power) and two-thirds by direct and indirect (other than hydropower) solar energy forms. The same percentage of energy demands by sectors as the above systems will be assumed. It will further be assumed that one half of the thermal energy will be achieved by flame combustion, one quarter by steam generation with hydrogen/oxygen steam generation and the last quarter by catalytic combustion; electric power will be generated by fuel cells; one half of the surface transportation will use gaseous hydrogen burning internal combustion engines and the other half will use fuel cells. In air transportation, both subsonic and supersonic, liquid hydrogen will be used.

5. Comparison of alternatives environmental impact of energy

It may be best to divide this into three sections, viz., pollution vapor generation, and environmental damage.

5.1. POLLUTION

Table 8 lists the pollutants for the three energy systems described. It can be seen that the coal/synthetic fossil system is the worst from the environmental point of view, while the solar–hydrogen energy system is the best. The solar–hydrogen system will not produce any CO_2, CO, SO_x, hydrocarbons, or particulates, except some NO_x. However, the solar–hydrogen-produced NOx is much less than those produced by the other energy *systems*. This is due to the fact that in the solar–hydrogen energy system only the flame combustion of hydrogen in air will generate NOx. The other utilization processes (such as direct steam generation, use of hydrogen in fuel cells, hydriding processes, etc.) will not produce any NOx.

TABLE 8. Pollutants produced by three energy systems

Pollutant	Fossil fuel system (kg/GJ)	Coal/synthetic fossil system (kg/GJ)	Solar–hydrogen system (kg/GJ)
CO_2	72.40	100.00	0
CO	0.80	0.65	0
SO_2	0.38	0.50	0
NO_x	0.34	0.32	0.10
HC	0.20	0.12	0
PM*	0.09	0.14	0

* Particulate matter.

5.2. VAPOR GENERATION

There is a notion that the hydrogen energy system would produce more water vapor than the other energy systems, since the fuel is pure hydrogen. When on considers the problem in detail, it is found to be not so.

Only the flame combustion of fuels in air or in oxygen will produce water vapor. In the case of hydrogen those other processes mentioned earlier will not produce any water vapor. Consequently, contrary to the popular belief, the solar–hydrogen energy system will produce less water vapor than the other systems.

Global warming, which is caused by the utilization of fossil fuels, also causes an increase in water vapor generation. Assuming that the Earth's mean temperature has increased by 0.5°C since the beginning of the Industrial revolution [25], this additional water vapor generation and that produced by the combustion of fuels have been calculated. The results are presented in Table 9. It can be seen that (1) the two fossil fuel systems generate much more additional (above natural) water vapor than the solar–hydrogen energy system, (2) the additional water vapor generated by global warming is much greater than that produced by the combustion of fuels, (3) the amount of water vapor generated by fuels is minimal compared to that generated naturally, and (4) the solar hydrogen system causes the smallest increase in vapor generation. Again, when the additional vapor generation is considered, the solar–hydrogen system becomes environmentally the most compatible system.

TABLE 9. Comparison of vapor generation by three energy systems (for 1998 energy consumption)

Item	Unit	Fossil fuel system	Coal/synthetic fossil system	Solar–hydrogen system
Annual vapor generation by energy System	10^{12} kg	8.9	9.300	6.0
Annual vapor generation due to global warming	10^{12} kg	3,900	3,900,000	0
Total vapor generation due to energy system and global warming	10^{12} kg	3,909	3,909,000	6.0
Total vapor generation as fraction of that produced naturally	%	0.782	0.782	0.001

Note: Annual vapor generation due to solar heating is 5 × 1,017 kg.

5.3. ENVIRONMENTAL DAMAGE

Table 10 presents the environmental damage per GJ of the energy consumed for each of the three energy systems considered and also for their fuel components in 1998 US dollars, as well as environmental compatibility factors, defined as the ratio of the environmental damage due to the hydrogen

TABLE 10. Environmental damage and environmental compatibility factors

Energy system and fuel	Environmental damage (1998 \$/GJ)	Environmental compatibility factor, ϕ_E
Fossil fuel system	12.47	0.055
Coal	14.51	
Oil	12.52	
Natural gas	8.26	
Coal/synthetic fossil system	15.46	0.044
Syn-gas	20.34	
SNG	13.49	
Solar–hydrogen energy system	0.68	1.000
Hydrogen	0.68	

energy system to that due to a given energy system. The environmental damage for the solar–hydrogen energy system is due to the NOx produced. It can be seen that the solar–hydrogen energy system is environmentally the most compatible system.

It should be mentioned that hydrogen also has the answer to the depletion of the ozone layer, mainly caused by chlorofluorocarbons. Refrigeration and air-conditioning systems based on the hydriding property of hydrogen do not need chlorofluorocarbons but need hydrogen, and any hydrogen leak would not cause ozone layer depletion. Such refrigeration systems are also very quiet, since they do not have any moving machinery.

6. Comparison of economics of energy alternatives

The economical comparison between competing energy system should be based on the effective costs of the services these fuels provide. The effective costs include the utilization energy, the east of fuel, and the costs associated with fuel consumption but which are not included in its price (so-called external costs). External costs include the costs of the physical damage done to humans, fauna, flora, and the environment due to harmful emissions, oil spills and leaks, and coal strip mining, as well as governmental expenditures for pollution abatement and expenditures for military protection of oil supplies.

In economic considerations, it is also important to compare the future costs of hydrogen (which will be considerably tower than they are today because of the assumed market and technology development) with the future costs, both internal and external, of fossil fuels (which will unavoidably be higher than today's prices due to depletion, international conflicts, and environmental impact).

The effective cast of a fuel can be calculated using the following relationship:

$$C_r = (C_i + C_e)\frac{\eta_{fk}}{\eta_{sk}} \tag{2}$$

where C_i is the internal cost or the conventional cost of the fuel, C_e the external cost including the environmental damage caused by the fuel η_{fk} the fossil fuel utilization efficiency for application k, and η_{sk} the synthetic fuel (inducing hydrogen) utilization efficiency for the same application or the end use.

In order to evaluate the overall cost (C_0) to society, the three scenarios considered earlier will be used. This cost can be calculated from the relationship:

$$C_0 = \sum_{n=1}^{n} \alpha_n C_m \tag{3}$$

where an is the fraction of energy used by the energy sector *n*, such as electricity generating, heat producing, surface transportation, subsonic air transportation, and supersonic air transportation. Since α_n is a fraction, their sum is

$$\sum_{n=1}^{n} \alpha_n = 1 \tag{4}$$

Substituting Eq. (2) into Eq. (3), one obtains

$$C_0 = \sum_{n=1}^{n} \alpha \left[(C_i + C_e) \frac{\eta_{fk}}{\eta_{sk}} \right]_n \tag{5}$$

Using Eqs. (2)–(5), Tables 11–13 have been prepared for the three energy scenarios, i.e., the fossil fuel system, the coal/synthetic fossil fuel system, and the solar–hydrogen energy system in 1998 US dollars. Comparing the results, it becomes dear that the solar–hydrogen energy system is the most cost–effective energy system, and results in the lowest overall effective cost to society.

TABLE 11. Effective east of fossil fuel system

Application	Fuel	Energy consumption fraction	Effective cost (1998 US $/GJ)
	Natural gas	0.20	17.46
Thermal energy	Petroleum fuels	0.10	27.56*
	Coal	0.10	17.75
Electric power	Coal	0.30	17.25
Surface transportation	Gasoline	0.20	31.61
Air transportation	Jet Fuel	0.10	25.98
TOTAL OF FRACTIONS		1.00	
OVERALL EFFECTIVE COST			22.11

* Average for residential and industrial sector.

7. Advantages of hydrogen and solar–hydrogen energy system

As a resu1t of the investigation presented above, it can be seen that hydrogen as a fuel and the solar hydrogen energy system have unmatched advantages as compared with fossil fuels and the fossil fuel system respectively.

TABLE 12. Effective cost of coal/synthetic fuel system

Application	Fuel	Energy Consumption factor	Effective cost (1998 US $/GJ)
Thermal energy	Goal	0.30	17.75
	SNG	0.10	36.64
Electric power	Goal	0.30	17.25
Surface transportation	SNG	0.10	36.64
	Syn-gasoline	0.10	51.65
Air transportation	Syn-jet	0.10	45.45
TOTAL OF FRACTIONS		1.00	
OVERALL EFFECTIVE COST			27.55

TABLE 13. Effective cost of solar–hydrogen energy system

Application	Fuel[a]	Energy Consumption factor	Effective cost (1998 US $/GJ)
Thermal energy			
Flame combustion	GH_2	0.20	26.04
Steam generation	GH_2	0.10	20.83
Catalytic combustion	GH_2	0.10	20.83
Electric power			
Fuel cells	GH_2	0.30	14.06
Surface transportation			
lC engines	GH_2	0.10	21.36
Fuel cells	GH_2	0.10	10.41
Air transportation			
Subsonic	LH_2	0.05	26.26
Supersonic	LH_2	0.05	22.51
TOTAL OF FRACTIONS		1.00	
OVERALL EFFECTIVE EAST			19.23

[a] It has been assumed that one-third of hydrogen will be produced from hydropower and/or wind power, and two-thirds from solar.

7.1. HYDROGEN

The advantages of hydrogen vis-á-vis fossil fuels can be listed as follows:

1. Liquid hydrogen is the best transportation fuel when compared to liquid fuels such as gasoline, jet fuel and alcohols, and gaseous hydrogen in the best gaseous transportation fuel.

2. While hydrogen can be converted to useful energy forms (thermal, mechanical, and electrical) at the user end through five different processes, fossil fuels can only be converted through one process, i.e., flame combustion. In other words, hydrogen is the most versatile fuel.
3. Hydrogen has the highest utilization efficiency when it comes to conversion to useful energy forms (thermal, mechanical, and electrical) at the user end. Overall, hydrogen is 39% more efficient than fossil fuels. In other words, hydrogen will save primary energy resources. It could also be termed as the most energy conserving fuel.
4. When fire hazards and toxicity are taken into account, hydrogen becomes the safest fuel.

7.2. SOLAR-HYDROGEN ENERGY SYSTEM

The advantages of the solar–hydrogen energy system vis-á-vis the present fossil fuel system and synthetic fossil fuel system can be listed as follows:

1. When the environmental impact is taken into consideration, the solar–hydrogen energy system becomes the most environmentally compatible energy system. It will not produce greenhouse gases, ozone layer damaging chemicals, oil spills, climate change, and little or no acid rain ingredients, and pollution. It will actually reverse the global warming and bring the Earth back to its normal temperatures by decreasing the CO_2 in the atmosphere to its pre-Industrial Revolution level.
2. The solar–hydrogen energy system has the lowest effective cost, when environmental damage and higher utilization efficiency of hydrogen are taken into account. In other words, the solar–hydrogen energy system will cost society least when compared with the present fossil fuel system and the synthetic fossil fuel system.

References

1. M. A. Elliot and N. C. Turner. "Estimating the Future Rate of Production of the World's Fossil Fuels," presented at the American Chemical Society's 163rd National Meeting, Division of Fuel Chemistry Symposium on "Non-Fossil Chemical Fuels," Boston, April 13, 1972.
2. D. Root and E. Attanasi, in *The American Association of Petroleum Geologists Bulletin* (1978).
3. J. D. Parent. "A Survey of the United States and Total World Production, Proves Reserves, and Remaining Recoverable Resources of Fossil Fuels and Uranium as of December 31, 1977," Institute of Gas Technology, Chicago, March (1979).

4. J. O. M. Bockris and T. Nejat Veziroglu. *Int. J. Hydrogen Energy* 8, 323 (1983).
5. T. N. Veziroglu and O. Basar. “Dynamics of a Universal Hydrogen Fuel System, Hydrogen Energy. Part B,” Plenum Press, pp. 1309–1326 (1974).
6. F. Barbir, T. N. Veziroglu and H. J. Plass, Jr. “Environmental Damage Due to Fossil Fuels Use,” *Int. J. Hydrogen Energy* 10, 739 (1990).
7. T. N. Veziroglu and F. Barbir. “Hydrogen: The Wonder Fuel,” *Int. J. Hydrogen Energy* 17, 391 (1992).
8. T. N. Veziroglu and Frano Barbir. “Transportation Fuel-Hydrogen,” *Energy Technology and the Environment*, Vol. 4, Wiley-Interscience, 2712–2730 (1995).
9. T. N. Veziroglu. “Hydrogen Technology for Energy Needs of Human Settlements,” *Int. J. Hydrogen Energy* 12(2), (1987).
10. T. N. Veziroglu, ed. *Hydrogen Energy*, Parts A and B. *Proceedings Hydrogen Economy Miami Energy Conference (THEME)*, Plenum Press, New York (1975).
11. T. N. Veziroglu, ed. *Proc. 1st World Hydrogen Energy Conference (WHEC)* (3 vols.), Clean Energy Research Institute, University of Miami, Coral Gables, FL (1976).
12. T. N. Veziroglu and W. Seifritz, eds. *Hydrogen Energy Progress* (4 vols.), *Proceedings of the 2nd WHEC*, Pergamon Press, Oxford (1979).
13. T. N. Veziroglu, K. Fueki and T. Ohta, eds. *Hydrogen Energy Progress* (4 vols.), *Proceedings of the 3rd WHEC*, Pergamon Press, Oxford (1981).
14. T. N. Veziroglu, W. D. Van Varst and J. H. Kelley, eds. *Hydrogen Energy Progress IV* (4 vols.), *Proceedings of the 4tlı WHEC*, Pergamon Press, Oxford (1982).
15. T. N. Veziroglu and J. B. Taylor, eds. *Hydrogen Energy Progress V* (4 vols.), *Proceedings of the 5th WHEC*, Pergamon Press, Oxford (1984).
16. T. N. Veziroglu, N. Getoff and P. Weinzierl, eds. *Hydrogen Energy Progress VI* (3 vols.), *Proceedings of the 6th WHEC*, Pergamon Press, Oxford (1986).
17. T. N. Veziroglu and A. N. Protsenka, eds. *Hydrogen Energy Progress VII* (3 vols.), *Proceedings of the 7th WHEC*, Pergamon Press, Oxford (1988).
18. T. N. Veziroglu and P. K. Takahashi, eds. *Hydrogen Energy Progress VII* (3 vols.), *Proceedings of the 8th WHEC*, Pergamon Press, Oxford (1990).
19. T. N. Veziroglu, C. Derive and J. Pottier, eds. *Hydrogen Energy Progress IX* (3 vols.), *Proceedings of the 9th WHEC*, International Association for Hydrogen Energy, Coral Gables, FL (1992).
20. D. L. Block and T. N. Veziroglu, eds. *Hydrogen Energy Progress X* (3 vols.), *Proceedings of the 10th WHEC*, International Association for Hydrogen Energy, Coral Gables, FL (1994).
21. T. N. Veziroglu, C.-J. Winter, J. P. Baselt and G. Kreysa, eds. *Hydrogen Energy Progress XI* (3 vols.), *Proceedings of the 11th WHEC*, International Association for Hydrogen Energy, Coral Gables, FL (1996).
22. J. C. Bolcich and T. N. Veziroglu, eds. *Hydrogen Energy Progress XII* (3 vols.), *Proceedings of the 12th WHEC*, International Association for Hydrogen Energy, Coral Gables, FL (1998).
23. John O’M. Bockris and T. N. Veziroglu with Debbi Smith. *Solar Hydrogen Energy: The Power to Save the Earth*, Optima, London (1991).
24. T. Nejat Veziroglu and Frano Barbir, *Hydrogen Energy Technologies,* UNIDO, A1400. Vienna, Austria (1998).

25. T. N. Veziroglu and F. Barbir. “Hydrogen Energy System: A Permanent Solution to the Global Energy-Environmental Problems,” *35th IUPAC Congress Proceedings*, Istanbul, Turkey, August 13–15, 1995.
26. W. Fulkerson, R. J. Judkins and M. K. Sanghvi. “Energy from Fossil Fuels,” *Scientific American* 263(3), pp. 129–135 (1990).
27. T. N. Veziroglu, I. Gurkan and M. M. Padki, “Remediation of Greenhouse Problem through Replacement of Fossil Fuels by Hydrogen,” *Int. J. Hydrogen Energy* 14(4), April (1989).

ENERGY POLICY IS TECHNOLOGY POLITICS – THE HYDROGEN ENERGY CASE

CARL-JOCHEN WINTER*
Ueberlingen, Germany

Abstract: As a typical example for an energy poor though technology rich industrialized nation, Germany's energy supply status shows both an accumulation of unsatisfactory sustainabilities putting the nation's energy security at risk, and a hopeful sign: the nation's supply dependence on foreign sources and the accordingly unavoidable price dictates the nation suffers under are almost life risking; the technological skill, however, of the nation's scientists, researchers, engineers, and industry staff materializes in a good percentage of the indigenous as well as the world's energy technology market, at present of some US$ 2,000 billion p.a.

Exemplified by the up and coming hydrogen energy economy this paper tries to advocate the 21st century's energy credo: energy policy is energy technology politics! Energy source thinking and acting is 19th and 20th centuries, energy efficient conversion technology thinking and acting as well as thinking and acting in terms of renewable energy and hydrogen energy utilization link-by-link along the complete energy conversion chain is 21st century!

Hydrogen energy is on the verge of becoming the centrefield of the world's energy interest. Hydrogen energy and its technologies are an epoch making development of necessity. Hydrogen energy is key for decarbonization and, thus, sustainabilization of fossil fuels, and as a storage and transport means for the introduction of otherwise non-operational and, thus, non-traded huge renewable sources in the world energy market. What, however, is the most important criterion among all others is hydrogen's thermodynamic ability to exergize (energy = exergy + anergy, with exergy as energy's maximum percentage of delivering technical work) the energy scheme, i.e., hydrogen's ability to make more technical work (exergy) available out of

---

* Prof. Dr.-Ing. C.-J. Winter, Vice President - The International Association of Hydrogen Energy (IAHE); author's address: Obere St. Leonhardstr. 9, D-88662 Ueberlingen, Germany, Tel/Fax +49 7551 944 5940/1

J.W. Sheffield and Ç. Sheffield (eds.), Assessment of Hydrogen Energy for Sustainable Development, 33–49.

less primary energy! Hydrogen is the better part of the hydrocarbons; hydrogen adds value through their decarbonization, hydrogenation and, as a consequence, dematerialization. Hydrogen energy plus the appropriate technologies are harbingers of the energy world's clean globalization. Firsthand, hydrogen energy and, in particular, hydrogen energy technologies, are to become part of industrialized nations', and here particularly Germany's, national energy identity; accordingly, national energy policy as energy technology politics needs to grow into the nation's awareness as common sense! Otherwise, Germany seems ill-equipped energetically, and its well-being hangs in the balance. Hydrogen energy grows into the nation's raison d'état! Hydrogen energy helps reinstitutionalize energy realpolitik, it is aiming high, though the goal is absolutely within reach!

1. Germany after 200 years of its energy history – bitter facts and a hopeful sign

1.1. FACTS – AN ACCUMULATION OF ENERGY SECURITY RISKS AND UNSATISFACTORY SUSTAINABILITIES

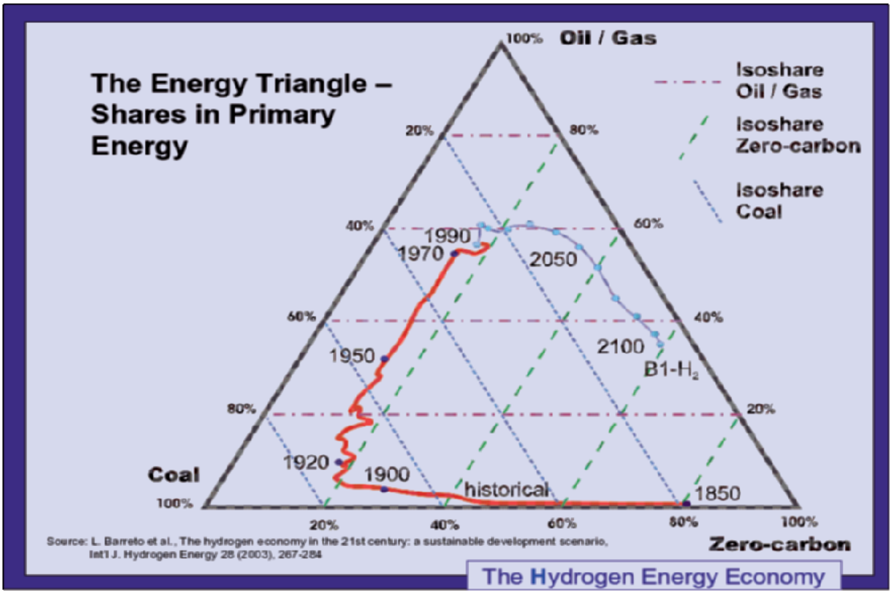
- The national energy efficiency is ~30% (world ~10%).
- The national exergy efficiency is ~15% (world a few %).
- Primary energy (raw materials) import dependence reaches ~75%.
- Dependence on crude oil imports for transport is ~97%, on natural gas 84%, and on hard coal 60%.
- New power plants supplying ~40,000 MWe will be required in the next few decades.
- In operation is a centrally organized national energy scheme; significant decentral energy potentials are lying fallow – more or less.
- No consistent future national energy concept is visible.
- According to the German Bundestag's decision, within 20 years there will be no more fission energy production.
- Renewable energies and national hard coal are highly subsidized.
- The nation "enjoys" Europe's second highest prices for electricity in industry.
- It has an environmental balance that is only just acceptable.
- And a climate change status which is – almost solely – only thanks to the post-unification deindustrialization of the former East Germany.

1.2. A HOPEFUL SIGN – VIRTUAL ENERGY, UNAPPRECIATED, BUT EXISTENT

- The important resource of the technology skill of the nation's engineers in a world energy market worth US$ 2,000 billion p.a., with an annual growth rate of 3%. Germany's energy industry provides all sorts of energy conversion equipment on the world market, such as the world's highest-efficiency power plants, refineries and nowadays in addition fuel cells and wind or solar photovoltaic energy converters, as well as efficiency-increasing and exergizing technologies which, of course, are not energy in themselves, but are just as good as energy because they deliver more energy services from less primary energy.

2. The energy history of humankind

- Never was only one energy form utilized, and a novel energy never completely replaced the "old ones", the continuously growing demand needed them all; consequently, energy diversity increased – and continues to increase. Humans lived and worked in energy centuries: until far into the 18th century the renewable energies of the first solar civilization were in use exclusively; the 19th century was the century of coal; towards its end and then in the 20th century oil, natural gas and, later, nuclear fission were added. And what will the 21st century bring? Three additions are clearly visible: (1) energy and above all exergy efficiency gains from link to link along the entire energy conversion chain, (2) the renewable energies, now of the second solar civilization, and (3) the secondary energy hydrogen, before the 22nd century becomes the first century of full energy sustainability – perhaps (Figure 1).
- The oligopolization of the fluid fossil fuels oil and gas grows. More and more energy sources are in less and less responsible hands – a not too comfortable situation for the world economy at large and, particularly, for nations depending on energy imports for an extremely high percentage of their need – to put it mildly! The bulk of the world's oil and gas resources is concentrated in the "energy strategic ellipse" spread out from the Persian Gulf via Iran, Iraq, and the central Asian states to as far as Siberia. It so seems that regional natural fossil energy source availability and the political stability of that region are mutually exclusive!?



Source: L. Barreto et al., The hydrogen economy in the 21st century: a sustainable development scenario, Int'l J. Hydrogen Energy 28 (2003), 267-284

Figure 1. The Energy Triangle – Shares in Primary Energy

- Nations rich in both indigenous energy (raw materials) and energy technology skills are seldom. Germany and Europe are poor in energy (raw materials), but rich in energy efficient technologies; historically, the one was conditional for the other: technology wealth grew out of energy poorness. For example, the German federal states of Baden-Württemberg and Bavaria, both absolutely energy poor but technology rich, as well as Switzerland or Japan, all now belong to the wealthiest regions in the world!
- For long, energy globalization has been a fact. Truly, today's world energy supply is a global supply; contributions from local, regional, or even national sources steadily lose importance. The consequence: the policy challenges facing efficient energy conversion technologies grow, and so does the need for an environmentally and climatically clean, storable, and transportable chemical energy carrier: hydrogen!

3. The energy centuries of mechanization, electrification and hydrogenation ("Technologies compete not fuels" David S. Scott)

- It is the energy technologies which compete with each other, not really the energy raw materials: technologies are the opening valves for fuels! No novel energy's entry into the energy supply and utilization scheme without prior availability of the appropriate technologies for their exploitation, storage and transport, and finally utilization!

- Coal was industrially unmined and almost useless until James Watt's steam engine could provide mechanical energy for the workplaces of English industry in the late 18th century: hand labour in manufacturing began to fade out, the mechanization of industry began.
- A good 100 years later, at the turn of the 19th and 20th centuries, electrification came into existence with Siemens' electrical generator and Edison's light bulb.
- Oil markets did not begin to develop before the petroleum lamp, later the Otto and Diesel engines, were on the market.
- Natural gas faced an easy task, since its markets could build on city gas or coke gas infrastructures; natural gas burner equipment and the gas turbine were added, and in these days the fuel cell is being developed as another opening valve for hydrogen rich natural gas or coal gas or biogas or – finally, pure hydrogen.
- Uranium was useless as long as the nuclear fuel energy cycle was not closed via uranium mining, uranium chemistry, uranium enrichment technologies, fuel rod production, nuclear reactors, to final storage or plutonium extraction of spent fuel rods.
- On principle, renewable energies are without operational primary energy raw materials per se, their conversion technologies are one and all – such as the wind energy converter, the photovoltaic cell, the hydro turbine, the heat pump, the biomass converter, or the solar-thermal power station.
- Most exciting is that human technology skill makes possible energy conversions which do not take place in nature! Examples are the solar-electric photovoltaic cell or the chemo-electric fuel cell, which apply in new ways dormant physical principles to energy conversion, so far non-operational in macroeconomic terms. It can be expected that further dormant novel energy conversion technologies await discovery – another mosaic stone in the "Energy Policy is Technology Politics" scheme!
- Technology-supported energy efficiency gains make more energy services from less primary energy sources which, in modern energy thinking and acting, is not the ultimate goal, but a means to an end, producing as many energy services from as little as possible of that primary source: examples are the gas- and steam-turbine combined heat and power cycle (CHP) with at present a (nearly) 60% electrical efficiency and potentially more, or the solar-hydrogen operated zero-energy home (zero = operational energy from the market), or the near 50% tank-to-wheel efficient

hydrogen fuelled optimized internal combustion engine (ICE). In any case, it is the efficient technologies which reduce the amount of primary energy raw materials necessary for the generation of more energy services. The Enquête Commission of the German Bundestag "Protection of the Earth's Atmosphere" in a unanimous vote stated that with marketed relevant technologies on hand in Germany the country could well be "operated" at a national energy efficiency of 60% instead of today's 30%. That is not a matter of available technologies, it is a matter of political will and economic viability!

- And finally, the secondary energy hydrogen, like the other major secondary energy within the mix, electricity, will be invariably generated from any conceivable primary energy: the hydrogenation of energy starts. Again, the technologies are dominant for hydrogen, particularly for its production, storage, transportation, or dissemination, finally for its end use. "Ecological reasoning not only asks for avoidance and *renunciation, but also and primarily for unparalleled technological development*"; no doubt, the road to the hydrogen energy economy is such an unparalleled technological development!
- Visions are conditional for any wise energy policy. Here, the vision reads: energy policy is technology politics! Albert Einstein's words, "*Visions are more important than knowledge because knowledge is finite*" are supplemented by Ernst Bloch's "*Visions need timetables!*" – or in other words: "*Visions without action degrade to illusions!*" Truly, the introduction of the hydrogen energy economy is one of these actions! And words shape actions!

4. Hydrogen energy, really? Hydrogen energy!

- "The hydrogen energy economy is not meant to take the world energy system to heaven, but to save it from fading out and from an environmental and climatic disaster" (Dag Hammarskjöld, paraphrased). World politics, economy, and ecology are the drivers, hydrogen technologies are the enablers.
- Hydrogen stands at the end of the historical trend of energy fluids from coal via oil and gas to hydrogen, from solids to liquids to gaseous energies, from *high carbon via low carbon to no-carbon, and consequently from (almost) no-hydrogen via low hydrogen to high hydrogen*! Year by year, with the ongoing switch from relatively less coal via more oil and gas, the relative carbon content of energy is continuously decreasing, and the hydrogen content grows: the atomic hydrogen/carbon ratios for coal, oil, natural gas, and hydrogen are $<1:2:4:\infty$. Decarboni-

zation of energy (relatively less carbon) and its hydrogenation (more hydrogen), and, since the atomic weights of carbon and hydrogen are 12 and 1, respectively, its dematerialization are in full swing. In the last 100 years the tonnage of carbon relative to the unit of energy used worldwide came down by 35% (Figure 2).

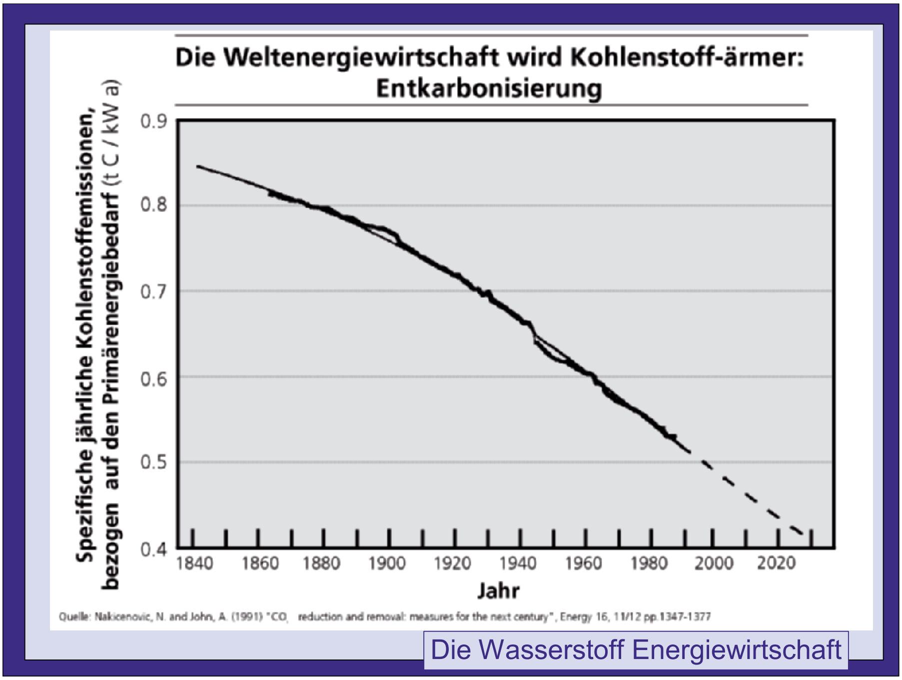


Figure 2. The World Energy Economy getting poorer in coal: Decarbonization

- Already today, two of three atoms of fossil fuels burnt are hydrogen atoms. Grid delivery of energy is increasing; it has become a standard and furthers energy ubiquity that applies to both secondary energy carriers: hydrogen energy and electricity.
- Taking on hydrogen is not really new: for long, the hydrogen economy which uses hydrogen non-energetically as a material commodity has been a profitable business. Particularly active are the commercial gas industry, hydrogen chemistry, and oil refineries. Clients are numerous and versatile: ammonia and methanol production, desulphurization of Diesel and reformulated hydrogenized gasoline fuel, glass manufacturing, the electronics and food industries, and many others. Energetically, the hydrogen amount needed in the refineries' operational process worldwide compares well with some 200 GW_{th}, which seems a rather big number; it is a little less, however, than the capacity of Germany's electrical online

power alone. Now, the switch to the hydrogen energy economy is ante portas. So far, only one industrial branch uses hydrogen energetically (and depends on it!), the space launching business (and German submersibles electrically propelled by hydrogen and oxygen fuelled fuel cells), both of which would not even exist without hydrogen as the fuel.

- Hydrogen contributes to the benignity of the environment and climate; hydrogen has the absolutely lightest ecological footprint: hydrogen, like electricity, belongs to the secondary energy realm; once generated, it is environmentally and climatically clean over the entire length of the subsequent energy conversion chain. And, hydrogen is environmentally and climatically neutral, if generated from renewable energies or from fossil fuels, in the latter case with capture and sequestration of co-produced carbon dioxide and its usage or final storage or mineralization such that release into the atmosphere is avoided. Electrolytic hydrogen comes from water and recombines to water again. The hydrogen energy economy concentrates the capture and sequestration of pollutants and greenhouse gases in one, the first, development step, the primary-to-secondary energy conversion step at the beginning of the hydrogen energy conversion chain. All the following steps down to the very end of the chain are environmentally and climatically clean! Clean secondary energy carriers make it unnecessary to burden the energy end-user – in most case a lay person – with the ecologically responsible disposal. It is to be expected that there will be no more widespread atmospheric or surface dissemination of pollutants.
- Hydrogen stimulates a technology innovation impetus par excellence: hydrogen supported fuel cells add to the accustomed thermoelectric conversion (turbines, reciprocating piston engines, others) a novel technology principle of energy conversion: fuel cells' chemo-electric conversion. Hydrogen fuelled fuel cells are compact with a rather small geometrical footprint, and their module output ranges from watts to a few megawatts over seven orders of magnitude; they are highly efficient, with low noise, without moving parts and, thus, without major dynamic forces or mechanical momentum; they are environmentally and climatically clean. They are being developed for portable electronics, for stationary combined heat, cold and power tri-generation, for mobile on-board electricity delivery in the electrical grids (APUs – auxiliary power units) and the drive trains of autos, buses, trucks and lorries, locomotives, later also for seagoing vessels and airplanes. Most of the technologies are already in their demonstration status, thousands of demonstration vehicles are on the road; the next steps into decisive economic viability are ahead, they need time, though (Figure 3).

Fuel cells have already been demonstrated in every imaginable application

- Automobiles
- Buses
- Scooters
- Bicycles
- Golf carts
- Space
- Airplanes
- Locomotives
- Boats
- Underwater vehicles
- Distributed power generation
- Cogeneration
- Back-up power
- Portable power

Source: F. Barbier (2005)

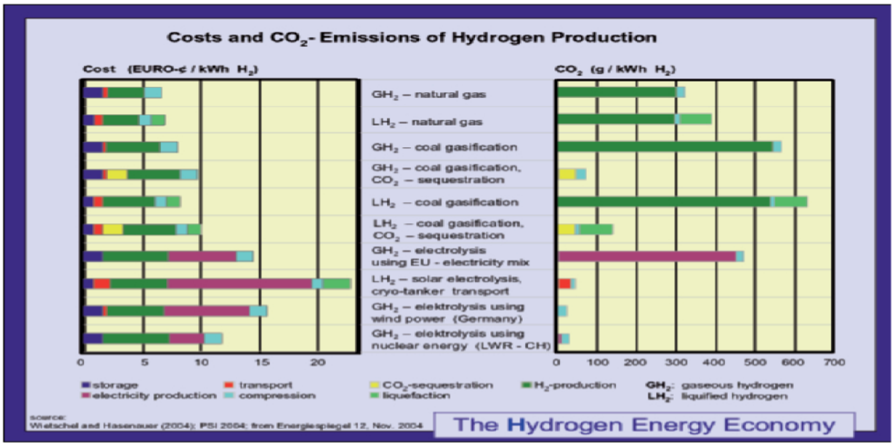
The **H**ydrogen Energy Economy

Figure 3. Applications of fuel cells

- Both secondary energy carriers: hydrogen and electricity, move the centre-of-interest within the energy conversion and utilization chain towards its back end: “all’s well that ends well.” But here, at the downstream end of the chain where the energy users live, energy cannot remain in the hands of 82 million laypersons (in Germany); professionalization is urgently needed. Professionalization as we are accustomed to have it at the beginning of the nation’s energy conversion, where the mines, the refineries, the power stations and the like are in the reliable hands of professionals.
- Hydrogen decentralizes the energy system: hydrogen-supported fuel cells provide heat, cold, and electricity where it is asked for – on the spot. Nationwide electricity wiring and cabling, sometimes over thousands of kilometres, which in Germany stands for a loss of some 4%, and sometimes much more in other parts of the world, becomes less necessary. Electricity capacities from the back end of the conversion chain start competition with electricity from the traditional front end. IT-controlled virtual power from millions of small-sized fuel cell electricity generators in residential energy systems, in office buildings, or small and medium-sized industries, much later even in autos parked and run as

power plants when not moving, easily sums up to the 100,000 MWs in Germany centrally online today: a thought experiment. Thought experiments seldom become real, but a real kernel is mostly in them somewhere. Here, that kernel reads: is it really responsible vis-à-vis urgently needed energy sustainabilization to negate a virtual electricity capacity of an amount almost equal to the traditional centralized online capacity?!

- Hydrogen enables an entry into the world energy trade for the huge renewable energy potentials of the world not or not fully operational so far: Patagonian wind sources, Canadian hydropower, Australian solar power and the like will be freed from their exclusive local, at most regional, utilization so far. Electrolytic hydrogen stores them and transports them worldwide; they become globally available and another powerful competitor in the electricity or hydrogen markets.
- Hydrogen offers the chance of decarbonization of fossil fuels already at the mine mouth or on top of the oil or gas field (Figure 4). Via hydrogen, shipping of coal, oil, or gas, gaseous or liquefied, over global distances will become environmentally and climatically clean. The energy seller takes over from the energy buyer the task to clean up the fuels intended for global trade. Henceforth, only hydrogen energy, gaseous or liquid, will be traded. Catastrophic oil tanker accidents with their devastating consequences will become a thing of the past. A time consuming diplomatic masterpiece is foreseeable, moving the guarantee for environmental and climatic cleanness from the energy buyer to the energy seller nation. The seller may be compensated with the added value related to the hydrogenation and, thus, sustainabilization of his product.



source:
Wietschel and Hasenauer (2004); PSI 2004; from Energiespiegel 12, Nov. 2004

Figure 4. Costs and CO_2 emissions of hydrogen production

- Hydrogen from coal offers coal a renaissance, returning – now in the form of gaseous, and in a next step, liquefied hydrogen – to the two end-user realms of transport and residential energy (which in Germany sum up to two-thirds of the nation's end energy demand!) from where it had to almost completely withdraw with the advent of oil and gas. Today, electricity and steel keep coal alive, tomorrow hydrogen will be giving clean coal a new life!
- Nature does not alter its laws, following them needs no justification. Hydrogen slows down the physically unavoidable entropy increase (= the energy degradation accompanied with each and every conversion step). Hydrogen is the better half of the hydrocarbons, and for renewable energies it is a storage and transport medium for continental, oceanic, even global distances. The two secondary energies, hydrogen and electricity, are interdependent via electrolysers and fuel cells. Shipping electricity is shipping electrons; shipping hydrogen is shipping electrons with a proton attached to it.
- In short: hydrogen is not a issue of tackling the day's unpleasant problems, as urgent as they may be, hydrogen asks for far-sightedness, hydrogen is a century's enterprise; hydrogen needs courage, not cowardice; big money, not small change; continuity, not ups and downs; and, perhaps the most important, conviction, not ambivalence!

5. Exergy, a few minutes of applied thermodynamics: it is needed, not only here!

- Energy = exergy + anergy. Exergy is the ability to perform technical work, exergy can be converted into any other energy form, anergy cannot. With a national exergy efficiency of c.15% in Germany, what the nation has really achieved in some 200 years of history of anthropogenic energy is an anergy economy, with a small addition of exergy – truly a bitter lesson! (With c.10% energy efficiency and a few percent exergy efficiency the world's situation is even grimmer!)
- Quite similar to electricity, its running mate in the secondary energy realm, hydrogen with the help of fuel cells exergizes the energy system; it makes available (in US literature exergy is sometimes called energy availability) more technical work (exergy) out of energy, it minimizes anergy. Examples: residential central heating system boilers are energetically excellent, almost 100% of the chemical energy of the fuel is converted into heat. They are exergetically, however, miserable, because it is exergetically absurd to generate 1,000°C combustion temperature simply in order to provide some 60–70°C room radiator temperature!

Hydrogen fuelled fuel cells, instead, with some 30% efficiency generate firsthand electricity (= pure exergy!), and the leftover heat still suffices to heat the house most of the year. Likewise, it is absurd to run on standstill at a red traffic light the on-board electrical generator of, say, 5 kW with the help of an internal combustion engine of some 100 kW; replaced by an engine-independent hydrogen fuelled fuel cell, the electricity supply is guaranteed even if the engine is cut. Again bitter to say, even after 100 years of automobilization the modern automobile generates mechanical traction (=exergy) with only 20–30% of the fuel's energy at most, the rest becomes heat. In reality the auto is – so to speak – a mobile stove which with at best some 20–30% of its on-board energy is also able to move humans or freight from A to B. Generally, when buying auto fuels it is done for kilometres, not for energy! And hydrogen stands for more kilometres. And a last example: geothermal power plants, because of the rather low temperature of the steam coming off the bore hole, have only meagre efficiencies of some 10–20%. Upgrading the steam's temperature to the usual steam power plant's 560–580°C with the help of a H_2/O_2 steam generator exergizes the system and delivers plant efficiencies which are customary for steam power plants, 40% or more!

6. Rebuttals, arguments

- At a standstill, the energy of motion is nil. Concentrating only on preserving assets leads to being overtaken. Innovations are the rule, deviating from that rule means slipping back. This kept in mind, the start into the hydrogen energy economy, of course, also shows counter-arguments and concerns! Addressing these concerns will help hydrogen energy succeed.
- Energy needs time. More time than is usually anticipated! Examples: the development of nuclear fission began with Otto Hahn's first nuclear fission experiment 1938 in Berlin, and has reached – now after almost 70 years – some 7–8% operational primary energy equivalent worldwide. Or another example, the gas turbine had its first application in the 1940s as the jet engine on-board Junkers' or Messerschmitt's aircraft; down on earth it today delivers, together with a steam turbine in combined cycles, an impressive 60% energy efficiency, or in future even more. And further, when in due time a high-temperature fuel cell will be added, a triple HT-fuel cell-gas turbine-steam turbine combined cycle's energy efficiency of some 70% will not be illusive! Can we really expect that hydrogen energy will be doing it any faster?

- As a rule, many decades up to half a century are needed for novel energies in the mix to deliver significant irreversible and indispensable contributions. The consequence: making a resolute start is almost always too late!
- "*Energies*-of-change," "*Technologies-of-change*" *are the rule; presservation of what came down to us is the exception.* An exception with sometimes immense negative consequences, as could be seen in the fading away of Germany's wharf industry in the North, or the clock industry in the Black Forest, or today's cellphones, cameras, portable electronics and the like, all are hurting, though they teach us beneficial lessons, if taken to heart!).
- "*Politics-of-change*" must anticipate and be visionary, but seldom are. *J.A. Schumpeter's "Innovations are the driving force for economic growth"* was valid, is valid, and will be valid – and seems to be forgotten!
- The consequence for the hydrogen energy economy: www.itsHYtime.de! It is almost always too late to start innovations and see them through. It is hydrogen time, it is high time to embark on the hydrogen energy economy and further its build-up! The invariable market results can be expected in years at the earliest, perhaps rather in decades. Decades are the typical time constraints of novel energies.

7. Added value

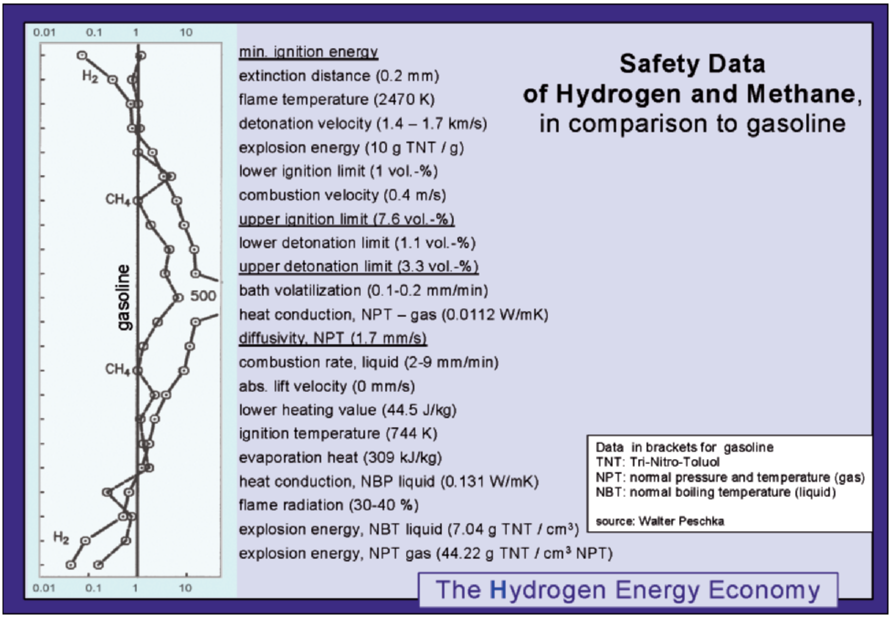
- Innovations achieve a breakthrough on the market if they demonstrate affordable added value. The triangulation of academia, industry, and politics is key.
- Not at all an euphemism, the added value of the hydrogen energy economy and its technologies is wide ranging and can be summarized as:
  - Its undoubted environmental and climatic benefits and its essential contribution to energy sustainability
  - The exergizing of the energy system: obtaining more useful technical work out of less energy
  - The slow-down of thermodynamically unavoidable energy degradation (=the entropy increase)
  - Making "national" energy operational in the form of national energy science and engineering skills
  - The reduction of primary energy raw material import dependence and, thus, the avoidance of price dictates, at least partially
  - Stimulating the export of innovative, efficient energy technologies

- Decentralizing the national energy system and thereby activating so far dormant downstream energy capacities and enabling competition with the operational centralized system
- The introduction of huge, so far untapped renewable energy sources into the world's energy trade
- The decarbonization of fossil fuels which, thus, become climatically as clean as renewable energies already are
- The professionalization of the energy realm at the end of the energy conversion chain

8. Safety of hydrogen in comparison to current fuels

Is hydrogen energy safe? First of all it is necessary to remind ourselves, even the engineers among us, that never and under no condition are technologies absolutely safe. That applies to energy technologies and here hydrogen energy technologies, too. Each and every energy material or energy technology adheres to its specific relative safety attributes. Minor or major positive and negative safety aspects are related to more or less all elements within the anthropogenic energy scheme. In addition, these aspects are dependent on time, location, and special conditions, e.g., coal mines in one country may enjoy an extremely high safety standard, whilst the standards another country suffers under may be disagreeably low; or, another example, a double-hull oil tanker's safety level is much higher than that of mono-hull tankers, but, so far the latter make up nearly 100% of the entire world fleet; or a last example, although renewable energies have a very low impact, if any, on the anthropogenic greenhouse effect, their contribution to the world mix grows rather slowly.

Now, how about hydrogen energy and safety? The safety relevance compares well with that of more or less all of its other competitors: it has safety advantages and disadvantages. Two overruling advantages are its lack of impact on the anthropogenic greenhouse effect, and its lack of radiotoxicity and radioactivity releases to the geosphere. Materially, electrolytic hydrogen forms a closed loop, it comes from water from the earth's inventory and recombines with oxygen (from air) to water again given back to that inventory. On principle, hydrogen from fossil fuels with carbon capture and sequestration or hydrogen from renewable energy compare well with respect to environmental and climatic cleanness. The comparatively low ignition energy of hydrogen, its wide ignition range, and its very high diffusivity in air, all have specific safety relevance (Figure 5).



Safety Data of Hydrogen and Methane, in comparison to gasoline

min. ignition energy
extinction distance (0.2 mm)
flame temperature (2470 K)
detonation velocity (1.4 – 1.7 km/s)
explosion energy (10 g TNT / g)
lower ignition limit (1 vol.-%)
combustion velocity (0.4 m/s)
upper ignition limit (7.6 vol.-%)
lower detonation limit (1.1 vol.-%)
upper detonation limit (3.3 vol.-%)
bath volatilization (0.1-0.2 mm/min)
heat conduction, NPT – gas (0.0112 W/mK)
diffusivity, NPT (1.7 mm/s)
combustion rate, liquid (2-9 mm/min)
abs. lift velocity (0 mm/s)
lower heating value (44.5 J/kg)
ignition temperature (744 K)
evaporation heat (309 kJ/kg)
heat conduction, NBP liquid (0.131 W/mK)
flame radiation (30-40 %)
explosion energy, NBT liquid (7.04 g TNT / cm³)
explosion energy, NPT gas (44.22 g TNT / cm³ NPT)

Data in brackets for gasoline
TNT: Tri-Nitro-Toluol
NPT: normal pressure and temperature (gas)
NBT: normal boiling temperature (liquid)

source: Walter Peschka

The Hydrogen Energy Economy

Figure 5. Safety Data of hydrogen and methane in comparison to gasoline

Since hydrogen, like electricity, is secondary energy, the energy chain's front end converters (the power plants, the reformers, the electrolysers, the liquefiers and others) have to be taken into the safety considerations, too!

Of particular indirect safety relevance is the fact that hydrogen-fuelled fuel cells exergize the energy scheme. They make more exergy out of less primary energy, or in other words, the exergy production needs less primary energy. Less energy is a positive safety aspect per se.

And a last very specific indirect safety aspect is allocated to solar hydrogen, i.e., to hydrogen from renewable energies. The primary energies are sunlight, wind, hydro, etc. Water for the electrolysis is taken from the earth's water inventory and is, after recombination with oxygen, returned to that inventory qualitatively and quantitatively unaltered. The solar water-to-hydrogen-to-water cycle is the only closed material cycle of any human energy scheme (Figure 6). All the others are open systems: they take something irrecoverable from the earth's crust, convert it chemically or nuclearly, and return it to the biosphere, sometimes toxic, sometimes radioactive, and sometimes of negative environmental or climatic influence.

9. In summary

Energy is never a monopole, energy is a dipole consisting of the primary energy raw materials and the efficient technologies which make a maximum

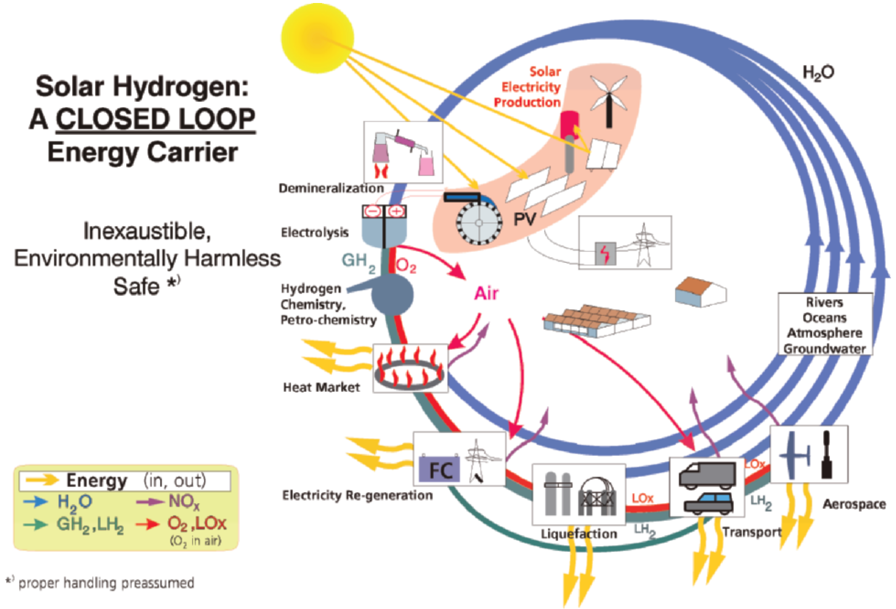


Figure 6. Solar Hydrogen: A Closed loop energy carrier

of energy services out of a minimum of those materials. With Germany dependent on imports to meet three quarters of its energy demand, wise energy related foreign policy is vital. All in all, the "forgotten pole" – efficient energy technologies along the complete energy conversion chain – compares well with energy; it is national "energy" for the energy poor country. The technology pole enables the country to compensate for the imponderabilities of potentially instable foreign energy markets. Efficient energy technologies are to become almost part of Germany's national identity. Wise and far-sighted national energy technology policy needs national common sense. Otherwise Germany would be ill prepared for what the energy world will encounter down the road!

Does hydrogen energy matter? Does it matter that hydrogen energy does not matter –so far?

What has to happen in order to create an affordable market from all the aforementioned technology related, in particular hydrogen energy technology related, arguments within a reasonable time? Addressing concerns will help the project succeed. Democratic communities require informed and aware voters, enterprises, and – not least – politicians. Getting there is a long-term process. It is necessary to keep the dispute on the hydrogen energy economy boiling gently, though continuously, and with an upward pointing positive gradient. Thinking and acting in terms of energy raw materials is 19th and 20th century, thinking and acting in terms of efficient energy technologies is 21st century! And no doubt, hydrogen energy technologies belong to the 21st century! Far-sightedness is in need, not present-day inconveniences tackling.

"It takes about 50 years for an idea to break through and become vogue, no one likes an intruder particularly when he is upsetting the commonplace" (Horace Kallen, 1972). Germany seems to be taking a back seat in establishing the hydrogen energy economy. Japan, the USA, Canada are the forerunners. In Germany the federal states of North Rhine-Westphalia, Bavaria, and Baden-Wuerttemberg are at the forefront.

Nature's does not change its laws. Nature's and the German Bundestag's laws increasingly diverge, and it is not reasonable to expect that nature's laws will be the ones to yield. In the search for technological knowledge the state can certainly lend a helping hand, financially and organizationally by structuring the appropriate energy framework, but in any case, it should not block the way! Wise German national energy policy asks for energy politics which give hydrogen energy its due.

PS: Regularly in springtime of even-numbered years the International German Hydrogen Energy Congress is scheduled; the next in the series will be in Essen, Germany, in early 2008.

The 18th World Hydrogen Energy Conference 2010 will also be in Essen. For more information visit: www.itsHYtime.de, www.18WHEC2010.de (Figure 7), and www.H2Congress.de.

The 18WEC2010 Chair Proudly Announces

18th World Hydrogen Energy Conference 2010
in Essen, Germany, May 16 - 21, 2010

Under the auspices of: International Association for Hydrogen Energy

Organized by: Landesinitiative Zukunftsenergien NRW

Hydrogen Energy

At home in Essen
Innovating Germany,
Host of the Energy World

www.18whec2010.de info@18whec2010.de

In cooperation with:

See you 2010 in Germany, please mark your calendar!

The Hydrogen Energy Economy

Figure 7. 18th World Hydrogen Energy Conference announcement

HYDROGEN FROM RENEWABLES

NICOLAS LYMBEROPOULOS[1]
Centre for Renewable Energy Sources, 19th km Marathonos
Av., Pikermi, 19009, Attica, Greece

Abstract: A review is presented of the various pathways for producing hydrogen from renewable energy sources as well as of various installations in Europe for the development and testing of integrated renewables and hydrogen technologies. Detailed information is given on a recently completed wind-hydrogen installation at the wind park of CRES in Attica, Greece. A Strengths, Weaknesses Opportunities and Threats analysis is also presented for the production of hydrogen from renewable energy sources. This review is based on a study performed under an EC PTA contract (Lymberopoulos, 2005).

Keywords: hydrogen, renewables, review, SWOT analysis

1. Introduction

Energy security and environmental protection issues lead to the conclusion that in the long term hydrogen will become a significant energy carrier, where hydrogen is expected to replace a significant part of the gaseous and liquid fuels in use today in stationary and transport applications. In the medium term, hydrogen could act as a storage medium for the excess energy produced by renewable energy technologies (RETs), where, in combination with fuel cells, RETs can have an increased penetration and provide guarantied power in autonomous electricity systems.

There are many paths that can be used to produce hydrogen from renewables:

---

[1] Correspondence Contact: Nicolas Lymberopoulos, CRES, 19th km Marathonos Av., Pikermi, 19009 Attica, Greece

J.W. Sheffield and Ç. Sheffield (eds.), Assessment of Hydrogen Energy for Sustainable Development, 51–57.

- Hydrogen from renewable electricity sources (wind, solar, geothermal, hydro, wave) through electrolysis
- Hydrogen from biomass-derived fuels through reforming
- Hydrogen from biomass through gasification or pyrolysis
- Biological and biomimetic hydrogen production (biophotolysis and fermentation)
- High temperature solar thermochemical production – thermolysis
- Photo-electrochemical production – photoelectrolysis

Electrolysis and reforming are well-established technologies but there are still many issues that need to be addressed to optimise their application and/or integration with renewable energy technologies or fuels. The remaining pathways however, are still in an early development phase, characterised by low efficiencies but also great potential for improvement. These, along with biomass gasification that has still not been commercialised, are briefly described hereafter.

2. Novel hydrogen from renewables pathways

2.1. HYDROGEN FROM BIOMASS

Gasification technology has been under intensive development over the last two decades and large-scale demonstration facilities have been tested with varying success. Until recently, biomass gasification has been employed to produce electricity or heat, which rarely justifies the capital and operating costs. No commercial plants exist today to produce hydrogen from biomass; however the increasing demand for hydrogen could provide a new incentive for more research and development of biomass gasification projects in the near future.

2.2. BIOPROCESSES FOR HYDROGEN PRODUCTION

Bioprocesses for hydrogen production are in an early stage of development. Processes are usually split in those requiring incident sunlight (bio-photolysis and photo-fermentation) and those that can be carried out in the absence of light (dark fermentations).

The starting process of bio-photolysis is photosynthesis, in which water is split into oxygen, protons and electrons (water splitting) with the aid of sunlight. In photo-fermentation hydrogen is produced by anaerobic photosynthetic bacteria employing nitrogenase instead of hydrogenase to transfer reducing power from organic substrates, preferably organic acids.

In dark fermentations hydrogen along with organic acids and CO_2 are produced in the absence of sunlight from organic substrates, in particular wet biomass, under anaerobic conditions by bacteria employing hydrogenases. Major breakthroughs are required before bioprocesses can meaningfully contribute to "sustainable hydrogen" production. These breakthroughs are needed both in relation to biological conversion efficiencies and yields, for which advances in biology and genetic engineering should provide input, but also in relation to reactor technology, specifically the design and construction of cheap, large bioreactors.

2.3. HIGH TEMPERATURE SOLAR – THERMOLYSIS

Thermolytic water splitting is the generic term for multi-step thermochemical processes that use high-temperature heat to split water into hydrogen and oxygen. The interest in this route stems from the theoretical potential that such a process could convert high-temperature heat into hydrogen with 50% efficiency, thereby outperforming the efficiency of the electricity/ electrolysis pathway and offering an alternative to electrolysis for renewable hydrogen generation. Thermolysis is mostly proposed in the context of advanced nuclear reactors and features prominently in the Technology Roadmap for Generation IV nuclear reactors.

2.4. PHOTO-ELECTROCHEMICAL PRODUCTION

Photo-electrochemical processes can produce hydrogen in one step – splitting water by illuminating a water-immersed semiconductor with sunlight. This is basically the combination of photovoltaic cells (PV) with in situ electrolysis of water. There are two types of photo-electrochemical processes. The first uses soluble metal complexes as catalysts and mimics photosynthesis; however, currently there is minimal experience in this process. The second method uses semi-conducting electrodes in a photochemical cell to convert light energy into chemical energy. The semiconductor surface serves two functions, to absorb solar energy and to act as an electrode.

3. Existing RES-hydrogen installations

There are a significant number of large-scale installations in Europe where hydrogen is produced from renewables, mostly realised in the context of research and demonstration projects. These are presented in the following table:

TABLE 1. Major European hydrogen and renewables installations

Site or Project	Country	Year	Features
HYSOLAR	Germany & S. Arabia	1985	10 kW PV, 2 × 10 kW electrolysers and 350 kW PV, 350 kW electrolyser
SWB	Germany	1986	370 kW PV, 111–100 kW electrolysers, 5,000 Nm^3 storage, 79–42 PAFC 10 kW PEM
Stralsund	Germany	1990s	100 kW wind turbine, 20 kW electrolyser, 200 Nm^3 storage, 21 kW burner
FIRST	Spain	1990s	8.5 kW PV, 5.2 kW electrolyser, 24 Nm^3 metal hydride, 10 kW PAFC, 2.5–5 kW PEM
PHOEBUS	Germany	1990s	43 kW PV, 26 kW electrolyser, 3,000 Nm^3 storage, 6.5 kW alkaline fuel cell
PVFSYS	France	2000	3.6 kW PV, 3.6 kW electrolyser, 4 kW PEMFC
UTSIRA ISLAND	Norway	2004	600 kW wind turbine, 10 Nm^3/h, 48 kW electrolyser, 10 kW fuel cell, 55 kW gen set, 2,400 Nm^3 storage
RES2H2 (Greek test site)	Greece	2005	500 kW wind turbine, 25 kW electrolyser, 40 Nm^3 metal hydride storage, compressor, filling station
PURE	UK	2005	2 × 15 kW wind turbines, 15 kW electrolyser, 44 Nm^3 storage, 5 kW PEMFC

Further to the previous installations that were run in autonomous or grid-connected mode, a number of hydrogen production, storage and filling installations were realised in the EC project CUTE that operate from the grid running on “Green certificates”.

4. The RES2H2 Greek test site wind-hydrogen installation

A wind-hydrogen installation was developed at the wind park of CRES in the context of the RES2H2 project, funded by the EC. The installation consists of a 25 kW water electrolyser (5 Nm^3/h) supplied by Casale Chemicals SA, operating under 20 bar pressure and capable to withstand rapid variations of input power (20–100% of nominal capacity in 1 sec). Hydrogen is purified up to 99.98%v. Metal hydride tanks have been installed with a total rated storage capacity of 3.78 kg hydrogen (42 Nm^3), filled with the metal alloy $La_{0.75}Ce_{0.25}Ni_5$. The mass specific hydrogen capacity is 1.28%w for the alloy and 0.66%w for the complete tanks that were designed by FIT, Cyprus, and manufactured by Labtech SA, Bulgaria.

A single stage triple metal diaphragm hydrogen compressor by PDC Machines, USA was installed, designed for an inlet pressure of 10–18 bar and an outlet pressure of 220 bar. A small conventional tank, of 0.36 m^3 volume, acts as hydrogen buffer to smooth the pressure and flow variations at the compressor inlet resulting from the variable production rate of the electrolyser. The hydrogen filling station is composed of two high pressure cylinders and one 12-cylinder stack of 0.6 m^3 volume, with a total hydrogen capacity of 10.7 kg (120 Nm^3). The focus of research is the operation of the electrolyser, the metal hydride tanks and the compressor under variable power input as produced by the wind turbine, at the component and at the system level. The following figure shows the operation of the electrolyser under variable input conditions.

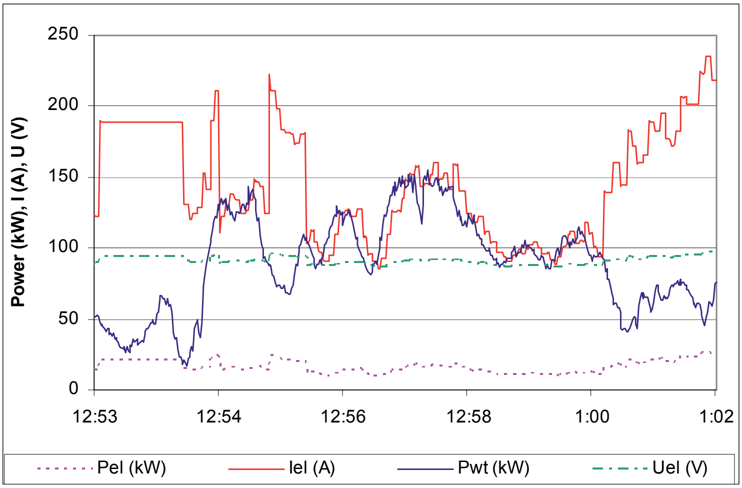


Figure 1. Electrolyser operation in time under variable power input

During the design and construction phase of the plant, several lessons were learned regarding transportation and installation issues, particularly important for plants to be erected in remote or poorly accessible areas. Preliminary results show an overall efficiency of 58%, calculated in relation to the hydrogen produced (high heating value) in relation to the power provided by the wind turbine (Varkaraki et al., 2006).

5. SWOT analysis for H_2 production from RES

Table 2 shows some of the strengths, weaknesses opportunities and threats for producing hydrogen from renewables.

TABLE 2. SWOT table for hydrogen production from renewables

Strengths	Weaknesses
Existing experience in handling compressed gases Seasonal energy storage without energy loss over time Able to handle power fluctuations and therefore ideal for integration with intermittent renewable energy sources Renewables can become "dispatchable" (guaranteed power from renewables) Potential for low and predictable O&M costs Reduced environmental impact compared to conventional energy systems	Technology immaturity of fuel cells and PEM electrolysers Low availability and high cost of small electrolysers Lack of component and system lifetime experience Low component efficiency Missing codes and standards Lack of after sales support Weak supply network (providers, installers, etc.) Lack of public awareness Lack of recycling and reuse schemes for hydrogen technology
Opportunities	Threats
Emergence of large-scale markets for hydrogen energy applications Already existing Stand-Alone Power Systems driven by Renewable Energy Sources in which hydrogen technologies can be incorporated as a replacement of batteries New job opportunities Diversification of companies involved in the energy sector Energy costs in conventional SAPS relatively high	Limited practical experience due to few true Stand-Alone Power Systems with hydrogen as an energy carrier (H-SAPS) installed Competing technologies have proved to be perfectly adequate Potential end users have no experience in H_2 technologies Inadequate legislative framework (standards, regulations, permissions of installation)

Acknowledgements

This review is based on work performed under EC contract NNE-PTA-2002-003/1.

References

Lymberopoulos, N., 2005, Hydrogen Production from Renewables, available from EC DG TREN at http://ec.europa.eu/energy/res/sectors/polygeneration_presentations_en.htm.

Varkaraki, E., Lymberopoulos, N., Zoulias, E., et al., 2006, Experiences from the operation of a wind-hydrogen pilot unit, CD ROM with proceedings from WHEC 16 / 13–16 June 2006 – Lyon France.

HYDROGEN FUELING SUSTAINABILITY OF ENERGY SYSTEMS, REGIONAL INTEGRATION, AND DEVELOPMENT: THE SAHARA WIND PROJECT

KHALID BENHAMOU*
Sahara Wind Inc., 32 rue Lalla Meryem Souissi, Rabat,
10100, Morocco

Abstract: With a 96% energy dependency from fossil fuel imports absorbing most of Morocco's export revenues, developing new sustainable energy consumption alternatives is of critical importance. Morocco's location on the main routes of migrant populations from Sub-Saharan Africa and being itself an exporter of immigrants, together constitute a significant security threat to both the region and NATO countries. The situation is fairly similar in Mauritania, whose scarce population is distributed over a vast territory in which access to electricity is difficult to grant through conventional grid infrastructures. Initially encouraged to provide employment in the relatively poor North Sea regions of Germany, the wind energy industry has emerged in the last ten years, as a major business providing most competitive prices of electricity even when operated under marginal European wind conditions. The trade winds that blow along the Atlantic coast from Morocco to Senegal represent the largest and most productive wind potential available on earth. Because of the erratic nature of winds, however, wind energy cannot be integrated locally on any significant scale unless far ranging, more advanced energy technologies are considered. Wind-electrolysis for the production of hydrogen offers great possibilities in absorbing large quantities of cheap generated wind electricity to maximize renewable energy uptake in the weak grids infrastructures of the region. This project is initiated by Sahara Wind Inc., a company from the private sector to serve as the foundation of an ambitious program supporting a vision highlighting possibilities for tackling energy scarcity and sustainable development objectives on a regional

---

* Khalid Benhamou, Managing Director, Sahara Wind Inc., 32 rue Lalla Meryem Souissi, Rabat, 10100, Morocco; tel: + 212 61 33 20 68; e-mail: kb@saharawind.com

J.W. Sheffield and Ç. Sheffield (eds.), Assessment of Hydrogen Energy for Sustainable Development, 59–73.

basis. This combination is likely to take advantage of the significant breakthroughs expected to happen in the near future regarding hydrogen technologies particularly through its association with large sources of renewable energies

Keywords: trade winds, renewable, wind energy, wind-electrolysis, electricity, grid stability, alternating current, high voltage direct current HVDC, European Union, electricity markets, infrastructure, applied research centers, carbon-free hydrogen, integration, pilot/demonstration project, Tarfaya, Morocco, Mauritania

1. Wind power, a vast renewable energy source

Close to the African coast, the junction of the Sahara desert with the Atlantic Ocean creates a zone of global energy exchange were the climate is dominated by steady winds: the trade winds. Local thermal winds coming inland from the Sahara's hot surfaces are actually superimposed upon the global trade wind system generated over the Atlantic and this creates one of the largest and steadiest wind systems available on earth. The higher latitude of such large wind resource (barely distant of 1,800 km south of the European continent) makes it rather compelling to envision the development of a clean, sustainable, and renewable integrated energy supply for our hemisphere.

The coastal plateaus that spread from Morocco through Mauritania and Senegal represent one of the largest, least populated, and windiest areas available worldwide, for the massive production of wind energy. These sites that are within reach of the European electricity grids can yield an expected yearly production of more than 4,500 full load hours (FLH), where recent wind measurements have been made. As a comparison, in Germany the world leader in wind power, the average productivity figures do not exceed 1,900 FLH. The size of the Saharan plateau's as wind catchments areas boasting far superior productivity figures is huge as the sole coastline, just to mention, spreads for over 3,000 km (Figure 2).

The Sahara wind resource that extends over thousands of kilometers of eroded plateaus and desert seacoasts (Figure 1), will take many years in order to be accurately evaluated. It represents to date, probably one of the world's largest untapped sources of wind energy. The size of this territory, the availability of the wind, and the relative geographical proximity of this region to Europe as one of the world's largest integrated electricity market provides tremendous development perspectives for the region's future and the wind energy industry overall.

In such context, the North West African vast endogenous wind resources are likely to provide significant opportunities for the region to cover domestic energy needs while supplying much larger electricity markets, namely that of the European Union to which these resources are currently linked via electricity gridline connections through the Iberian Peninsula. Provided an appropriate framework is developed, the broader North West African region could seize the industrial opportunities associated with the manufacturing of various equipment parts for the large-scale wind-project envisaged, to ensure full integration of local industries that are likely to lower individual component costs while generating jobs and boosting local labor markets (www.saharawind.com).

Figure 1. Arial view of Saharan coastal plateaus (source Sahara Wind Inc.)

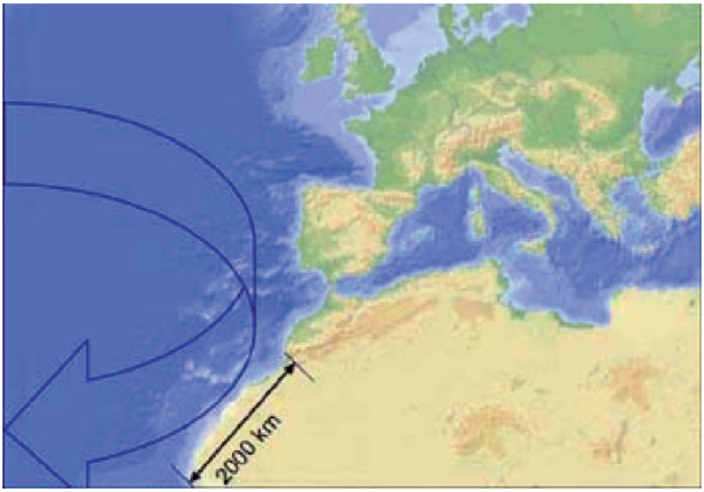


Figure 2. Global trade winds over North West Africa

2. Harnessing wind energy and its industry into regional energy markets

Although the trade winds that extend from Morocco through Senegal represent the largest wind potential available on earth, their erratic nature undermines any optimal utilization possibilities, to the extent that only a marginal proportion of that wind energy can be fed into the region's weaker grids infrastructure. This prevents local industrial and economic integration from taking place on any significant scale. Thus, a conventional approach to wind energy developments to feed smaller local electricity markets cannot enable a viable wind energy industry to be established, which could be essential for tackling the regions economic challenges currently under pressure from sub-Saharan migrant populations. A large renewable energy industry accompanied by many social benefits and job creations could indeed improve the region's economics particularly as it would be based on the sustainable utilization of one of the world's largest wind energy resources.

2.1. TECHNICAL LIMITATIONS: GRID STABILITY

With a total 4,508 MW of installed capacity, the size of Morocco electricity grid which represents North West Africa's largest, is a relatively small grid that can hardly cope with very large amounts of wind generated electricity before encountering grid stability problems unless precautions are taken. Common issues associated with high wind penetration rates such as generation intermittency, dispatching, power margins, reactive compensation, voltage, frequency regulation, flickers, harmonics, and all other effects are likely to create significant challenges on Morocco's grid. This problematic would be even more acute in Mauritania which has a grid extending over a very large territory (about twice the size of a country like France) with an installed capacity of less then 120 MW. Thus, it is important to mention that unless wind energy developments are part of a regionally integrated, comprehensive strategy where state-of-the-art energy technologies can be engaged, spare threshold capacities must be kept available for the grid infrastructure not to saturate.

2.2. INDUSTRIAL INTEGRATION

Unless a common strategy is developed, through elaborated energy research platforms with key local stakeholders brought together in a well-coordinated framework of action, experience has often shown that efforts aimed at introducing (new) wind energy technologies in developing countries amounts ultimately to the simple export of equipment through concessionary sources of financing and export credit packages. These policies have done very little in terms of local capacity building and industrial integration, for a technology that could have been promising in terms of economic returns, addressing energy security, and the creation of an accessible integrated industrial activity.

Ignoring a domestic wind power industry that was already building wind turbine prototypes of up to 250 kW of rated power five years ago, Egypt's public utility resorted to import 60 MW of Danish wind turbines that were barely twice that size. The utility's further expansions involved the purchase of several hundred megawatts of wind turbines for the Zafarana desert region involving Danish, German, and Japanese manufactured machines financed through their respective concessionary loans or export credit packages. With the growing size of the individual wind turbines whose technologies are less likely transferable and the saturation of Egypt's smaller electricity grid to further wind developments, the Egyptian utility has prevented any industrial integration from taking place, displacing some of the country's energy dependency from hydrocarbons to actual wind turbine imports, while making their servicing rather costly.

If lessons are not drawn from the aforementioned to develop a comprehensive and more sustainable approach, regional utilities from Morocco through Senegal may be led to follow the very same path whereas most wind turbine components can be easily integrated within the region's existing industrial infrastructures and know-how. Morocco's industries for instance already manufactures, assembles, and exports a variety of industrial components into world markets ranging from preassembled control cables, electro-switching equipment, transformers, spare parts, to automobiles.

As it is common practice within the wind industry, a first step toward developing wind energy in a remote market begins generally with the on-site manufacturing of wind turbine blade components that are too bulky, labor intensive, and fairly simple to build using simple moldings and wood epoxy coating techniques. It is rather compelling to notice in our case that the very molds used for building the "Cayucos" (long polyester vessels currently used in smuggling illegal immigrants out of Mauritania and Senegal into the Canaries Islands) are almost identical to the ones that would be required in the manufacturing of wind turbine blades. Thus the capacities do exist in the region; they just need to be appropriately mobilized and integrated for far ranging, better suited, more sustainable economic purposes.

2.3. REGIONAL ENERGY MARKETS

Since this region is located on the edge of one of the largest electricity grids (the European Union's grid), its vast renewable energy potential could be used to produce significant amounts of cheaply generated wind energy that could end up supplying European commercial electricity markets through appropriate electricity transfer infrastructures utilizing High Voltage Direct Current lines (Figure 3) as envisioned by our large wind energy development project (www.saharawind.com). This however, will require an effect of scale; and developing mechanisms to firm this energy locally is very important initially, as it lies in the critical path of major alternative energy developments.

Figure 3. Comparison Left, power line: HVDC, 3,000 MW, +/– 500 kV bipole. Right, high voltage AC 400 MW line. (Pacific Direct Current Intertie PDCI near Bishop, CA)

As of today, no technology currently exists for enabling the uptake of significant wind energy potentials on a reliable basis. Being erratic by nature countries that have achieved the highest wind penetration rates did not manage to cover 25% of domestic energy consumptions while relying on extremely high interconnected backup capabilities (Denmark). Taking the same proportions in the Saharan region in countries like Mauritania or further into sub-Saharan Africa, will as mentioned previously, translate into very little installed wind power capacities.

Therefore research ought to be conducted into alternative options for integrating widely available wind/renewable energy resource into grids and or other viable energy infrastructures. Such combinations are likely to take advantage of the significant breakthroughs expected to happen in the near future, regarding hydrogen energy technologies particularly through its association with large sources of renewable energies.

3. Hydrogen, a revolution in energy technology developments

Because of the world's current energy deadlock, and regardless of any environmental considerations, the 21st century is bound to be one where energy breakthroughs will have to be found in order to preserve mankind's economic activities and making them a little more sustainable. As an alternative to hydrocarbons, hydrogen promises to become a universal energy carrier in the future. Therefore and particularly since the technologies already exist, any applied research conducted on hydrogen energy technologies are likely to be very promising in terms of results as they are of strategic dimension. Thus, in order to introduce these state of the art technologies, our initial steps are aimed at building up capacities, training engineers, doctoral, and postdoctoral students, who are likely to reinforce more sustainable energy generation system, through our ambitious and wide ranging cooperative project development activities.

3.1. INTEGRATED REGIONAL APPLIED RESEARCH PROJECTS

Developing a new energy economy will require a global strategy to be progressively implemented. The introduction of these technologies at an early stage, through regional applied research projects will likely contribute to establish and identify areas where the potential breakthroughs can become significant in the future. The region disposes of a qualified pool of university professors, engineers, and scientists that currently lack appropriate research infrastructures. Equipping and networking are the two main research institutions in Morocco and Mauritania through the financing of Wind/Hydrogen/fuel cell test benches as we envision could be considered as a first step toward a successful, gradual introduction of state-of-the-art energy technologies. While this will also prevent any research and technological gaps to widen between countries that dispose of large research facilities and others that do not, the networking of these facilities and their activities are necessary for developing a comprehensive approach toward new sustainable energy alternatives. For that matter, the Hydrogen Economy vision of the International Partnership for the Hydrogen Economy (IPHE) clearly states that energy systems of the future must be cleaner, much more efficient, flexible, and reliable to meet the growing global demand for energy. Besides offering a potential solution to satisfy global energy requirements while reducing (and eventually eliminating) CO_2 (and other GHG emissions) and improving energy security, a hydrogen economy is one in which hydrogen is produced cleanly and cost-effectively.

3.2. HYDROGEN APPLIED RESEARCH, CONTEXT, AND NEW ENERGY DEVELOPMENT POSSIBILITIES

Mauritania and Morocco's energy challenges are part of a broader energy context pertaining to energy access, resource limitations, and sustainability issues. Further, the region's decentralized grid infrastructures require site specific solutions. Integrating the production of hydrogen as an energy carrier utilizing regional electricity market opportunities and its vast renewable energy potential provides an ideal testing ground for applying the latest research and technological breakthroughs in the development of a renewable driven hydrogen economy. As no applied research programs in hydrogen or fuel cells currently exists in both countries, this would contribute to bridge hydrogen technology divides, highlighting a comprehensive approach to the role of hydrogen (and hydrogen applied research) in fulfilling sustainable development objectives. Hydrogen is scalable, and can be worked into modules – small, medium, and large integrated applications. Applied hydrogen research will reinforce a complementary vision in handling intermittent sources of energy (wind) both in decentralized productions of energy and in possible future massively centralized large-scale Wind/HVDC transfer infrastructures. Involving domestic scientific communities at an early stage may contribute to develop newer, wide-ranging approaches that may be better integrated to the regions real potentials. Hydrogen could be integrated to the region's industries and main export commodities; mining, phosphate processing, and fertilizer industries (already big customers of electrolysers worldwide). Wind-electrolysis in Morocco and Mauritania's (trade wind regions) can be duplicated on a large scale and produce hydrogen at competitive costs. Hydrogen from fossil fuel reforming represents the vast majority of today's hydrogen production, emitting 6 tons of CO_2 per single ton of hydrogen in the process. It is therefore important to differentiate hydrogen production alternatives at an early stage (carbon- and noncarbon-generated hydrogen) and encourage countries with similar potentials to collaborate and exchange expertise through excellence centers located in their universities. This will expand applications and developments further into sub-Saharan Africa with hydrogen and fuel cell technology solutions. Such vision supported by NATO would provide a strategic approach to renewable energies which, coupled with a sustainable integrated hydrogen economy, could contribute to building tomorrow's energy solutions.

3.3. HYDROGEN TECHNOLOGIES TO IMPROVE SECURITY IN THE REGION

North West African countries dispose of skilled human capacities and a scientist pool capable of getting involved and conducting such applied research. It is essential to foster regional (south/south) collaboration in clean energy technologies for tackling energy access, environment and sustainable development issues. Collaboration between Morocco and Mauritania's scientific communities is very important in providing focus, sensitizing, and developing alternatives to handle the economic consequences of high energy dependencies or limited energy access which could in the long run if combined with environmental challenges causes, such as land degradation, desertification, and demographic pressure, generate economic distress. Both largely agricultural-based societies are indeed threatened by environmental challenges. Building scientific capacities, and developing a vision that can generate a dynamic around fast growing energy and sustainable industries (wind energy has 25% growth rates worldwide focused essentially in Europe) could in the long term, become an alternative in fixing migrant population, and contribute to their social integration. Further integrating hydrogen production and the development of fuel cell research could contribute to improve decentralized electrification prospects and fixing populations as well, thus reducing migration fluxes which are currently the region's main security challenges.

3.4. HYDROGEN, THE MISSING LINK IN SOLVING RENEWABLE ENERGIES INTERMITTENCY

Throughout sub-Sahara Africa, electricity grids are still decentralized whereas wind resources are widely available in both Morocco and Mauritania. Access to energy is a key social priority. Hydrogen can improve renewable energy absorption of grids as a decentralized energy source of nonfossil origin fostering sustainable development (capacity is built on-site). Hydrogen is a new process, which will be used in small scale but it can also grow in size and end up ultimately being integrated with large wind infrastructures to supply electricity markets with appropriate electric HVDC line infrastructures. So in a way, hydrogen is complementary to both remote decentralized or large-scale energy firming applications, actually facilitating the transition from decentralized to centralized energy evacuation networks. Traditional centralized electric generation from fossil fuels are not adapted to supply weak AC grids with lack of loads to supply and long distances to cover. Losses can be as high as 70% over a few 100 km in standard AC grids whereas hydrogen-related technologies enable more decentralized approaches and novel integration perspectives.

The Norwegian Utsira island wind/hydrogen energy demonstration project is very recent as it highlights stand alone insular systems which addresses the possibilities of utilizing hydrogen as a storage medium for intermittent sources of renewable energies (i.e., wind energy). In our case, however, we have the possibility to evaluate the utilization of hydrogen for the very same purposes while assessing a more progressive, complementary integration of this technology to large-scale transmission networks that are likely to be integrated in the region. Being located at the edge of a very large European electricity market, the role and utilization of hydrogen could be catalytic, as it may in both cases facilitate the transition from decentralized to centralized energy evacuation networks.

4. A phased approach to integrating hydrogen technologies

4.1. INITIAL STEP: EQUIPPING PUBLIC LAB FACILITIES

The objective of the project is to reinforce capacities by fostering a regional collaboration between Morocco and Mauritania through facilities that will be interconnected with other research centers. By equipping existing lab facilities, the scientists, engineers, and doctoral students in the main public university/research centers will be able to evaluate the integration possibilities of wind into grids, wind/hydrogen electrolysis, stationary fuel cell technologies and their applications in weak grids and/or isolated sites. This will be part of a project aimed at highlighting the region's vast trade wind energy potential and developing ways to integrate this resource within the countries' infrastructures, economies, and into a broader sustainable energy vision being developed worldwide (www.iphe.net). The interactions between hydrogen as renewable energy storage, grid stabilization, and the maximization of renewable energy intakes on remote or weak grid conditions will be studied and evaluated. Nonenergy applications of hydrogen can be looked into as well as the labs will be connected to wind measurement instruments on coastal desert sites disposing of high wind potentials. Production scenarios of commercial hydrogen for nonenergy uses will be looked into as well, through the lab analysis of data gathered. Wind modeling software would then determine the electricity and hydrogen production that can be generated over wider areas by extrapolating the results.

4.2. WIND MAPPING – HYDROGEN PRODUCTION TECHNIQUES

Developing a new comprehensive vision of sustainable energy production, utilizing the latest state-of-the-art energy technologies will enable us to forecast and model sustainable consumption trends with plenty of renewable resources. Utilizing wind mapping techniques within the hydrogen applied research centers will facilitate the assessment of hydrogen production possibilities on a wider scale. Mapping techniques and regional computer models could be applied that are similar to the US model for market expansion of wind energy and hydrogen production from wind and other sources over the next 50 years in the region. The loads and resources being more easily assessed, a Wind-Hydrogen Deployment Systems (WinHDS) model can be developed to forecast the expansion of generation and transmission capacity in the region spanning the next 50 years and minimize system-wide costs of meeting loads, reserve requirements, and emission constraints. While all major types of conventional generators will be included, the WinHDS model will address market issues of greatest significance to wind – specifically issues of electricity transmission and intermittency.

4.3. SECOND STEP: THE SAHARA WIND-HYDROGEN PILOT/DEMO PROJECT

This applied research could serve as basis for the Sahara Wind-Hydrogen demonstration project that Sahara Wind Inc. intends to build as part of its large-scale commercial wind energy developments currently under way, and carried out in conjunction with several multilateral development institutions. Being faster to set up then successive wind power capacities aimed at feeding large commercial electricity markets, the hydrogen production perspectives to be developed with the support of the United Nations Industrial Development Organization are likely to demonstrate the complementarities that the hydrogen economy provides in the development of sustainable energy systems. The Sahara Wind-Hydrogen Energy Project in Tarfaya is likely to provide an operational research platform that addresses innovative and sustainable hydrogen production technologies with several industry and research partners with appropriate levels of funding around this pilot project.

Several interesting and complementary options available in the recent research conducted in the USA and Europe have highlighted several key aspects of the wind/hydrogen association:

- The characterization of cooperation of wind turbines and electrolizers, in some instances coupled.
- The wheeling of power from wind turbines to electrolizers on strong transmission networks.
- The use of hydrogen as a storage mechanism in small-scale remote wind and PV applications.

Although each of these activities represents important investigations, they only go part of the way in addressing the technical challenges when developing a large wind-based hydrogen production system. Looking into these perspectives, two different possibilities are available. It is important to mention that merging their respective advantages represents the most compelling of all options. The first option would consider Wind turbines that are designed to produce hydrogen directly, either independent of the grid or at least independent from a power processing perspective, the second being wind turbines that are connected to a transmission network and may, depending on loading and resource, produce either hydrogen or electricity for direct sale. The Sahara Wind-Hydrogen Energy Project located in Tarfaya is likely to provide an operational research platform that addresses the latter of these two options.

It is nevertheless important to expect that such wind/hydrogen park would be installed in a manner that the total rating of the installed wind capacity would be much larger than the available grid capacity is able to absorb. Indeed, a wind farm designed to produce hydrogen should not mobilize any further investments into transformer stations and secure grid capacities, when only a fraction of its global output is expected to be fed into the grid. Hence, this would result in large buffered power generating sources which, connected to a weak grid, provide significant energy handling capabilities likely to enhance the systems stability and reliability. Such approach, even if it is internal to the wind farm, enables a significant valorization of the fluctuating wind energy resource in addition to the use of complementary mechanisms such as power conditioning schemes and other optimized transfer infrastructures likely to be envisioned in the Tarfaya region.

The application of the results, their expansion and replication into remote grids will be carried out in the region by Mauritania's electric utility, its agency for rural electrification (ADER), and Morocco's utility (ONE) along with other public structures with whom Sahara Wind Inc. is already engaged in years of collaborative project development work aimed at large-scale wind energy integration. Finally, the integration of nonenergy hydrogen applications is likely to be of interest to both countries' main industrial conglomerates operating in the mining, phosphate processing, and fertilizer industries.

4.4. DEVELOPING LOCAL HYDROGEN END-USER MARKETS

4.4.1. Phosphate mining and processing industry

Morocco's first export commodity and foreign currency earner remains the phosphate industry. Disposing of the world's largest mineral reserves, Morocco is currently the world's leading Phosphate exporter. The availability of Oxygen, a hydrogen by-product in the water electrolysis process would enable Morocco's phosphate-based industry to eliminate all SO_2 emissions (estimated at 2.5 million tons/year) from its sulfuric acid production facilities. The availability of hydrogen would also enable local production of ammonia, an essential component required in the production of fertilizers that is currently imported. Ammonia can also be used as stable storage means for hydrogen, which is much easier to handle then pure hydrogen in its gaseous form. In Mozambique for instance, fertilizer industries are already utilizing surpluses of renewable hydro-generated electricity to produce hydrogen through electrolysis for fertilizer products. Instead exporting mostly raw phosphates, the utilization of any available hydrogen would enable Morocco to develop and integrate its fertilizer industry most comprehensively, beyond exporting solely phosphate-based fertilizers. Finally, in the process for the current production of sulfuric acid, that utilizes phosphor-gypsum in Morocco the availability of hydrogen could enable a joint production of clean Portland cement, without any CO_2 emissions. The production of cement could create a significant added value in the production of sulfuric acid (prices of cement being generally linked to costs of energy) and will avoid the environmental nuisance in the current dumping of over 12 million tons/year of phosphor-gypsum into the Atlantic Ocean.

4.4.2. Fishing, mining, and other industries

The active regional fishing industry and labor intensive processing plants in the region could make use of significant amounts of hydrogen in their respective processes. Their needs for a firm source of energy are high and the use of chemical derivatives from the local phosphate processing could be also considered. The region's mining and mine processing plants, besides requiring a reliable source of energy, could consider the use of hydrogen and other hydrogen related chemicals that are generally part of mineral-ore refining processes that contribute significantly to the added value of raw mining exports commodities. Finally, as all these activities do generate larger pools of labor employments, the agglomerations of the regions are likely to grow in size and require larger amounts of freshwater supplies for urban consumption. As most of the cities on the Saharan coastline already get their water produced through reverse-osmosis desalination processes, any electricity generated from large integrated wind energy operations would reinforce further freshwater supply capabilities of these cities, making them more autonomous from expensive fossil fuels energy imports.

5. Conclusions

The aforementioned activities are essential in evaluating the possible utilization of hydrogen technologies to enhance the critical uptake of renewable energy in the weak grids infrastructures of the region. While the Sahara Wind-Hydrogen demo/pilot projects are likely to be included into the International Partnership for the Hydrogen Economy's future list of collaborative projects involving several IPHE member countries, these activities could also bridge hydrogen production technologies with the needs of different countries, particularly developing countries to determine how technology transfer will be affected. Finally, the objective of the project is to build capacity and enable applied research to be conducted on hydrogen energy technologies in both Morocco and Mauritania, and stimulate wider regional cooperation to support large-scale production of carbon-free hydrogen from wind-electrolysis on an unprecedented scale.

References

Agbossou A., Hamelin J., Chahine R. (2000). Fuel cell and hydrogen storage for stand alone renewable energy system. International Journal of Renewable Energy Engineering, 2(3), pp. 254–259.

Benhamou K., Sahara Wind Inc. Engineering Report on the Perspectives of Wind-Hydrogen Energy Production in Morocco, (contract TF/INT/03/002/11-68) for the United Nations Industrial Development Organization UNIDO International Centre for Hydrogen Energy technologies (ICHET), Istanbul, Turkey 2005.

Benhamou K., "Policies for the future: spreading awareness of wind opportunities (North Africa)" Proceedings of the CD World Wind Energy Conference, November 23–26 Cape Town, South Africa 2003.

Fingersh L.J. (2003). "Optimized Hydrogen and Electricity Generation from Wind" – Technical report (NREL/TP-500-34364), National Renewable Energy Laboratory, Golden, Colorado, USA.

Gonzalez A., McKeogh E., Gallachoir B.O. (2003). The role of hydrogen in high wind energy penetration electricity systems. The Irish case. Renewable Energy, 29, pp. 471–489.

"IPHE Renewable Hydrogen" workshop of the IPHE, 24–26 October 2005, Seville, Spain.

Implementation and Liaison Committee (ILC) meeting of the IPHE, 22–24 June 2006, Lyon, France.

Leighty W., Keith G. (2001). "Transmitting 4,000 MW of New Windpower from North Dakota to Chicago: New HVDC Electric Lines or Hydrogen Pipeline". Proceedings of the International Conference on Hydrogen Age of Asia, 27–28 November 2001, Tokyo, Japan.

Kottenstette R., J. Cottrell, NREL, (2003). Hydrogen Storage in Wind Generator Towers, NREL/TP-500-34656 2006.

UNDP/GEF “PIMS#3292 UNDP/GEF Morocco: Sahara Wind Phase I/Tarfaya (400–500 MW) on–Grid Wind Electricity in a Liberalized Market” United Nations Development Program/Global Environment Facility-World Bank, Washington DC, USA (2005).

www.eia.doe.gov/emeu/iea/Notes_for_Table_6_4TimeSeries.html - Energy Information Agency, United States Department of Energy Washington DC, USA (2006).

www.iphe.net International Partnership for the Hydrogen Economy.

www.saharawind.com Sahara Wind Inc., “Sahara Wind Energy Development Company” the Sahara Wind Energy Development Project.

PATHWAY FOR HYDROGEN IN URBAN TRANSIT SYSTEM

TAPAN K. BOSE [*]
Hydrogen Engine Center Canada and Hydrogen Research Institute, UQTR, PO Box 500, Trois-Rivières, Qc, Canada G9A 5H7

AHMED HOURRI
Hydrogen Research Institute, Université du Québec à Trois-Rivières, PO Box, Trois-Rivières, Qc, Canada G9A 5H7

GILLES Y. CHAMPAGNE
E-H2 (Energy-Hydrogen) Inc., Canada

R. P. FOURNIER
Université du Québec à Trois-Rivières (UQTR)

Abstract: According to the Intergovernmental Panel on Climate Change (IPCC), the average global temperature has risen over the last century. The changes in climate could adversely impact human health, agriculture, water resources, and ecosystems. Most national and international agencies have concluded that our use of carbon-rich fuel is responsible for global warming through the greenhouse effect. Automotive exhaust emissions are the largest single source of air pollution in the world today, especially in urban areas. Natural gas, a fossil fuel that offers substantial advantages over oil-derived fuels, can facilitate the transition to hydrogen fuel. Advanced natural gas-fueled vehicles have the potential to reduce carbon monoxide and reactive hydrocarbon emissions substantially compared to gasoline vehicles. Further environmental benefits can be realized by using a blend of natural gas and hydrogen. Such an approach will help create an infrastructure for an eventual transition to hydrogen.

Keywords: hydrogen, fuel, natural gas, transportation

---

[*] To whom correspondence should be addressed: Tapan K. Bose, Hydrogen Research Institute, Université du Québec à Trois-Rivières C.P. 500, Trois-Rivières, Qc, Canada G9A 5H7; e-mail: tbose@hydrogenenginecenter.com

J.W. Sheffield and Ç. Sheffield (eds.), Assessment of Hydrogen Energy for Sustainable Development, 75–82.

1. Introduction

The Intergovernmental Panel on Climate Change (IPCC) has concluded that the average global temperature has risen by 0.3–0.6°C and the sea level by 10–25 cm during the 20th century. The ten warmest years of the century have occurred over the last 15 years. If this trend continues over the next century, the IPCC projects a temperature increase of 1.4–5.8°C, a rise in sea level of 90 cm and a likely increase in precipitation intensity. The changes in climate could adversely impact human health, agriculture, water resources, and ecosystems. Most national and international agencies have concluded that our use of carbon-rich fuel is responsible for global warming through the greenhouse effect.

According to the World Energy Outlook 2002 (report published by international Energy Agency),[1] the geographic location of new emissions will shift dramatically from the industrialized countries to the developing world in 2030. The developing countries' share of global emissions will jump from 34% in 2000 to 47% in 2030 (see Figure 1).

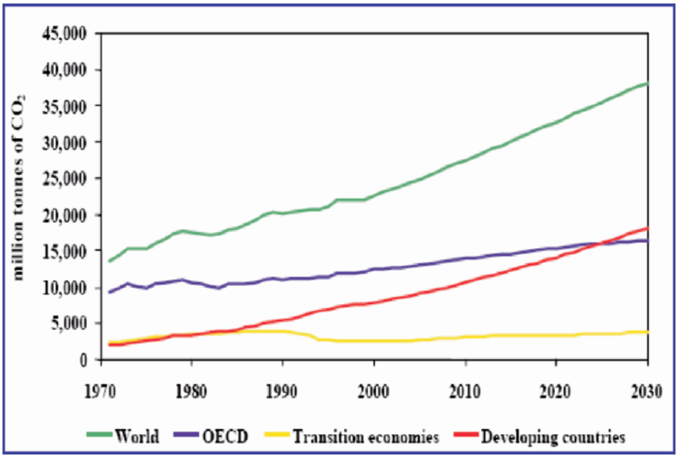


Figure 1. Energy-related CO_2 emissions by regions[1]

China alone will contribute a quarter of the increase in CO_2 emissions or 3.6 billion tons, bringing its total emissions to 6.7 billion tons per year in 2030. However, Chinese emissions will still be well below those of the USA. A projected increase in fossil fuel consumption is largely responsible for fast-paced growth in CO_2 emissions. Of the fossil fuels, coal and oil account currently for the major part of the total energy-related CO_2 emissions. Factors such as population growth, rising personal incomes, improved standards of living, and further industrialization are expected to have a much greater influence on levels of energy consumption in developing countries where oil consumption is projected to increase for all end uses.[2]

In the industrialized world, increases in oil use are projected primarily in the transportation sector, where there are currently no available fuels to compete significantly with oil products. The International Energy Outlook 2004 case projects declining oil use for electricity generation, with other fuels (especially natural gas) expected to provide more favorable alternatives to oil- or coal-fired generation. Natural gas is projected to be the fastest growing primary energy source worldwide, maintaining average growth of 2.2% annually over the 2001–2025 period.[3]

Two major environmental issues, global climate change and local or regional air pollution, could affect energy use throughout the world in the coming decades. Reducing the greenhouse gas (GHG) emissions requires major changes to the way energy is produced and used. This will create pathways for a transition to a new energy system with no adverse impact on the environment.

Many countries have introduced regulations targeting petrol- and diesel-fueled vehicles and coal-fired power generation. Compressed Natural Gas (CNG) is slowly finding a niche as a vehicle fuel as governments strive to cut air pollution from gasoline and diesel and reduce their reliance on imported crude oil. Burning natural gas is the cleanest source of energy among the fossil fuels. Higher efficiency and further environmental benefits can be realized by using a blend of natural gas and hydrogen. The use of a mixture of hydrogen and natural gas as a vehicle fuel has been proposed to take advantage of the low emission potential of hydrogen. Hydrogen ICEs, hydrogen ICE hybrids could also be used in the near term. This paper looks at strategies for the transition to hydrogen-based energy systems in urban transportation.

2. Urban transit: pathway to hydrogen vehicles

2.1. THE NATURAL GAS BRIDGE

It is well documented that the transportation sector in urban areas produces the major part of GHG as well as harmful emissions. Hydrogen systems could provide both immediate and long-term reductions of global CO_2 emissions and criteria pollutants in transportation systems. Recently, many countries initiated a program to promote the use of CNG in vehicles. The natural gas vehicle (NGV) utilization started in Italy and reached Argentina in the early 1980s where a local technology has developed with great success and expanded to Brazil and Latin America in general.[4] Argentina has adopted a program for large-scale conversion of vehicles to natural gas and building of new CNG fueling stations. As a result, many vehicles (taxis and private cars) use natural gas supplied by an extensive network of fueling stations. Thus, this fuel can be used not only in the major cities but also for some intercity travel. Argentina's fleet of NGV is the largest in the world (see Table 1).[5]

TABLE 1. Top ten countries in terms of natural gas vehicles (NGV) in the world

Country	Rank	Vehicles	Refueling stations
Argentina	1	1,459,263	1,400
Brazil	2	1,117,885	1,227
Pakistan	3	1,000,000	930
Italy	4	382,000	509
India	5	248,000	198
USA	6	130,000	1,340
Iran	7	115,479	137
China	8	97,200	355
Ukraine	9	67,000	147
Egypt	10	63,135	95

Recently, the Chinese government passed legislations imposing stricter environmental protection standards and greater use of clean fuels, particularly, alternative cleaner energy, in the country. Elsewhere in Asia, the increased availability of natural gas is also giving a big boost to the cleaner vehicles. In June 2001, the European Commission's green paper on security of energy supply suggested a target of 20% alternative motor fuels to be achieved by 2020. The most powerful options being: bio fuels including biogas, natural gas, and hydrogen. NGV could account for 10–12% of that target.[6]

Current generation NGVs produce much less pollution compared to the traditional fuels such as gasoline and diesel (8). Of all the fossil fuels, natural gas (methane) has the highest hydrogen to carbon ratio. This means that substituting gasoline (0.26 kg CO_2/kWh fuel) by natural gas (0.2 kg CO_2/kWh fuel) reduces overall CO_2 as well as harmful emissions considerably.[7] Further environmental benefits can be achieved by using a blend of natural gas and hydrogen.

2.2. THE NATURAL GAS AND HYDROGEN MIXTURE PATHWAY

The use of a mixture of hydrogen and natural gas as a vehicle fuel has been proposed as a way of harnessing the low emission potential of hydrogen without the complications associated with a dedicated hydrogen-fueled vehicle. Blended at the point of refueling, it may be used in natural gas vehicles without modification of the vehicle's fuel storage system. By limiting the amount of hydrogen in the mixture, natural gas carburation or fuel injection systems can be used without encountering the combustion difficulties associated with pure hydrogen fueling.[8]

The addition of hydrogen to a natural gas engine increases the flame speed, which reduces unburned hydrocarbons. The hydrogen would also displace carbon that would be available to produce CO and CO_2 during combustion process. Due to the faster flame speed and broader flammability limits of hydrogen, addition of hydrogen to natural gas should result in an overall increase in the laminar burning velocity, and lean operating limit.[9]

Two urban buses have been demonstrated in Montreal. The applied fuel (volumetric) mixture of 20% hydrogen and 80% natural gas, showed more than 40% NO_x reduction compared with pure natural gas during engine testing.[10] The 20% hydrogen in the fuel contributes only about 3% of the fuel mass and about 7% of the fuel energy. For the same volumetric composition of the fuel (20% hydrogen and 80% natural gas), the Westport-Cummins (a Vancouver-based company) Hydrogen–CNG engine upgrade led to a reduction of nitrous oxide (NO_x) and non-methane hydrocarbon (nmHC) emissions by 50%. This was achieved while retaining the performance and efficiency of the engine and creating a slight reduction in CO and CH_4 emission levels. In addition, CO_2 emissions were reduced by 7% compared to pure natural gas operation.[11] This means that in operation, this bus would produce 65% less NO_x, 80% less particulate matter (PM) and about 10 tons per year less GHG versus a bus featuring the newest diesel engines certified to the 2002 emissions levels established by the US Environmental Protection Agency.[11] SunLine Services Group of California is partnering with Cummins Westport to demonstrate the HCNG engines.

Vehicles with internal combustion engines burning hydrogen–natural gas blends require the same infrastructure as natural gas. Both require a large-scale distribution network and compression facilities. A hydrogen pathway strategy for transportation must also consider the status of hydrogen production. Central production of hydrogen might not be the most economic pathway for hydrogen production especially for HCNG vehicles needs. Hydrogen produced at a central plant must either be pressurized and delivered by tube trailer or by hydrogen pipeline, or it can be liquefied and shipped in cryogenic tanker trucks. Either transportation option increases the cost of hydrogen dramatically.[12]

Distributed hydrogen production via small-scale reforming is less costly than centralized production. Distributed hydrogen production would be attractive especially in the early stages of a hydrogen economy. Hydrogen could be provided where it was needed, allowing supply to match demand.

Therefore, by taking advantage of the natural gas network, onsite production of hydrogen by steam methane reforming is the likely route to achieve cost-effectiveness.[13]

Hydrogen ICEs, hydrogen ICE hybrids will not only reduce GHG emissions but will also improve efficiency, thus serving as a transition technologies. In the near term, while the development and demonstration of FCVs continues, hydrogen ICEs could be commercialized for applications such as transit buses. The efficiency and cost of an optimized, high-compression hydrogen ICE has the potential to reach the level of a diesel vehicle.[14] Powering a hybrid platform, the fuel efficiency of the high-compression hydrogen ICE hybrid could approach that of the diesel hybrid. Emissions from a hydrogen ICE, although not zero, are very low, with more than 99% reduction in CO_2 compared to fossil fuels.[14] Hydrogen ICE hybrid could easily be a long-term solution. Gasoline ICE hybrid gives 52 miles/gallon for a compact car. It is expected that the mileage and efficiency of the hydrogen ICE hybrid would be considerably better because of the higher compression ratio of hydrogen as compared to gasoline.

Hydrogen penetration in the transportation sector will likely be led by fleet vehicles, i.e., transit buses, courier, delivery, and light-duty utility vehicles that refuel at home base. Niche applications could also play a strategic role in developing hydrogen infrastructures and energy systems. Such end-use applications include forklifts and off-road vehicles.

Other end use include stationary power generation. According to the Energy Information Administration (EIA), natural gas fired electricity generation is expected to increase dramatically over the next 20 years.[3] By taking advantage of the natural gas infrastructure already in place, distributed production of hydrogen is possible (with carbon sequestration). Therefore hydrogen-powered fuel cells and hydrogen ICE generators can be used as a back up power units to provide on-site generation of electricity for residential buildings, hospitals, commercial, and industrial sites. They can also be used for electricity generation during hours of high demand. The reformer will produce and supply hydrogen for on-site electricity generation, and the excess hydrogen could be provided to a nearby vehicle refueling station. The waste heat from the reformer would eventually be used for water or space heating for the site. The International Energy Agency projects that fuel cells will contribute significantly to power production as of 2020. Fuel cells are expected to become competitive in distributed generation when capital costs fall below $1,000/kW, just over a quarter of current costs and their efficiency approaches 60%.[1]

3. Conclusion

Energy needs in the world are rising fast and climate-change concerns are certainly very pressing. Clearly, the use of natural gas in the transportation sector and efficient power generation are among the most effective tools to respond to the climate-change problem in the near term. But developing skills and technologies in renewable and alternative energies would help economic growth with least impact on the environment. We have shown that there are great opportunities for a rapid, practical, and profitable path for introducing gradually hydrogen energy technologies in the transportation sector. The use of hydrogen fuel holds significant potential for diversifying the world's energy mix, especially in the transportation and distributed power-generation sectors. It is believed that this could lead to higher energy efficiencies and a reduction in polluting emissions and GHG.

References

1. International Energy Agency, "World Energy Outlook 2002" (www.worldenergyoutlook.org).
2. Energy Information Administration. International Energy Outlook 2003: Environmental Issues and World Energy Use. Report #DOE/EIA-0484 (2003).
3. Energy Information Administration. International Energy Outlook 2004: Environmental Issues and World Energy Use. Report #DOE/EIA-0484 (2004).
4. J. C. Fracchia, "Global Natural Gas Vehicle review". Paper presented at the 9th International Association for Natural Gas Vehicles conference (NGV 2004). October 2004, Buenos Aires, Argentina.
5. "Latest International NGV Statistics". International Association for Natural Gas Vehicles at www.iangv.org
6. J. Henningsen, "Transportation Fuel Diversity and Environment from a Global Perspective: The bright outlook for NGVs". Presentation at the 22nd National NGV Conference Exhibition, September 2004, San Antonio, Texas.
7. C. J. Winter, On Energies of Changes-The Hydrogen Solution. Edited by C.J. Winter, Gerling Akademie Verlage, pp. 67–82, (2000).
8. S. P. Salanki, J. S. Wallace, "The use of Hydrogen-Natural Gas Mixtures in a lean-Burn IC engine". Proceedings of the Hydrogen and Fuel Cell Conference. Vancouver 2003, Canada (2003).
9. S. P. Salanki, J. S. Wallace, "Combustion of Hythane in alean burn IC Engine". Final report submitted to Institut de Recherche sur l'hydrogène-Université du Québec à Trois-Rivières, 1998.
10. R. Wurster, Ludwig-B.lkow-Systemtechnik GmbH, "Hydrogen Bus Demonstration Projects". Published at the VDI/GET-Fachtagung Energieversorgung mit Brennstoffzellenanlagen - Stand und Perspektiven, Technische Hochschule Darmstadt, VDI Düsseldorf. Germany, February 15–16, 1995.

11. Westport Innovations Inc. “Hydrogen Blended Natural Gas Program Overview”. www.westport.com/pdf/WPT-HCNG__Tech_Med.pdf.
12. C. E. Thomas, “Hydrogen-fuelled vehicles: hybrids vs fuel cells”. Presented to the International Vehicle Technology Symposium On Climate Change. March 2003, Sacramento, California.
13. J. M. Ogden, “Review of small stationary reformers for hydrogen production”. Report to the International Energy Agency. March 2001.
14. M. Dyck, M. Fairlie, R. S. Mc Millan, and V. Scepanovic, “Hydrogen Systems: A Canadian Opportunity for Greenhouse Gas Reduction and Economic Growth”. Paper presented at the EIC Climate Change Technology Conference, Ottawa, Canada, May (2006).

ENERGY TRANSITIONS IN TRANSPORTATION:
IS IT A TECHNOLOGY OR A POLICY-DRIVEN PROCESS?

ROSÀRIO MACÁRIO*
IST – Instituto Superior Técnico
TIS.PT, Consultores em Transportes Inovação e Sistemas, s.a.
Portugal

Abstract: Last decades observed an outstanding increase in traffic generated by mobility needs, both in passenger and freight. This is largely a consequence of the global trend of last years when we moved from a stock economy to a flow economy and with it substantial change was introduced in logistic processes and transportation became of the production process in most industry and also in services. Mobility was transformed into an opportunity factor both for industries (business opportunity) and for individuals (personal opportunity) and today transport is a key factor of any vigorous economy.

However, transportation as we have it today is largely unsustainable. In the EU-25 transportation is the fastest growing source of CO_2. According to the EC White Paper on Transport (issued in 2001), transport was at the time responsible for 28% of EU's greenhouse gas emissions in 1998, of which 84% was generated by road transport. Despite this striking evidence of disturbance of the current technological paradigm of fossil fuels in which transportation is still largely supported and the fact that technology is dominated and ready to offer reliable alternatives we face a number of other "soft" barriers hindering the adoption of more sustainable sources of energy to support transportation.

We show the evidence that for an energy paradigm to succeed the merits of technology do not suffice; instead four factors have to be well aligned with articulated actions: the sustainability factor; the technological; the market factors; and the policy factors. But it is on top of this common action of these factors the political process which takes the lead in the change process.

---

* Professor Rosário Macário, Instituto Superior Técnico, Departament of Civil Engineering and Architecture, Lisbon Technical University, Av Rovisco Pais 1, 1049-001 Lisboa, Portugal; e-mail: rosariomacario@civil.ist.utl.pt

J.W. Sheffield and Ç. Sheffield (eds.), Assessment of Hydrogen Energy for Sustainable Development, 83–96.

Being so, the most critical element of the change process is how and when to succeed placing the change process in the political agenda. This means putting together a coalition and creating the momentum for a transport policy window. This paper discusses this issue and presents the structure of the process of opening the window opportunity for a change of energy paradigm in the transport sector, standing for the thesis that energy transition in transportation (a very likely elsewhere) is a policy-driven process.

Keywords: decision-making, policy agenda, energy transition, coalition, transport policy

1. Introduction

Nearly all modes of transportation still use carbon-based fuels, either directly (in the case of petrol or diesel fuel) or even indirectly (in the case of electricity or innovative energy carriers like Hydrogen), whenever energy sources rely on nonrenewable energy sources like coal. Either way, CO_2 is released into the atmosphere, and is the most common source of man-made greenhouse gases (GHG) contributing to global warming, as acknowledged by the European Commission in its statement "transportation is clearly a fundamental cause of climate change" (EC, 2004), becoming therefore urgent to take proactive measures to reverse this trend.

This is of extreme importance, not only due to unsustainable behavior patterns such as the market pull for larger vehicles with greater performance and more features, e.g., so-called sport utility vehicles (SUVs), but also in result of increased energy consumption of "on board" applications not directly related to vehicle displacement, namely safety and comfort..

Today, car manufacturers face an increasing pressure for greater environmental compliance while the challenge lies in anticipating policy trends and market demands, supporting its strategic positioning with respect to which technological pathways they should follow. But setting up their "strategy" requires a basic understanding on the strategic process itself. As suggested by Mintzberg (1994), strategy can be seen as a compound of four basic concepts: plan, pattern, position, and perspective. Car manufacturers develop their own plans for the future (the intended strategy), and they also evolve patterns out of their past (the realized strategy). The answer on whether realized strategies of car manufactures should always be "intended", remains uncertain. The emerging strategies that each car manufacturer adopts along the way will therefore play a crucial role in this process, enabling its prompt adaptation to market trends, e.g., by keeping technological options open (see Figure 1).

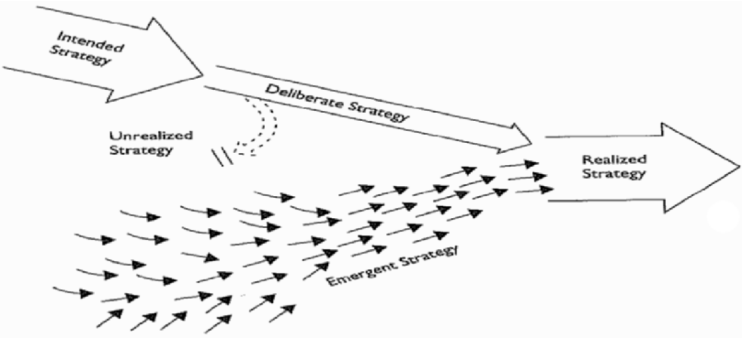


Figure 1. Forms of strategy (Mintzberg, 1994)

But while carmakers have indeed increased their technological capacity, productivity, and competitiveness, the conditions in which they operate have worsened, and the overall economic context remains challenging. Despite its fundamental impact on modern society in both economic and social terms, the car industry is characterized by declining average profit margins, from more than 20% in the 1920s to around 10% in the 1960s and less than 5% today. The ability of the car industry to invest and deliver new alternatives into the mass market, is to some extent constrained by the costs of doing business in Europe and the increasingly complex, dense set of regulations weighing on the industry (ACEA, 2004). At the same time, there is an ongoing shift of knowledge from the greater manufacturers toward suppliers, who play an important role in the development of innovative components, yet with no participation in the development of engine design itself.

Actually, modern car-making plants manufacture virtually nothing; merely assembling and putting together the parts manufactured elsewhere, while manufacturing process as such is carried out externally by a broad range of different ancillary companies. Moreover, in order to estimate energy needs and chances for renewables in transportation, it is necessary to have a clear picture on the fundamental driving forces in transportation.

2. Sustainability and beyond

The fundamental assumption is that economic growth implies increased demand for mobility, hence transport, which inevitably brings demand for more energy. A closed loop that can only be mitigated by means of improvements in vehicle and engine efficiency or optimized mobility management. Yet, although often unrealized, a fixed economic growth percentage translates into its exponential rise. As a consequence, also the mobility and the demand for energy resources will rise exponentially.

Common sense's misperception about this fact leads often to argue from a position of belief rather than a position of knowledge, when it comes to discuss sustainability issues.

It is therefore crucial to understand how much economic growth, and consequent transportation, represents a fair wish, inasmuch as it brings along a higher risk of energy supply shortage, should energy upstream production throughput and refining capacity is not able to keep up with exponential growth patterns, in the context of a worldwide oil-based economy.

Altogether, these are some of the core issues that characterize the current context to which transportation sector in general and the car industry in particular, are subject, envisaging anticipating structural changes in the nature of energy supply to the transport system and vehicle-related technologies.

According to IEA (2001c), achieving a truly sustainable energy system will depend on technological breakthroughs that radically alter how we produce and use energy. This calls on governments to take the lead in acelerating the development and deployment of new technologies "allowing meeting our growing energy needs without compromising our energy security and the environment." The World Energy Council (WEC) has published in 2004 its report on the "Drivers of the Energy Scene", focusing primarily on past and current trends in oil and natural gas (NG) markets, further addressing the functioning of the energy system and how the energy availability and energy acceptability goals could impact on GDP growth and energy accessibility in the future.

This report is remarkably original for its positioning among international organizations, as it points to developments, both qualitative and quantitative, running against most common analysis found. It challenges widespread forecasts on GDP growth and oil price, proposing that GDP growth in the coming years is likely to remain below the commonly accepted forecasts of 3% in the early years of this decade. At the same time, it also suggests that real primary and final energy prices are likely to rise in the coming years, a perspective that the recent evolution in oil prices seems to confirm.

According to the EC Green paper of Security of Energy Supply (2000), domestic resources are indeed running out, while Europe does not enjoy large domestic resources. Hence, expectations are that EU energy resources will steadily fall. The pace at which they will run out depend on world oil prices and technological progress. EU enlargement will not improve this situation. Still according to the EC Green Paper, in the North Sea, oil extraction costs are much higher than in the Middle East, while reserves are limited. In the best case, these would represent a further 25 years of production or eight years of consumption at current levels, from 2001.

NG from the North Sea, is following the same pattern as oil. Still, production from NG reserves in Norway, a member of the European Economic Area, may represent 23 years of consumption at current levels. However, we should consider that, on the one hand, consumption of NG is likely to increase in result of a partial shift from “dirty” fossil fuel to a somewhat “cleaner” NG is some applications, including transportation.

Yet, the potential of renewable energy sources, hardly materialized up to now, remains to be exploited. Should cost and technological-related problems be overcome, renewables could become a key energy source for the future in the EU (EC, 2000). But shifting from an oil-based transport system will also require adapting infrastructure of supply depending on choice of technology. The required large-scale expansion of innovative technologies relying on renewable energy sources will be heavily dependent on the attainment of network economies.

The major problem in attaining such stage in alternative energy sources stems from the fact that none of these alternatives has yet emerged as clearly promising. In a situation like this, it is legitimate to expect that the relevant economic agents will not embark in the necessary investments to provide energy supply to whatever new technology might be proposed, unless costs are either low or strongly subsidized. If contention of costs is possible beyond a certain threshold scale of production, subsidization might be the leveraging solution to launch new technologies, but long-term cost-benefit analysis encompassing strategic environmental assessment is required to support this decision.

Consequently, currently existing supply networks of alternative fuels tends to concentrate in those cases where the need for a supply network to be built does not imply very high costs. This is the case for biofuels sharing existing supply networks while enjoying similar physical and chemical characteristics and to a different extent, NG, already relatively wide spread for industrial and domestic consumption. In the case of public transport operators (UPT), these may enjoy by itself sufficient scale to allow for dedicated supply – for example, a NG storage facility in central maintenance and refueling premises of a bus operator.

NG is enlarging its network through pipelines across Europe and represents a comparatively inexpensive alternative in terms of its distribution, when we look at other more demanding options, such as hydrogen. A remarkable NG supply infrastructure’s growth is experienced in several countries, Germany and Italy being the best examples. NG supply infrastructure in Germany is supported by local gas utility companies collaborating to rapidly grow the natural gas vehicles (NGVs), taking the lead in Europe regarding plans to introduce NGVs. There are about 20,000 vehicles and until 2006 this figure is expected to increase to a total of 70,000 supported by the

German federal government which committed national Policy to maintain low tax rates on NG through the year 2020, while consistently increasing the taxes on both gasoline and diesel, an example that sends a consistent message about its long-range plans to the car companies.

On the other hand hydrogen supply network is still far from a complete implementation. All transport-related initiatives on hydrogen buses depend on facilities that produce H_2 either locally through hydrolysis (expensive and insufficient) or through compressed H_2 transported from production centres (suppliers such as BP, Air Liquid, Linde Gas, etc.). Besides the cost of changes in the supply infrastructure, the most important balance will be the well to wheel balancing, ensuring that effective improvements in energy dependence from fossil fuels and their external consequences are taken into account.

However, despite all the stress around the development of new alternatives to fossil fuels, the world is not at all running out of oil. In fact, and in parallel to the sustainability dilemma, we are confronted with the challenge of economic definitions and harmonization of concepts given the uncertainty that surrounds the definition of "remaining reserves", reinforced by the lack of data to support better estimations. Consequently, as observed by Mitchell et al. (2001) there is a definitional problem since "remaining reserves" means the quantity of in-place resources that can be recovered economically, and this is far from a consensus around the world.

This drives us to the basic assumption that the sustainability problem is not only of technological character or even economic and that a considerable political- and market-driven dimensions are also at stake as identified in Marques (2006).[*] In fact it has proven in Marques (2006) that the Kuhn's conditions for a scientific revolution are present in the energy field. According to Kuhn's conditions for a paradigm shift occur whenever scientists find anomalies in the current paradigms which cannot be explained. The sustainability factor is by itself the representation of these anomalies.

In parallel the acknowledgment that the current technological paradigm in transportation is unsustainable is the driving force for the development of new technology, which evolution represents the technological factor. However, there are vested interests very closely associated to the current paradigms so a window of opportunity is needed to introduce the new technologies and the consequent associated changes in function, processes, interactions, and even in institutions. The dynamics of this complex network

---

[*] Thesis for Master in Transportation at IST (Lisbon, Portugal), student Carlos Marques with scientific supervision of the author, presented and approved in 2006 under the title "*Factors for a technological paradigm shift in road transportation*"

of cause–effect relations form the political factor for change, which has the potential to bridge the gap between disruptive technologies and the market place, by creating favorable legal and regulatory frameworks, providing crucial signals to the market. Good signaling will promote trust in agents and enable materialization of investments in order to make change effective at a large scale, that is the required scale for economic feasibility and thus survival of the new paradigm.

3. The political decision process

For many years the implementation of transportation policies, and all others, followed a logically structured cycle of allocative decisions based on a rational approach that is usually illustrated with four main steps: specification of objectives; development of alternatives by which the objectives may be accomplished; evaluation of the consequences of each alternative; and finally, selection of the action that maximizes the net benefit according to decision-makers criteria and valuations.

This conceptual approach assumes a unitary decision-making, or considers a group acting as a unit, and ignores situations of conflict, which arise whenever social activities are at stake and the different interests of societal groups (or stakeholders) are confronted. However, today policy definition is a much more demanding process as it requires the ability to define a problem lying on a multi-perspective environment, and considering coalition effects, to draw arguments from a diversity of sources, to adapt the argument to the audience (also a multi-stakeholder audience), and finally to educate public opinion in order to achieve consensus around policy objectives and design as envisaged by Majone (1989).

This means policy definition requires understanding the diversity of personalities represented by the stakeholders, the interests they represent, and the interdependence those interests impose in the different stages of policy definition, given the subjective nature of the citizens' decisions, in particular when called to express their public opinions, for example through voting mechanisms (Lau and Redlawsk in Kuklinsky, 2001). That is, today policy definition in democratic societies requires a participatory approach not envisaged before.

The conceptual abstraction of a policy cycle provides a good level of adaptation when applied to decision processes related to mobility systems. In particular, the incorporation of interaction with stakeholders seems to be possible from the practical point of view as well as theoretically robust.

The several stages of a policy decision-making process close to the current reality of democratic societies can be represented by the following steps[†]:

Stage 1. Definition of problems and objectives:

- Perception of problems and dynamics of environment (by decision-makers)
- Disseminate perception of problem so that stakeholders gain awareness
- Definition of objectives
- Gaining acceptance from stakeholders in setting the goals based on problem perceptions (including feedback and possible redefinition of objectives)

Stage 2. Policy design:

- Identification of alternative solutions/responses to the problem
- Planning concepts/future scenarios, including determination of favorable and unfavorable patterns
- Selection of policy instruments
- Gaining acceptance from stakeholders for the selection of instruments which can reach the preferred defined patterns, assuming that each policy/instrument has its own goals and effects
- Assessment of expected impacts and stakeholders reactions (including possible feedback for redefinition of policy instruments)

Stage 3. Policy implementation:

- Deployment of policy instruments including detailed design of legal, organizational, financial, and operational instruments for the effective implementation of the policy
- Identifying and bringing together "implementers", that is all individual and institutions involved in the set up of policy organization, including gaining acceptance from stakeholders for that organization
- Definition of an implementation plan, setting up resources, time, and space scales

Stage 4. Policy evaluation:

- Checking stakeholders reactions

[†] This policy cycle was developed by the author in the framework of a EC research project designated as TRANSTALK, in 2002, "Involving stakeholders in the evaluation of transport pricing policies"

- Monitoring and evaluation of implementation
- Evaluation of policy impacts, side effects and overall outcome, by measuring the impact and policy success
- If necessary return to stage 2 for fine-tuning (feedback mechanism) and reconsideration of initial stages, whenever evaluation results in low effeciveness

Despite the positive aspect of including an interaction process, this staged approach can still be criticized for oversimplifying the possible involvement of multiple levels of government in the decision process, which can result in the existence of interacting cycles to consider the negotiation and bargaining process between the institutions engaged in the process. In addition, this approach is also unable to reflect policy motivation to move from one stage to the next, neither to assess potential negative political balance that might lead to policy disruption in the middle of the process.

The reflection over these flaws will certainly lead us to the conclusion that the best analytical model would be a multi-framed one, although we must also recognize that its main disadvantage would be the degree of complexity and the strong growth of interacting cycles that would considerably reduce our capacity of understanding the decision process entailed in each of its steps.

4. Building the political agenda: creating policy windows

When applying this cycle in the real world what happens is that we execute the stakeholder consultation step entailed in each stage as many times as the number of group of stakeholders we have, which represents the multi-frame image in the theoretical modeling. While moving from one group to the other we enter into an incremental learning process on public acceptability of the proposals being discussed and, quite often, in between those incremental steps we make adjustments based on trade-offs between the different groups of stakeholders.

Therefore, stakeholders are the key stone of current paradigm of political decision. They act as clients of this decision process, consequently the problem awareness is of critical importance for the creation of momentum for public intervention. This supports the view, for which many authors stand, that ignorance is the main threat to sustainability.

The importance of the groups of stakeholders in the public agenda is due to the fact that they have the capacity to promote new items in the public agenda, with a strong influence in public opinion, or advocate certain proposals within the existing agenda. In fact as (Kingdon, 1995) says much of stakeholder's group activity consists mostly of negative blocking and not positive promotion. A good example is the action of transportation unions, which usually seeks to preserve prerogatives and benefits they are currently enjoying.

The term stakeholder or interest group is not very precise. Theoretically these groups can be a reduced number of executives within a public or private company, or an industrial association representing the all country, or still an individual of public standing. Even government officials, their associations, and their departments or agencies are more recently being considered as a stakeholder group (Lindblom and Woodhouse, 1993, pp 74).

Organized groups of interest are an important function in today's society for they are able not only to influence the political agenda, but mainly because they do effectively have a surveillance function of the decision-makers action. However, identification of these groups and even articulation of their interests is extremely important but it is not enough. There is often the need to put them in action for which effective coalition is needed.

In resume interest groups help to form the agenda by clarifying what the citizens want, they monitor the action of governments and provide valuable feedback, they are also an important source of information for policymakers and they can help in building coalitions. The formation of groups of stakeholders is very dependent on local and national circumstances and even within them geometry varies according to the issues at stake.

The start of this learning process is inevitably marked by the setting of the political agenda that is the element that establishes the public prominence of the issue at stake. A governmental agenda is made of a list of subjects to which government officials pay more attention at any given time. Hence, the agenda setting process is a narrowing process since it narrows the set of subjects that could potentially occupy the officials attention and priority to the set of subjects over which they will effectively focus. In addition, there are agendas within agendas as Kingdon (1995) points out, and subjects do inevitably compete for a position in the agendas.

What explains the ability of a given item to succeed in being placed in the agenda? Three explanations are advanced by Kingdon (1995): problems, politics, and visible participants. The chances of a political proposal or subject being accepted increases substantially if it is understood as an answer to a problem that is already seen as such by a considerable number of citizens.

There are evidences in many public domains that political events flow along their own dynamics where consensus is more of a consequence of bargaining then by persuasion, as Kingdon puts it (pp 199)" *trading provisions for support, adding elected officials to coalitions by giving them concessions that they demand, or compromising from ideal positions that will gain wider acceptance*". Finally, there is a distinction between visible and invisible participants. The first are those actors who receive press and public attention, the later are the influent opinion makers. Experiences in several sectors provide the evidence that the visible participants are very effective influencing the agenda while the invisible are effective influencing the alternatives to the political proposal at stake

Another relevant instrument is the policy window, which is an opportunity to push a pet solution or, in alternative, to call the attention to a given problem. In practical terms officers or advocates in general keep their ammunitions at hand waiting for these opportunities which are open by events either in political or problem streams. These policy entrepreneurs usually are good readers of the stakeholders of a given problem or policy and use them as influencing instrument to weight their competing pets.

Considering these elements the life cycle of any energy policy has to be exposed to four distinct stages: the invisible (or generation) stage; the momentum stage; the accountable stage; and the contestable stage. After these four phases a policy either regenerates or is replaced by another in the political agenda.

In the invisible stage the issue is generated for political purposes. This stage can last years or be rather fast. It is charaterized by two parallel streams of action that converge in a more or less conscious way. On the one hand symptoms of malfunction start to emerge in the society that initiates the process of gaining awareness of the problem, while on the other hand the research community and the industry prepare usually away from channels of communication the technology that will support a reliable technical solution. When these two streams converge the agenda starts building – it is the issue generation stage – and the process enters the momentum stage. This is when public acceptability of the problem and respective solution upsurge and the political window (or momentum) occurs enable a movement forward in the implementation, usually leading to the enactment of a given policy. From this moment on the policy becomes accountable and actions of promotion, devising incentives, ensuring enforcement, and monitoring results and impacts occurs. We often observe that at this stage subsidization upsurges as an important instrument to promote a given policy. The first results represent the milestone to start the contestablility stage. That is, improvements are thought with special focus on efficiency and effectiveness of the policy and alternative solutions start to emerge as competitors for similar results and impacts. Afterward the next stage is either regeneration to keep it in the political agenda or simply replacement by other important issues.

In the case of energy, security plays a determinant role in several of these stages: in the generation stage to ensure the reliability of the technical solution envisaged; in the momentum stage to ensure political acceptability;

in the contestable stage for the credits on past performance but also as a comparative advantage with all possible alternatives.

5. Conclusions

In this short paper we present the streamline of a research area that we consider of major importance to pursue the objectives of energy transition in the transportation sector and elsewhere.

The following aspects are made evident along this paper:

- There are four influencing factors for energy transition[‡] in transportation: the sustainability; the technological; the policy; and the market
- The decision-making process reinforces the importance to observe and understand the synergies between factors and in particular the dynamics between the political and market factor
- The need for participatory approaches in support of political decision-making gives capacitation to citizens, society, and institutions prime priority in any strategy to evolve to a new energy transition stage
- Building the political agenda and creating the political window requires in-depth analysis of the articulation of all these factors to go through the four stages of the political cycle: generation; momentum; accountability; contestability

Finally, we believe that a first demonstration is done that successful energy transition requires a policy-driven process, the technological factor being only the sine qua non condition to move forward. The fast track for energy transition lies in highlighting short- and long-term results and effects so that it can gain priority to be placed in the political agenda.

References

Arthur, D. Little, 2001, “Future Powertrain Technologies: The Next Generation” – Final Report

Bauen, A. & Hart, D., 1998, Further Assessment of the Environmental Characteristics of Fuel Cells and Competing Technologies. A study conducted for the UK DTI Fuel Cell Programme – http://www.env.ic.ac.uk/research/epmg/DavidFur-ass.html

---

[‡] We understand transition as a consecutive stage in an evolutionary process. The evolution of energy was made through clear stages dominated by different technological paradigms

Campbell, C.J., Laherrère, J.H., 1998, "The End of Cheap Oil" in Scientific American, pp 140, March

Conte M., et al., 2001, "Hydrogen economy for a sustainable development: state-of-the-art and technological perspectives". Journal of Power SourcesCowi, 2002, "Fiscal Measures to reduce CO_2 Emissions from New passenger cars" – Final Report, EC DG ENV

Economides, M.J., 2002, "Petroleum", University of Houston, Houston, Texas, USA

EIA – Energy Information Administration, 2002 "International Energy Outlook 2002", National Energy Information Center, Washington, DC, USA

European Commission, 2000, Green Paper – Towards a European strategy for the security of energy supply, COM (2000) 769, November

European Commission, 2001a, The European Union's Oil Supply

European Commission, 2001b, Future Needs and Challenges for Non-Nuclear Energy Research in the European Union, Discussion Paper

European Commission, 2001c, White Paper – European transport policy for 2010: time to decide, COM (2001) 370

European Commission, 2003, "Renewable Fuels for Cross Border Transportation" – Final Report – Study contract ENV.C1/ETU/2001/0092 – Directorate-General for Environment

European Commission, 2004, "Energy and transport: Report 2000–2004", ISBN 92-894-74572

Howe, Charles W., 1979, "Natural Resource Economics", Wiley, Chchester

Hubbert, K., 1971, World Oil, from Energy and Power

Kingdon, J.W., 1995, "Agendas, Alternatives, and Public Policies", Addison Wesley Longman, New York

Larsen, H., Sønderberg, L., 2002, "Risø Energy Report, New and emerging technologies – options for the future", Risø National Laborator, October

Macário, R., Marques C., 2005, "Policy Drivers to Change Energy Supply in Transportation System", Proceedings International Hydrogen Energy Congress and Exhibition IHEC 2005, Istanbul, Turkey, July 13–15

Marques, C., 2006, "Factors for a technological paradigm shift in road transportation", M. Sc. in Transportation, IST, Lisbon, Portugal

Mintzberg, H., 1994, "The Rise and Fall of Strategic Planning, Financial Times", Prentice-Hall, London

Mitchell, J., Morita K., Selley N., Stern J., 2001, "The new economy of Oil, Impacts on Business, Geopolitics and Society", The Royal Institute on International Affairs

Nielsen, L.H., Jørgensen K., 2000, "Electric Vehicles and Renewable Energy in the Transport Sector". Main focus: Battery electric vehicles and hydrogen based fuel cell vehicles, RISØ-R-1187, Risø National Laboratory

OECD/IEA, 1997, "Energy Technologies for the 21st Century", OECD, Paris

OECD/IEA, 2001a, World Energy Outlook, Paris

OECD/IEA, 2001b, Energy Policies of IEA Countries, Paris

OECD/IEA, 2001c, Towards a Sustainable Energy Future, Paris

OECD/IEA, 2001d, Energy Policies of IEA Countries, Paris

OECD/IEA, 2002, Vision for the 21st Century. Zero Emissions Technologies for Fossil Fuels. Technology Status Report", OECD, Paris

World Energy Council, 2004, Drivers of the Energy Scene

Ramesohl, S., Fischedick, M., "Dynamic Energy Systems Analysis for the Assessment of the Perspectives of New Energy Technologies", Wuppertal Institute for Climate Environment Energy, Wuppertal, Germany

Rogers, E.M., 1995, "Diffusion of Innovations", 4th Ed., The Free Press, New York

Rubin, J., 2003, "Driving to New Sources of Energy, Gaining Flexibility, Ensuring Supply, and Reducing Emissions", TRB News, Washington, DC

TIS.PT, 2002, "Vehicle Taxation Study", DG Taxation – European Commission

TIS.PT, 2005, "State-of-the-Art for developing Scenarios for the Transport systems and Energy Supplies and their Effects" Deliverable 1

T&E, 2004, "Reducing CO_2 Emissions from New Cars" by Per Kågeson

UIC, 2004, "EVENT – Evaluation of Energy Efficiency Technologies for Rolling Stock and Train Operation of Railways", Paris

PROSPECTS FOR HYDROGEN AS A MILITARY FUEL

KEVIN D. POINTON
J. BARRY LAKEMAN*
Department of Physical Sciences
Dstl Porton Down, Salisbury SP4 0JQ, UK

Abstract: Hydrogen faces considerable technical barriers as a military fuel, not the least of which are the safety engineering necessary, the lower effective energy storage density and the production and distribution issues. These and other issues will prompt considerable institutional resistance to hydrogen in the armed services and are discussed in more detail. While there are alternatives that meet the need better than hydrogen, the armed forces will continue to demand high flashpoint, liquid fuels regardless of cost. In the future, fuel costs will be higher, and fuel will be extracted from currently uneconomic sources, such as oil shale and coal. The best prospects for hydrogen would appear to be in niche vehicle applications that do not represent a significant fuel consumption. Hydrogen may also have a part to play in portable fuel cell power systems. In the UK, non-reversible chemical hydrides are being investigated as an energy dense source of hydrogen for soldier power.

Keywords: fuel cells, synthetic fuels, hydrogen, portable power

1. Introduction

As oil production from available crude oil stocks declines, UK Land Forces and the Royal Navy will continue to demand fuels that meet its existing technical, safety and environmental requirements, most of which were written around the existing technology-fuel model. For the Navy, these

---

* To whom correspondence should be addressed. Barry Lakeman, Department of Physical Sciences, Dstl Porton Down, Salisbury SP4 0JQ, UK, e-mail: jblakeman@dstl.gov.uk

J.W. Sheffield and Ç. Sheffield (eds.), Assessment of Hydrogen Energy for Sustainable Development, 97–106.

requirements will include suitability for seawater compensated tanks, rapid underway refuelling and fire safety under battle conditions, none of which can be met by hydrogen without great difficulty. For the Army, rapid refuelling, security and efficiency of the logistics chain and fire safety under battle conditions will be key decision-making factors. Similarly, the Royal Air Force would probably have to sacrifice significant capability in order to use alternative fuels such as hydrogen, since the severely weight constrained vehicles would be adversely affected by hydrogen's poor effective energy storage density.

The case for hydrogen as a military fuel is considered in more depth below.

2. Fuel flexibility

The nature of existing fuels as a complex liquid mixture of hydrocarbons lends itself well to adjustment of properties by choice of fraction, blending, treatment, etc., so that the properties of the fuel can be tailored to meet the demands of particular applications. The fuels are essentially non-polar organic solvents, and readily dissolve a variety of additives. Thus, military fuels can be based on commercial fuels, but with adjusted properties. For example, JP 8 is essentially identical to commercial Jet A-1, but with the addition of a military additive pack to account for the more demanding military requirements. This includes antioxidants to prevent fuel oxidation, metal deactivators to counteract metals, fuel system icing inhibitor to prevent water in fuel from freezing, and a corrosion inhibitor/lubricity enhancer to prevent corrosion and fuel pump failure.[1]

Flexibility is largely an advantage for petroleum-based fuels only because it allows them to be fine tuned to meet the needs of combustion-based technology, generally internal combustion engines and gas turbines. Assuming that hydrogen would be targeted primarily as a fuel for fuel cell technology, much of this flexibility becomes obsolete. Fuel cells are technically better suited to pure hydrogen, with no technological requirement for additives. The temperatures at which hydrogen undergoes phase change are extreme relative to ambient temperature, and growth of water producing micro-organisms in the hydrogen is not an issue. Therefore, anti-icing additives would not be needed. Corrosion within the fuel cell is preventable by materials selection and operating point choices, so that anti-corrosion additives would be equally pointless.

It may become necessary to add an odorant on safety grounds. This is mandatory for other colourless, odourless, gaseous fuels such as natural gas and propane. When stored as a high pressure gas, additives can be accommodated provided their useful partial pressure is less than their vapour pressure. Such potential odorants have been reported in the literature. It is unlikely that an odorant could be found that would be effective in liquid hydrogen systems, since it would need to be accepted into a liquid under the most extreme conditions and co-vaporise at cryogenic temperatures.

Hydrogen can also be used in existing combustion technology. For example, Bayerische Motoren Werke (BMW) are developing hydrogen-fuelled passenger cars powered by internal combustion engines. Since hydrogen possesses a high flame speed, ignition timing must be carefully adjusted and measures taken to avoid knock. The same high flame speeds and hydrogen's small quenching distance mean that hydrogen flames can pass through relatively narrow inlet valve openings and cause flashback. Various techniques are available to mitigate these problems, but there is no simple conversion of existing engines to run on pure hydrogen, such as can be achieved with liquified petroleum gas (LPG).

The attributes of fuel cells, e.g., relative stealth, high efficiency, etc., are sufficiently compelling that they could be the future technology of choice should hydrogen be the mandated fuel. However, the transition to a possible hydrogen economy would be a lengthy one, and would be eased by the ability to fuel multiple technologies.

3. Energy storage density

Existing fuels deliver remarkably high energy storage density. Generally speaking, the combustion enthalpy of petroleum fuels does not vary greatly with the fuel type, typically being around 45 MJ/kg based on the higher heating value (HHV), depending on the density. They compare well with alternative liquid fuels, such as ethanol (30 MJ/kg), methanol (22 MJ/kg) and bio-diesel (36–42 MJ/kg). The energy storage densities of selected fuels, without their storage systems, are shown in Figure 1.

Hydrogen possesses an exceptionally high combustion enthalpy, i.e., 141 MJ/kg based on the HHV-factor of 3 better than an oil-based fuel. However, hydrogen is a permanent gas, extremely fugitive and difficult to store densely. As a fuel storage system, the effective energy density can reduce to less than a third of the effective energy density of a hydrocarbon fuel. Considerable research is being undertaken in order to provide the required storage capacity, acceptable weight and compactness and adequate responsiveness. Three types of storage system have emerged as the most promising: high pressure storage in advanced composite cylinders, storage of hydrogen as a cryogenic liquid and storage as a reversible metal hydride. Each of these has been deployed in prototype fuel cell vehicles.

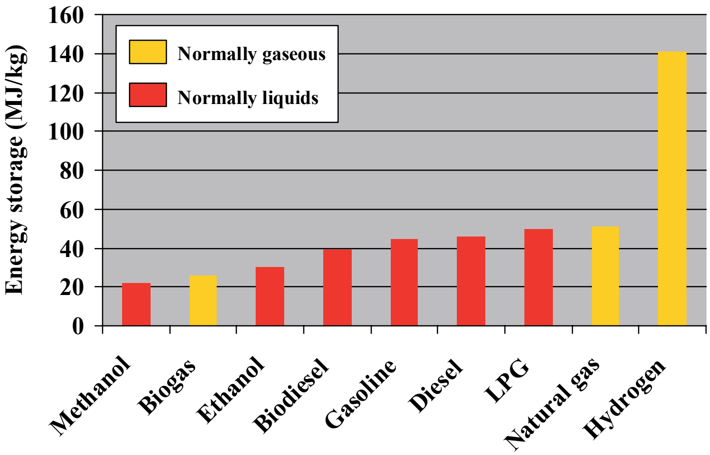


Figure 1. Energy content (higher heating value) of various fuels excluding their storage systems

High pressure, composite storage cylinders generally comprise a relatively thin and weak, but impermeable, liner, with a strong carbon fibre overwrap. The result is a cylinder with a much higher strength/weight ratio than traditional steel cylinders. Cylinders capable of storing hydrogen at up to 700 bar have been qualified for civilian vehicle use, but at only a third of the energy storage density of a petroleum-based fuel. Figure 2 illustrates the gravimetric hydrogen storage for different weights of hydrogen at different pressures. At the best, only 7 wt.% hydrogen is stored at 700 bar. This decreases substantially as the amount of hydrogen stored decreases.

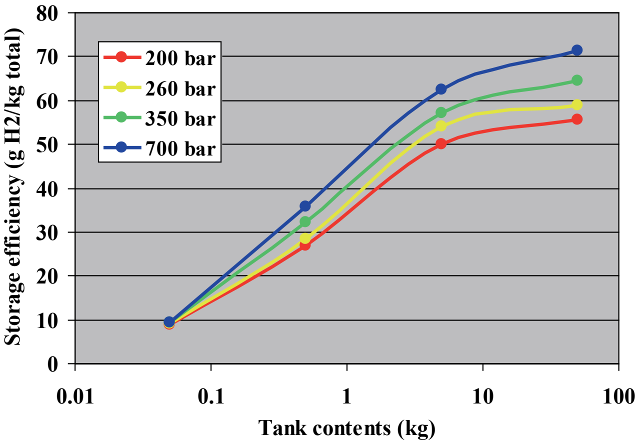


Figure 2. Gravimetric storage efficiency of composite cylinders (including peripherals)

Hydrogen can also be stored as a liquid at low temperatures, e.g., at its boiling point of –253°C, at a similar energy storage density to storage at 700 bar. This is illustrated in Figure 3. However, for hydrogen to remain liquid at such low temperatures, tanks with highly effective and efficient insulation must be used. Liquid hydrogen containers have been made sufficiently compact to fit into the boot (trunk) space of a passenger car and contain perhaps 5 kg of hydrogen. A further problem with liquid hydrogen storage is one of boil-off. The insulation system is not perfect and some heat ingress and consequent vaporisation occurs. This leads to a steady pressure increase within the tank, which needs to be vented before the pressure approaches the vessel's rated safe operating pressure. This is a function of tank size, design and insulation used. For a small vehicle-sized tank, as much as 4% of the tank's contents can be lost per day. Larger vessels can have boil-off rates below 0.2% per day.

An alternative to storing hydrogen as a gas or liquid is to store it by absorption into metal hydrides. These have the advantage of low volume over most other storage methods, but tend to be heavier. Additionally, the pressures of operation are typically below 10 bar, much lower than compressed gas cylinders. This allows the tank to be constructed in geometries not used for pressure vessels, which facilitates better space utilisation.

The weights of power systems using hydrogen or diesel have been estimated for the medium weight, tracked Warrior armoured vehicle, assuing the use of a hybrid electric drive (see Table 1). The estimates include hydrogen storage with its ancillary equipment, such as pressure regulators and heat exchangers, proton exchange membrane fuel cell (PEMFC)

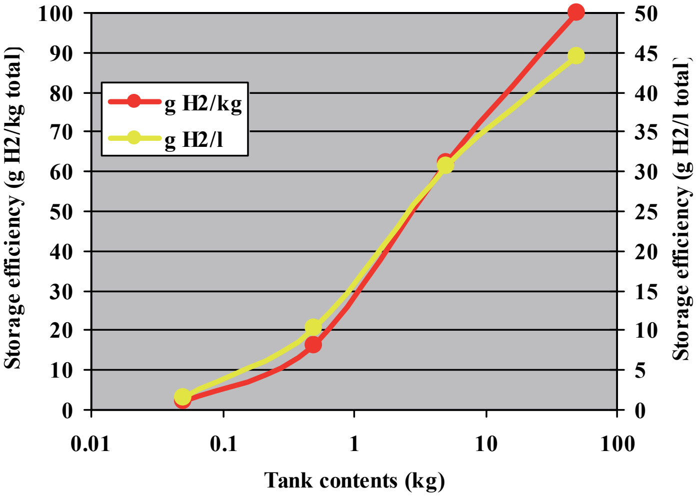


Figure 3. Volumetric storage efficiency of composite cylinders (including peripherals)

including balance of plant, and diesel engine generator with its ancillaries, such as air filtration unit and cooling fan.

TABLE 1. Weight and volume estimates for PEMFC power plants with hydrogen stored in 3 forms, compared with a diesel generator for powering a Warrior armoured vehicle. Fuel tank capacity is 11,100 MJ

Technology	Weight/kg	Volume/litres
PEM fuel cell + reversible metal hydride	5,930	4,780
PEM fuel cell with liquid hydrogen	1,952	4,297
PEM fuel cell with compressed hydrogen	2,140	5,173
Diesel generator	2,291	2,101

The electric drive is not included. The delivery of 11,100 MJ of usable energy is assumed, similar to the content of Warrior's fuel tank.

These figures indicate that hydrogen fuelled fuel cell systems, using either compressed or cryogenic hydrogen storage, may compete with diesel engine technology on a weight basis, but the systems will be bulkier by at least a factor of 2. Adoption of hydrogen would therefore mean less space available for personnel or equipment or a larger vehicle. If the vehicle has to larger, this has significant implications for the increased armour requirement and gross weight of the vehicle.

Similarly, a hydrogen fuelled aircraft would require a much greater volume for fuel storage space if hydrogen was to be adopted as the propulsion fuel. This would lead to military aircraft of reduced capability compared with their conventionally fuelled counterparts.

It is clear that conventional metal hydride hydrogen storage is not a feasible option for storage of land or air vehicle propulsion fuel. However, metal hydride hydrogen storage has been successfully employed on the German, Class 212, fuel cell-powered submarine, where very long underwater endurance is not required.

4. Refuelling rate

The high energy density of liquid hydrocarbons is conducive to fast filling of fuel tanks in seconds.

Compressed hydrogen cylinders for passenger cars, with 350 bar working pressure, can be filled in about 2 minutes,[2] at ambient temperatures lower than 20°C. However, the military can be operating in much higher ambient temperatures, which would result in a lower fill speed. The fill time of the larger tanks that would be needed for vehicles such as Challenger or Warrior, would be greatly extended due to the lower surface area/volume ratio.

It is unknown how fast 700 bar cylinders can be filled, but this will be considerably longer than their 350 bar counterparts, again because of the need to dissipate much more heat through the side wall.

In the case of metal hydrides, recharging the system requires the chemical heat of reaction between the metal and the hydride to be removed (via an in-tank heat exchanger). Large tanks, as used on the German Class 212 submarine, require long recharge times, of the order of one day.

It will take significantly longer to charge a liquid hydrogen tank than a diesel tank (the effective energy density of liquid hydrogen is only one-third that of diesel. Couplings for dispensing liquid hydrogen are complex. They require evacuation of the transfer lines to remove water vapour and air, liquid dispensing and vapour return via concentric passages, leak monitoring and avoidance of air-condensation by design.[3]

5. Safety

The specific physical characteristics of hydrogen are quite different from those of common fuels. This, combined with the fact that the nature of the safety hazards will depend on the situation considered, means that there is no simple answer to the issue of whether hydrogen is a more or less hazardous fuel. Some of hydrogen's properties make it potentially less dangerous, while other hydrogen characteristics could potentially make it more dangerous in certain situations. Generally, hydrogen probably presents a broadly similar level of risk to other volatile fuels, but clearly has significantly more hazards than involatile ones. The use of hydrogen will therefore likely require considerable safety engineering, such as active ventilation in garaging and installation of adequate safety interlocks in vehicle systems to mitigate the risks.

Demonstrations of simulated leaks of hydrogen as compared to petroleum on automobiles are well documented. The demonstrations clearly show that a hydrogen leak is less catastrophic than a petroleum leak following ignition. However, there will be no direct read across to a complex military vehicle, such as a ship, where there could be numerous watertight bulkheads and enclosures, which could render hydrogen more hazardous under battle damage than the current navy diesel fuel.

6. Hydrogen as a military vehicle fuel

Hydrogen faces considerable technical barriers as a military vehicle fuel, not least of which are the safety engineering necessary, the lower energy storage density and the production and distribution issues. In a military context, the use of hydrogen as a vehicle fuel will result in bulkier power systems and introduce more severe safety considerations than existing, low flashpoint fuels. The armed forces will need to decide on whether to bear these disadvantages or choose synthetic liquid fuels, which may involve a significant cost penalty.

However, the military user is a relatively small fuel consumer when compared with the civilian market. This military user is also a relatively small player in the land vehicle market, and the propulsion and fuel technologies that are available to the military customer will be strongly influenced by the prevailing civilian markets. That is, the military customer will have to buy the propulsion technology produced by manufacturers for the dominant civilian market, particularly in the case of land vehicles where complex engine management systems mean that there is little scope for producing military specials at an economic cost.

7. Hydrogen as a civilian vehicle fuel

In 2003, the total daily oil-based consumption in the USA was 16 million barrels per day, of which only 1.8% was consumed by the US Department of Defense (US DoD) – equivalent to 330,000 barrels per day. This indicates that the civil sector accounts for 98.2% of US oil-based consumption, and indicates that the civil sector will strongly influence the availability of propulsion and fuel technologies for the military customer.

The key question that must be answered is whether hydrogen will be adopted as the fuel of choice for civilian vehicles, particularly trucks, ships and planes. In regards to energy density, safety, etc., the considerations listed above will apply. If civilian trucks will be required to undertake long journeys, with minimal stops for refuelling it is hard to see that hydrogen would be the fuel of choice for the vehicle operators. Similar arguments will apply to marine and air transport.

In the USA, research and development is heavily focused on the security of the energy supply, and the large native reserves of coal and oil shale could be used for the manufacture of sulphur-free, synthetic fuels, which could be used in existing internal combustion engine technologies. This would seem a likely way forward for vehicle propulsion, although the ultimate direction will be dictated by environmental and political considerations.

8. Alternative fuels

A synthetic fuel economy must be regarded as a possible adjunct to a hydrogen economy. The US DoD is considering the use of synthetic liquid fuels and a tri-service effort is developing the use of synthetic JP-5 and JP-8, initially as blend stocks, but fully synthetic fuels eventually.[4]

Synthetic fuels are seen as easing sulphur content issues and reforming to hydrogen for fuel cells as well, as being capable of meeting military requirements. The world's large stocks of oil shale, coal and natural gas can all be converted by "gas-to-liquids" technology into synthetic fuel. The technology is nearing maturity, with all major oil companies investing heavily in this area. Typically, larger hydrocarbon molecules are assembled from synthesis gas (carbon monoxide and hydrogen) in a Fischer-Tropsh (FT) synthesis. The resulting hydrocarbon mixture can be further processed to give a range of fractions resembling existing fuels, but without the contaminating sulphur.

The Sasol Fischer-Tropsch plant in Secunda, South Africa, produces 28,000 barrels of synthetic hydrocarbon fuel per day. Ten of these plants would satisfy all the US DoD needs. The adoption of this option will be strongly dependent on political forces.

9. Military applications for hydrogen

The best prospects for hydrogen would appear to be in niche applications that do not represent a major fuel consumption, or where the power requirement is a small fraction of the vehicle's propulsion power. An example of this is the air-independent propulsion system on board the German Class 212 submarine. The particular requirements of this vehicle allow the use of heavy hydrogen storage as a metal hydride.

A further example would be the silent watch auxiliary power unit developed by Hydrogenics for the Canadian Coyote armoured vehicle. This proton exchange membrane (PEM) fuel cell APU also uses hydrogen stored as a metal hydride. Hydrogen is produced using an on-board electrolyser powered during operation of the diesel engine.

In the UK, QinetiQ are developing a novel hydrogen generator for portable power, for future soldier applications. Hydrogen is generated by the thermolysis of ammonia borane, NH_3BH_3, which has a hydrogen content of 19.6 wt.%. The thermolysis products are boron nitride (BN) and hydrogen, which makes this hydride an attractive hydrogen storage medium. Assuming that the total power system comprises a small PEM fuel cell of 10 W, hybridised with a small battery for air-independent operation, and a hydrogen generation system capable of providing at least 48 h mission capability, a specific energy of 600 Wh/kg should be achievable, making this technology at least a factor of 4 times more energy dense than a rechargeable lithium-ion battery.

References

1. "Future Technological and Operational Challenges Associated with the Single Fuel Concept", NATO RTO technical report TR-066.
2. S. Rau, "Dynetek Europe GmbH", Synnogy New Energy Consortium meeting, Guildford, UK, June 2003.
3. California Hydrogen Fuel Cell Station Guidelines, September 2004.
4. P. Muzzel, "Reforming and Synthetic JP-8 Programs", 4th DoD Logistics Fuel Reforming Conference, Philadelphia, USA, October 22–23, 2003.

THE US MILITARY AND HYDROGEN IN MISSOURI

STEVEN TUPPER*
University of Missouri-Rolla,
Rolla, MO 65409-0050, USA

Abstract: The US military is a heavy user of energy both in mobile applications and for its large infrastructure base. One US installation, Fort Leonard Wood, is a training center for all the US services (Army, Air Force, Navy, Marine, and Coast Guard) as well as a school center for the Corps of Engineers, Military Police, and "Chemical" (read as chemical, biological, radiological, nuclear, and explosives defense) branches of the Army. The installation is also an international crossroad with many nations' officers training there and permanent military liaison missions from several NATO countries. The University of Missouri is located near the installation and operates a technology park on the military base. The University is engaged is a series of alternative energy projects with the US military to make Fort Leonard Wood an alternative energy "poster child" which means both a test bed and a model operation for emulation. The projects include the use of hydrogen as a transportation fuel. The hydrogen initiatives are to address the challenge of ensuring reliable, domestic, diverse energy sources while reducing US dependence on foreign oil and protecting the environment, the University of Missouri-Rolla (UMR) is establishing a Hydrogen Center to research and develop technologies for the next generation hydrogen-powered transportation systems.

Keywords: US military, hydrogen, transportation, alternative energy, transit system, on-site production, commuter service, refueling station, public perception, nondestructive evaluation, codes, standards, permitting, safety, first responders, reliability, maintainability, hydrogen highway

---

* To whom correspondence should be addressed: Stephen Tupper, tel: 1 (573) 329-8515, e-mail: tuppers@umr.edu

J.W. Sheffield and Ç. Sheffield (eds.), Assessment of Hydrogen Energy for Sustainable Development, 107–112.

1. US Army's Fort Leonard Wood

1.1. WHAT, WHERE, AND WHO

Fort Leonard Wood, in the beautiful south central Missouri Ozarks, covers more than 61,000 acres. The fort is located in Pulaski County, which has a population of 38,320. It lies centered between the towns of Rolla and Lebanon. The University of Missouri-Rolla (UMR) is located 30 miles east on Interstate 44. The fort and campus are strong partners in science and technology interests that affect military considerations.

Fort Leonard Wood's major military mission is the US Army Maneuver Support Center (MANSCEN) and, where all chemical, engineer, and military police Soldiers, plus many Marines, Airmen, Sailors, Coastguardsmen, and international students from allied nations receive training. Several NATO countries station part of their formal military liaison missions at Fort Leonard Wood.

1.2. ALTERNATIVE ENERGY INTEREST AREA

MANSCEN has requested that Missouri Transportation Institute (MTI) establish a commuter service between FLW and the cities of Rolla and Lebanon, which are located about 25 miles to the east and west of the fort, respectively. This request results from significant growth in the fort's population, which has almost doubled to around 40,000 people on the base. The increase in commuter traffic, coupled with the US Army's interest in reducing single-occupant auto trips to the fort and its willingness to provide each federal employee with a $105 per month tax-free benefit, makes the long-term operation of a commuter bus service viable. MTI in partnership with UMR is exploring the possibility of using the commuter bus service as a hydrogen transportation validation and deployment platform, and as a test bed for advanced hydrogen fuel cell vehicles in a real-world environment.

The military interest in alternative fuels proposes to focus on Fort Leonard Wood as part of the alternative fuels test bed. The military's interest stems from economic reasons and meeting a Presidential challenge to achieve a very short-term measured objective to achieve a shift to 3% of fuels used as renewable fuels. The economic reasons are further defined in environmental, operating as well as public relations costs. UMR is also interested in alternative fuels and supports establishing Fort Leonard Wood as a test bed. UMR's research interest reflects its strength areas in engineering, energy, and materials and matches well with the State of Missouri's economic foundations. UMR is working three thrust areas. First is the integration of alternative fuels – and primarily hydrogen – as transportation fuels. UMR is working a promising proposal that would establish a multi-fuel and on-site hydrogen generation refueling station that would be coupled with the commuter service. Second is waste to energy conversion schemes applicable to domestic military bases and to military base camps for deployed troops. This thrust accomplishes both electrical power generation and waste conversion in a coupled set. Third is the use of woody biomass for generation of alternative fuels and its military application is to allow continuity of operations under emergency conditions.

2. A hydrogen center

2.1. STRATEGIC PLAN

UMR and MTI are working with the US Army, US Department of Transportation's Research and Innovative Technology Administration, National Association of State Fire Marshals, the Missouri State Fire Marshal, Missouri Department of Transportation, Missouri Department of Economic Development, and the private sector in proposing a holistic approach to address not just the technology but public perception; permitting; safety standards; education and training of operators, code officials, and first responders; reliability; long-term operations inspection and maintenance; functionality of equipment; and alternative fuels to create the "Hydrogen Highway" in Missouri. The proposed Hydrogen Center to be established at UMR will pursue a broad research, training, and education agenda to develop a rural hydrogen transportation test bed for developing, demonstrating, evaluating, and promoting hydrogen-based technologies in a real-world environment. Lessons learned and technologies developed will be transferred to support national efforts, and critical links will be maintained with other national hydrogen centers.

2.2. HYDROGEN CENTER OBJECTIVES

The test bed will serve as the focal point for the proposed Hydrogen Center activities, focusing on the overarching goals of collecting and evaluating the real-world performance and utility of hydrogen-powered vehicles and benchmarking issues related to the safety, operation, and maintenance of hydrogen-powered vehicles with other alternative fuel-powered vehicles.

The goal of making commercialization decisions within ten years has led to the creation of eight principal objectives. The successful operation of the center will lead to the realization of those objectives, which are as follows:

- Evaluate and validate, under real-world and heavy-load conditions, emerging multi-fuel energy concepts for deployment of hydrogen-powered vehicles in suburban and rural regions.
- Collect and evaluate real-world data to address safety and environmental issues, develop statistically validated codes and standards, formulate policies and regulations, and understand reliability and large-scale deployment of hydrogen technology under diverse operating conditions.
- Develop, validate, and transition to a manufacturing environment, commercially ready, nondestructive testing technologies for hydrogen storage and transport systems that may be used by an unskilled or semiskilled workforce.
- Test, demonstrate, and validate hydrogen fuel cell vehicles, hydrogen transportation infrastructure, and vehicle and infrastructure interfaces for complete system solutions.
- Provide commuter service customers with a positive experience, helping to overcome fears of hydrogen technology and helping to promote hydrogen energy systems.
- Integrate research results into a comprehensive undergraduate and graduate curriculum to educate the future workforce on hydrogen technologies.
- Develop and implement an outreach program, in collaboration with other national programs, which has a special emphasis on safety training for operators, maintainers, code officials, and first responders.
- Expand the hydrogen energy infrastructure along the I-44 corridor between St. Louis and Springfield/Branson and along the I-70 corridor between St. Louis and Kansas City.

2.3. THE INITIAL PROJECTS TO BE CONDUCTED INCLUDE

- Development of the hydrogen demonstration test bed
- On-site generation of hydrogen using ethanol
- Modeling of composite hydrogen storage tanks
- Nondestructive testing and evaluation of composite hydrogen storage tanks

- Development of statistically validated codes and standards for a few selected critical components in the hydrogen transportation infrastructure
- Development of safety guidelines for designing infrastructure and transportation vehicles

3. University of Missouri

3.1. INSTITUTIONAL UNIQUENESS

UMR and MTI are well positioned to implement the test bed and conduct the related research activities to meet the needs of the next generation transportation fuel systems. Based on the interest, encouragement, and support of the US Department of Transportation, the UMR is willing to invest resources toward these important issues. UMR and MTI along with the other state, federal, and industry partners represent the full breadth of the hydrogen initiative program, from basic research to full-scale deployment and operations capability. The elements are connected through a university, government, and industry partnership that brings together unique perspectives and skill sets necessary to achieve breakthroughs and meaningful results. Because the proper application, interpretation of codes and standards, and appropriate permitting requires early involvement of these groups, key partners who are already engaged include the fire marshals and other agencies that are responsible for emergency response.

UMR has the expertise in energy and environmental engineering to help the US industrial base modify waste to energy technologies operating at commercial demonstration scale. Modifications will transfer the developing technology to military use both on domestic bases and for base camps where the twin and equal goals of energy production and waste management can be accomplished synchronously. UMR researchers anticipate further steps can be ganged to the waste to energy processes to generate hydrogen rather than fuel oils. UMR is experienced agriculture to wood gas production and can develop the technologies and economies for woody biomass to hydrogen in parallel.

3.2. LINKAGE BETWEEN UNIVERSITY OF MISSOURI AND FORT LEONARD WOOD

The University of Missouri is tightly integrated with the fort. It operates the nation’s first technology park on an active Army post. The park includes a Business Center provides immediate access to military contacts for suppliers, researchers, contractors, and other businesses that work closely with the Army. The University of Missouri Technology Park mission is

to provide a modern, fully furnished, and technologically advanced office location to businesses, agencies, and organizations that support or enhance the missions, activities, and strategic goals of Fort Leonard Wood.

The University also maintains a full-time liaison at the fort to expedite research, education, and economic development consistent both with the military needs and the university mission.

4. Conclusion

The State of Missouri is ideally suited to develop and demonstrate the proper operation of hydrogen highways in a rural setting, which represents over 25% of the US transportation needs and which is not well represented in the current major national projects. Large-scale demonstrations in a diverse set of real-world conditions are needed to allow for evaluating new technologies from a theoretical standpoint and in real-world applications used by a workforce representative of the national norm. UMR has the strong cross-linkages with the US military through Fort Leonard Wood to succeed in both waste to oil and eventually hydrogen as well as woody-biomass to hydrogen efforts. Fort Leonard Wood, as a US military alternative fuels test bed (poster child), should be considered to serve in that same capacity to NATO as well.

FUEL CELLS FOR CLEAN POWER GENERATION: STATUS AND PERSPECTIVES

FRANO BARBIR*
UNIDO-International Centre for Hydrogen Energy
Technologies, 38 Sabri Ülker Sk., 34015 Istanbul, Turkey

Abstract: Fuel cells are an emerging technology with applications in transportation, stationary power, and portable power generation, with power outputs ranging from mW to MW. State of the art in fuel cell technology and challenges for their development and widespread applications are discussed.

Keywords: fuel cells, applications, challenges, power generation

1. Introduction

A fuel cell is an electrochemical energy converter that converts chemical energy of fuel (typically hydrogen) directly into electricity. A fuel cell is like a battery but with constant fuel and oxidant supply. The fuel cells have been used in the space program since the Gemini program, but the interest in terrestrial applications emerged in the 1990s. Since then, the fuel cells found applications in military and research submarines, and they are being demonstrated in automobiles, buses, and utility vehicles. Also fuel cells are being demonstrated in stationary power generation as well as in portable power, especially for military applications.

There are several reasons why fuel cells have drawn this much attention, such as:

- They potentially may have a high efficiency, theoretically 83% but in practice around 40%.

---

* To whom correspondence should be addressed. Frano Barbir, UNIDO-ICHET, Sabri Ulker Sk. 38/4 Cevizlibag, Zeytinburnu, 34015 Istanbul, Turkey; e-mail: barbir@unido-ichet.org

J.W. Sheffield and Ç. Sheffield (eds.), Assessment of Hydrogen Energy for Sustainable Development, 113–121.

- When hydrogen is used as fuel, the fuel cells have no emissions other than water.
- Hydrogen as fuel may be produced from indigenous sources, which is an attractive option from the national security aspect.
- Fuel cells are simple, consisting of repetitive planar components and therefore could be produced at low cost.
- Fuel cells have no moving parts so a long life may be expected.
- Fuel cells are modular and can be produced at any size to generate any amount of power (from mW to MW).
- They are quiet which makes them attractive for some applications.

Based on electrolyte used there are different types of fuel cells:

- Alkaline fuel cells, mainly used in the space program
- Acid polymer membrane or Polymer Electrolyte Membrane or Proton Exchange Membrane fuel cells (also known as PEMFC)
- Phosphoric acid fuel cells (PAFC)
- Molten carbonate fuel cells (MCFC)
- Solid oxide fuel cells (SOFC)

Direct methanol fuel cell is actually a PEM fuel cell that uses methanol as fuel. Zinc/air fuel cell by definition is not a fuel cell (or at best it is a semifuel cell). Each type of fuel cells has different chemistry, operates at different temperatures and is at a different stage of development. Most of the development and demonstration to date has been with the PEM fuel cells.

PEM Fuel Cells are simple, operate at relatively low temperature (up to 80°C), have quick start-up and fast response to change of load, have high efficiency and high power density (both in terms of kW/kg and kW/l), and when they use hydrogen as fuel they have zero emissions. PEM fuel cells have already been demonstrated in every imaginable application such as automobiles, buses, scooters, bicycles, golf carts, fork lifts, airplanes, locomotives, boats, underwater vehicles, distributed power generation, cogeneration, back-up power, and portable power.

A logical question is "Why fuel cells are not on the market if they are so good?" The next several sections will attempt to answer this question through an analysis of the key issues and challenges in fuel cell state-of-the-art technology, applications, and commercialization.

2. Challenges in fuel cell stack development

2.1. POWER DENSITY

Fuel cells have achieved >1 W/cm^2 peak power, but in normal operation ($V_{cell} \geq 0.6$ V) achievable power density is 0.6–0.7 W/cm^2 and 0.3–0.4 W/cm^2 in high efficiency operation ($V_{cell} \geq 0.7$ V). The goal of fuel cell development is to keep increasing power density. This is possible through improvements in key materials, such as catalyst and electrolyte, as well as through improvements in fuel cell design.

2.2. UNIFORMITY OF CELLS

Performance of a stack of cells is limited by performance of the weakest cell in stack. It is therefore important to achieve high uniformity in performance of the individual cells in the stack, through stack design, mass production techniques, quality control, and automated stack assembly process. Optimum flow field design may be obtained by careful Computational Fluid Mechanic techniques and experimental validation including flow visualization techniques.

2.3. WATER MANAGEMENT

Water plays a crucial role in operation of a fuel cell stack. The membrane's ionic conductivity is a strong function of its hydration state. Although water is produced in the cathode some water still has to be brought in the fuel cell to prevent the membrane from drying. Too little water may cause polymer drying and too much water may cause electrode flooding. The form of water depends on local conditions primarily flow rate, pressure, and temperature. The stack design, selection, and control of operating conditions affect water management and therefore, the stack performance.

2.4. OPERATING CONDITIONS

Operation with low relative humidity of the gases at the stack inlet is preferred because it simplifies the system (humidification of reactant gases and water recovery). PEM fuel cells are operational even at room temperature, but the typical operating temperature is between 60°C and 80°C. In order to reduce the size of the heat rejection equipment there is a lot of reserch and development (R&D) on high temperature membranes that would allow operation at 130–140°C.

2.5. SIZE AND WEIGHT

For most mobile applications size and weight of the fuel cell is very important. Automotive fuel cell stacks have gravimetric and volumetric power density >1 kW/kg and >1 kW/l, respectively. For smaller stacks <10 kW, power density is significantly lower.

2.6. SENSITIVITY TO CONTAMINANTS

Sensitivity to contaminants, both in fuel and oxidant and in fuel cell construction materials, surprisingly has not been studied enough. There is a very corrosive environment inside a fuel cell (hot, humid, and presence of sulfuric acid) which limits the choice of materials. Both catalyst and polymer membrane may be extremely sensitive to contaminants, particularly metal ions. More research in this area is required.

2.7. DURABILITY

Although PEM fuel cells exhibited several thousand hours of either continuous or intermittent operation, this may not be sufficient for most of the potential applications. It has been found that the operating conditions have a strong effect on durability decay rates. This has been utilized to develop the accelerated life tests. Long life times (in excess of 10,000 hours) have been achieved with good diligence in cell design and control of operating conditions. But durability continues to be one of the most critical challenges for fuel cell commercialization. The exact mechanism(s) of PEM failure is(are) not yet well understood. The researchers often chase the symptoms of performance degradation, such as hydrogen crossover, fluoride emissions rate or Pt particle size distribution, instead of addressing the causes. There are several possible PEM fuel cell failure mechanisms, such as:

- Manufacturing defects
- Unwanted chemical reactions, caused by either contaminants or by-products
- Polymer/catalyst stability
- Mechanical forces
- Thermal effects (insufficient local heat removal rate)
- Combination of two or more mechanisms from the above list.

2.8. COST

The fuel cells are still too expensive for most applications (several thousand US Dollars per kW). This is due to the amount and kind of materials, manufacturing processes and manufacturing volumes. The most critical components are the catalyst and the membrane materials. Pt loading in today's fuel cells is typically around 0.3 mg/cm^2 of electrode active area, which corresponds to 0.6 mg/peak Watt (or 0.6 g/kW). The cost of the membrane material is expected to decrease by half for every two orders of magnitude increase in manufacturing volume.

3. Challenges in fuel cell system development

The following are the challenges on the fuel cell system level:

3.1. SYSTEM EFFICIENCY

The system efficiency is lower than the stack efficiency due to power requirements for auxiliary components and due to power conversion. A well-designed system should not use more than 10% of the fuel cell output power for auxiliary components. The efficiency of DC/DC or DC/AC converters is relatively high (typically >90%) but their number and configurations must be optimized for given application.

3.2. OPERATION AT HIGHER TEMPERATURES

The need for operation at high temperatures has already been mentioned. A higher operating temperature would reduce the size of the heat rejection equipment. In addition, operation at >100°C would greatly simplify water management inside the fuel cell because all water inside the fuel cell would be in vapor phase. The challenge is to develop a polymer membrane that can operate at high temperature.

3.3. WATER BALANCE

Water is produced in the electrochemical reaction inside the fuel cell. At the same time water is needed for humidification of reactant gases. The system design must ensure that there is no need for supplying additional water to the system, which may be impractical for transportation applications.

3.4. FREEZING

For many potential applications a fuel cell system must be capable of surviving and operating in extreme conditions. Presence of water in the membrane and fuel cell requires special attention to fuel cell stack and system design to allow system survival and start-up in extremely cold conditions. Most automotive systems have already demonstrated this capability.

3.5. FUEL ISSUES

In order to bring the fuel cell systems to the market sooner than hydrogen may become widely available fuel, fuel cell systems may be equipped with a reformer that generates hydrogen-rich gas from hydrocarbon fuels. This poses several challenges to the fuel cell stack and system design. CO even in small quantities is a poison for Pt catalyst at normal operating temperatures. Controlling a fuel cell/reformer system in variable power mode and maintaining low CO level all the time is a very challenging task. In addition, several other contaminants may be generated in the reforming process which may have detrimental effect on fuel cell stack performance and durability. US Department of Energy in April 2004 stopped supporting on-board reformer development, putting more emphasis on on-board hydrogen storage development, yet another critical issue for fuel cell acceptance.

4. Fuel cell applications

4.1. TRANSPORTATION

Almost every car manufacturer has already developed and demonstrated at least one fuel cell vehicles, and some have already went through several iterations/generations of fuel cell vehicles. Fuel cells in transportation offer clean alternative to gasoline and diesel internal combustion engines. For some countries, such as US, the ability to generate it is own fuel is a more important driver for fuel cell vehicles development than low emissions. Fuel cell vehicles are in general more efficient than those with the internal combustion engine (although this advantage diminishes with the hybrid vehicles). The main challenge for fuel cell vehicles is the size of hydrogen storage needed for an acceptable range, and the cost of the fuel cells. Automotive engines, produced by mass production techniques, are very cheap, <50 kW, about two order of magnitude lower than today's fuel cells (although such comparison is not fair because of the even bigger difference in manufacturing scales. Some studies conducted by automotive companies and their consultants indicate that the fuel cells could be produced at this cost.

Fuel cell buses do not have a problem with storing relatively large amounts of hydrogen (40–50 kg). Hydrogen is typically stored in the double roof space, which also appears to be a very safe solution. There are some 100 fuel cell buses being demonstrated on the streets of major cities in USA and Europe. Recent program CUTE (Clean Urban Transport for Europe) had logged more than a million miles with fuel cell buses operating in major European cities.

Possible niche market for fuel cells may be forklifts used indoors. Fuel cells may have a distinct advantage over batteries because they may be refueled much faster than the batteries can be recharged.

4.2. STATIONARY POWER GENERATION

Fuel cells may be used for stationary power generation, although PEM fuel cells have been limited to 200 kW level. Typically, stationary fuel cells are high temperature fuel cells such as PAFC, MCFC, and SOFC. Some systems may be combined with turbines resulting in very high efficiency (>70%). Stationary fuel cells are suitable for distributed power generation sited close to the customer load, can enable utilities to defer or eliminate costly investments in transmission and distribution system upgrades, and provide customers with better quality, more reliable energy supplies, and a cleaner environment. In addition, distributed power may provide better security and lower risk of terrorist attack.

4.3. RESIDENTIAL POWER GENERATION AND COGENERATION

Smaller fuel cells (<20 kW, but more typically <5 kW) are being developed for residential applications, particularly in Japan and Europe. These fuel cells use natural gas as fuel (therefore they are equipped with a reformer). Most often they also enable capture and utilization of waste heat and use it for space and/or hot water heating in combination with a natural gas boiler, resulting in high overall efficiency.

4.4. PORTABLE POWER

Smaller fuel cells (1 kW and lower) may be used as portable power as well as back-up power (uninterruptible power supply) or as battery chargers. Small fuel cells are also being developed as battery replacement which would enable longer operation time for consumer electronics (such as laptop computers, cell phones, cameras, and music players). There is a wide array of possible fuel cell applications in military: battery chargers, telecommunications, navigation systems, soldier power, computers, various power tools, exoskeletons, auxiliary power unit for vehicles, unmanned aerial vehicles, small autonomous robot vehicles, unattended sensors and munitions, ocean sensors, and transponders, etc.

5. Challenges in fuel cell commercialization

The most critical issues for fuel cell commercialization are:

- High cost for most applications
- Low durability
- Nonexistence of hydrogen infrastructure

The cost and durability issues have already been discussed above. Hydrogen is being considered as future replacement for fossil fuels. Commercial hydrogen is today primarily being used as industrial gas and it is very expensive. Most of hydrogen is today produced from natural gas. However, as a replacement for fossil fuels, hydrogen from natural gas does not make much sense. It may be justified only in a transition period to allow commercialization of promising hydrogen technologies such as fuel cells. Fuel cells with their numerous possible applications may actually be the main driver for hydrogen economy. In hydrogen economy, hydrogen, together with electricity, will be produced from clean renewable energy sources and will be used instead of fossil fuels to satisfy all the energy needs. Changing of the entire energy system is a gigantic endeavor on global scale, which may have already started, but which may take several decades to complete. Individual hydrogen energy technologies, including fuel cells, do not make much sense and may not compete with incumbent technologies if considered outside the context and the benefits of the entire energy system.

6. Conclusions

Fuel cells are being developed and demonstrated in many applications that may have relevance to international security. This includes clean transportation, clean power generation, distributed power generation, and military applications. Fuel cells are versatile, efficient, clean, and modular. They are close to commercialization and there are some niche markets which could enable early penetration. There are a few technical challenges, such as high cost, low durability, and nonexistence of hydrogen infrastructure, but there are no “show-stoppers.”

Fuel cells are only a part of a bigger energy system chain, and it may be difficult to commercialize only one component of that chain. However, the fuel cells may be the enabling technology to pave the road toward hydrogen economy. Transition from the fossil fuels-based system seems to be inevitable, due to environmental concerns, due to geopolitical problems and ultimately due to depletion of fluid fuels (oil and natural gas). Hydrogen in conjunction with renewable energy sources offers an attractive and feasible solution. Hydrogen complements the renewable energy sources by allowing their use in virtually every application. A shift to renewable energy sources will require a major shift in our mind-sets, culture, and policies, such as:

- Shift from the goals of continuous growth to the goals of sustainable development
- Promote energy and resources conservation
- Prioritize protection of the environment
- Moreover, this shift will have to be coordinated on a global scale

PERFORMANCE OF SINGLE-CHAMBER SOLID OXIDE FUEL CELLS

ISAIAH KELLOGG[1, 2], UMIT KOYLU[1],
AND FATIH DOĞAN[2*]
[1]*Department of Mechanical and Aerospace Engineering*
[2]*Department of Materials Science and Engineering*
University of Missouri-Rolla, Rolla, MO-65409, USA

Abstract: Single-chamber solid oxide fuel cells (SC-SOFCs) immerse the entire cell in a mixture of fuel and oxidizer gases within a single chamber, which eliminates the need for high temperature sealant, simplifies construction, and increases reliability over traditional double-chamber cells. However, there are challenges, such as low fuel utilization and electrode catalytic selectivity, that need to be overcome. This brief review paper looks at recent improvements in materials, processing, and operation of SC-SOFCs, which are rapidly approaching the performances of the double-chamber fuel cells and may become attractive for specific fuel cell applications.

Keywords: solid oxide fuel cell, SOFC, hydrogen, hydrocarbon, single chamber, SC-SOFC

1. Introduction

A single-chamber solid oxide fuel cell (SC-SOFC), which operates using a mixture of fuel and oxidant gases, provides several advantages over the conventional double-chamber SOFC, such as simplified cell structure with no sealing required and direct use of hydrocarbon fuel [1, 2]. The oxygen activity at the electrodes of the SC-SOFC is not fixed and one electrode (anode) has a higher electrocatalytic activity for the oxidation of the fuel than the other (cathode). Oxidation reactions of a hydrocarbon fuel can

---

[*] Fatih Dogan, Department of Materials Science and Engineering, University of Missouri-Rolla, Rolla, MO 65409 U.S.A.; e-mail: doganf@umr.edu

J.W. Sheffield and Ç. Sheffield (eds.), Assessment of Hydrogen Energy for Sustainable Development, 123–134.

be represented with a simplified multistep, quasi-general mechanism as follows:

$$CnHm + (n/2)O_2 \rightarrow nCO + (m/2)H_2 \quad (1)$$

$$H_2 + O^{2-} \rightarrow H_2O + 2e^- \quad (2)$$

$$CO + O^{2-} \rightarrow CO_2 + 2e^- \quad (3)$$

The cathode has a higher electrocatalytic activity for the reduction of oxygen according to the reaction:

$$½O_2 + 2e^- \rightarrow O^{2-} \quad (4)$$

These reactions lead to a low oxygen partial pressure at the anode locally, while the oxygen partial pressure at the cathode remains relatively high. As a result, an electromotive force (emf) between two electrodes is generated using a mixed gas of fuel and air. The SC-SOFC is not affected by the problems associated with carbon deposition, which is a significant drawback for double-chamber SOFCs when Ni-cermet used as anode material. Another advantage of SC-SOFC is that it converts hydrocarbon fuels into hydrogen and other reaction products in addition to electrical power generation. Hence, SC-SOFC has a potential for cogeneration of hydrogen and electrical power simultaneously by controlling Reaction (1). In this paper, recent developments on SC-SOFC in this laboratory are reviewed with respect to fuel cell materials, electrochemical performance of the cells, fuel utilization, and hydrogen generation [3, 4].

2. Experimental methods

The fuel/air mixtures for SC-SOFC were generally chosen to be richer than the upper explosion limits, yet they were fuel lean enough to prevent carbon deposition, which has been a significant problem in double-chamber SOFCs [5]. However, the local mixture ratios were also dependent on catalytic activity and testing conditions and varied accordingly for the optimum [1].

A typical experimental setup is illustrated in Figure 1. Typical measurements were conducted in a tube furnace consisting of an alumina tube through which mixed fuel and air flowed. Current collectors of Pt or Au mesh for the anode or cathode, respectively, were used to gather electronic data while thermocouples were used to monitor the temperature, although some researchers avoided the use of Pt due to catalytic reactions which can raise the measured temperature [6, 7]. It may also be useful to coat the thermocouples with a nonreactive epoxy to prevent a catalytic reaction on the thermocouple from causing a false high temperature measurement [6] or embed a tiny thermocouple directly into the cell itself [7]. The furnace was preheated to different temperatures varying from 300°C to over 700°C but the reactions at the cell surface raised the cell temperature above the furnace set temperature, sometimes enough to sustain the cell without a powered furnace [8].

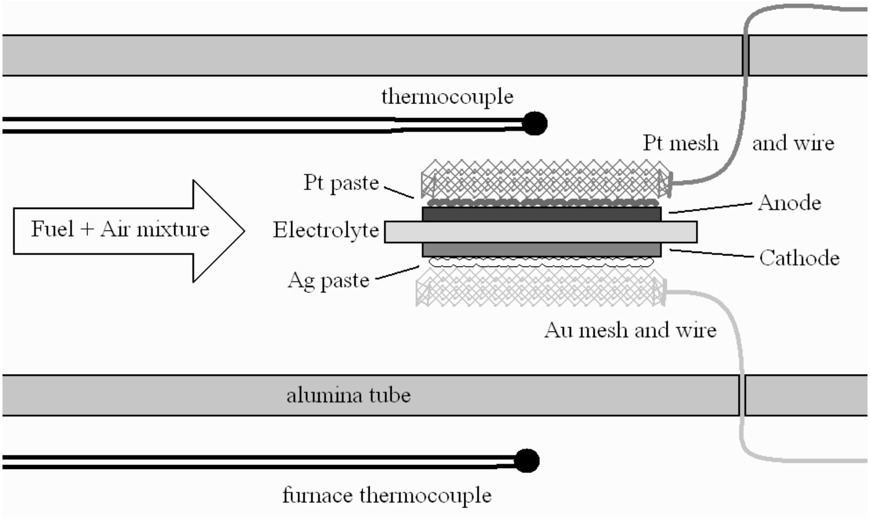


Figure 1. Experimental setup for SC-SOFC

3. Fuel cell materials

Several electrolyte materials have been tested including various compositions of Sm-doped ceria (SDC) and Y-doped ZrO_2 (YSZ). Electrolyte or electrode supported fuel cells were processed to control the thickness of electrolyte layers within submicrometer up to several hundred micrometer. While a dense electrolyte for a double-chamber fuel cell is required, a single-chamber configuration allows the use of porous electrolytes. Figure 2 shows a typical microstructure of a porous YSZ used in SC-SOFC. Many research groups [9–19] are attempting to improve the strength (and therefore reduce the minimum thickness) or increase the ionic conductivity of electrolyte materials so that the resistance of the electrolyte can be reduced.

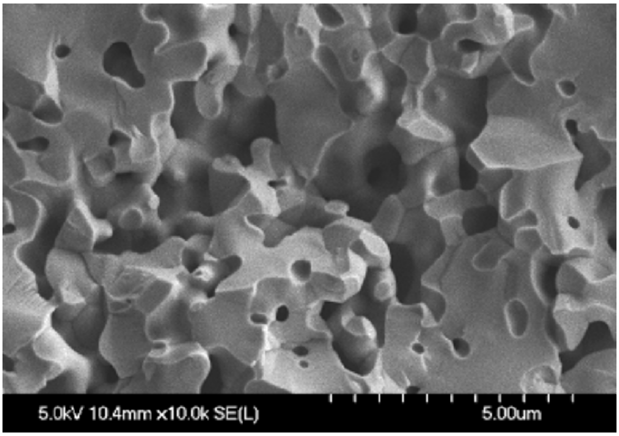


Figure 2. Fracture surface SEM image of porous YSZ electrolyte [4]

Anode materials are required to have a high electrocatalytic activity for the partial oxidation of the fuel in order to facilitate Reaction (1). Consequently, several anode materials have been tested including various compositions of Ni-cermets such as 70 wt.% Ni/30 wt.% YSZ (Ni + YSZ), 70 wt.% Ni/30 wt.% $Sm_{0.2}Ce_{0.8}O_x$ (Ni + CSO), and 60 wt.% Ni/40 wt.% $Gd_{0.1}Ce_{0.9}O_x$ (Ni + CGO). Because cathode materials exhibit a high electrocatalytic activity for the reduction of the oxygen in order to facilitate reaction (4), several cathode materials have also been tested, including various compositions of (La, Sr) (Co, Fe)O_3 (LSCF), and CSO-LSCF.

If the electrode materials are not sufficiently selective, a parasitic reaction creates mixed potentials at the electrodes which reduces the efficiency of the cell. The electrode materials must not only be selective but also impede unwanted fuel reactions [20]. Compared to traditional double-chamber fuel cells, parasitic reactions in a single-chamber fuel cell have historically reduced the open circuit voltage (OCV) by about half [21]. This is analogous to a leak that allows the fuel to seep into the oxidizer side of a double-chamber fuel cell [22]. Another concern is that the SC-SOFC operates in a narrow range of oxygen partial pressures that are near the ranges where both Ni-based anodes and LSCF-based cathodes may undergo undesirable oxidation/reduction reactions, although new research is directed towards creating more redox stable electrodes [23, 24]. Although the current choices of selective electrode materials are relatively poor, recent advances in materials have helped narrow the performance gap between double- and single-chamber fuel cells, and future advances are expected to further increase the performance of single-chamber fuel cells [4, 25–29].

4. Electrochemical performance

An ideal SC-SOFC has the same OCV and I–V output as a double-chamber cell, given a uniform oxygen partial pressure. A difference in catalytic properties of the electrodes must be sufficient to cause a substantial difference in oxygen partial pressure between the electrodes. For the ideal SC-SOFC, one electrode would be reversible toward oxygen adsorption and inert to fuel, while the other electrode would be reversible toward fuel adsorption and completely inert to oxygen [30]. Advances in electrode catalyst materials are needed for SC-SOFC to have the same performance as conventional double-chamber SOFC with a significant reduction in complexity and cost.

The power generation of SC-SOFC is dependent on the resistance of the materials. The electrolyte itself, the chemical reactions, and the overpotential contribute to the impedance, which is measured with a load of half the short circuit current applied to the cell. Figure 3 shows the impedance spectra of a particular cell, fitted to an equivalent resistor/capacitor (RC) circuit. Usually, R1 is considered to be the electrolyte resistance with R2 and R3 as the overpotential of the electrodes. The inductance of the cables and the relaxation frequency of R2 and C2 tended to introduce error into the measurement of R1. Therefore, R1 is usually measured together with R2 as R1 + R2 [31]. Some cells may be significantly affected by the electrolyte resistance, which depends on thickness.

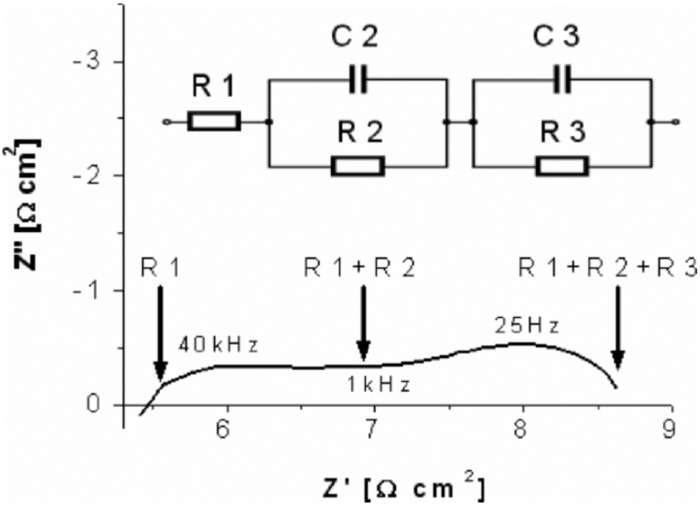


Figure 3. Typical impedance spectra of the cell (Ni + CGO anode under 50 mA/cm^2 load at 630°C) [31]

The impedance is dependent on temperature, as can be seen in Figure 4, which shows the area specific resistance (ASR) of a cell as a function of cell temperature for different gas flow rates. For the same cell temperatures, lower ASR was observed for increasing gas flow rates due to the increased gas diffusion near the electrodes that effectively reduced the overpotential resistances [4]. Because the anode and cathode are often conductive, the impedance of the cell is dependent largely on the thickness of the electrolyte. Using an anode supported cell structure, a YSZ electrolyte can be used as thin as 10–20 μm or even 1–2 μm [32, 33] as compared to 0.5 mm for a typical electrolyte supported cell [26].

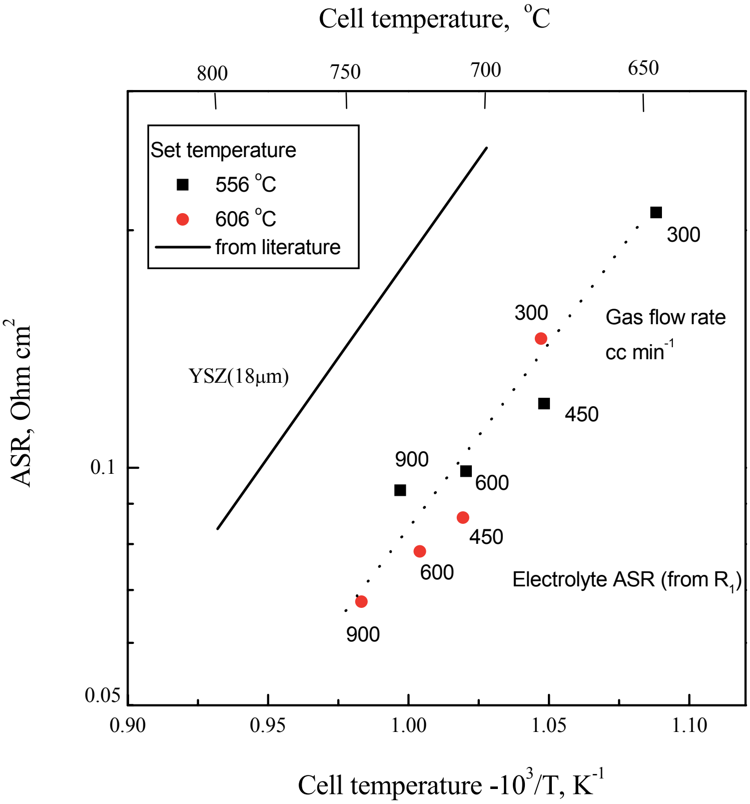


Figure 4. ASRs of a 16% YSZ electrolyte. The ASRs of YSZ were calculated from literature using 18 μm thick. Numbers in the figure indicate the value of gas flow rate where data were acquired [4]

The reactions at the surface of the present fuel cell increased with the temperature. This effect was also dependent on gas flow rate, as shown in Figure 5. The performance of the fuel cell was controlled to a degree with the gas flow rate in addition to the furnace set temperature [4]. The configuration of the cell also affected performance due to its effect on gas composition in the locality of each electrode [34, 35]. Although power increased with increasing flow rates, the amount of unutilized fuel increased as well. Only 4–8% of the fuel was utilized, even in tests with high power density of 0.6 W/cm² or higher [4].

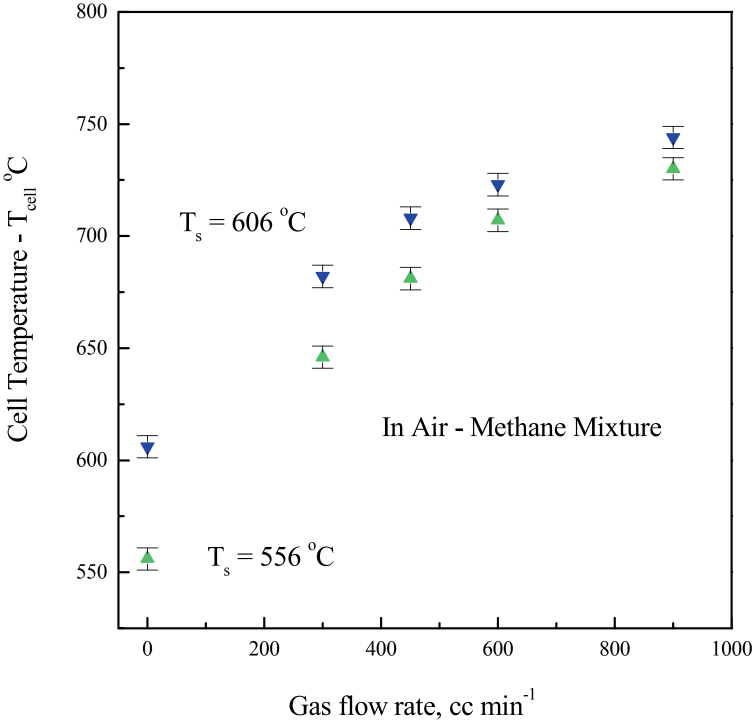


Figure 5. Cell temperature as a function of gas flow rate with a different set of temperatures [4]

The reaction rate was in turn affected by the cell temperature, as shown in Figure 6. The reaction rates generally followed the Arrhenius relation, i.e.,

$$r = A\exp\left(-\frac{E_a}{kT}\right) \tag{5}$$

where A is a nearly temperature-independent constant, E_a is the activation energy of the reaction in molecular units, k is Boltzmann’s constant, and T

is the temperature in Kelvin [4]. The interactions between cell temperature, gas flow rate, reaction rate, and cell performance are very complex and not yet fully understood. Some researchers have used three dimensional modeling of electrical, chemical, and mass transfer in order to evaluate the performance of a SOFC in part or in whole [36–38].

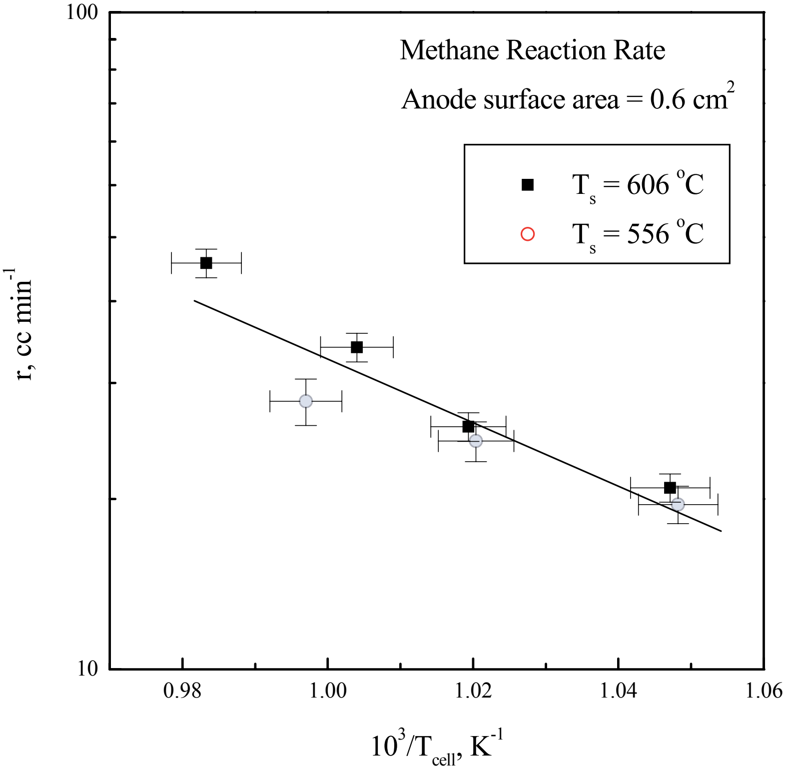


Figure 6. Methane reaction rate as a function of reciprocal cell temperature [4]

Figure 7 shows a double-cell module and the temperature response of the voltage generated. The double-cell modules suffered a decrease in voltage as temperature increased, possibly due to a change in oxygen activity on the electrodes or electron leakage of the interconnecting Au wire. The decrease in voltage with the smaller cells suggests that there might be a size limitation for this type of fuel cell [3].

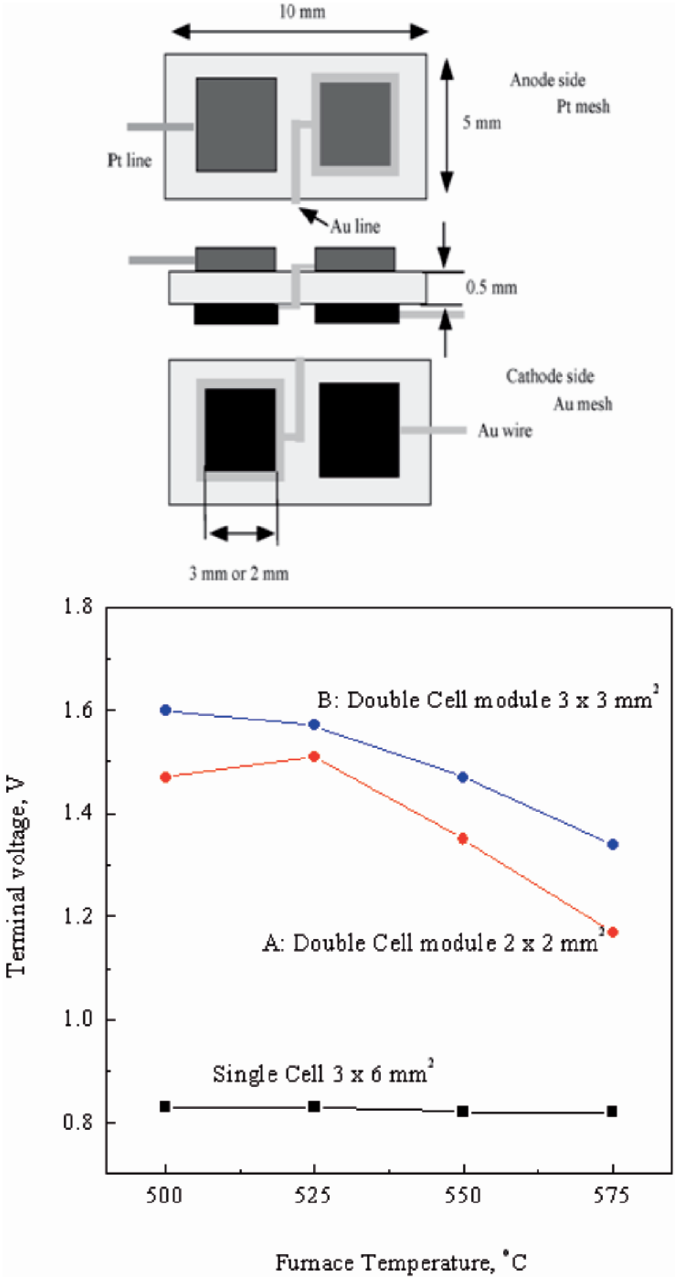


Figure 7. Double-cell module and open circuit voltage as a function of furnace temperature [3]

Figure 8 shows the discharge profile of a cell with different gas flow rates heated to a furnace set temperature of 606°C. A maximum power density of about 0.66 W/cm^2 (corresponding to 0.44 V) was obtained at a cell temperature of 744°C using a porous electrolyte. Performance of the cell increased with increasing gas flow rate; however, this could usually be attributed to an increase in temperature [4].

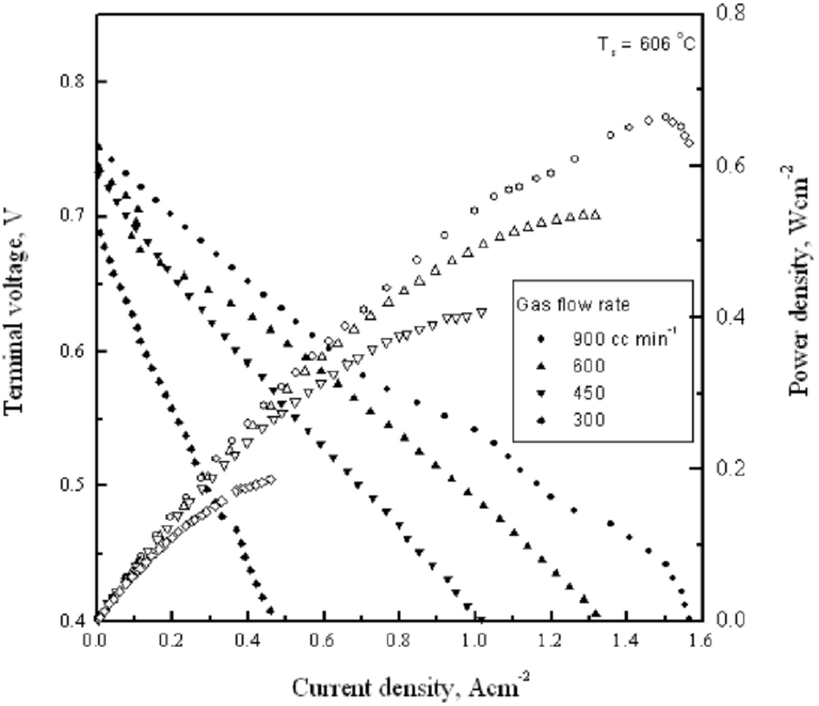


Figure 8. I–V discharge profile (solid symbols) and power density (open symbols) of the porous electrolyte SC-SOFC. Data collected at a set temperature of 606°C [4]

5. Summary

Significant improvements in the performance of single-chamber solid oxide fuel cells have been achieved in recent years. Since SC-SOFC does not require high temperature sealing materials to prevent the mixing of fuel gas and oxygen at operation temperatures, it offers a robust and more reliable alternative to double-chamber SOFC for special applications. As further advances are made towards controlling the catalytic activity of electrode materials, electrolyte resistance particularly at lower operating temperatures, optimizing of the gas flow rate and the cell configuration, SC-SOFC may find widespread implementation as compact power sources in the future.

References

1. Hibino, T., Hashimoto, A., Inoue, T., Tokuno, S., and Sano, M. A Low-Operating-Temperature Solid Oxide Fuel Cell in Hydrocarbon-Air Mixtures, *Science*, 288, 2031 (2000).
2. Hibino, T., Hashimoto, A., Yano, M., Suzuki, M., Yoshida, S., and Sano, M. A Solid Oxide Fuel Cell Using an Exothermic Reaction as the Heat Source, *Journal of the Electrochem. Soc.*, 148, A544 (2001).
3. Suzuki, T., Jasinski, P., Anderson, H., and Dogan, F. Role of Composite Cathodes in Single Chamber SOFC, *Journal of the Electrochem. Soc.*, 151, A1678 (2004).
4. Suzuki, T., Jasinski, P., Petrovsky, V., Anderson, H., and Dogan, F. Performance of a Porous Electrolyte in Single-chamber SOFCs, *Journal of the Electrochem. Soc.*, 152, 1 (2005).
5. Steele, B. C. H. Survey of Materials Selection for Ceramic Fuel Cells II. Cathodes and Anodes, *Solid State Ionics*, 86–88, 1223 (1996).
6. Napporn, T. W., Morin, F., and Meunier, M. Evaluation of the Actual Working Temperature of a Single-chamber SOFC, *Electrochem. and Solid-State Letters*, 7, A60 (2004).
7. Napporn, T. W., Jacques-Bédard, X., Morin, F., and Meunier, M. Operating Conditions of a Single-chamber SOFC, *Journal of the Electrochem. Soc.*, 151, A2088 (2004).
8. Hibino, T., Hashimoto, A., Inoue, T., Tokuno, J., Yoshida, S., and Sano, M. A Solid Oxide Fuel Cell Using an Exothermic Reaction as the Heat Source, *Journal of the Electrochem. Soc.*, 148, A5449 (2001).
9. Adler, S.B. Factors Governing Oxygen Reduction in Solid Oxide Fuel Cell Cathodes, *Chem. Rev.* 104, 4791 (2004).
10. Hibino, T., Wang, S., Kakimoto, S., and Sano, M. Single Chamber Solid Oxide Fuel Cell Constructed from an Yttria-Stabilized Zirconia Electrolyte, *Electrochem. Solid-State Letters*, 2, 317 (1999).
11. Hibino, T., Tsunekawa, H., Tanimoto, S., and Sano, M. Improvement of a Single-chamber Solid-oxide Fuel Cell and Evaluation of New Cell Designs, *Journal of the Electrochem. Soc.*, 147, 1338 (2000).
12. Hibino, T., Hashimoto, A., Inoue, T., Tokuno, J., Yoshida, S., and Sano, M. Single-chamber Solid Oxide Fuel Cells at Intermediate Temperatures with Various Hydrocarbon-air Mixtures, *Journal of the Electrochem. Soc.*, 147, 2888 (2000).
13. Babilo, P. and Haile, S. M. Enhanced Sintering of Yttrium-Doped Barium Zirconate by Addition of ZnO, *Journal of the American Ceram. Soc.*, 88, 2362 (2005).
14. Uda, T., Boysen, D. A., Chisholm, C. R. I., and Haile, S. M. Alcohol Fuel Cells at Optimal Temperatures, *Electrochem. and Solid-State Letters*, 9, A261 (2006).
15. Shao, Z., Haile, S. M. A High Performance Cathode for the Next Generation of Solid Oxide Fuel Cells, *Nature*, 431, 170 (2004).
16. Petrovsky, V., Suzuki, T., Jasinski, P., and Anderson, H. U. Low-temperature Processed Anode for Solid Oxide Fuel Cells, *Electrochem. and Solid-State Letters*, 8, A341 (2005).
17. Chiba, R., Yoshimura, F., Sakurai, Y., Tabata, Y., and Arakawa, M. A Study of Cathode Materials for Intermediate Temperature SOFCs Prepared by the Sol-gel Method, *Solid State Ionics*, 175, 23 (2004).
18. Hibino, T., Hashimoto, A., Yano, M., Suzuki, M., Yoshida, S., and Sano, M. High Performance Anodes for SOFCs Operating in Methane-air Mixture at Reduced Temperatures, *Journal of the Electrochem. Soc.*, 149, A133 (2002).
19. Gorte, R. J., Vohs, J. M., and McIntosh, S. Recent Developments on Anodes for Direct Fuel Utilization in SOFC, *Solid State Ionics*, 175, 1 (2004).

20. Riess, I. The Significance of Impeded Reactions in Solid State Electrochemistry, *Solid State Ionics*, 176, 1667 (2005).
21. Grimes, P., Fielder, B., and Adam, J. Liquid-Alkaline Fuel Cells, *15th Annual Power Sources Conference*, 292 (1961).
22. Priestnall, M., Kotzeva, V., Fish, D., and Nilsson, E. Compact Mixed Reactant Fuel Cells, *Journal of Power Sources*, 106, 21 (2002).
23. Tao, S. and Irvine, J. T. S. A Redox-Stable Efficient Anode for Solid-oxide Fuel Cells, *Nature Materials*, 2, 320 (2003).
24. Tikekar, N. M., Armstrong, T. J., and Virkar, A. V. Reduction and Reoxidation Kinetics of Nickel-based SOFC Anodes, *Journal of the Electrochem. Soc.*, 153, A654 (2006).
25. Jasinski, P., Petrovsky, V., Suzuki, T., Petrovsky, T., and Anderson, H. U. Electrical Properties of YSZ Films Prepared by NetShape Technology, *Journal of the Electrochem. Soc.*, 152, A454 (2005).
26. Suzuki, T., Jasinski, P., Anderson, H., and Dogan, F. Single Chamber Electrolyte Supported SOFC Module, *Electrochem. Solid-State Letters*, 7, A391, (2004).
27. Asahara, S., Michiba, D., Hibino, M., and Yao, T. Single Chamber SOFC Using $BaLaIn_2O_{5.5}$ Solid Electrolyte, *Electrochem. Solid-State Letters*, 8, A449 (2005).
28. Shao, Z., Haile, S. M., Ahn, J., Ronney, P. D., Zhan, Z., and Barnett, S. A. A Thermally Self-Sustained Micro Solid-oxide Fuel-cell Stack with High Power Density, *Nature*, 435, 795 (2005).
29. Haile, S. M., Staneff, G., and Ryu, K. H. Non-stoichiometry, Grain Boundary Transport and Chemical Stability of Proton Conducting Perovskites, *Journal of Materials Science*, 36, 1149 (2001).
30. Riess, I., van der Put, P. J., and Schoonman, J. Solid Oxide Fuel Cells Operating on Uniform Mixtures of Fuel and Air, *Solid State Ionics*, 82, 1 (1995).
31. Jasinski, P., Suzuki, T., Dogan, F., and Anderson, H. Impedance Spectroscopy of Single Chamber SOFC, *Solid State Ionics*, 175, 35 (2004).
32. Shao, Z., Kwak, C., and Haile, S. M. Anode-Supported Thin-film Fuel Cells Operated in a Single Chamber Configuration, *Solid State Ionics*, 175, 39 (2004).
33. Suzuki, T., Jasinski, P., Petrovsky, V., Anderson, H., and Dogan, F. Anode Supported Single Chamber Solid Oxide Fuel Cell in CH_4-air Mixture, *Journal of the Electrochem. Soc.*, 151, A1473 (2004).
34. Hibino, T., Hashimoto, A., Inoue, T., Tokuno, J., Yoshida, S., and Sano, M. A Solid Oxide Fuel Cell Using an Exothermic Reaction as the Heat Source, *Journal of the Electrochem. Soc.*, 148, A5449 (2001).
35. Hibino, T., Hashimoto, A., Suzuki, M., Yano, M., Yoshida, S., and Sano, M. A Solid Oxide Fuel Cell with a Novel Geometry that Eliminates the Need for Preparing a Thin Electrolyte Film, *Journal of the Electrochem. Soc.*, 149, A195 (2002).
36. Yuan, J. and Sundén, B. Analysis of Intermediate Temperature Solid Oxide Fuel Cell Transport Processes and Performance, *ASME Journal of Heat Transfer*, 127, 1380 (2005).
37. Sheng, C. Y. and Dean, A. M. Importance of Gas-phase Kinetics within the Anode Channel of a Solid-oxide Fuel Cell, *Journal of Physical Chemistry*, 108, 3772, (2004).
38. Li, P. W. and Chyu, M. K. Electrochemical and Transport Phenomena in Solid Oxide Fuel Cells, *ASME Journal of Heat Transfer*, 127, 1344 (2005).

HYDROGEN PRODUCTION FROM SOLAR ENERGY

I. ENGIN TÜRE*
UNIDO-ICHET
Sabri Ulker Sok. 38/4, Cevizlibag, Zeytinburnu
34015, Istanbul, Turkey

Abstract: Solar energy is potentially the most abundant renewable energy resource available to us and hydrogen production from solar energy is considered to be the ultimate solution for sustainable energy. The various methods for utilizing solar energy for hydrogen production are examined and both their advantages and disadvantages are compared. The technology of splitting water using solar energy can be divided into the four main topics: photochemical systems; semiconductor systems; photobiological systems; and hybrid and other systems. Concentrated solar energy can also be used for the direct decomposition of water to produce hydrogen. As a result of the great potential promised by solar energy technologies, low cost, high efficiency hydrogen production systems utilizing solar energy are the subject of intense investigation. The most common method of solar-based hydrogen production utilizes photovoltaic (PV) cells in combination with water electrolysis. In this system, PV cells are used to create electrical energy. An electrolyzer passes this electric current through water, causing the water molecules to separate into hydrogen and oxygen gases. Older electrolyzer designs are operated using water premixed with a caustic electrolyte, most often potassium hydroxide. While this design has proven to be relatively efficient, the corrosive nature of the electrolyte adds to the operational complexities of the system. Nearly all modern electrolyzers use a proton exchange membrane (PEM) as a catalyst in the electrolysis process. In comparison to electrolyzers employing a liquid electrolyte needing frequent replenishment, PEM electrolyzers have the advantage of producing very pure hydrogen and at the same time requiring much less maintenance. However, they must use distilled or deionized water instead of tap water. Another major benefit of using PEM electrolyzer cells is that they are easily scalable, and by simply

---

* To whom the correspondence should be addressed. Engin Ture, UNIDO-ICHET, Sabri Ulker Sok. 38/4 Cevizlibag, Zeytinburnu 34015 Istanbul, Turkey; e-mail: eture@unido-ichet.org

J.W. Sheffield and Ç. Sheffield (eds.), Assessment of Hydrogen Energy for Sustainable Development, 135–146.

adding more cells, the system can easily be matched to the desired rate of hydrogen production, or to the amount of electricity produced from the PV cells. Other systems utilizing photochemical or biological technologies to produce hydrogen are small-scale units that are currently intended for educational and research purposes only. These systems produce small amounts of hydrogen and are often used to power small fuel cells of only a few watts. There are also a number of systems designed to create larger amounts of hydrogen from solar power but these systems are still under development.

Keywords: hydrogen, solar energy, photovoltaics, electrolyzer, photochemical

1. Introduction

There are a number of methods of producing hydrogen utilizing solar energy and a summary of these is shown in Figure 1.

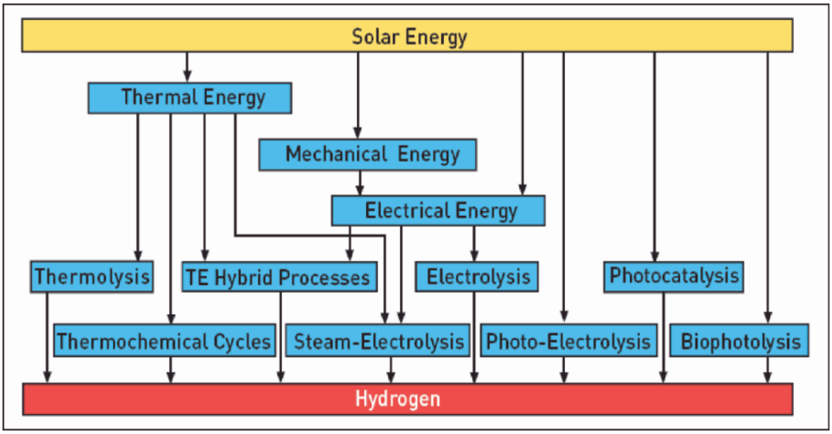


Figure 1. Pathways to hydrogen via solar energy [1]

The photoproduction of hydrogen from the decomposition of water using power derived from solar energy has been the goal of scientists and engineers since the early 1970s when Fujishima and Honda first reported the generation of hydrogen and oxygen gases in a photoelectrochemical cell (PEC) using a titanium dioxide electrode illuminated with near ultraviolet light [2]. In such solar photonic processes, photons are incident directly on an absorber which may convert part of the photon energy to electricity (PV cell) or store part as chemical energy in an endergonic chemical reaction (conversion of water to hydrogen and oxygen).

Four types of solar photochemical hydrogen systems have been identified that show sufficient promise for further research and development:

1. Semiconductor systems
2. Photochemical systems
3. Photobiological systems
4. Hybrid and other systems

Among these methods, the only technique developed sufficiently for commercialization, is that where electrical energy produced by solar PV panels is fed into an electrolyzer to produce gaseous hydrogen.

2. Semiconductor Systems

If photons of sufficient energy are incident on a semiconductor, excess electrons and holes are created in the semiconductor conduction and valence bands respectively. Further, if the semiconductor is fabricated to contain one or more p–n junctions, the chemical potential of the excess carriers can be converted into a flow of charges resulting in an electric current. This current can then be used to power the direct electrolysis of water. Alternatively, the excess charge carriers can migrate to the semiconductor surface where they initiate chemical reactions and produce H_2 and/or O_2 in the surrounding medium either in a PEC or in a suspension of semiconductor particles.

2.1. PHOTOVOLTAIC – ELECTROLYZER SYSTEMS

This is the most developed option at present, since the typical efficiency of silicon PV cells is better than 15%, and the efficiency of electrolyzers is often better than 75%. There is extensive fundamental work underway to improve the performance of PV cells. However, research is needed to explore the special requirements of a coupled PV cell/electrolyzer system. Computer simulations of a PV-electrolyzer system have now been developed. At the scale of around 10 kW_e, the best overall efficiency for H_2 generation from water is 6% [2].

2.1.1. Photovoltaic electricity generation

PV cells convert photon energy into electrical energy. Two conditions must exist inside a PV material to for a PV electricity generation to occur: (1) incident light energy must be sufficiently high to break a chemical bond in the material and thus create a free electron/hole pair; and (2) an electrical asymmetry in the form of a p–n junction must be present [3].

Every semiconductor material has a very important characteristic property called its band gap (E_g) which is the minimum energy difference between its valance and conduction bands. The semiconductor can only absorb photons of energy higher than this value. The optimum band gap for an ideal p–n junction PV cell lies in the 1.4–1.5 eV range, corresponding to the peak intensity of visible solar light. The efficiencies of various PV cells illuminated by sunlight as functions of band gap are shown in Figure 2.

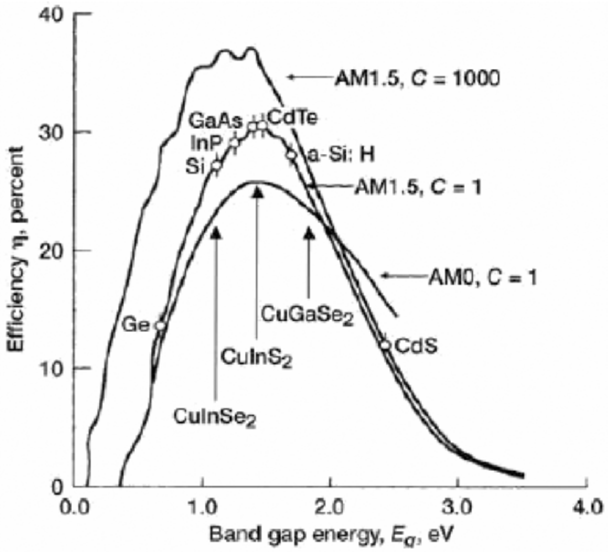


Figure 2. Ideal p–n junction solar cell efficiencies plotted against band gap energy [3]

To date, PV technology has had two main thrusts: (1) the development of high efficiency cells with high cost; and (2) the development of low efficiency cells with low cost. PV technology needs to combine these two extremes into a high efficiency, low cost cell. Along these lines, existing PV cell technologies are often described in terms of three technology generations, as illustrated in Figure 3.

Generation I consisting of wafer-based PV cell technologies is the most mature technology group. It includes single-crystal and polycrystal silicon as well as III–V materials such as gallium arsenide [3]. The single-crystal and polycrystalline silicon technologies both require extremely high purity fabrication materials to produce defect free insulating wafers for processing into junctions. Approximately 80% of all PV cells currently sold are silicon based [4] with typical efficiencies less than 20%.

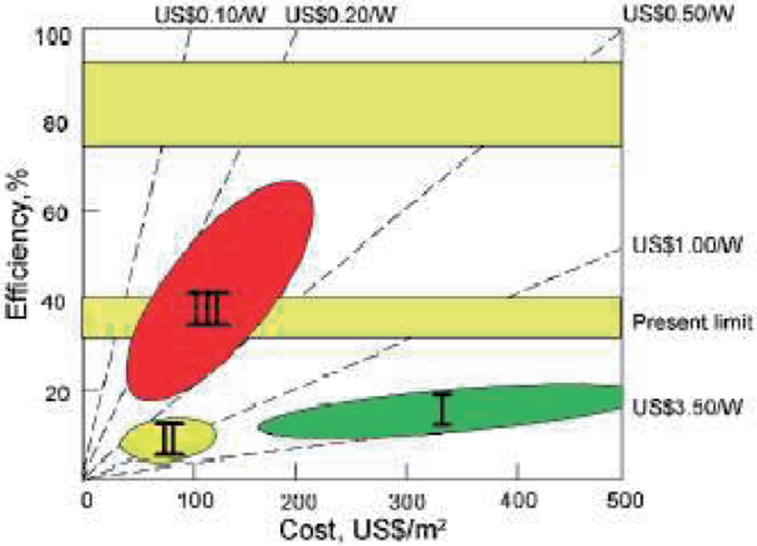


Figure 3. Plot of efficiency versus cost for the three generations of solar cells [3]

Generation II PV technologies use thin-films of semiconductor materials deposited onto substrates. As this process is less technically demanding than wafer production, the material cost of Generation II is relatively lower than Generation I technologies. The primary Generation II technologies are $CuInGaSe_2$ (CIGS), CdTe, and amorphous Si (a-Si). The maximum efficiencies achieved for these technologies in the laboratory were 18.4%, 16.4%, and 12.7%, respectively in 2001 [5], and are significantly lower than those for Generation I technologies. The main reason is the presence of many crystalline imperfections in these thin-films due to the uncontrolled way they are fabricated.

The most well-developed Generation III concept is that of tandem PV cells. These consist of layers of semiconductors having different band gaps, each layer being optimized for absorption of light with energy close to its band gap. Theoretically, with enough individual layers an efficiency of 87% can be achieved [5].

2.2. ELECTROLYZER TECHNOLOGY FOR HYDROGEN PRODUCTION

Electrolyzers convert water into hydrogen and oxygen using electric energy. When electrodes are placed in water and a sufficiently large voltage is applied between them, it becomes energetically favorable for oxygen gas to form at one electrode and hydrogen gas at the other. The water is reduced to hydrogen gas at the cathode, while water is oxidized to oxygen at the anode, as illustrated in Figure 4. The theoretical minimum voltage required to drive this water-splitting process is 1.23V. The reactions that occur at the electrodes are as follows:

Cathode (positive voltage): $2H^+ + 2e^- \rightarrow H_2$
Anode (negative voltage): $H_2O \rightarrow ½\, O_2 + 2H^+ + 2e^-$

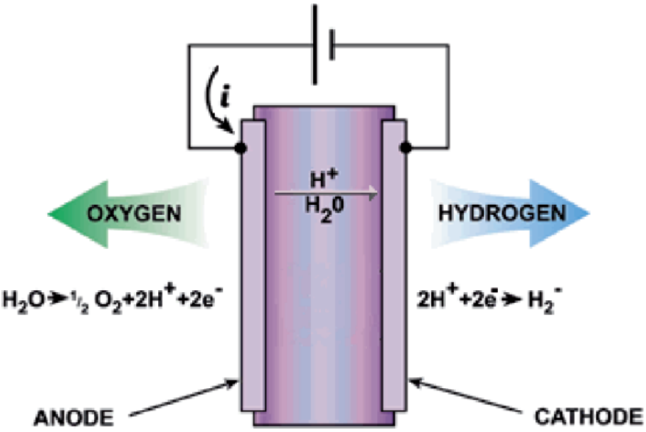


Figure 4. Electrolysis schematic [3]

Currently there are two primary distributed electrolyzer technologies in development and use: (1) Alkaline electrolyte electrolyzers and (2) Proton-exchange membrane electrolyzers.

Alkaline electrolyte electrolyzers represent a very mature technology. The anode and cathode materials in these systems are typically made of nickel-plated steel and bare steel, respectively. The electrolyte is a liquid based on highly caustic KOH solution.

Proton-exchange membrane (PEM) electrolyzers are a newer and more rapidly evolving water electrolysis technology. PEM technology is a completely solid-state technology, with cathode and anode each consisting of a highly porous network of graphite-like material having small platinum particles embedded inside. The graphite-like material serves as a conductive electrode while the embedded platinum particles serve to catalyze electrochemical reactions. The electrolyte is formed from a solid-polymer. Table 1 contains a summary of key advantages and disadvantages for the two technologies.

TABLE 1. Summary of strengths and weaknesses of alkaline and PEM electrolyzers [3]

	Strengths	Weaknesses
Electrolyzers		
Alkaline	High voltage efficiency	High parasitic power consumption
	Durable	Complex gas handing
	Compact	Liquid electrolyte (KOH)
Solid polymer	Low parasitic power consumption	
	High overall efficiency	High purity water needed
	Pressure difference allowed between H_2 and O_2 sides	High over potentials in some electrolyzers

3. Photochemical systems

Any photochemical process to drive the water splitting reaction must involve a sensitizer, that is, a molecule or semiconductor that can absorb sunlight and stimulate photochemical reactions. The absorption of a single photon in the solar wavelength ranges can cause the transfer of one electron in a photoredox process. The water splitting reaction is a two-electron process, hence, catalysts for the storage of electrochemical equivalents are necessary in practical schemes. Figure 5 shows a minimal scheme for a process to split water involving a photochemical sensitizer S with redox storage catalysts for oxidation and reduction.

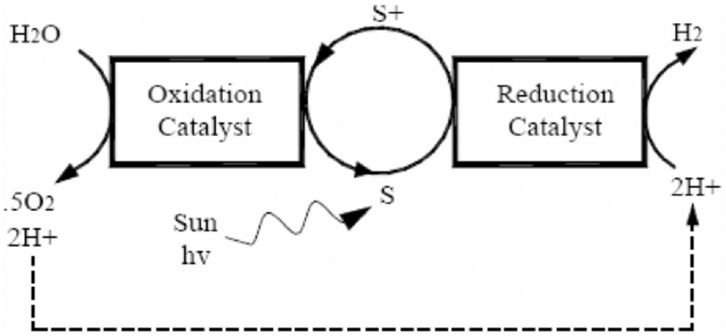


Figure 5. Photochemical hydrogen production [6]

No photochemical system investigated has yet approached an efficiency of 10%. Photochemical systems suffer from several difficulties:

- The molecular absorber must remain robust through millions of cycles. The quantum yield for photodegradation reactions must be lower than 10^{-6}. This is a very severe constraint.
- Unless contained in a highly ordered system, excited-state molecules formed by light absorption must migrate through diffusion to the sites of quenchers where electron-transfer can take place. Diffusion in a liquid is a relatively slow process and so excited-state lifetimes must be sufficiently long to allow this primary photochemical process to take place.
- Even if the primary electron-transfer process occurs efficiently, spontaneous energy-wasting back-electron transfer can always occur unless elaborate methods are employed to minimize this ubiquitous reaction.
- All systems studied to date produce H_2 and O_2 gases together, and these bubble out as a 2:1 highly explosive mixture. Some method must be employed to separate the gases. This brings additional costs.

4. Photoelectrochemical cells for direct hydrogen production

The essence of a PEC is that PV electric power and electrolytic decomposition of water are integrated into a single device. In its simplest form, a PEC hydrogen production cell consists of a light absorbing semiconductor electrode connected electrically to a metal counter electrode, both immersed in an electrolyte.

When light of sufficient energy is incident upon the semiconductor electrode, free electrons and holes are created. Similar to the case of the p–n junction, a potential drop occurs at the semiconductor-liquid interface as a result of the electronic asymmetry and subsequent formation of opposing charged layers at the interface. For n-type material, these results in free holes are being driven to the interface and free electrons being driven out from the semiconductor to the counterelectrode. For p-type semiconductor electrodes the situation is reversed with electrons and holes being driven to the interface and counterelectrode respectively. For the n-type case, the free holes that go to the interface then oxidize water through the reaction:

$$H_2O + 2h^+ = \tfrac{1}{2}\,O_2 + 2H^+ \text{ (Anode)}$$

while free electrons flow to the counterelectrode and reduce hydrogen ions to hydrogen gas. In this way, the PV semiconductor both generates the required voltage for electrolysis and participates in the required electrochemical reactions itself.

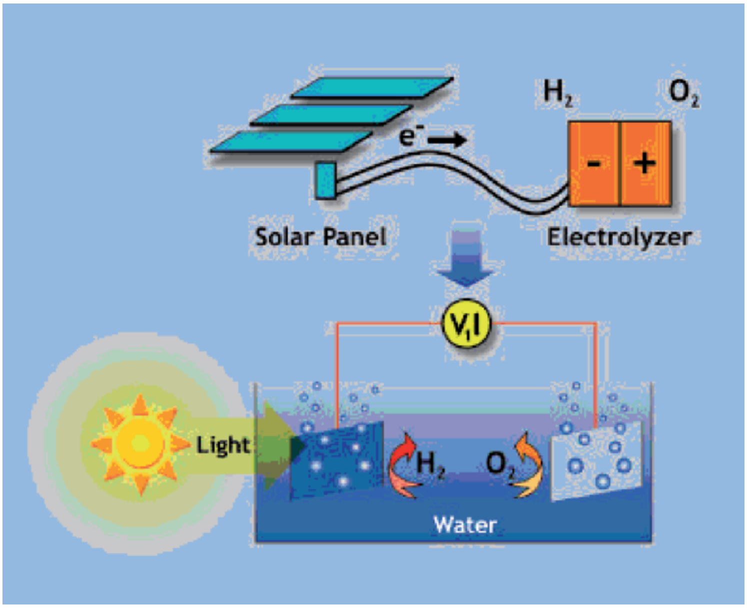


Figure 6. A monolithic PEC [7]

There are a number of key materials requirements for the semiconductor electrode material in order for the cell to operate effectively. First and foremost, the band gap of the semiconductor electrode material is an absolutely critical parameter. There exists an optimum band gap for PV power generation from terrestrial sunlight that is about 1.4 eV. Furthermore, the band gap must be large enough to provide for greater than the 1.23 V required to split water. However, for two reasons, only materials with very high band gaps (~3 eV) can be used in direct PEC systems. Figure 6 shows a typical monolithic PEC. Firstly, due to losses in the system such as system resistance and electrode over potential, only a fraction of the total band gap energy is harnessed as useful voltage. Secondly, and very importantly, all materials with band gaps below approximately 3 eV have been found to lack stability and undergo electrochemical corrosion during PEC operation.

Hybrid photoelectrodes are used in the most promising current approaches to PEC hydrogen generation. In this approach, a stable high-band gap material such as TiO_2 is stacked on top of a standard p–n junction PV cell with a band gap tuned to the solar spectrum. It simultaneously provides high photo-conversion efficiency and photoelectrode stability, with the use of a standard platinum counterelectrode. A hybrid photoelectrode device based on AlGaAs on a Si substrate has demonstrated a short-lived light to hydrogen efficiency of 18.3% [8].

Dye-sensitized or Gratzel PV cells use a porous TiO_2 photoelectrode with a ruthenium-based light absorbing dye. The light-absorbing dye, called a sensitizer, absorbs sunlight to create an electron-hole pair, and then transfers the electron to the TiO_2 electrode. In turn this causes H^+ ions to be reduced to H_2 at the counterelectrode and water molecules to be oxidized by the hole at the dye molecule. Zayat and coworkers have developed a $SrTiO_3$ photoelectrode based dye-sensitized PEC cell based on this concept. The PEC solar to hydrogen efficiency of this is 4.46% [9].

5. Photobiological systems

In photobiological systems, certain types of organism such algae and bacteria produce hydrogen when illuminated by light. A Schematic of an indirect photobiological hydrogen production system is shown in Figure 7. Whereas algae use the reversible hydrogenase enzyme to generate hydrogen from protons in anaerobic conditions, cyanobacteria use nitrogenase enzymes to generate hydrogen in anaerobic conditions.

Hydrogen production by green algae has significant advantages over other photobiological systems. Firstly, ATP production is not required. Secondly, high theoretical efficiencies are possible. Moreover, water is used directly as the source of reductant without the need to produce biomass or to store intermediary carbon metabolites. However, green algae also photosynthesize under illumination and the resulting O_2 production depresses the algal photoproduction of H_2. This sensitivity is the major obstacle limiting the use of algal systems for H_2 production. Several studies have indicated that mutagenesis can be used to decrease the O_2 sensitivity of the hydrogenase and thus can eventually lead to a system that produces H_2 under aerobic conditions [10].

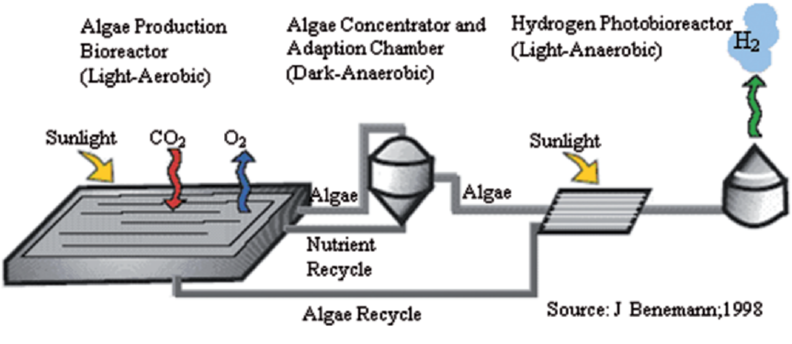


Figure 7. Schematic of an indirect photobiological hydrogen production system [11]

Photobiological systems have the distinct advantage that the collector system self assembles. Although the capital costs of such systems are potentially quite low, there may be considerable costs involved in the fabrication of reactor systems necessary to maintain the organisms under optimum conditions. Another major disadvantage is that hydrogen and oxygen are generated together to cause a potentially explosive mixture, and rapid separation of the two gases must be employed to prevent this possibility. Benemann has proposed a two-stage process, in which green algae are cultivated in large open ponds to produce a high carbohydrate algal biomass [12]. The biomass then becomes the substrate for the production of hydrogen in closed tubular photobioreactors.

6. Hybrid and other systems

Semiconductors can only absorb photons of light with energies greater than the band gap energy of the semiconductor. By treating the surface of a semiconductor so that molecular dyes are adsorbed, it becomes possible to produce electron-hole pairs at the lower energies characterized by the dye. In this manner the efficiency of the system can be raised to take advantage of a larger part of the available solar spectrum. There have been reports of PEC based on chloroplast preparations in the electrolyte or adsorbed onto an electrode. However, these systems have not yet been developed to give significant amounts of water splitting.

7. Photodegradation systems

An organic molecule can be used as the sacrificial donor in a reduction half reaction. Generally there is no net energy storage, but (depending on the reaction) hydrogen may be evolved at the same time as a surplus reaction product. For example, the reaction

$$CH_3COOH(aq) + O_2 \longrightarrow 2CO_2 + 2\,H_2$$

is exergonic by 392 kJ but the fuel value of the H_2 produced is 474 kJ [2]. The process involves the conversion of one fuel (CH_3COOH, with a fuel value of 866 kJ) into another ($2H_2$, with a fuel value of 474 kJ).

By using solar energy to couple hydrogen evolution to the photodegradation of organic pollutants, value is added to the photodegradation process. The use of UV or solar light to destroy organic pollutants in contaminated waters is quite expensive, with treatment costs varying between \$1 and \$50 per kg of pollutant removed. If hydrogen could be evolved at the same time as organic pollutants are photodegraded, considerable value could be added to the process.

8. Summary

Among renewable energy sources, solar energy is likely to become the dominant energy resource for hydrogen production. Of the various techniques for harnessing solar energy, those of photoelectrochemical and biological hydrogen production have the potentials to achieve the desired goals of high efficiencies and low costs. These systems are inherently low cost despite problems associated with gas separation and have already achieved significant efficiencies.

References

1. Luzzi, A., Bonadio, L., McCann, M., *In Pursuit of the Future:25 Years of IEA Research Towards the Realisation of Hydrogen Energy Systems*, International Energy Agency Hydrogen Implementing Agreement, 2004.
2. Bolton, J. R., *Solar Photoproduction of Hydrogen*, IEA Technical Report, IEA Agreement on the Production and Utilisation of Hydrogen, September 1996.
3. Danielson, D., *The Prospects for Solar-powered Distributed Hydrogen Production*, Term Paper Sustainable Energy, 2004.
4. Maycock, P., *The World PV Market: Production Increases 36%*, Renewable Energy World, July/August 2002, http://www.jxj.com/magsandj/rew/2002_04/world_pv_market.html.
5. Green, M. et al., *Solar Cell Efficiency Tables*, Key Center for Photovoltaics, University of New South Wales (2001) http://www.pv.unsw.edu.au/eff/.
6. Goel, N., Mirabai, S. T., Ingley, H., Goswami, Y., *Hydrogen Production,* Mechanical and Aerospace Engineering Department, University of Florida.
7. Turner, J. A., *Direct Photoelectrochemical Production of Hydrogen*, Solar-Hydrogen Workshop, November 9, 2004.
8. Licht, S. et al., *Efficient water splitting by RuO2-catalyzed AlGaAs/Si photoelectrolysis*, Journal of Physical Chemistry 104 (2000) p. 8920.
9. El Zayat, M. Y. et al., *Photoelectrochemical properties of dye sensitized Zr-doped SrTiO3 electrodes*, International Journal of Hydrogen Energy 23 (1998) p. 259.
10. Benemann, J., (1998), *Process Analysis and Economics of Biophotolysis of Water*, IEA-HIA Technical Report, March 1998.
11. Benemann, J. R., (1998), *Process Analysis and Economics of Biophotolysis of Water*, IEA-HIA Technical Report, March 1998.
12. Benemann, J. R., *Feasibility Analysis of Photobiological Hydrogen Production* in D. L. Block and T. N. Veziroglu, eds., Hydrogen Energy Progress X, Proc. 10th World Hydrogen Energy Conf., Cocoa Beach, Florida, June 20–24, 1994, pp. 931–940 (1995).

CHEMICAL SYNTHESIS OF MIXED OXIDE POWDERS FOR SOLID OXIDE FUEL CELL (SOFC) ELECTROLYTE AND ELECTRODES

ÇINAR ÖNCEL
MEHMET ALI GÜLGÜN*
Sabanci University,
FENS, Tuzla, 34956
Istanbul, Turkey

Abstract: Synthesis of LSGM ($La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$), LSFM ($La_{0.9}Sr_{0.1}Fe_{0.8}Mg_{0.2}O_{3-\delta}$), and LSCM ($La_{0.9}Sr_{0.1}Cr_{0.8}Mg_{0.2}O_{3-\delta}$) powders were achieved via an organic precursor method. Different organic "carrier" molecules were used for powder synthesis. Citric acid (CA), tartaric acid (TA), Pechini precursors, polyvinyl alcohol, and ethylenediaminetetraacetic acid (EDTA) were selected as organic carriers for their ability to stabilize the metal ions. Each organic carrier material exhibited a different degree of effectiveness in the synthesis of the mixed oxide powders. One of the main factors affecting the phase purity appears to be the interaction of the functional groups with the constituent cations. It was determined that amorphous LSGM first crystallizes at 625°C. However, elimination of undesired phases requires higher temperatures. Possible implications of limited MgO solubility on the ionic conductivity are presented. Impedance measurements as a function of temperature up to 545°C revealed that the x-ray phase pure pellets may have extrapolated ionic conductivity values as high as 0.14–0.16 S/cm at 800°C.

---

* To whom the correspondence should be addressed. Mehmet Ali Gulgun, Sabanci University, FENS, Tuzla, 34956, Istanbul, Turkey; e-mail: m-gulgun@sabanciuniv.edu

J.W. Sheffield and Ç. Sheffield (eds.), Assessment of Hydrogen Energy for Sustainable Development, 147–159.

1. Introduction

Solid oxide fuel cells are regarded as the energy production systems for 21st century due to their high efficiency, utilization of a variety of the fuel resources, and environmental friendliness.

Strontium and magnesium-doped lanthanum gallate (LSGM, e.g., La1-xSrxGa1-yMgyO3-(x + y)/2) is a perovskite-type oxide and one of the most promising electrolyte materials for Intermediate Temperature-SOFC applications. Its ionic conductivity values are much higher than the one of YSZ electrolyte, and comparable to that of ceria-based electrolytes in the high and intermediate temperature ranges. Ionic conductivities of YSZ, LSGM, and CGO electrolytes at temperatures 600°C, 800°C, and 1,000°C are tabulated in Table 1.4.

TABLE 1. Ionic conductivities of YSZ, LSGM, and CGO for 600°C, 800°C, and 1,000°C

Electrolyte	600°C	800°C	1,000°C
YSZ	0.003 S/cm	0.03 S/cm	0.1 S/cm
LSGM	0.02 S/cm^2	0.12–0.17 S/cm	0.25 S/cm^2
CGO	0.025 S/cm	0.1 S/cm^2	0.25 S/cm

Each electrolyte material in SOFC construction is designed to exhibit the best performance under SOFC operating conditions. Small discrepancies in the composition results in a poorer performance of SOFC. For example, excellent ionic conductivity was achieved with Sr and Mg-doped $LaGaO_3$ electrolyte material of the following composition ($La_{0.9}Sr_{0.1}Ga_{0.83}Mg_{0.17}O_{3-\delta}$).[3] Small deviations from composition resulted in a decrease in the ionic conductivity in Figure 1. Therefore, it is important to produce pure and single-phase SOFC components with the desired compositions.

Organic precursor technique is a method widely used in mixed oxide powder synthesis.[5–8] The predicted mechanism in organic precursor method for achieving a stable precursor is the chelating/complexing of the metal cations by the functional groups of the organic carrier materials in the solution.[9] This stabilization action is believed to be due to columbic attraction forces between the carboxylic or hydroxyl groups of the carrier materials and metal cations. The molecular geometry of the functional groups is also believed to play an important role in the chelating/complexing ability. As a result of this stabilization, metal cations are believed to have a homogeneous distribution in the solution and in the preceramic precursor after solvent removal. During calcination, after the organic burnout, an amorphous powder

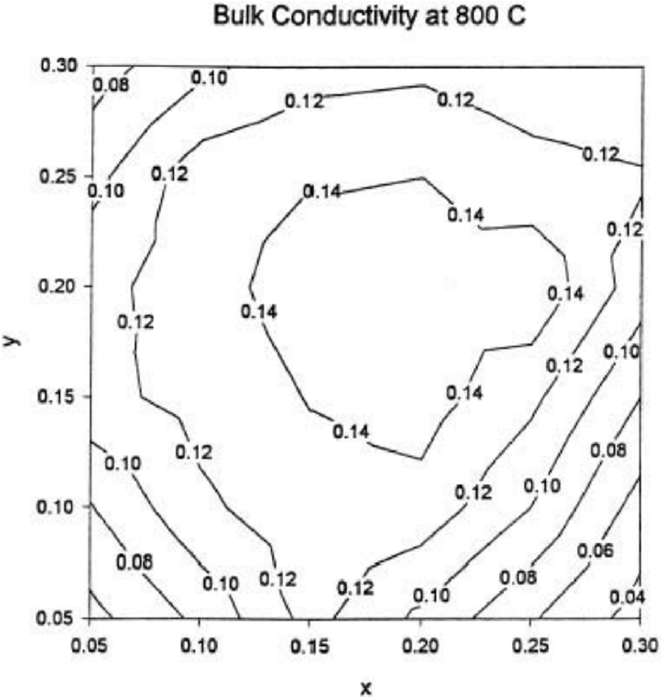


Figure 1. Bulk electrical conductivity versus Sr and Mg concentrations in LS_xGM_y. Bulk conductivities are given a S/cm[4]

is obtained. At higher temperatures, crystallization of the desired phases takes place. Due to the homogeneity in molecular level, lower diffusion distances for the cations are required to obtain the desired crystal phase. This in turn may result in lower temperatures for phase formation compared to the solid-state reaction technique.[10] Moreover, combustion of the organic materials results in local temperature increases, that help diffusion process and final crystallization.

Different types of the organic carrier materials can be used in oxide synthesis. One of the successful techniques for single-phase mixed oxide powders is Pechini process.[11] Pechini process operates through polyesterfication between hydrocarboxylic acids such as citric acid (CA), and polyhydroxy alcohols such as ethylene glycol.[11] According to the ester reaction shown below, carboxyl end of CA and hydroxyl end of ethylene glycol react and water molecule is released. The acid acts as a chelating agent that chemically binds the cations dissolved in the solution.

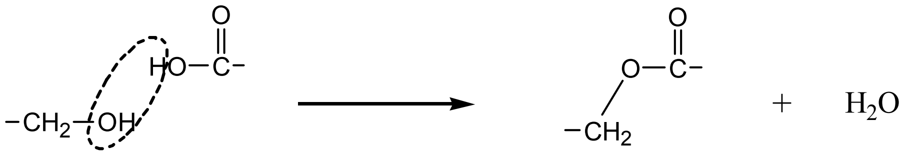


Figure 2. Ester reaction

The polymerization is based on the polyesterfication between the metal-chelate complexes and polyhdroxyl alcohols. By polyesterification process, randomly coiled macromolecular chains are obtained. These chains may chelate cations uniformly and form very stable metal-organic complexes. Moreover, due to chelating action and high viscosity polymeric network, cation segregation during solvent evaporation is hindered. The resultant ceramic powders possess better chemical homogeneity and smaller particle size. Organic precursor methods with different organic carrier materials, such as citrate synthesis, polymeric precursor synthesis, and urea method have been employed in various oxide syntheses; however, there are few studies on the chemical synthesis of SOFC components via different carrier materials.[12–13]

In this study LSGM synthesis was conducted via various organic precursor methods. Effects of different carrier materials on phase purity and crystallization behavior were investigated.

Additionally, LSFMand LSCM powders were synthesized with same synthesis route and organic carrier materials. In synthesis of LSFM and LSCM powders, the stoichiometry used in LSGM synthesis was kept to investigate the effects of different cations (Fe^{3+} or Cr^{3+} in place of Ga^{3+}). Iron and chromium were chosen to replace gallium such that the new materials can be evaluated as candidates for SOFC interconnect and cathode materials.

2. Experimental procedure

Cation sources were nitrate salts of the desired cations selected for their high solubility in cold water. Lanthanum nitrate hexahydrate ($La(NO_3)_3{\cdot}6H_2O$, >99%, Sigma Aldrich Chemie GmbH, Taufkirchen, Germany), gallium nitrate nanohydrate ($Ga(NO_3)_3{\cdot}9H_2O$, 99.9%, ChemPur Feinchemikalien und Forschungbedarf GmbH, Karlsruhe, Germany), strontium nitrate ($Sr(NO_3)_2$, >99%, Sigma Aldrich Chemie GmbH, Taufkirchen, Germany), magnesium nitrate hexahydrate ($Mg(NO_3)_2{\cdot}6H_2O$), iron nitrate nanohydrate ($Fe(NO_3)_3{\cdot}9H_2O$), chromium nitrate nanohydrate ($Cr(NO_3)_3{\cdot}9H_2O$, all three salts >99%, Merck KgaA, Darmstadt, Germany) were the sources of lanthanum, gallium, strontium, magnesium, iron, and chromium, respectively.

Polyvinyl alcohol, PVA (n C_2H_4O, MW = 72,000, >98%, Merck KgaA, Darmstadt, Germany), CA ($C_6H_8O_7$, >99.5%, Sigma Aldrich Chemie GmbH, Taufkirchen, Germany), EDTA ($C_{10}H_{16}N_2O_8$, 98%, Sigma Aldrich Chemie GmbH, Taufkirchen, Germany), Ta ($C_4H_6O_2$, 99.7%, Sigma Aldrich Chemie GmbH, Taufkirchen, Germany), and ethylene glycol, EG ($C_2H_6O_2$, 99.5%, Carlo Erba Reagenti, Mendetison Group) were the organic/polymeric materials used as "carriers" for the cations.

Distilled water and nitric acid (HNO_3, 65% solution, Sigma Aldrich Chemie GmbH, Taufkirchen, Germany) were utilized as solvents in the experiments where indicated.

Low temperature chemical synthesis of three different mixed oxides with four-cations, LSGM, LSCM, and LSFM was investigated to produce these mixed oxides as single phase, fine powders.

For the synthesis, desired amounts of cation salts were dissolved in distilled water/organic carrier solutions to obtain exact stoichiometry. In the organic precursor route with organic/polymeric carrier materials, the amounts of carrier materials were determined to obtain 1:1 cation to organic molecule ratio in the solution.

For the synthesis of LSGM, two different synthesis concepts were applied. In both routes, nitrate salts of each constituent cation were selected as the cation source. PVA (Steric entrapment method[14]), CA, TA, EDTA, or Pechini precursors (with 60% CA – 40% and EG, or 90% CA – 10% EG mixtures) were used as the organic carrier materials in solution. In the synthesis of LSGM with EDTA as the carrier material, nitric acid was the solvent. In the second production route, nitrate salt of each constituent cation was dissolved in distilled water without any organic molecule.

Solutions were mixed with a magnetic stirrer and heated up to 300°C to evaporate the solvents and to obtain a crisp powder. These organo-metallic precursors were ground and calcined in pure alumina crucibles at 700°C, 800°C, 900°C, 1,000°C, 1,050°C, 1,100°C, 1,150°C, or 1,200°C in a box furnace (in air) with 10°C/min heating rate. After reaching the final temperature the furnace was turned of immediately and the powders were allowed to cool in the furnace.

In LSFM and LSCM synthesis, calcination temperatures, 500°C, 550°C, 600°C, 650°C, 700°C, 750°C, 800°C, and 850°C were used.

Crystal structure and phase distribution of the powders at room temperature were studied with an x-ray powder diffractometer (Bruker AXS-D8, Karlsruhe, Germany). The measurements were performed in the 2θ range of 10–90°C at 40 kV and 40 mA, using Cu–K_α radiation. In all measurements, the step size was 0.03°C, and data collection period was 2 sec. in each step. $K\alpha_2$ peaks are suppressed in the x-ray diffraction measurements.

In x-ray diffraction plots, the percentages of each phase are calculated by taking the ratio of the height in the intensity axis of the main peak (100% peak) of each phase, to the sum of the height of the main peaks of all phases. Prior to the peak-height measurements, background subtraction is performed. For phase identification, the experimental spectra were compared to the characteristic x-ray card files in the JCPDS database. For phases that are synthesized in this work for the first time, the experimental spectra were compared to the JCPDS file for the compound from which the new mixed cation oxide is derived, i.e., the LSFM x-ray spectrum was compared to the JCPDS file for $LaFeO_3$ and $La_{0.9}Sr_{0.1}FeO_{2.95}$; while the LSCM x-ray spectrum was compared to the JCPDS file for $LaCrO_3$.

Synthesized LSGM powders were biaxially pressed into pellets under 70 MPa, and then isostatically pressed under 350 MPa. These pellets were heated up to 1,350°C and held 6 h at this temperature. XRD, SEM (FEG-SEM Leo Supra 35, Oberkochen, Germany), and energy dispersive X-ray spectrometry (EDS) studies were conducted on these pellets. Amorphous LSGM ($La_{0.9}Sr_{0.1}Ga_{0.85}Mg_{0.15}O_{3-d}$) films were deposited on pure gold substrates from synthesized pure LSGM pellets. The crystallization behavior of these amorphous films was studied using differential thermal analysis (Netzsch STA 449C Jupiter, Selb, Germany) and X-ray diffraction. Complex-plane impedance measurements were performed via Solartron Impedance Analyzer 1260 with Solartron 1296 dielectric interface. Ohmic resistivities of the samples were estimated by fitting of the high-frequency arc to a semicircle and calculating the real impedance difference. The measurements were done in the frequency range from 5 Hz to 13 MHz between room temperature and 545°C.

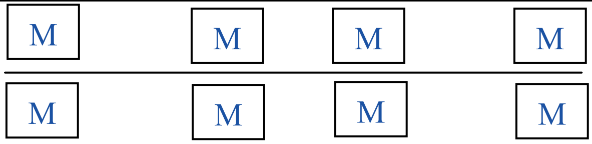
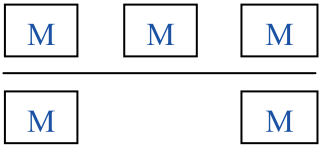
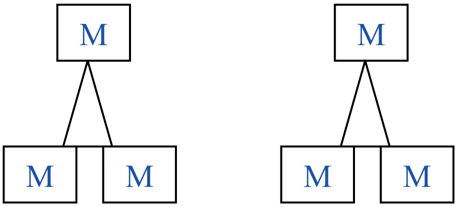
3. Results and discussion

3.1. LSGM SYNTHESIS

Table 2 lists the percent amounts of phases in the powders obtained with a different organic carrier molecule and calcined at 900°C. The amounts are determined from the XRD intensities.

As the EG amount in the Pechini precursor was decreased from 60:40 to 90:10 to 100:0 CA:EG, the amount of LSGM appeared to increase at the given calcination temperature (see Table 2). This may be due to an increased number of active carboxylic ends of CA compared to the 60:40 CA:EG precursor. To this end, the use of CA alone could give better phase distribution due to a more effective chelating action. When CA alone was used as the organic carrier, a strong increase in the percentage of LSGM

TABLE 2. Phase percentages of powders for three different Pechini precursors

Precursor	Configuration	Amount of LSGM
Pechini 60% CA–40% EG		13% LSGM
Pechini 90% CA–10% EG		76% LSGM
Pechini 100% CA–0% EG		95% LSGM

phase was observed in powders calcined at 900°C (Table 2). The better LSGM yield of the CA as the carrier material, compared to Pechini process may be explained by the large number of free active carboxylic groups of the CA, without the EG to esterify with. The effectiveness of the CA in stabilizing cations stems from the "claw" shape arrangement of carboxylic groups of the CA, which is suitable to chelate cations. In Pechini process, EG molecules attach to the carboxylic ends of CA molecules according to the reaction in Figure 2 and thereby decrease the number of active carboxylic ends. This in turn decreased the effectiveness of CA molecules for chelating La^{+3}, Sr^{+2}, Ga^{+3}, and Mg^{+2} ions in the Pechini solution.

To see the effect of the number of carboxylic ends in the chelating cations, different acids with two or four carboxylic ends (TA and EDTA) were used as the carrier material. TA has two carboxylic groups in its molecular structure. As mentioned before, the chelating ability of CA is due to its three carboxylic ends. Therefore TA with two carboxylic groups may be less effective, resulting in a lower LSGM phase amount for the same temperatures. Also the geometry of these molecules may play an important role in the chelating action. Experiments with TA confirmed the expected relationship between the number of carboxylic ends, geometry of the carrier molecule, and the chelating ability. In LSGM powder synthesis with TA as the carrier material, lower amounts of LSGM phase were obtained (28.8% and 62.7% at 900°C and 1,000°C, respectively) in comparison to the LSGM powder synthesized with CA (94.2% and 96.4% at 900°C and 1,000°C, respectively) as the carrier material at low temperatures. However, the amount of LSGM phase calcined from TA-acid precursors at temperatures above 1,050°C was larger than those prepared with CA-based precursors.

EDTA was also used as the carrier material in the LSGM synthesis. EDTA appears to be more efficient than TA but still less effective than CA. If a simple relationship between the number of carboxylic acid ends of a molecule and its effectiveness in chelating various cations were to be expected, EDTA should have been a more effective carrier molecule for mixed cations.

In the experiments conducted with the carrier materials that have carboxylic ends, such as Pechini precursors, CA, TA, and EDTA; the percentage of $LaSrGa_3O_7$ phase was higher than $La_4Ga_2O_9$ phase below 1,000°C. However, in LSGM synthesis with PVA, the percentage of $La_4Ga_2O_9$ phase was higher than the $LaSrGa_3O_7$ phase. Obviously, $La_4Ga_2O_9$ phase is lanthanum-rich, $LaSrGa_3O_7$ phase is gallium-rich. Therefore, it appears that an interaction (complexing) of PVA with lanthanum ions may be less favored compared to gallium ions in a system composed of these four cations. Thus, an early crystallization of $La_4Ga_2O_9$ phase is more favorable than the other phases because of the loosely held La^{3+} ions in PVA-cation polymeric network at low temperatures (below 800°C). Also, LSGM percentage in the resulting powders calcined up to 1,100°C was considerably small compared to the LSGM percentage in the powders synthesized with Pechini precursors, CA, TA, or EDTA.

LSGM powders synthesized using nitrate sources of all cations without using any complexing or chelating agent yielded much lower amounts of LSGM at any calcinations temperature. The results once more confirmed the effectiveness of carrier material in mixed oxide synthesis. The highest amount of LSGM phase obtained without any organic carrier in the process is 58.6% at 1,200°C.

3.2. LSFM AND LSCM SYNTHESIS

Since ionic radii and valences of iron and chromium ions are similar to gallium ion, substitution of these cations with gallium ion may result in powders with similar crystal structure and properties to LSGM. Moreover, $LaFeO_3$- and $LaCrO_3$-based oxides are candidate cathode and anode materials for SOFC, respectively.

X-ray diffraction results of the calcined powders at different temperatures showed that, single-phase LSFM powders were obtained at 550°C with PVA, CA, or EDTA as the carrier materials. This result indicated that organic precursor method is an efficient technique to synthesize multication oxides. According to the author's best knowledge, Sr-doped $LaFeO_3$, a three-cation oxide material, could be synthesized at 1,200°C with some amount of undesired phases.[15] However, synthesis of LSFM is reported here for the first time.

In LSCM synthesis, 96.9% LSCM powders were obtained at 850°C with PVA as the organic carrier material. Sauvet et al. synthesized Sr-doped $LaCrO_3$ at 1,000°C as single-phase powder.[16] The result in this study may still seem to be promising in light of the difficulty of synthesizing a four-cation oxide rather than a three-cation oxide.

The most intriguing result of this study is the inconsistency of the effectiveness of the organic carrier materials for different powders. In LSGM synthesis CA seems to be the best and PVA seems to be the worst carrier material for low temperature synthesis. A similar tendency was also observed in LSFM synthesis. However, in LSCM synthesis, PVA was the most effective organic carrier among all the others. Moreover, CA was the one of the worst carrier material. These results emphasize the need for studying the effectiveness of "chelating" action to obtain single-phase oxide powders. If a strong chelating was the only necessary criterium for desired phase formation, CA should be also effective in LSCM synthesis.

3.3. CRYSTALLIZATION OF LSGM

X-ray diffraction analysis of the LSGM films deposited on gold substrates before and after heat treatment revealed that as-deposited films and films heat treated at 600°C for 48 h are x-ray amorphous (Figure 3 curve (a)). The only visible peaks in the spectrum belong to the gold substrate. Figure 3 curve (b) illustrates the x-ray diffraction data of the same sample after heat treatment at 655°C for 72 h. Besides the gold-diffraction peaks one can discern only the 100% crystalline peak of LSGM at 32.471°. Figure 4 shows the DTA analysis results of the films on gold substrate. The exothermic peak at around 660° is associated with the crystallization of the LSGM film. The edge onset for the crystallization peak is at a temperature of 625°C.

Sintered pellets with $x = 0.1$, $y = 0.15$ and 0.17 were used in the impedance analyses at temperatures between room temperature and 545°C. The ohmic bulk conductivity of pellets is defined as:

$$\sigma_{ohm} = \frac{1}{R_{ohm}} \times \frac{t}{A} \qquad (1)$$

where R_{ohm} is ohmic resistance of the grains, t and A are the thickness and the electrode surface area of the sample, respectively. The R_{ohm} is measured from the high-frequency semicircle in the complex plane impedance analysis results.

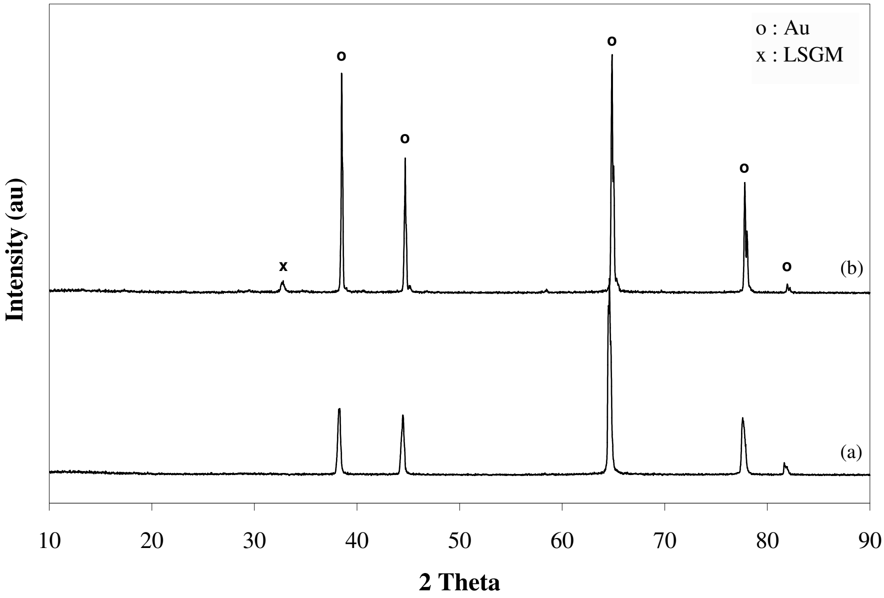


Figure 3. XRD plot of the LSGM deposited onto 99.99% Au plate (a) annealed at 600°C for 48 h, (b) annealed at 655°C for 72 h

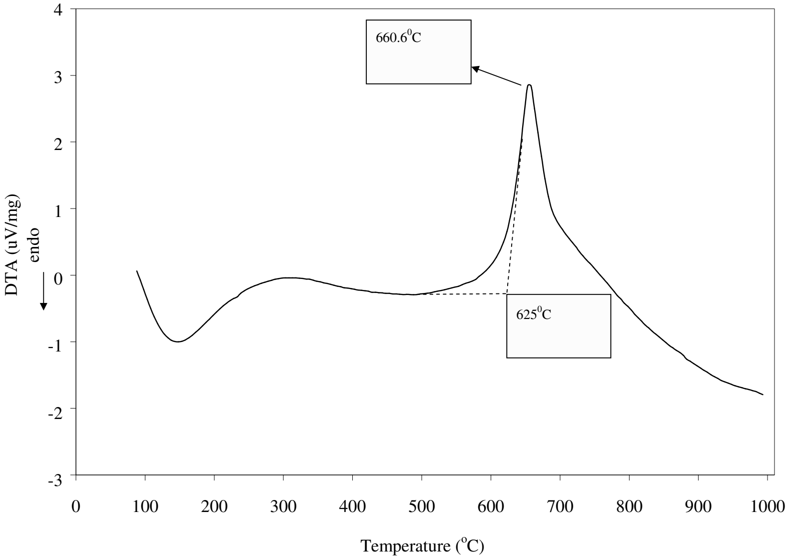


Figure 4. DTA plot of the amorphous LSGM film deposited on a pure gold substrate

Figure 5 is the plot of log(σT) vs 1/T for LSGM samples with 15% and 17% Mg between room temperature and 545°C. Data for both compositions lie on straight lines Along with the experimental data, best linear fits to the data for the two samples are also shown. From these linear fits the ionic bulk conductivities for LSGM at 800°C were estimated by extrapolating to be 0.14–1.16 S/cm for 17% and 15% Mg containing samples, respectively.

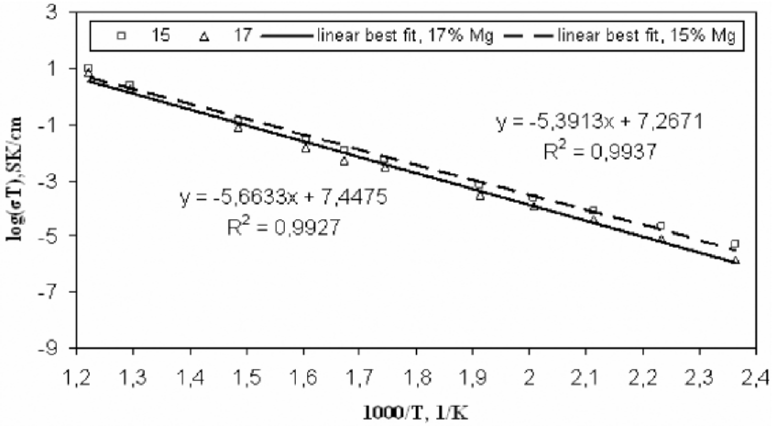


Figure 5. Ohmic bulk conductivities as a function of temperature for two LSGM pellets with 15% and 17% Mg concentration. Linear best fit to the data is also superimposed on the plots

4. Conclusion

In this study, synthesis of LSGM, LSFM, and LSCM powders were performed via organic precursor method by using different organic carrier materials.

When calcined at a low temperature (<1,000°C), precursors synthesized using CA as the organic carrier material yielded 95% LSGM phase in the powders. Maximum LSGM concentration (99%) in the synthesized powders was obtained at 1,150°C using TA as the organic carrier material. In contrast to LSGM, single-phase LSFM was obtained with relative ease from the precursors calcined at 550°C. CA appeared to be most effective precursor for low temperature synthesis of LSFM. The best concentration of LSCM phase in the synthesized powders was 96.9%, when PVA was used as the organic carrier material.

Every organic carrier material has exhibited a different performance for the synthesis of mixed oxide powders. Moreover, the performance of one organic carrier material varied for each type of mixed oxide powder synthesis. TA was the best organic carrier material for LSGM synthesis at calcination temperatures larger than 1,000°C, but it performed poorly in LSCM synthesis when compared to PVA at all calcination temperatures.

Cation chelating and/or stabilizing ability of the functional groups of the organic carrier materials does not appear to be scaling just with the number of functional groups of the carrier molecule. An ore complex interaction of the organic carrier with different cations may play an important role in synthesis of single-phase mixed oxide powders at relatively low temperatures.

Crystallization temperature of an amorphous LSGM film was determined as ~625°C. This is most likely the theoretical lower temperature limit for the single-phase LSGM synthesis

Bulk ionic conductivities of the samples were measured by impedance analysis between room temperature and 545°C. The extrapolated ionic conductivity could be as high as 0.14–0.16 S/cm at 800°C. This value is very promising, however, caution should be exercised in interpreting this extrapolated ionic conductivity value. A change in the slope of log(σT) versus 1/T plot is suspected in the literature above 550°C.

References

1. J. Fleig, K. D. Kreuer, J. Maier, "Handbook of Advanced Ceramics", *Materials, Applications, and Processing*, Academic Press, 1–60 (2001).
2. Helmut Ullmann, Nikolai Trofimenko, "Composition, structure and transport properties of perovskite-type oxides", *Solid State Ionics* **119**, 1–8 (1999).
3. S. P. S. Badwal, "Stability of solid oxide fuel cell components", *Solid State Ionics* **143**, 39–46 (2001).
4. K. Huang, J. B. Goodenough, "A solid oxide fuel cell based on Sr- and Mg-doped $LaGaO_3$ electrolyte: the role of a rare-earth oxide Buffer", *Journal of Alloys and Compounds* **303–304**, 454–464 (2000).
5. G. Ch. Kostogloudis, Ch. Ftikos, A. Ahmad-Khanlou, A. Naoumidis, D. Stöver, "Chemical compatibility of alternative perovskite oxide SOFC cathodes with doped lanthanum gallate solid electrolyte", *Solid State Ionics* **134**, 127–138 (2000).
6. A. Cüneyt Taş, Peter J. Majewski, Fritz Aldinger, "Chemical preparation of pure and strontium- and/or magnesium-doped lanthanum gallate powders", *Journal of American Ceramic Society* **83**[12], 2954–2960 (2000).
7. F. Riza, Ch. Ftikos, F. Tietz, W. Fischer, "Preparation and characterization of $Ln_{0.8}Sr_{0.2}Fe_{0.8}Co_{0.2}O_{3-\delta}$ (Ln = La, Pr, Nd, Sm, Eu, Gd)", *Journal of the European Ceramic Society* **21**, 1769–1773 (2001).
8. Marko Hrovat, Ariane Ahmad-Khanlou, Zoran Samadzija, Janez Holc, "Interactions between lanthanum gallate based solid electrolyte and ceria", *Materials Research Bulletin*, **34**[12/13], 2027–2034 (1999).
9. Mehmet A. Gülgün, My H. Nguyen, Waltraud M. Kriven, "Polymerized organic-inorganic synthesis of mixed oxides", *Journal of American Ceramic Society* **82**[3], 556–560 (1999).

10. Mehmet A. Gülgün, Oludele O. Popoola, Waltraud M. Kriven, “Chemical synthesis and characterization of calcium aluminate powders”, *Journal of American Creamic Society* **77**[2], 531–539 (1994).
11. M. P. Pechini, US Patent No. 3, 330, 697, July (1967).
12. M. Marinsek, K. Zupan, J. Maeek, “Ni-YSZ cermet anodes prepared by citrate/nitrate combustion synthesis”, *Journal of Power Sources* **106**, 178–188 (2002).
13. K. Zupan, S. Pejovnik, J. Maeek, “Synthesis of nanometer crystalline lanthanum chromite powders by the citrate-nitrate autoignition reaction”, *Acta Chim. Slov.* **48**[1], 137–145 (2001).
14. Mehmet. A. Gülgün, W. M. Kriven, “Polymerized Organic-Inorganic Complex Route for Mixed-Oxide Synthesis”, US patent# 6,482,387.
15. S. P. Simner, J. R. Bonnett, N. L. Canfield, K. D. Meinhardt, V. L. Sprenkle, J. W. Stevenson, “Development of lanthanum ferrite SOFC cathodes”, *Journal of Power Sources* **113**[1], 1–10 (2003).
16. A.-L. Sauvet, J. Fouletier, F. Gaillard, M. Primet, “Doped lanthanum chromites as SOFC anode materials”, *Journal of Catalysis* **209**[1], 25–34 (2002).

SOLAR HYDROGEN PRODUCTION IN ALGERIA: PERSPECTIVES AND APPLICATIONS

S. LABED[*]
Centre de Développement des Energies Renouvelables,
CDER, BP. 62-Bouzaréah, Alger (16340), Algerie

Abstract: This article considers Algeria as a case study for the evaluation of the hydrogen production potential when using both decentralized and centralized solar PV installations. An in-depth analysis is proposed herein and concerns some figures of merit of solar PV technology and hydrogen production with today and future technologies. Cost of energy production is also viewed in detail at the light of a life cycle cost analysis that targets a typical solar PV – hydrogen unit production. Security aspects of hydrogen production, transport and use are also discussed, especially those regarding the option of H_2 export to Europe via the Algerian pipelines of gas across Spain and Italy.

Keywords: solar radiation, photovoltaic, hydrogen, cost analysis

1. Introduction

The evolution of mankind has always been tightly linked to energy since the appearance of human being on earth. The change from one type of energy to another has frequently been a complicated but necessary process. The examples are numerous: the man used in the first times his own force and that of his specie (slaves) afterwards. Later, he turned to underground resources and exploited coal, hydrocarbons, uranium, etc. The same constant is observed along the ages: the depletion of any energy source provokes an

---

[*] Correspondance to Dr. S. Labed, Centre de Développement des Energies Renouvelables - CDER BP. 62–Bouzaréah - Alger (16340)/ALGERIA Tél: 00 213.21.901503, 00213.21.901446 Fax: 00.213.21. 901560, 00.213.21.901654; e-mail: labed@cder.dz

J.W. Sheffield and Ç. Sheffield (eds.), Assessment of Hydrogen Energy for Sustainable Development, 161–175.

energy *crisis* which imposes the search of another one (substitution). Even if the *new* found source is more powerful, it always produces more *wastes*. The consequence of such problematic relationship man–energy is still matter of today's debate. The unprecedented frenetic use of energy resources this last century menaces not only the environment but also the human specie itself. Even if the awareness about the effects of various climatic phenomena contributing in the constant heating of the planet was late, it is worth to mention that many countries are looking presently for other energy consumption models, and also for clean energy sources. Consequently, renewable energies have been pushed to the front of the world scene. Despite the reticence of *ones* and the hesitation of *others*, renewable energies were finally considered as a *complementary option* sometimes and as an *alternative* some other times. Later, the concept of hydrogen economy appeared given the worldwide abundance of such gas. Today, it is well accepted to consider that future energy option will be the combination of renewables; as the *energy source*, and the hydrogen as the energy *vector*.

Algeria with an economy fully dependent on hydrocarbon incomes is not an exception to the rule and is also concerned about energy substitution even with many underestimated and unexplored energy resources. On a medium term, the development of the above mentioned vision, i.e., combination of renewables and hydrogen will obey to an economic necessity rather than to policy considerations. The decentralized nature of renewables make them economically viable for the development of a territory composed essentially of more than of 85% of arid zones and low population density. Moreover, Algeria has to face many challenges on medium and long terms. The first one, is on a national level, and comes from a constant increase in energy demand issued from a high population growth. The second one, is on international level, and is basically linked to energy export and a safe security supply of the Mediterranean region. Fortunately, the country is blessed by a huge solar energy potential, the equivalent of more than 30 times the annual world energy consumption, which can be used judiciously for a sustainable development.

This article considers Algeria as a case study in order to investigate the technical and the economical facets of the combination of solar PV and hydrogen. An in-depth analysis is proposed herein and concerns some figures of merit of solar PV and hydrogen production with today and future technologies. Cost of energy production is also viewed in detail at the light of a life cycle cost analysis that targets a typical solar PV – hydrogen unit production. Safety aspects of hydrogen production, transport, and use are also considered especially those linked with the option of exporting H_2 to Europe via the Algerian pipeline gas.

2. The solar potential

The North African region in general and Algeria in particular are considered as one of the sunniest in the world according to many recorded data and satellite observations.

TABLE 1. List of the country wilayates and their geographical locations with daily average of horizontal annual solar irradiation, *Gy*(H)

Code	Wilaya	Latitude (°)	Longitude (°)	G_y(H) (kWh/m^2)
1	Adrar	27.9	–0.3	5.83
2	Chlef	36.2	1.3	4.92
3	Laghouat	33.8	2.9	4.54
4	O.El. Bouaghi	35.9	7.1	4.47
5	Batna	35.6	6.2	4.48
6	Béjaïa	36.7	5.1	4.61
7	Biskra	34.8	5.7	4.76
8	Béchar	31.6	–2.2	5
9	Blida	36.3	2.8	4.73
10	Bouira	36.4	3.9	4.69
11	Tamanrasset	22.8	5.5	5.7
12	Tébessa	35.5	8.1	4.53
13	Tlemcen	35	–1.5	5.37
14	Tiaret	35.3	1.4	4.58
15	Tizi-Ouzou	36.7	4.1	4.58
16	Alger	36.8	3.1	4.69
17	Djelfa	34.7	3.3	4.8
18	Jijel	36.8	5.8	4.61
19	Sétif	36.2	5.4	4.61
20	Saida	34.9	0.2	4.75
21	Skikda	36.9	7	4.39
22	S. Belabbès	35.2	–2.6	5.41
23	Annaba	36.8	7.8	4.39
24	Guelma	36.5	7.5	4.39
25	Constantine	36.3	6.6	4.37
26	Médéa	36.3	2.8	4.73
27	Mostaganem	35.9	0.1	4.7
28	M'Sila	35.7	4.5	4.66
29	Mascara	35.3	0.2	4.7
30	Ouargla	31.9	5.4	5.46

Code	Wilaya	Longitude (°)	Longitude (°)	G_y(H) (kWh/m^2)
31	Oran	35.5	−0.5	4.9
32	El-Bayadh	33.7	1.0	4.59
33	Illizi	26.5	8.4	5.67
34	B-B-Arreridj	36.1	4.8	4.58
35	Boumerdès	36.6	3.6	4.69
36	El-Taref	36.8	8.3	4.36
37	Tindouf	27.7	−8.1	5.9
38	Tissemsilt	35.5	1.5	4.58
39	El-Oued	33.5	6.1	5.05
40	Khenchela	35.4	7.2	4.47
41	Souk-Ahras	36.3	8	4.36
42	Tipaza	36.4	2.3	4.73
43	Mila	36.3	6.2	4.37
44	Aïn-Defla	36.1	2	4.73
45	Naâma	33.3	−0.3	5.04
46	A.Témouchent	35.3	−1.1	5.37
47	Ghardaia	32.4	3.8	5.21
48	Relizane	35.8	0.5	4.7

In the case of Algeria, the distribution of the solar resource can be subdivided into three zones: *coast al* (humid climate), *atlas* (cold in winter and hot in summer), and *Saharan* (dry desert climate) with typical average values of annual daily horizontal irradiation: 4 kWh/m^2, 5 kWh/m^2, and 6 kWh/m^2, respectively. Unfortunately the solar potential is still not accurately known because of the lack of data recordings.[1] Thus, to overcome such problem one needs to search for other data sources. Among the existing ones,[2, 3, 4, 5] we have chosen the NASA website which proposes a ten-year solar radiation database that covers globally the whole Algerian territory.

Though, the first step was the collection the daily average of the yearly solar irradiation, G_y(H), falling on a horizontal surface. Table 1 resumes such data for the 48 wilayates (provinces or states) of the country, while Figure 1 shows the country map and the corresponding wilayate's code.

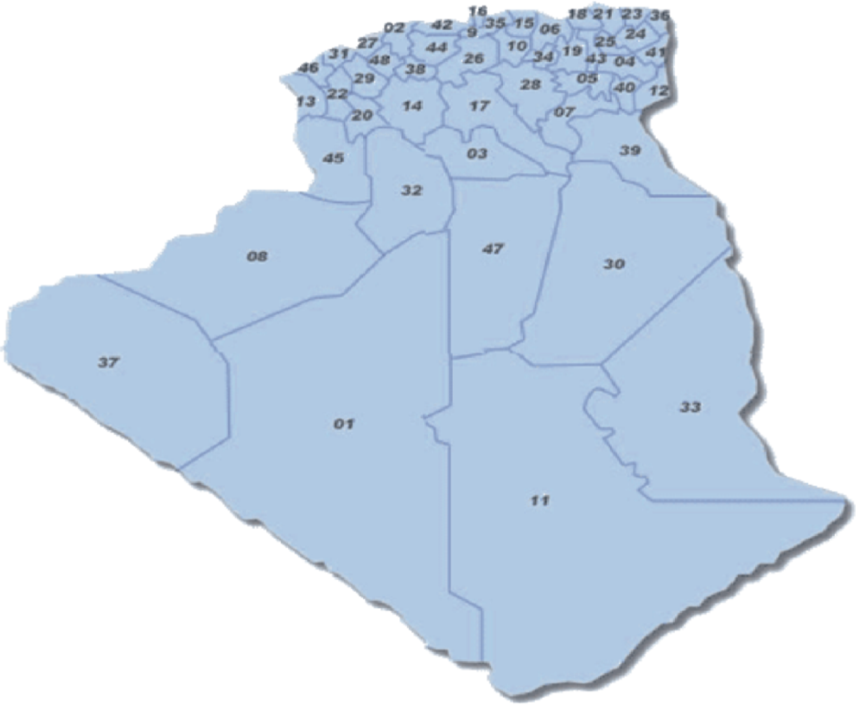


Figure 1. Country's map and wilayate's code.

3. Evaluation of the PV solar hydrogen potential

3.1. SYSTEM'S DESCRIPTION AND SIMULATION CODE

The purpose of the study is to evaluate the hydrogen potential for the different wilayates of the country by mean of a typical solar PV system composed of the following: a PV array for both configurations fixed at latitude's site and with a two-axis tracker, DC/DC converter and an electrolyzer system. The electrolyzer system is a turn-key installation consisting of electrolyzer cells, a water treatment unit, and a compressor for compressing the generated hydrogen. All calculated data are normalized for a 1 kWp installation in order to appreciate the results on the country scale.

TABLE 2. Life cycle cost analysis equations

Cost	Analytical expression	Legend and Nomenclature
Initial	$Cin = C_{PV}.P_G + C_{elec}.P_{elec} + (C_{Tr}.\ P_{Tr})^{*}$	Cin Initial cost C_{PV} Installed PV array cost (\$/Wp) P_G PV array nominal power (Wp) C_{elec} Electrolyzer unit cost (\$/Wp) P_{elec} Electrolyzer nominal power (Wp) C_{Tr} Tracker unit cost (\$/Wp) P_{Tr} Tracker nominal power (Wp) OM Operation and Maintenance costs (\$) OM_0 1st year maintenance costs (\$) M Actualization factor of maintenance costs t Discount rate gm Inflation maintenance cost rate g_{elec}, g_{Tr} Inflation replacement cost rate n electrolyzer and tracker life (years) I_{elec} Electrolyzer initial cost (\$) I_{Tr} Tracker initial cost (\$) R_{Tr}.R_{elec} Replacement costs of Tracker or electrolyzer R Actualization factor of replacement costs
Operation and Maintenance	$OM_{PV} = OM_0 \cdot M,$ $M = \frac{1+g_m}{t-g_m} \cdot \left[1 - \left(\frac{1+g_m}{1+t}\right)^N\right]$ $OM_0 = f_{OMO} . C_{in}, f_{OMO} \sim 0.02$	
Replacement	$R_{electr} = I_{elec} \cdot R,$ $R = \sum_{i=1}^{n} \left(\frac{1+g_{elec}}{1+t}\right)^{\frac{N}{n+1}}.$ $R_{Tr} = I_{Tr} \cdot R,$ $R = \sum_{i=1}^{n} \left(\frac{1+g_{Tr}}{1+t}\right)^{\frac{N}{n+1}}.$	
Life cycle	$P_{PV} = C_{in} + OM_{PV} + R_{elecr} + (R_{Tr})^{*}$	
kWh	$kWh_{PV} = \left[\frac{P_{PV}}{Ey.N}\right]$	
Kg H_2	$C_{H2} = \left[\frac{P_{PV}}{W_{H2}.N}\right]$	

---

[*] Only when a tracking system and DC/DC converter are used

		P_{PV} Life cycle costs N life of system (years) Ey Annual energy produced by the system W_{H2} Annual weight of H_2 produced by the system

The simulation code consists in the following steps as detailed in Table 2:

- Converting horizontal to tilted irradiation [6, 7]
- Generating hourly irradiance from daily values [8, 9]
- Estimating diffuse irradiance [10, 11]
- Calculating hourly ambient temperatures from daily min and max values[12]
- Calculating daily solar irradiation for both cases: Tilt angle = Latitude, and a two-axis tracking system
- Calculating hydrogen production by the electrolyzer system for both configuration
- Performing life cycle cost analysis and calculate cost production of H_2

The energy supplied by the PV array, E_{PV} is given by:

$$E_{PV} = \eta_{PV}.G.A_{PV} \tag{1}$$

$$\eta_{PV} = \eta_0.[1-\gamma(T_c-25)] \tag{2}$$

$$T_c = T_a + \left[\frac{NOCT-20}{800}\right].G_{in} \tag{3}$$

$$v = 1.22.10^{-7}.I \tag{4}$$

where G and A_{PV} are the in plane tilted irradiation (kWh/m^2) and the array surface (m^2) respectively. While η_0, γ, T_c are the reference PV module efficiency, the PV module's efficiency variation with temperature, T_c the PV cell average temperature (°C) respectively. Finally, T_a, $NOCT$, and G_{in} are the ambient average temperature (°C), the Nominal Operating Cell Temperature (°C), and the in plane tilted irradiance (W/m^2) respectively. v, is H_2 flow (m^3/s), I, is the array average DC current (amp).

Table 3 summarizes the list of the economic and technological parameters used in the simulation with typical values.

TABLE 3. Summary of technological and economic parameters

Module's values (Si-Mono)	NOCT (°C)	47
	η_{PV}	0.17
	γ (%/°C)	0.004
Typical unit costs	C_{PV} ($/Wp)	5
	C_{elec} ($/W)	5
	C_{Tr} ($/Wp)	0.5
Nominal power	P_G (Wp)	1,000
	P_{elec} (W)	700
	P_{Tr} (W)	1,400
Economic parameters	g_m	0.06
	t	0.12
	$gr_{elec.}$	0.04
	gr_{Tr}	0.04
System or component life	N (years)	30
	N_{elec}, N_{Tr} (years)	15

4. Results and discussions

The analysis of the simulation results concern many parameters from which some figures of merit and typical values are drawn in order to serve as reference for any future energy planning.

4.1. THE PV ARRAY ENERGY YIELD

The average values of the annual energy yields of PV array generators installed in the Algerian territory are fairly high as it may be expected. Figure 2 compiles these values for the 48 wilayates and indicates clearly the linear relationship between the incident solar irradiation and the collected energy. The tendency line for both curves (fixed tilt and two-axis tracking) present a good correlation factor $R^2 = 0.95$. The later suggests the consideration of the slope of both tendencies as a figure of merit. Thus we obtain 1.3 kWh/kWh/m^2 and 1.5 kWh/kWh/m^2 for each installed kWp for a fixed tilt and a two-axis tracking respectively.

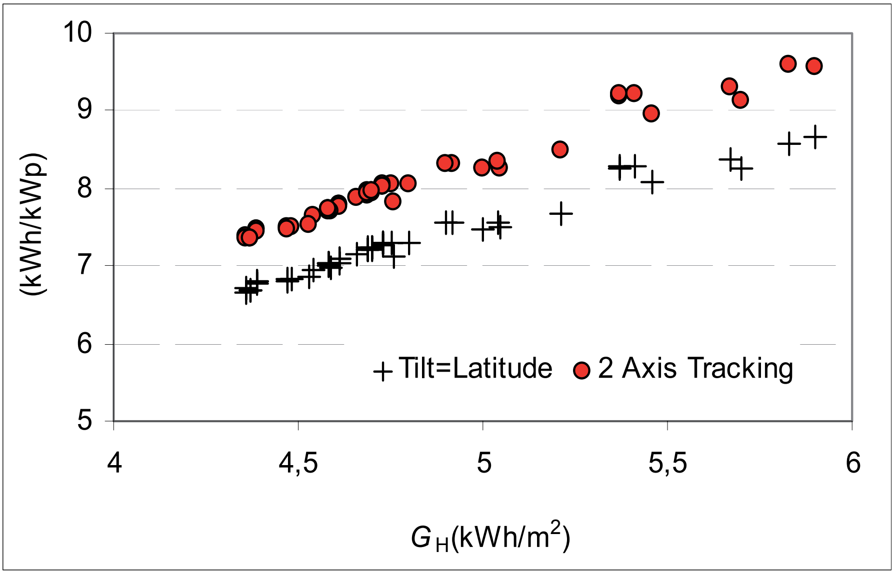


Figure 2. Average PV array energy yield Vs incident horizontal solar irradiation G_H(kWh/m^2)

4.2. THE AVERAGE VOLUME YIELD OF H_2 PRODUCTION

The second parameter is the volume of H_2 produced by a standardized 1 kWp PV generator as indicated in Figure 3. The above mentioned linear tendency is also valid in this case, and let us extracting some typical values from the slopes of both curves. This means that 0.25 m^3/kWh/m^2 and 0.33 m^3/kWh/m^2 of H_2 can be supplied by a standard 1 kWp PV system. On a yearly basis if we consider as an example the corresponding horizontal solar irradiation of wilaya 16 (Algiers) and wilaya 11 (Tamanrasset) we may obtain: 640 m^3/kWp and 720 m^3/kWp, for fixed tilt and two-axis tracking respectively.

4.3. THE AVERAGE WEIGHT YIELD OF H_2 PRODUCTION

Another interesting parameter may be the average yield of weight of H_2 production. The corresponding average values for both fixed tilt and two-axis tracking systems are: 0.022 kg/kWh/m^2 and 0.028 kg/kWh/m^2 for each PV kWp installed. In the same manner if we consider the total annual output for both wilayates 16 and 11, we obtain respectively: 54 kg H_2/kWp and 60 kg H_2/kWp.

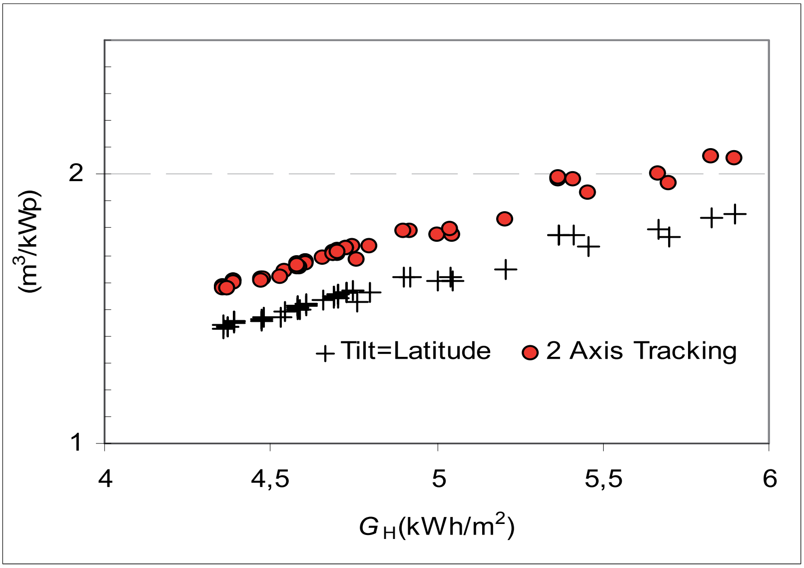


Figure 3. Average volume yield of H_2 production Vs incident horizontal solar irradiation G_H(kWh/m^2).

4.4. THE HYDROGEN COST PRODUCTION

The cost of H_2 production may be the most important parameter not only for keeping a reference in mind but also to compare with other energy alternatives. The general tendency lines for both cost curves of Figure 4 are best described by power expressions: 26.4 $(G_H)^{-0.85}$ for a fixed tilt, and 27.0 $(G_H)^{-0.90}$ with a correlation factor $R^2 > 0.97$. It is worth to note that the large difference in cost production of H_2 for relatively non-sunny ($G_H < 4.5$ kWh/m^2) and very sunny regions ($G_H > 5.5$ kWh/m^2). The impact in terms of cost production lies between \$7.5/kg H_2 and \$5.8/kg H_2 for a fixed tilt, and between \$7.0/kg H_2 and \$5.5/kg H_2. Such results are also comparable to those obtained by other references[13] for what concerns fixed flate plate PV modules, as resumed in Table 4. While the results obtained with the axis tracking system are comparable to those obtained with wind energy.[14]

TABLE 4. Cost comparison with other energy sources

Process	Hydrogen cost (\$/kg H_2)
Gas reformation[14]	1.15
Wind electrolysis[14]	3.10
PV flate plate[13]	7.40
CPV electrolysis[15]	3.63

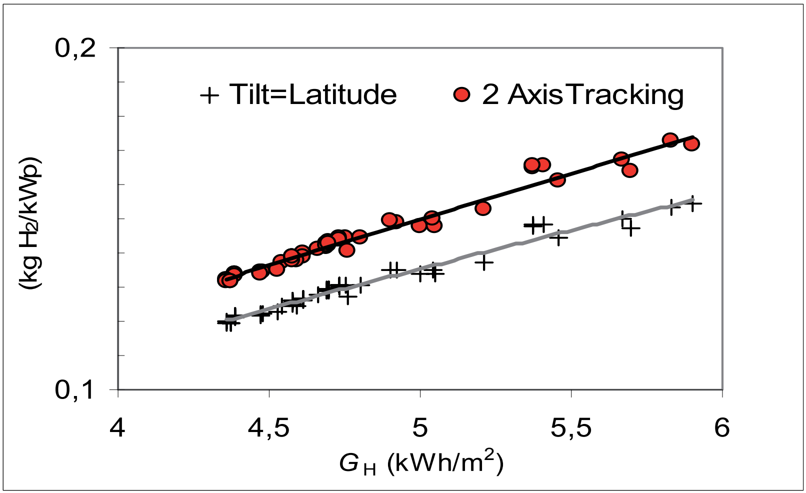


Figure 4. Average weight yield of H_2 production Vs incident horizontal solar irradiation G_H(kWh/m^2).

Nevertheless, if we suppose that future PV module's cost may be as cheaper as $1/Wp then one can find that cost production of 1 kg H_2 may be below 3.7 for a fixed tilt and around $3.2/kg H_2 for a tracking system. In our belief, such results open wide perspectives for solar hydrogen production in sunny regions and encourage future developments in all other technologies linked directly to hydrogen production among which the direct cost of the electrolyzer and the systematic recourse to intermediate PV concentration CPV[15] would have a non negligible impact on the final cost.

5. Hydrogen applications

Even if hydrogen applications are numerous but we may regroup them for the case of Algeria into three potential categories according to the country particularities and the population needs.

5.1. STAND ALONE INSTALLATIONS

The distribution of the population density is highly concentrated on the coastal regions, 60% (out of 33 millions) in a land area that represents less than 6% of the whole territory. Such situation imposes the recourse to the *Atlas* and desert regions in order to host future population. The last requires the building of thousands of houses and even new cities. On-site electricity production is suitable since grid extension is not economically viable in most cases. In this regard, small-scale PV solar hydrogen units would be ideal and fit perfectly with the availability of solar and water resources, on the one hand, and the population energy needs, on the other hand. Typical sizes for either individual or collective use can lie between 5 kWp and 50 kWp.

5.2. CENTRALIZED ELECTRICITY PRODUCTION

Algeria, as a developing country is expecting its energy needs to triple within the next decade, because of combined effect of high population growth and an increasing industrialization activity. The energy sector is planning to more than quadruple the national installed electric capacities. PV solar hydrogen can play an important role in the frame of such scheme. A combined strategy leaning on centralized electricity production as well as large central solar hydrogen plants would be suitable. In our belief both options, i.e., exporting solar hydrogen electricity via high voltage transmission lines (HVTL), or exporting compressed hydrogen via pipeline gas should be considered as complementary rather than antagonist.

5.3. AUTOMOTIVE APPLICATIONS

Even if Algeria is one of the biggest exporter of natural gas but still most of the national automotive park runs with gasoline and diesel. Only less than 1% of the vehicles are equipped with liquefied propane gas (LPG) kits. Consequently, most of the pollution problems in urban cities come from the transport sector. Moreover, it is likely that this high-increasing tendency will follow in the future as shown in Figure 6.

The environmental national norms and standards are imposing nowadays the conformity to certain level of gas emissions especially in high concentrated cities. The transport sector is thus obliged to convert gradually the major part of the present and future vehicles with cleaner energies. A serious option would be the use of LPG in a first time, and a combination of hydrogen and gas in an intermediate phase, and totally with fuel cells and hydrogen in a final phase. It is worth to note that approximately 180 buses will be put into service in the framework of a National Demonstration Program that introduces a new natural gas for vehicles (NGV) that seems to be mixable with H_2, resulting to a more energetic gas propulsion.

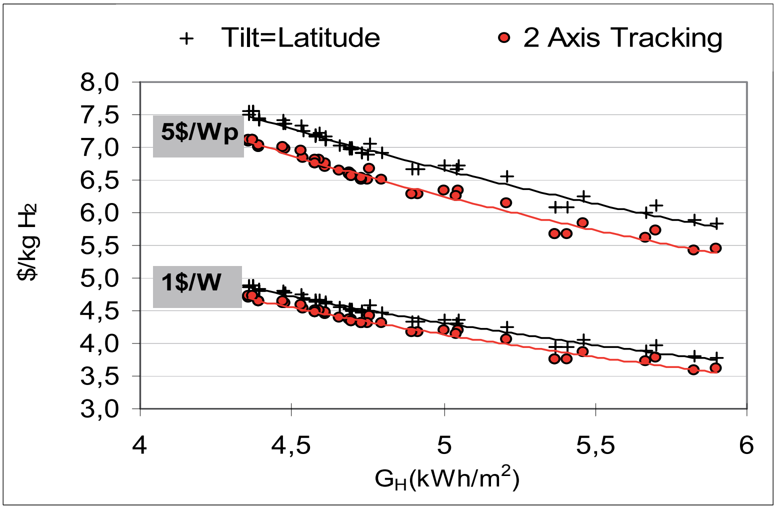


Figure 5. Cost of H_2 production en Vs unit cost of PV modules (Present & Future).

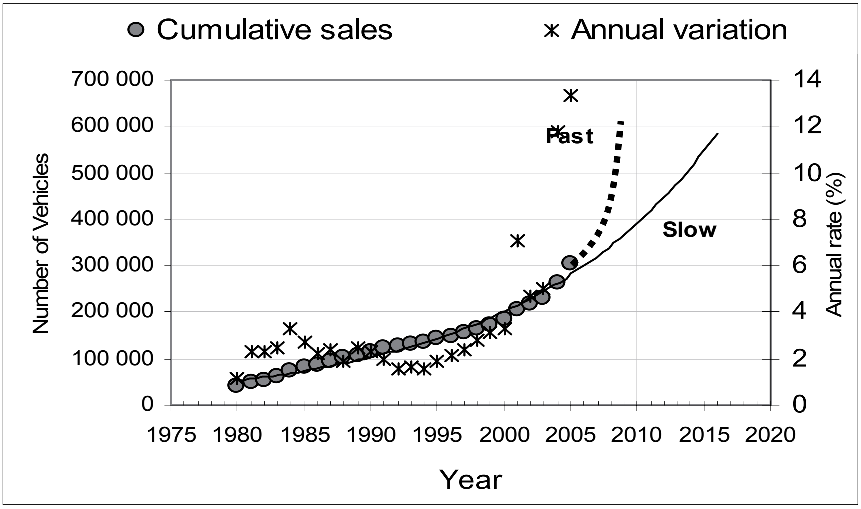


Figure 6. Yearly cumulative sales of vehicles 1975-2005 and beyond.

6. Safety and Security aspects

Hydrogen is certainly a clean and abundant energy but in the same time its large-scale use still suffers from a psychological handicap linked to safety aspects given some of its properties,[16, 17, 18] particularly its inflammability and the high risk of detonation (subsonic or supersonic). This is clearly indicated in Table 5 where some of the properties are compared with another industrial gas, the propane.

TABLE 5. Comparison of some typical properties of hydrogen and propane

Properties	Units	Hydrogen	Propane
Domain of inflammability	% vol.	Apr-75	2.1–9.5
Minimal energy of inflammation	mJ	0.02	0.26
Auto-Inflammation temperature	K	585	760
Combustion velocity in the air (TPN)	cm/sec	265–325	30–40
Explosion energy (mass)	gr TNT/ gr product	24	10
Explosion energy (volume)	kg TNT/ cm^3 gas	2.02	20.3

It is shown that the hydrogen domain of inflammability is ten times of the propane, while its combustion velocity in the air is eight times greater than that of the propane. Moreover, the risk level depends also on the state of hydrogen (gas, liquid, etc.) and the storage type (pressure storage, cryogenic storage, metal hydride storage, carbon nanofiber storage). In addition, the evaluation of the risk in any hydrogen installation will certainly vary with the site: urban, isolated region, pressurized tanks, long-distance pipelines, etc. This means that hydrogen utilization, transport, or manipulation should be subject to more severe norms and standards in order to ensure a safe use of such future energy vector. In this regard, we believe that more research is still needed as well a high tight scientific international cooperation.

7. Conclusions

Hydrogen economy is becoming from day to day an unavoidable reality that seems to be only a matter of time since the depletion of hydrocarbon reserves is accelerated because of excessive use of energy worldwide. Algeria as a gas and oil producer is concerned by the search of energy alternatives on medium and long terms. Among the potential energy options the combination of renewables, particularly PV solar and hydrogen is certainly interesting and may be a good answer to future centralized and decentralized energy needs. The simulation results presented in this article are in a large extent in favor of such scenario and may serve as a basis for further detailed studies.

References

1. Labed S., Lorenzo E., The impact of solar radiation variability and data discrepancies on the design of PV systems. Renewable Energy 2004; 29: 1007–1022.
2. Capderou, Atlas solaire de l'Algérie. Edition EPAU; 1985.
3. Censolar atlas, Mean values of solar irradiation on horizontal surface, Solar International H-World-Edition Progensa, 1993.
4. Meteonorm, Solar engineering handbook, part 2, version 4.0 Theory part 1: radiation. Swiss Federal Office of Energy; 1999. http://eosweb.larc.nasa.gov/sse
5. Aguiar R., Collares-Pereira M., Conde J. P., Simple procedure for generating sequences of daily values using a library of Markov transition matrices. Solar Energy 1988; 40(3): 269–279.
6. Collares-Pereira M., Rabl A., The average distribution of solar radiation correlations between diffuse and hemispherical and between daily and hourly insolation values. Solar Energy 1979; 22: 155–164.
7. Liu Byh, Jordan R. C., The interrelationship and characteristic distribution of direct, diffuse and total solar radiation. Solar Energy 1960; 4: 1–9.
8. Whillier A., The determination of hourly values of total solar radiation from daily summations. Archiv fur Meteorologie, geophysik und Bioklimatologie, B 1956; 197–244.
9. Perez R., Seals R., Ineichen P., Stewart R., Meniccucci D., A New Simplified version of the Perez diffuse irradiance model for tilted surfaces. Solar Energy 1987; 39: 221–231.
10. Perez R., Stewart R., Arbogast C., Seals R., Scott J., An anisotropic hourly diffuse radiation model for sloping surfaces: description, performance validation, site dependency evaluation. Solar Energy 1986; 36: 481–497.
11. Lorenzo E. et al., Solar Electricity. Progensa: Madrid, Spain, 1994; 192–193.
12. Kazmerski L., "PV Electrolysis," ASES Renewable Hydrogen Forum Proceedings, October 1, 2003.
13. Mears D., Mann M., Ivy J., Rutkowski M., "Overview of Central H2A Results," 2004 US Hydrogen Conference Proceedings, April 26–30, 2004.
14. McConnell R., Generating Hydrogen through Water Electrolysis Using Concentrator Photovoltaics – DOE Solar Energy Technologies, October 25–28, 2004. Denver, Colorado, USA.
15. Ogden, J. M., Prospects for Building a Hydrogen Energy Infrastructure, Annual Review of Energy and the Environment, 1999; 24: 227–279.
16. Safety Standard for Hydrogen and Hydrogen Systems, Guidelines for Hydrogen System design, Materials selection, Operations, Storage, and Transportation, Document NSS 1740.16, NASA.
17. Association française de l'hydrogène (www.afh2.org).
18. Paillère H., Studer E., Chaudourne S., Dossier la filière hydrogène - Le risqué hydrogène revisité CLEFS CEA No. 50/51 Hiver 2004–2005.

BIOHYDROGEN PRODUCTION BY ANAEROBIC BIOLOGICAL FERMENTATION OF AGRICULTURE WASTE

MU'TAZ AL-ALAWI[*]
Mu'tah University,
Karak, Jordan

Abstract: Efficient conversion of corn stalk wastes into biohydrogen gas by microorganisms was reported for the first time. Batch tests were carried out to analyze influences of several environmental factors on biohydrogen production from corn stalk wastes. The maximum yield of hydrogen 58.6 ml H_2/g TVS was observed at 100 h, the value is about 22-fold as compared with that of raw corn stalk wastes. The results indicated that the HCl pretreatment of the substrate plays a key role in the conversion of the corn stalk wastes into biohydrogen.

Keywords: biohydrogen production, corn stalk wastes, biological fermentation

1. Introduction

Hydrogen is an environmentally friendly fuel; it produces only water upon combustion. Many believe that hydrogen will replace fossil fuel as the energy source of the next generation. Hydrogen is conventionally produced by chemical or electrolytical means. But, it may also be produced.

Earlier studies have been done by pure cultures of anaerobic bacteria to study the conversion of carbohydrates (such as glucose and starch) to hydrogen gas, e.g., *Aspergillus terreus* (Emtiazi et al., 2001) and *Clostridium* (Taguchi et al., 1994). Recently, the considerable attention of research activity on fermentative hydrogen-production has been focused on the conversion of biomass reproducible resources to hydrogen by mixed cultures

---

[*] To whom correspondence should be addressed. Mu'taz Al-Alawi, Water and Environmental Research Center, Mu'tah University, Mail box: P.O. Box 16, Karak 61110, Jordan; e-mail: alawi1979@yahoo.com

J.W. Sheffield and Ç. Sheffield (eds.), Assessment of Hydrogen Energy for Sustainable Development, 177–185.

(Lay et al., 1999; Fan et al., 2002). For example, Fan et al. have successfully used a heat-shocked cow dung compost to convert a simulated organic wastewater into hydrogen gas (Fan et al., 2003).

However, the research of the conversion of the biomass containing cellulose, such as corn stalk, into biohydrogen is lacking. In general, it is hard to convert directly raw crop stalk wastes into biohydrogen gas by microbe anaerobic fermentation because of their complex chemical composition, e.g., cellulose, hemicellulose, lignin, protein, fat.

It is well known that cellulose in nature substrates, such as corn stalk wastes, is persistent in the environment and remains as an environmental pollutant. Except that some of them were employed as feedstuff of livestock and fowl, most of them were set on fire or discarded as environmental pollutants. Cellulosic materials can, however, be a valuable and vast renewable resource.

Here, our research interest is to convert the biomass containing cellulose, such as corn stalk wastes into hydrogen gas by natural anaerobic microorganism. For this purpose, several environmental factors, such as pretreatment of substrate, initial pH and substrate concentration, were selected as target factors in conversion of corn stalk wastes into biohydrogen gas by cow dung composts.

2. Experimental methods

2.1. SEED MICROFLORA

Hydrogen-producing microfora were taken from cow dung compost in the suburb of Amman City. Before it is used, cow dung compost was placed into a stainless-steel pizza pan to a depth of 1 cm and broken up in the infrared oven for 2 h in order to inhibit the bioactivity of hydrogen consumers and to harvest hydrogen-producing sporeforming anaerobes.

2.2. CHEMICAL PRETREATMENT OF THE SUBSTRATE

The corn stalk wastes used as substrate were obtained from the suburbs of Amman city. Before the substrate were degraded by microorganisms, the mixture of corn stalk and dilute HCl (or NaOH) solution was boiled 30 min in beakers, and then neutralized to pH = 7 with either dilute NaOH or HCl solution. TVS value was determined as follows:

$$\mathrm{TVS} = \frac{\mathrm{W}_{\text{dry corn stalk}} - \mathrm{W}_{\text{ash}}}{\mathrm{W}_{\text{dry corn stalk}}} \times 100\%.$$

2.3. EXPERIMENTAL PROCEDURE

The batch experiments were performed with 250 ml serum vials as batch reactors filled to 150 ml comprising the mixture of the composts, the pretreated corn stalk, and 3 ml of nutrient stock solution. These vials were purged with nitrogen gas to remove oxygen and the headspace of the reactors to keep the anaerobic environment. The bottles were incubated at 36 ± 1°C and operated in an orbital shaker with a rotation speed of 90 rpm to provide better contact among substrates. The compost concentration of 80 g/l was maintained in the batch reactors. The volume of biogas was determined using glass syringes of 5–100 ml. Each liter of nutrient stock solution containing 80 g of NH_4HCO_3, 12.4 g of KH_2PO_4, 0.1 g of $MgSO_4{\cdot}7H_2O$, 0.01 g of NaCl, 0.01 g of $Na_2MoO_4{\cdot}2H_2O$, 0.01 g of $CaCl_2{\cdot}2H_2O$, 0.015 g of $MnSO_4{\cdot}7H_2O$, 0.0278 g of $FeCl_2$, which was slightly modified from Lay et al. (1999).

2.4. ANALYTICAL METHODS

The hydrogen gas percentage was calculated by comparing the sample biogas with a standard of pure hydrogen using a gas chromatograph (GC, Shimadzu 190D) equipped with a thermal conductivity detector (TCD) and 6 ft stainless column packed with Porapak Q (80/100 mesh). The operational temperatures of the injection port, the oven and the detector were 100°C, 80°C, and 150°C, respectively. Nitrogen was used as the carrier gas at a flow rate of 20 ml/min. The concentrations of the volatile fatty acids (VFAs) and the alcohols were analyzed using another GC of the same model with a flame ionization detector (FID) and a 8 ft stainless column packed with 10% PEG-20M and 2% H_3PO_4 (80/100 mesh). The temperature of the injection port, the detector, and the oven were 200°C, 240°C and a programmed column temperature of 130–175°C, respectively. Nitrogen was the carrier gas at a flow rate of 20 ml/min. The pH values inside the reactors were determined using a microcomputer pH-vision 8911.

3. Results and discussion

3.1. EFFECT OF PRETREATMENT OF SUBSTRATE ON HYDROGEN YIELD

To the best of our knowledge, the direct conversion of raw corn stalk into biohydrogen gas by microorganisms is difficult, e.g., the maximal hydrogen yield of raw beer lees, wheat straw and corn stalk wastes is only 6.8, 0.5, and 2.68 ml H_2/g TVS, respectively (Fan et al., 2003). Therefore, the pretreatment of the substrate is quite indispensable in order to enhance the hydrolyzation of raw corn stalk wastes.

Figure 1 represents the effects of the changes in the HCl concentration on hydrogen production yield at the fixed initial pH = 7 and substrate concentration 25 g/l. As can be seen from Figure 1, the cumulative hydrogen yield increased sharply with the increase of the concentration of HCl in the range of 0.5–1.0%, and then decreased slowly with the increase of the HCl concentration.

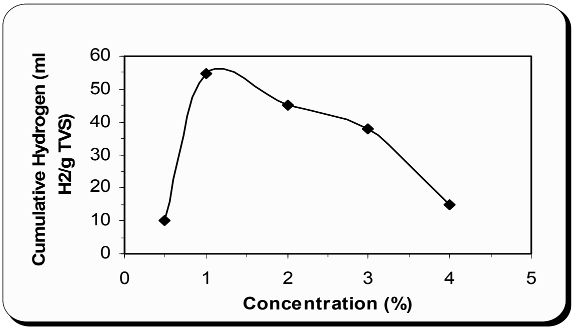


Figure 1. The effect of HCL pretreatment of corn stalk on hydrogen yield. Other variables are constant at their respective levels as follows: initial pH = 7, concentration of substrate 25g/l

Maximum hydrogen yield of 54.9 ml H_2/g TVS was obtained at HCl concentration of 1.0%. Then, the hydrogen yield gradually declined as HCl concentration increased from 54.9 ml H_2/g TVS at HCl concentration of 1.0% to 15 ml H_2/ g TVS at HCl concentration of 4.0%. Although the higher HCl concentration was in favor of the hydrolyzation ofcorn stalk (substrate), but the high Cl^- anion concentration heavily inhibited the growth of hydrogen production bacteria (Wang et al., 1995).

As far as we know, the direct conversion of raw corn stalk into hydrogen gas by anaerobic fermentation is very difficult because of its complex-polymer structure such as cellulose, hemicellulose and lignin, e.g., the maximal hydrogen yield was only 2.68 ml H2/g TVS by the cow dung compost in the test using the raw corn stalk. In order to explain the experiment phenomena, the composition of the corn stalk was analyzed in the test. Compared with the raw corn stalk, we found that the soluble sugar content increased from 0.5% to 12%, and the cellulose and hemicellulose contents decreased from 25.3% and 20% to 10.78% and 11.3% for the acid pretreated corn stalk, respectively. Accordingly, we deduced that an increase in the hydrogen yield possibly was due to an increase in the soluble sugar in the composition of the acid pretreated substrate. Our experiment results proved that HCl pretreatment of the substrate plays a key role in conversion of the corn stalk wastes into biohydrogen gas by the cow dung composts.

3.2. EFFECT OF THE SUBSTRATE CONCENTRATION ON HYDROGEN YIELD

Figure 2 depicts the effects of the pretreated substrate concentration vs cumulative hydrogen yield by microorganism. As can be seen from Figure 2, the cumulative hydrogen yield increases with increasing the concentration of the pretreated substrate in the range of 5–25 g/l, the maximum hydrogen yield of 55.5 ml H_2/g TVS occurred at the pretreated corn stalk of 25 g/l and then the hydrogen yield gradually decreases with the increases of the substrate concentration.

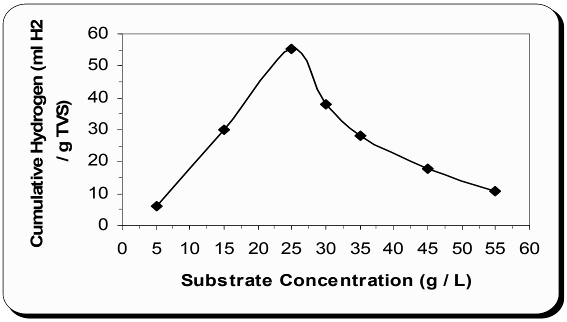


Figure 2. The effect of substrate concentration on hydrogen yield. Other variables are constant at their respective levels as follows: initial pH = 7; 1.0% HCl pretreated substrate

Our test results showed that the change of the substrate concentration remarkably affected the hydrogen yield. Although increase of substrate concentration could enhance the hydrogen yield, but the higher substrate concentration also results in the accumulation of the VFAs and fall of pH value, which inhibited the growth of hydrogen-producing bacteria. In addition, the partial pressure of hydrogen in the reactor rose with the increases of substrate concentration. While the partial pressure of hydrogen increased to a certain level in the headspace of reactor, the microorganisms would switch to alcohol production, thus inhibiting hydrogen production (Fan et al., 2004).

3.3. EFFECT OF INITIAL PH VALUE ON HYDROGEN YIELD

The changes of the cumulative hydrogen yields over the pH range of 4.5–9.0 at the fixed substrate concentration of 25 g/l were plotted in Figure 3. As can be seen from Figure 3, while the initial pH level rose from 4.5 to 6.0, the cumulative hydrogen yield increased from 5 to 58.6 ml H_2/g TVS, and then gradually decreased with the increase in the initial pH of the culture medium in the range of 7.0–9.0. Obviously, the initial pH values of "6.0–7.0" and "5.5–7.0" may represent the "optimum" and "acceptable" ranges of pH for the hydrogen production of the substrate, whereas the hydrogen yield sharply dropped while the pH was lower than 5.5 or higher than 7.0. The results implied that the pH control could stimulate the microorganisms to produce hydrogen and would achieve the system having maximum hydrogen production ability, because the activity of hydrogenase would be inhibited by low or high pH in overall hydrogen fermentation (Fan et al., 2004; Lay et al., 1999).

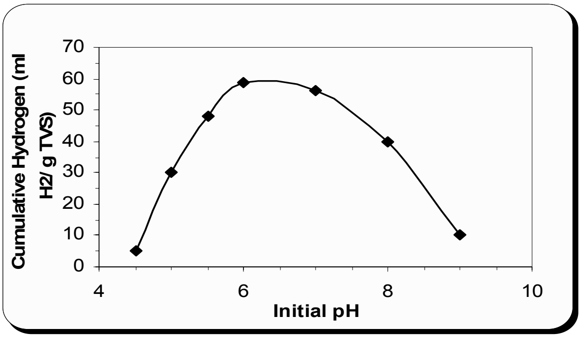


Figure 3. The effect of varied pH value on hydrogen yield. Other variables are constant at their respective levels as follows: substrate concentration of 25 g/l, 1.0% HCl pretreated substrate

3.4. BIODEGRADATION CHARACTERISTICS OF THE SUBSTRATE

Here, VFAs and alcohol were selected as main by-products of the composts consuming the substrate. Figure 4 illustrated the changes of the accumulative hydrogen yield (a), pH value (b), VFAs (c), and alcohol (d) during the conversion of the pretreated corn stalk wastes to biohydrogen by cow dung compost. As shown in Figure 4(a), the hydrogen evolution began to occur after 10 h of cultivation. The maximum hydrogen yield of 58.6 ml H_2/g TVS was observed at 100 h. The hydrogen percentage in the biogas was 55% and there was no significant methane observed in this study.

The medium pH decreased from 7.0 at 10 h to about 4.7 at 70 h with the progress of hydrogen evolution and substrate decomposition, the optimum pH value of hydrogen production appeared in the range of 5.25–4.6 (Figure 4(b)). Hydrogen production was accompanied with the formation of VFAs and alcohol throughout the beer lees fermentation (Figures 4(c) and (d)). During this period, the concentration of acetate and butyrate achieved the

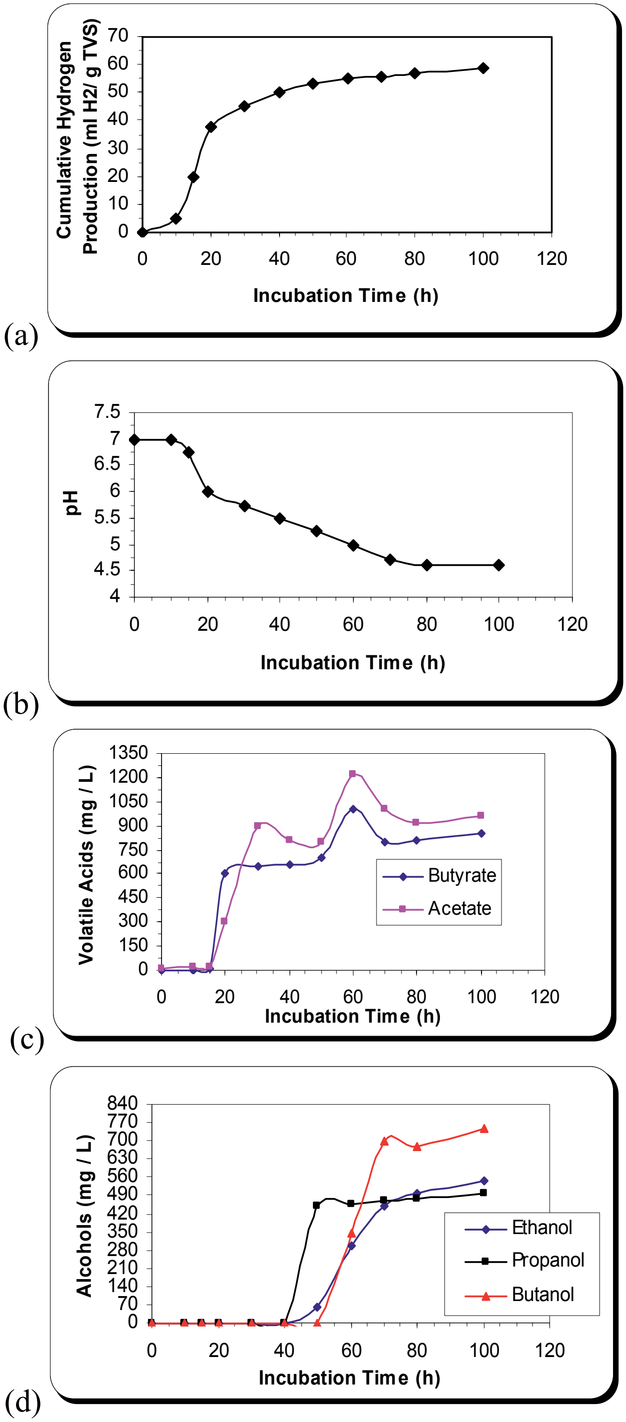


Figure 4. Developments of cumulative hydrogen yield, pH value, volatile fatty acids (VFAs) and alcohols in the batch reactor during the conversion of the substrate to biohydrogen under the pretreated condition of microwave heating

maximum value 1,225–1,000 mg/l at 60 h, respectively. Furthermore, the concentration of ethanol, propanol, and butanol achieved the maximum value 550, 500, and 750 mg/l at 100 h, respectively. Hydrogen production stopped when the available substrate was consumed up, and the ethanol, acetate, and butyrate as significant by-products were left in the batch reactor, but amounts of propionate were not observed in total VFAs. However, the biodegradation characteristics of the pretreated corn stalk waste was similar to that of sucrose and starch, in which VFAs mainly consists of acetate and butyrate (Fan et al., 2004).

These phenomena were expected because hydrogen production appears to be usually accompanied with the formation of VFAs and alcohol while both of them are the main by-product in the metabolism of hydrogen fermentation. However, under the optimum pH condition of hydrogen production, the acetate and butyrate producers were active and competed with the propionate producer (Fan et al., 2004). In order to effectively convert the corn stalk into biohydrogen by the microorganisms, the activity of the propionate producer should be suppressed.

4. Conclusion

The HCl pretreatment of the substrate plays a key role in conversion of the corn stalk wastes into biohydrogen gas by the cow dung composts. The maximum hydrogen yield of 58.6 ml H_2/g TVS was observed at the fixed initial pH of 7.0 and substrate concentration of 25 g/l, the value was about 22-fold higher than that of raw corn stalk wastes. The hydrogen percent in the biogas was more than 55% and there was no significant methane observed in the experiments. The result is encouraging because of its potential commercial and environmental benefits in the future.

References

Emtiazi, G., Naghavi, N., and Bordbar, A., 2001, Biodegradation of lignocellulosic waste by *Aspergillous terreus*, *Biodegradation*. **12**: 259–263.

Fan, Y. T., Li, Ch. L., Hou, H. W., Lu, H. J., and Lay, J. J., 2002, Studies on biohydrogen production by biohydrogen fermentation of natural anaerobic microorganism, *China Environ. Sci*. **22**(4): 370–374.

Fan, Y. T., Li, Ch. L., Lay, J. J., Hou, H. W., and Zhang, G. Sh., 2004, Optimization of initial substrate and pH levels for germination of sporing hydrogen-producing anaerobes in cow dung compost, *Bioresour. Technol*. **91**: 189–193.

Fan, Y. T., Liao, X. Ch., Lu, H. J., and Hou, H. W., 2003, Study on biohydrogen production by anaerobic biological fermentation of organic wasters, *Environ. Sci.* **24**(3): 152–155 (in Chinese).

Fang, H. H. P., Zhang, T., and Liu, H., 2002, Effect of pH on hydrogen production from glucose by a mixed culture, *Bioresour. Technol.* **82**: 87–93.

Lay, J. J., Lee, Y. J., and Noike, T., 1999, Feasibility of biological hydrogen production from organic fraction of municipal solid waste, *Water Res.* **33**(11): 2579–2586.

Wang, J. S., Zhao, L. H., Jia, Z. P., Wang, Z. L., and Guo, Y., 1995, Inhibition of sulphates and chlorides to anaerobic digestion, *Environ. Sci.* **16**: 3–7 (in Chinese).

HYDROGEN ENERGY SYSTEM FOR SUSTAINABLE DEVELOPMENT

NAIM H. AFGAN*
Instituto Superior Tecnico, Lisbon, Portugal
MARIA G. CARVALHO
BEPA – Bureau of European Policy Advisers,
European Commission, Brussels

Abstract: Complexity is the property which describes the state of complex system. It is multidimensional indicator which comprises all individual characteristics of the system. Complex system is the entity which characterizes the structure with a large number of elements interacting among themselves. The main energy resources: fossil fuels, nuclear energy, geothermal energy, hydro-potential and solar energy are essential sources of primary energy. The conversion of primary energy resources in the finale energy is a chain of processes leading to usable form of energy. The electricity can be used to produce hydrogen which may be used as the fuel in the fuel cells. There are many different sources of energy on our planet. Among those sources are wind and solar energy. Conversion of wind and solar energy to electricity and to hydrogen is opening a new venue for the efficient utilization of renewable energy sources. Sustainable development is strategic goal of modern society reflecting contemporary demand for economic, social, political and environmental development. It is of fundamental importance for the world to join this movement and promote future strategy in the economic development based on the vision of sustainability criteria. The energy strategy in this respect plays the most important role in the design of the sustainability concept development. Access to affordable and reliable energy, drawn from environmentally acceptable sources of supply, is an important feature of sustainable development. The lecture gives an overview on the potential on multi-criteria assessment of hydrogen systems. With respective selection of the criteria comprising performance,

---

* To whom the correspondence should be addressed. Naim Hamdia Afgan; Instituto Superior Tecnico, Lisbon, Portugal; e-mail: nafgan@navier.ist.utl.pt

J.W. Sheffield and Ç. Sheffield (eds.), Assessment of Hydrogen Energy for Sustainable Development, 187–209.

environment, market and social indicators the assessment procedure is adapted for the assessment of the selected options of the hydrogen energy systems and their comparison with new and renewable energy systems. The multi-criteria procedure is based on the Sustainability Index rating composed by linear aggregative function of all indicators with respective weighting function. The hydrogen systems options are designed on two hydrogen production processes: reforming hydrogen production and electrolysis. Power production units are hydrogen gas turbine, fuel cell and internal combustion engine. Solar and wind energy systems representing renewable power plant options. These options are evaluated with multi-criteria method comprising following indicators: fuel, electricity, fixed cost, capital cost and CO_2. The example of multi-criteria procedure for the assessment of hydrogen systems proves that the Sustainability General Index rating is the effective tool for the decision-making procedure.

Keywords: hydrogen energy system, hydrogen production, hydrogen consumption, multi-criteria assessment, sustainability index

1. Introduction

Any energy system is characterized by interactions of number of different elements reflecting its functionality and structure as the complex system, defined by the complexity as the integral parameter of the system. Complexity is the property which describes the state of complex system [1, 2]. It is multi-dimensional indicator which comprises all individual characteristics of the system. Complex system is the entity which characterizes the structure with a large number of elements interacting among themselves. There are different structures of elements. Elements in biology are structured to perform specific function. Typical example is DNK molecule, comprising large number of elements interacting among themselves. In the information theory the structure of elements is described as the Internet network with large number of nodes for information exchange. In energy system we can describe complex system as the system which produces, transport and utilize different energy sources. The complexity of these systems is the internal property of the system expressed as the wholeness property. This imply that the complexity describe the essential characteristic of the system. If the complexity is described in thermodynamic words, it represents the internal parameter of the system expressed by agglomerated indicators describing specific property of the system. If we take into a consideration only material system, we can take the entropy of the system as the macroscopic property of the system. These can be applied to chemically bounded molecules. Prigogine [3, 4] has determined the characteristic property of these systems as the entropy generation. This means that every interaction between elements accompanying with mass, momentum and energy exchange ultimately is connected and contribute to the entropy generation in the system. It should be taken into a consideration that the entropy generation is defined per unit mass of the system and represent specific property of the system. So the entropy generation represents the complexity property of the system.

If we take into a consideration non-material system where complex properties include entities which are not defined per unit mass of the system, we have to introduce notion which represents wholeness of the system. Good example for this type of complex system Internet system. Large numbers of nodes are connected in large net serving to transfer information among nodes. If we assume that transfer of information contribute to the increase of informativity of the system, we can see that the increase of informatively is equivalent to the increase of the complexity of the system. In this respect the informativity is equivalent to complexity.

There are three interrelated approaches to the modern study of complex systems:

1. How interactions give rise to patterns of behaviour
2. Understanding the ways of describing complex systems
3. The process of formation of complex systems through pattern formation and evolution

In dealing with energy systems it is of interest to focus our attention to the description of complex system. The energy system is composed of number of element with functionally defined role within the system. Each of the elements will be described by the appropriate indicators in order to accommodate differences in the energy system. Elements are agglomeration of the potential option of management systems. As the example we can describe financing element as the set of options meeting different criteria in validation of the management system. The same feature is exercised with other elements leading to the potential of the large number of management systems. In order to mathematically define variation of the management system we can introduce notion of the complexity as the property of the management system. It was verified that the sustainability is property of the complex system. In this respect by the appropriate definition of General Sustainability Index as the parameter of complex system, we can have measuring characteristic for the assessment of hydrogen system.

If the multi-criteria evaluation of energy system is introduced in this analysis, indicators which are reflecting all potential interaction of the system and surrounding must be also recognized. In this respect, the indicators the integral parameters of the system, which comprise resource, economic, environment and social indicators will be used.

Since these indicators are given in different scales it is necessary to convert them into the specific quantities which are expressed in the same scale. Convolution of these indicators wills represent an integral measuring parameter which will reflect the total quality of the system. Any degradation of the system will lead to the decrease of Sustainability Index.

The preset dilemma reflecting different approaches to the potential use of hydrogen is attracting scientists, engineers and academic society in large to discuss potentiality of the options under consideration. The main energy resources: fossil fuels, nuclear energy, geothermal energy, hydro-potential and solar energy are essential sources of primary energy. The conversion of primary energy resources in the finale energy is a chain of processes leading to usable form of energy.

There are several ways to produce hydrogen, by electrolysis of water, by splitting water using light, by collecting and reforming gas from biomass, by reforming natural gas or any other fossil fuel. Each of these processes is extremely energy intensive and always results in hydrogen with negative net energy. There are three energy sources to be used. The potential use of the renewable energy for hydrogen production is opening a new venue for utilization of hydrogen. In particular this advantage is seen in the hydrogen use in transport. Conversion of wind and solar energy to electricity and to hydrogen is opening a new venue for the efficient utilization of renewable energy sources. With abundant renewable energy resources the hydrogen rout is gaining economic prestige to be fuel of the future. If we take into consideration the environment effect of fossil fuel the hydrogen rout will definitely be the obvious future of the energy strategy.

In order to evaluate potential options for the future energy strategy it is of interest to evaluate hydrogen energy system. It has become of great interest to evaluate power system using different criteria. In this respect there are a number of methods, which are used with respective procedure in presenting quantitative merits for the rating of different power system designs [5, 6]. Among popular methods applied in the evaluation of power system are: thermodynamic method, energy-cost evaluation method and life cycle method. Each of the methods is based on the optimization function reflecting a single indicator in evaluation of individual options of power plant design. It has been noted that the energy system complexity requires multivariable assessment taking into a consideration different aspect of power system. It is obvious that beside the economic valorization of the power system the modern approach has to take into a consideration other aspect of the individual design of power system. Since energy production in the power system is based on different physical principles each power system option will reflect the importance of different optimization parameter. Also, each power system option will use different energy source, which conversion in the finale energy will impose different interaction with its environment [7].

The decision-making method based on the probabilistic assessment of fuzzy set of indicators with information deficiency has proved to be a powerful tool for the evaluation of complex systems defined by with multi-parameters [8, 9, 10]. It has become obvious that comparing the desirability of different means of action leading to the sustainability of products or determining “optimal” solutions in many cases by using simple criteria or a simple objective function. This area, multi-criteria decision-making has lead to numerous evolution schemes and to the formation of vector-maximum problem in mathematical programming.

2. Selection of options and indicators for energy systems

2.1. OPTION SELECTION

Potential options of Hydrogen systems are objects with number of attributes defining feedstock, energy sources, hydrogen production process and hydrogen utilization system. Among the energy resources are fossil fuels, nuclear fuel and renewable energy sources. Hydrogen production process comprise electrolysis, gas reforming process and light splitting process Finally, the attribute describing hydrogen utilisation process include fuel cell, reciprocication engine and gas turbine. Figure 1 presents Hydrogen System Structure Object.

In Object Oriented language the potential options of Hydrogen Energy Systems can be defined as:

> HES [Feedstock (Water, Coal, Oil, Gas, Biomass); Electric Energy (Nuclear PP, Renewable PP, Fossil PP), H_2 Production (Electrolysis, Reforming, Gasification); H_2Utilisation (Fuel Cell, Gas Turbine, Internal Combustion Engine)]

In evaluation of the potential objects which are to define respective options to be taken into a consideration there are 99 objects. In this exercise we will focus our attention on the following hydrogen energy systems: Fossil–Reforming–Internal Combustion Engine System, Natural Gas Steam Reforming–Fuel Cell System, Nuclear Power–Electrolysis–Fuel Cell System, Solar Power–Electrolysis–Fuel Cell System, Wind Power–Electrolysis–Fuel Cell System, Biomass–Reforming–Gas Turbine System.

In the evaluation of Hydrogen energy system a following option are used: For all systems are anticipated power production 400 kW.

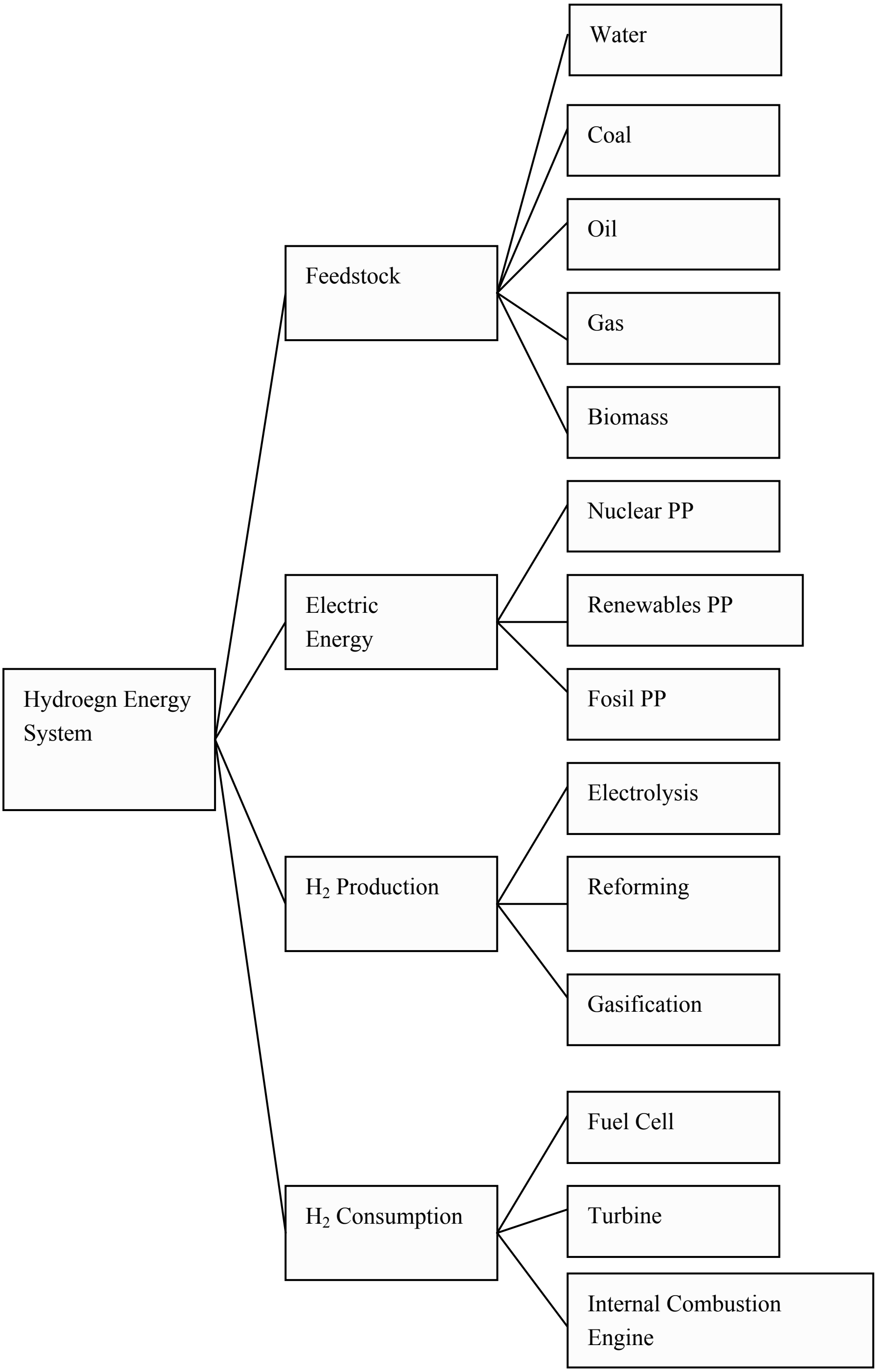


Figure 1. The Hydrogen System Structure Object

2.1.1. *Organic fuel reforming–storage–internal combustion engine system*

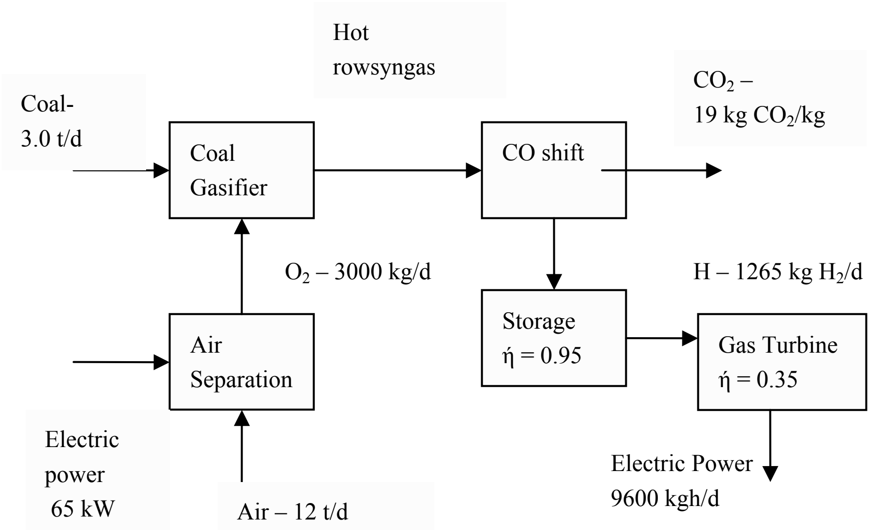


Figure 2. Organic fuel reforming–storage–internal combustion engine system (ORSICES) [7]

2.1.2. *Natural gas reforming–storage–fuel cell–system (NGRSFCS)*

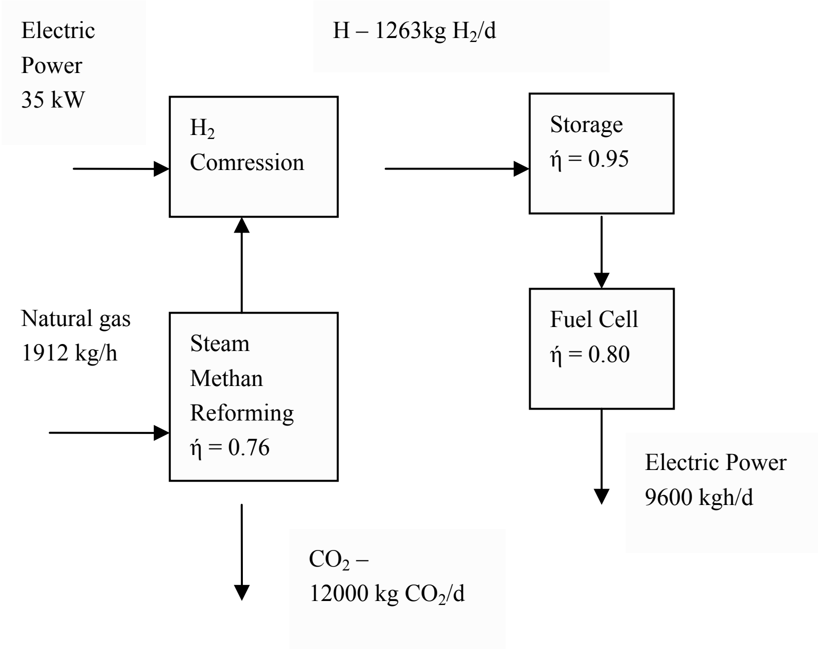


Figure 3. Natural gas reforming–storage–fuel cell – system (NGRSFCS) [7]

2.1.3. Nuclear power electrolysis–storage–fuel cell (NPESFC)

In the definition of this system it is anticipated that the mean energy source is coal with Low Caloric Value 7,000 kJ/kg. The efficiency of the coal reforming system is 73%. The efficiency of reciprocication engine with hydrogen fuel is 35%. Combustion of coal in reforming process is accompanied with production of chemical products which are considered as the pollutant of environment. In order to justify the effect of pollution problem with this hydrogen energy system a following emission is anticipated: CO_2. In this system it assumed that there is a storage facility. Total investment cost for the system is divided in following items: reforming plant, reciprocication engine. The use of nuclear energy for the hydrogen production was advocated many years ago as the promoting advantage of the utilization of nuclear power plants. Now, when hydrogen is close to its strategic acceptance, the same idea is again actual. Present cost of electricity from modern nuclear power plant is estimated as 7 c/kWh. Use of the low cost of electricity for the electrolysis in hydrogen production has become challenging issue for the potential of the hydrogen production. With electrolysis efficiency 75% the price of hydrogen can be as low as 47 c/kg. In this hydrogen system the need for storage is fundamental importance. Estimated cost for large volume hydrogen tanks is $399/m^3. PAFCs have been in “commercial” production for more than five years, with about 200 kW units installed or in production. These have historically been expensive at $3,000/kW, though assistance for purchasers has come through US Government programme.

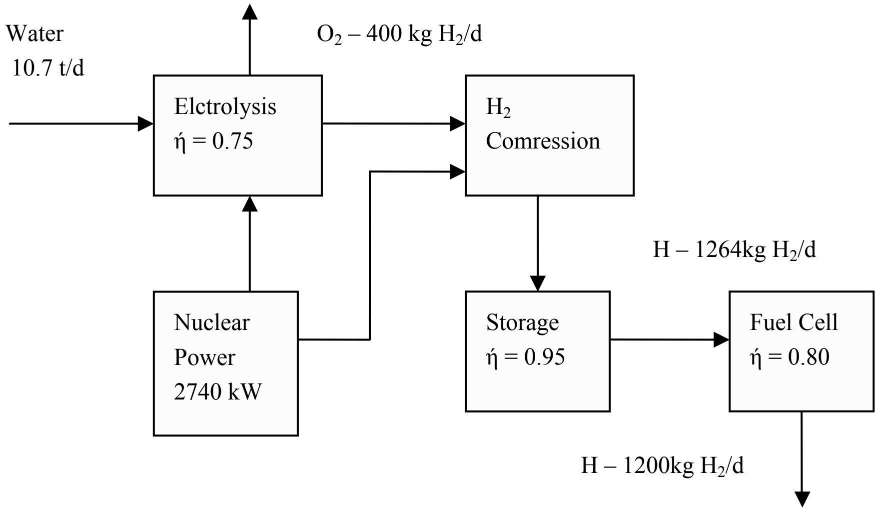


Figure 4. Nuclear power electrolysis–storage–fuel cell (NPESFC) [7]

The price, even at that stage, was subsidized internally, and the current market price is \$3,750/kW. This may seem like an increase but for the first time actually covers all of the costs of production.

The PAFC represents the first generation of "commercial" fuel cells. Although successful in terms of technical performance, questions are raised with regard to its cost reduction potential and whether may be a more competitive option in the future.

2.1.4. Solar power–electrolysis–storage–fuel cell system (SPESFCS)

The abundant solar energy resources are challenging potential option for hydrogen production. The solar cell costs are important element of the PV economic viability. The modules account for about 50% of cost of a PV power plant. The solar cells themselves account about half of the module cost, or 20% of total system cost. Thin film polycrystalline technology may make possible to have the module cost about 50 USD/m and electricity price of 6 cents/kWh. This is only a planning target for 10% efficiency.

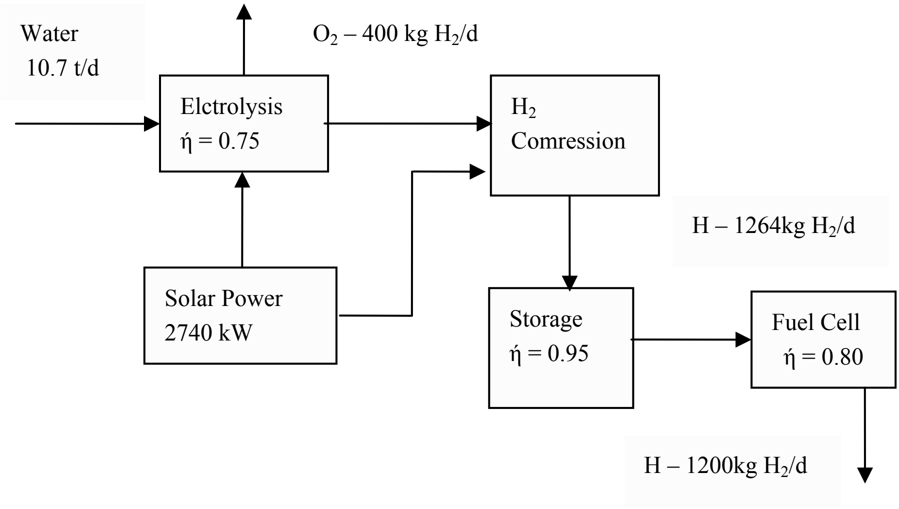


Figure 5. Solar power–electrolysis–storage–fuel cell system (SPESFCS) [7]

Electrolysis is the decomposition of water into hydrogen and oxygen. Electrolyzers essentially consist of a negative and a positive electrode as well as an electrolyte. Electrolyzers are characterized by their very simple and compact construction. Only 4% of hydrogen is made from water via electrolysis. Since most electricity comes from fossil fuels in plants that are 30% efficient, and electrolysis is 70% efficient, you end up using four units of energy to create one unit of hydrogen energy: 70% * 30% = 20% efficiency.

2.1.5. Wind power–electrolysis–storage–fuel cell system (WPESFCS)

Wind energy can be harvested to provide electricity at the low cost. Coupling wind turbine by hydrogen-generating electrolyzer has potential to provide low cost, environment friendly, distributed generation of hydrogen in edition to electricity. In this way hydrogen generation can be pathway for the wind generation of hydrogen. Wind electricity generation unit has efficiency 35% and lifetime 20 years. Investment cost of the wind generation unit is 1,000–1,100 Euro/kW with cost of land 300–400 Euro/m. Electricity cost is 0.03–0.07 Euro/kWh.

The goal is to use renewable energy to make hydrogen from water via electrolysis. When the wind with current wind turbines which can perform at 30–40% efficiency, producing hydrogen at an overall 25% efficiency.

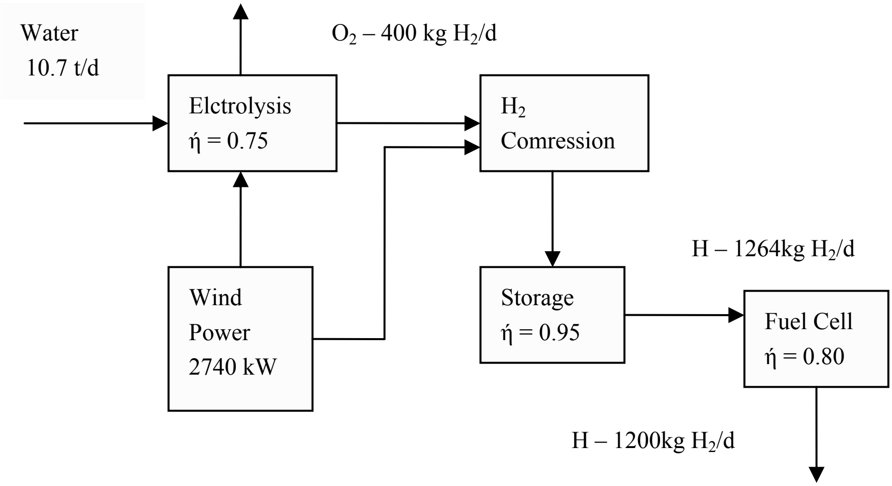


Figure 6. Wind power–electrolysis–storage–fuel cell system (WPESFCS) [7]

2.1.6. Biomass gasifier–compression–gas turbine CPH

The main goal of the gasification process is production of the high quality and quantity of gaseous fuel from the biomass. The gasification process is performed at the high temperature of 700–1,000°C and under the stoichiometric conditions ($\lambda < 1$), which don't allow to develop the combustion process and also to consume the all fuel. This hydrogen system is composed of air separation unit, biomass gasifier, CO shift, storage and gas turbine in CHP cycle.

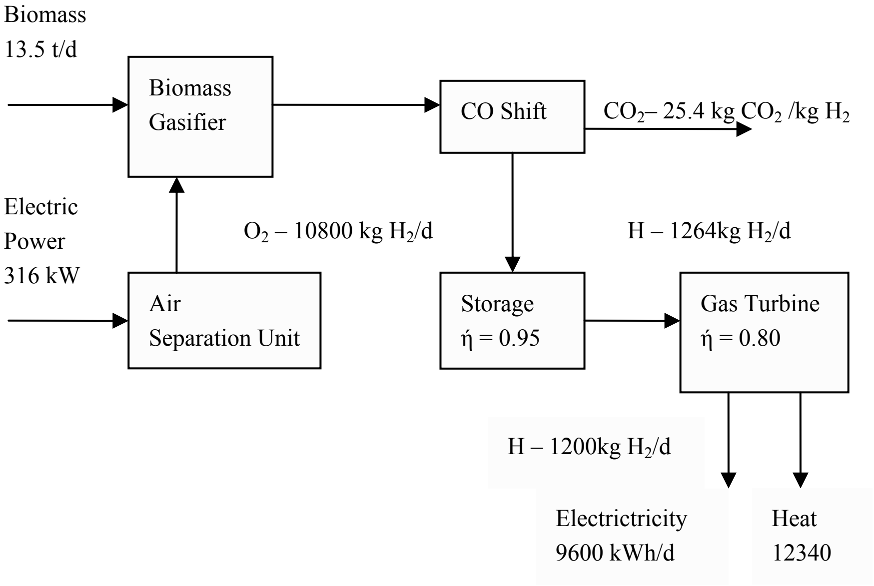


Figure 7. Biomass gasifier–compression–gas turbine CPH (BGCSGTCHPS) [6]

3. Sustainability assessment

Measuring sustainability is a major issue as well as a driving force of the discussion on sustainability development. Developing tools that is reliable measure sustainability is a prerequisite for identifying non-sustainable processes, informing design-makers of the quality of products and monitoring impacts to the social environment. The multiplicity of indicators and measuring tools being developed in this fast-growing field shows the importance of the conceptual and methodological work in this area. The development and selection of indicators require parameters related to the reliability, appropriateness, practicality and limitations of measurement.

The effective indicator has to meet characteristics reflecting a problem and criteria to be considered [7]. Its purpose is to show how well system is working. In the case there is a problem an indicator has to indicate its origin and direction to take to solve the problem. Indicators are strongly dependent on the type of the system they monitor.

It is known that any numerical number, semantic expression or mathematical sign are information. Examples of these types of information can be found in any reading of temperature or other time dependent variables describing state of the system. Information is also parameters used in the design of respective system. Also, positive or negative sign of the variable is also the information.

Collecting information and its processing will convert them in data. So, data represent agglomerated information, which are partially or finally processed. Examples of data can be found as a parameter, which describe evaluated information to be used for the specific purpose. In this respect the average inlet temperature of cooling water in the condenser is data obtained by the averaging procedure adapted for this purpose. Also heat transfer coefficient used in the design of condenser is the data obtained by the experimental procedure for the heat transfer evaluation.

In order to use the data for the assessment of respective system, it is necessary to convert them into the indicator. So, the indicator represents the measuring parameter for the comparison between the different states or structure of the system. As example, the efficiency of system is an indicator for the quality of energy use in respective system. Also, we can evaluate different structure of the systems by indicator representing respective entities of the system. In this direction is the assessment of intelligence use in the improvement of the system compatibility with its surrounding is measured by the respective indicators.

3.1. INDICATORS

For the sustainability assessment of HE system a following indicators are used:

1. Fuel Indicator – Fuel
2. Electricity Indicator – Electricity
3. Fixed Cost Indicator – Fixed
4. Capital Indicator – Capital
5. Environment Indicator – EI

3.1.1. Fuel indicator (fuel)

Since every system under consideration is subject to different efficiency, it is of interest to have efficiency as the integral parameter of the system which comprises element characteristics of the system. The performance indicator in this assessment procedure is composed of number of sub-indicators: efficiency, total energy cost, capital cost and lifetime. The efficiency of the system is considered as the integral parameter for the performance validation. The total energy cost is result of the system optimization with minimum energy cost constrain. The capital cost is a measure of the investment per unit energy produced in the lifetime of the system. Also, the important parameter in the assessment of performance of the energy system is the lifetime of system.

3.1.2. Electricity indicator (electricity)

For any hydrogen system electricity is needed. In this respect utilization of the electricity is an important indicator in evaluation of the hydrogen systems. It is used in the system with electrolysis and compression of all hydrogen systems. In option with electrolysis, it is anticipated electricity production within the system and for the reforming system the electricity is considered to be imported outside of the hydrogen system with respective commercial prices.

3.1.3. Fixed cost indicator (fixed)

Fixed cost indicator is derived form the total capital cost of the system. It defined as 5% of capital cost. It comprise operational and maintenance cost for whole system, including hydrogen production and its utilization for the electric energy production.

3.1.4. Capital cost indicator (capital)

Capital cost indicator is defined as the 18% of total capital cost for the hydrogen production and utilization elements. For each option the total capital cost is obtained forms the scale down of the hydrogen system as they are defined in the evaluation of larger system.

3.1.5. Environment indicator (CO_2)

Present strategy in hydrogen system design is strongly related to the modern approach in gas emission control. Due to the global effect of CO_2, its monitoring has become of paramount interest in the design of new hydrogen system. For this reason, any design of hydrogen system has to incorporate those features which are related to decease of CO_2 emission per unit energy produced. The environment indicators are composed of tree element:CO_2. CO_2, Indicators is represented by the respective concentration of gases.

4. Multicriteria sustainability assessment

The multi-criteria assessment is based on the decision-making procedure reflecting combined effect of all criteria under consideration and is expressed in the form of General Index of Sustainability [8, 9, 10]. Selected numbers of indicators are taken as measure of the criteria comprising specific information of the options under consideration. The procedure is aimed to express options property by the respective set of indicators.

4.1. SUSTAINABILITY INDEX DEFINITION

The decision-making procedure comprise several steps in order to obtain mathematical tool for the assessment of the rating among the options under consideration. In order to prepare respective data for the hydrogen systems assessment, Table 1 presents the data to be used in the analysis.

TABLE 1. Technical data of hydrogen systems

	Fuel $/kg H_2	Electricity $/kg H_2	Fixed (O&M) $/kg H_2	Capital (18%/y) $/kg H_2	CO_2 kgCO_2/kg H_2
ORSICES	0.20	0.16	0.58	2.09	19
NGRSFCS	0.58	0.03	0.56	2.07	9.5
NPESFCS	0	2.45	1.09	3.92	0
SPESFCS	0	8.93	1.09	3.92	0
WPESFCS	0	3.68	1.09	3.92	0
BGCSGTS	0.64	0.28	0.69	2.48	25

General indices method comprises formation of an aggregative function with the weighted arithmetic mean as the synthesizing function defined as:

$$Q(q;w) = \sum_{i=1}^{m} w_i r_i \tag{1}$$

where

$Q\ (q,w)$ – General Sustainability Index
w_i – weight-coefficients elements of vector w
r_i – aggregated indicators of specific criteria

The probability of dominancy is factor which defines the preference relation between objects by the inequality $\overline{Q}_+(q^{(j)};I) > \overline{Q}_+(q^{(l)};I)$.

$$R(j,l;I) = \frac{|\{s: Q_+^{(s)}(q^{(j)}) > Q_+^{(s)}(q^{(l)})\}|}{N(I;m,n)} \tag{2}$$

where

$Q_+^{(i)}(q^{(i)})$ – General Sustainability Index
N (I, m, n) – Number of combinations satisfying prescribed condition

In order to define weight-coefficient vector the randomization of uncertainty is introduced. Randomization produces stochastic with realizations from corresponding sets of functions and a random weight-vector. It is assumed that the measurement of the weight coefficients is accurate to within a steps h = 1/n, with n a positive integer. In this case the infinite set of all possible vectors may be approximated by the finite set W (m, n) of all possible weight vectors with discrete components. In our case, we will use m = 5, and n = 40 so that the total number of elements of the set W (m, n) is N (m, n) = 135,751.

For non-numeric, inexact and incomplete information I = OI U II used for the reduction of the set W (m, n) of all possible vectors w to obtain the discrete components set W (I;n, m) is defined a number of constrain reflecting non-numeric information about mutual relation among the criteria under consideration.

5. Multi-criteria evaluation of hydrogen systems

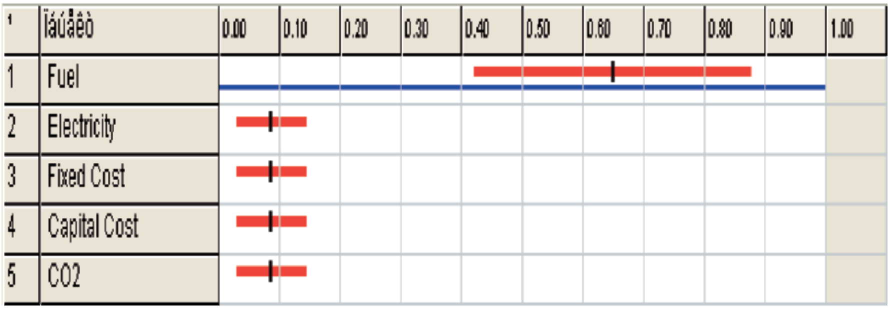
The evaluation of options under consideration is based on the selection of respective conditions to be satisfied as defined in individual cases. There are two groups of cases. Single indicator priority with other weighting factors having the same values and second group includes those cases with priority given stepwise change in pairs defined by economic and capital indicators.

Evaluation is obtained for following cases:

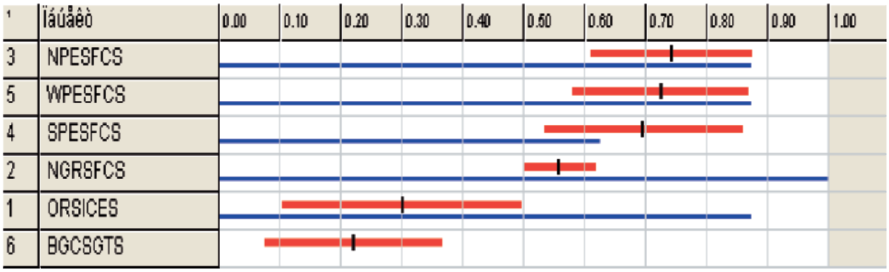
5.1. GROUP 1

5.1.1. Case 1 – *fuel > electricity = fixed = capital =* CO_2

Weighting coefficients



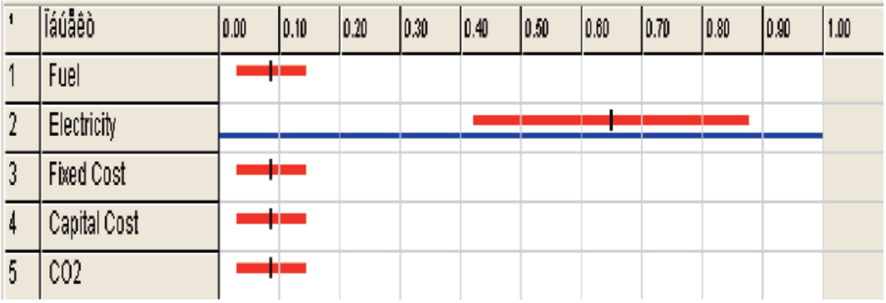
General sustainability index



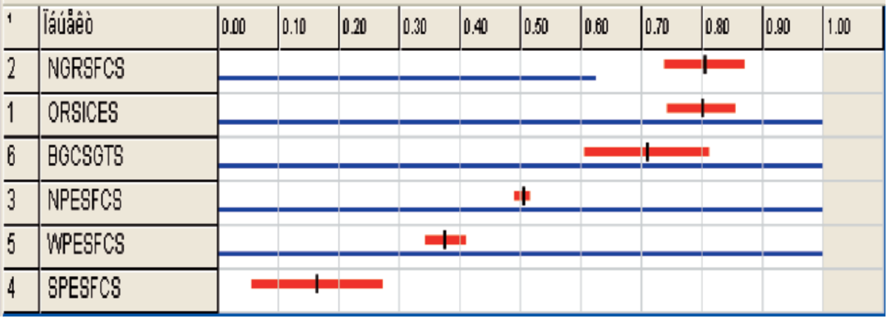
In this case we can notice that nuclear, wind and solar options are in the first group of options under consideration. It is obvious expectation since these three options are not using any fuel for its operation. Water for the electrolysis is not taken into a consideration. It should be emphasized that this case the probability of dominancy is higher then 50% for all options. This proves that this case is highly probable case.

5.1.2. Case 2 – electricity > fuel = fixed = capital = CO_2

Weighting coefficients



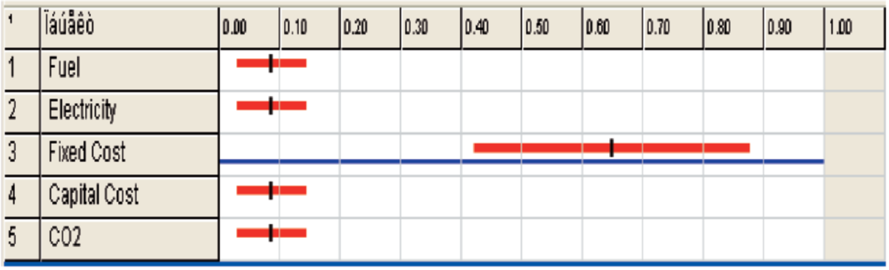
General sustainability index



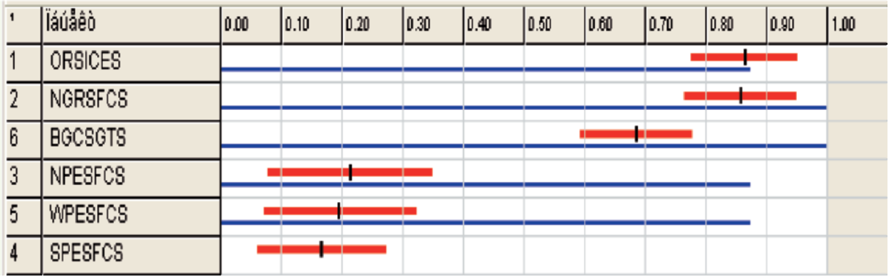
The Case 2 – Electricity > fuel = fixed = capital = CO_2 gives priority to the electricity cost with other indicators having the same value. Priority is obtained for the NGRSFCS and ORSICS options. As in the Case 1 this case is having probability of dominancy.

5.1.3. Case 3 – fixed > fuel = electricity = capital = CO_2

Weighting coefficients



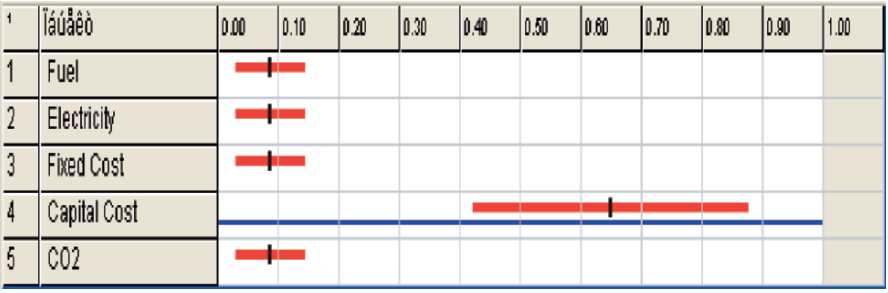
General sustainability index



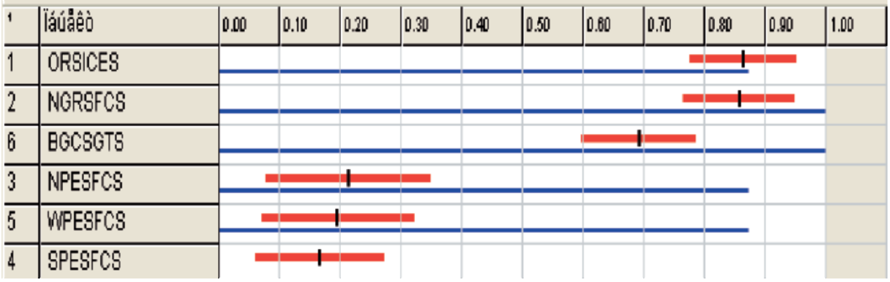
Case with priority given to fixed cost emphasizes options with refinery hydrogen production including coal option and natural gas option. Options with renewable energy sources are having low rating among options in this case. Due to the high investment capital for renewable options the effect of fixed charge is influencing the low rating of options with renewable sources.

5.1.4. Case 4 – capital > fuel = electricity = fixed = CO_2

Weighting coefficients



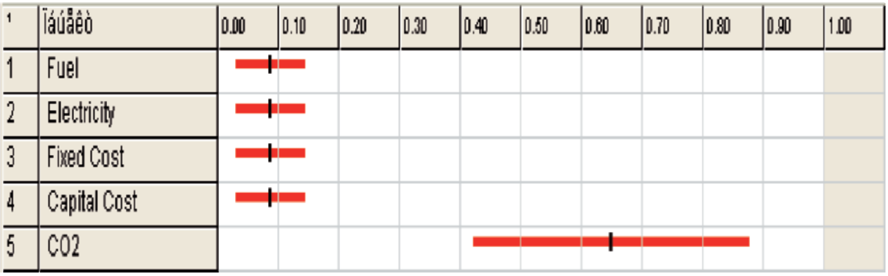
General sustainability index



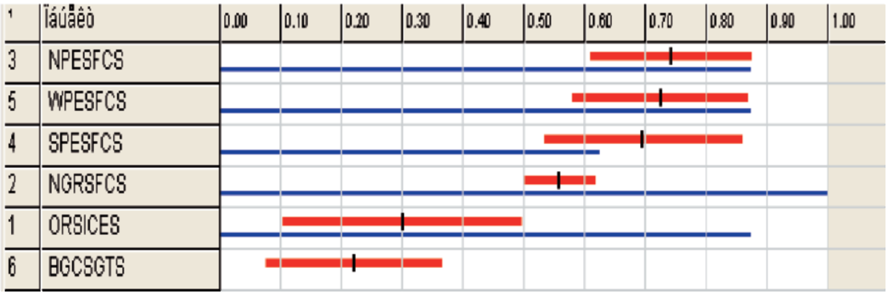
Similar situation is as in the Case 3 .In this case with priority to the capital cost in the hydrogen cost is having the same affect. It is obvious that these two cases are reflecting the same influence to the rating priority among options under consideration. This case belongs to the group with the high value of probability of dominancy proving that this case is highly probable.

5.1.5. Case 5 – CO_2 >fuel = electricity = fixed = capital

Weighting coefficients



General sustainability index

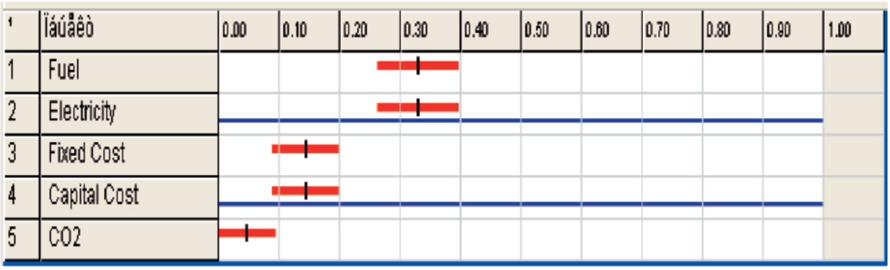


If priority is given to CO_2 indicator the results obtained favours nuclear, wind and solar options. Low rating is obtained for the options with reforming processes and high CO_2 concentration.

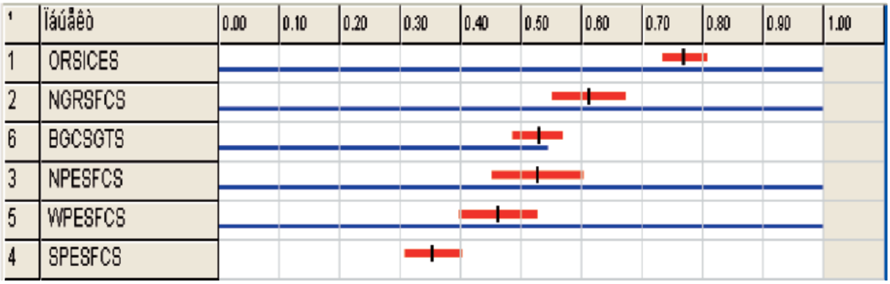
5.2. GROUP 2

5.2.1. Case 6 – fuel = electricity > fixed = capital > CO_2

Weighting coefficients



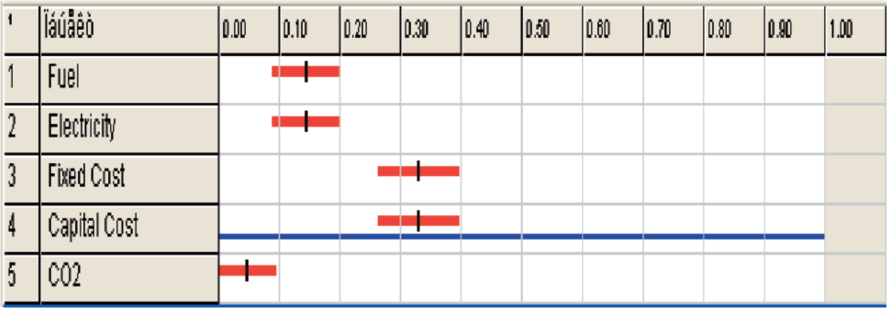
General sustainability index



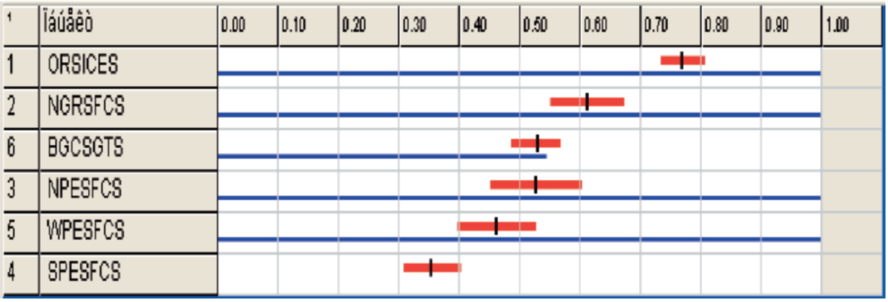
This case is designed with priority given to the economic indicators in comparison with to the capital costs. An this interesting observation is obtained if the priority is given to the fuel and electricity indicators in comparison to the fixed and capital cost. In this case the highest priority on the rating list is obtained for the coal reforming options.

5.2.2. Case 7 – capital =fuel > electricity = fixed > CO_2

Weighting coefficients



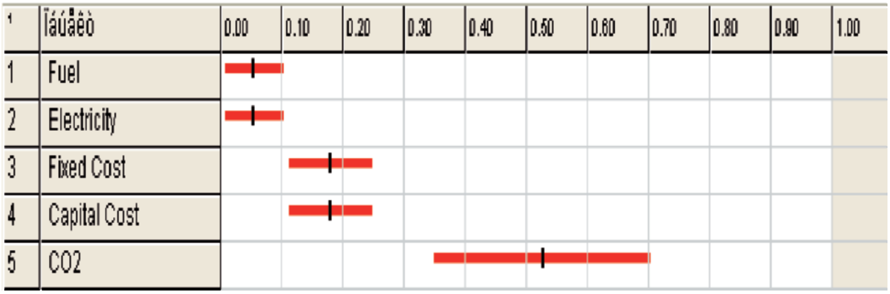
General sustainability index



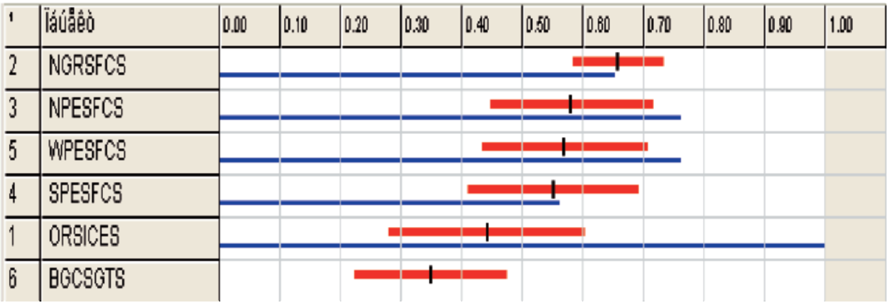
As in the Case 7, the priority is given fixed and capital cost in comparison with fuel and electricity cost .The coal reforming options is having priority in comparison with other options under consideration.

5.2.3. Case 8 – CO_2 > fixed = capital > fuel = electricity

Weighting coefficients



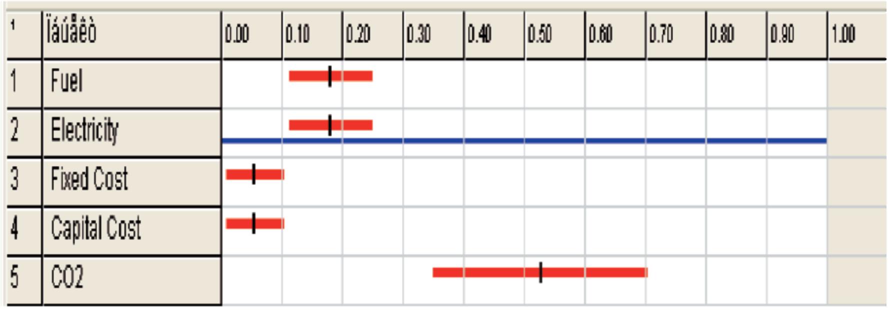
General sustainability index



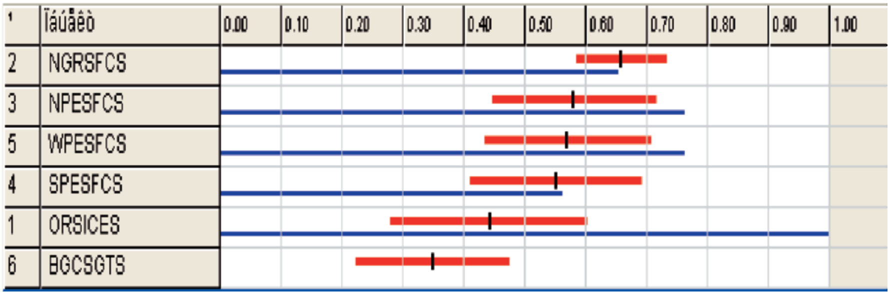
In order to investigate the effect of the CO_2 indicator on the priority list the priority is given to CO_2 indicator and fixed and capital indicators in comparison with fuel and electricity indicators. With marginal differences GSI, all options are composing single group without substantial difference.

5.2.4. *Case 9 – CO_2 >fuel = electricity > fixed = capital*

Weighting coefficients



General sustainability index



This case is reflecting the same situation as in the Case 8 with priority given to CO_2 indicator and having opposite ration among fixed and capital indicators in comparison with fuel and electricity indicators. The rating among options is similar as in the Case 8.

6. Conclusion

Multi-criteria evaluation of hydrogen systems is an exercise showing potential possibility of the analysis of complex systems. In the general terms it could be said that the complexity of hydrogen systems can be defined as the multidimensional space of different indicators. Every hydrogen system under consideration is entity by itself, defined by the respective number of parameters which are deterministically related according the physical laws describing individual processes in the system. The differences expressed by selected indicators are reflecting complexity of the individual structure of options under consideration.

Use of multi-criteria decision-making procedure requests a new method for evaluation of the potential options of energy systems. Its purpose is mainly oriented to the evaluation of options in order to investigate the effect of individual criteria on the priority list for decision-making process. In the evaluation procedure it is possible to investigate effects of mutual relation of the criteria on the finale priority list. This evaluation procedure could be imagined as the useful tool for the analysis of the individual criteria.

Since this evaluation is only demonstration of the method and procedure, it would be inappropriate to make any finale conclusion of the potential selection of the hydrogen system as it was demonstrated in this evolution. But, still it can be concluded that under circumstances demonstrated in this evaluation coal and natural gas with fuel cell systems are presently the most attractive potential systems to be selected among the options under consideration. Also, natural gas and nuclear systems with fuel cell and gas turbine options are potentially acceptable solution for the situation where it can be in accordance with respective local condition. It should be emphasized that the utilization options are not substantially affecting priority of the options under consideration.

References

1. Gianpiero M., Mayuari K., Postar G., Energy Analysis as a Tool for Sustainability: Lessens for Complex System Theory. Annals of the New York Academy of Sciences, 879, pp. 344–367, 1999
2. Heylighen F., The Science of Self-organization and Adaptively, Free University of Brussels, Belgium
3. Progogine I., Evaluation Criteria, Variational Properties and Fluctuations, Non-equlibrium Thermodynamics Variational Techniques and Stability, Ed. R. J. Donnely, R. Herman, I. Prigogine, The University of Chicago Press, Chicago, 1966
4. Prigogine I., Kondepudi D., Modern Thermodynamics: From Heat Engine to Dissipative Processes, Wiley, Chichester, 1998
5. Naim H. Afgan, Maria G. Carvalho, Sustainability Assessment Method for Energy Systems, Kluwer Academic, Boston, 2000
6. Naim H. Afgan, Maria G. Carvalho, Sustainability Assessment of Hydrogen Energy Systems, Int. Journal on Hydrogen Energy, Vol. 29, Issue 13, pp. 1327–1342
7. Simbeck D., Chang E., Hydrogen Supply: Cost Estimate for Hydrogen Pathways, National Renewable Energy Laboratory - NREL/SR-540-32525
8. Hovanov N., Fedotov Yu., Zakharov V., The Making of Index Numbers Under Uncertainty, Environmental Indices: Systems Analysis Approach, EOLSS, Oxford, pp. 83–99, 1999

9. Hovanov N., Analysis and Synthesis of Parameters under Information Deficiency. St. Petersburg, St. Petersburg State University Press, 1996 (Monograph, in Russian)
10. Hovanov N., Kornikov V., Seregin I., Qualitative Information Processing in DSS ASPID-3W for Complex Objects Estimation Under Uncertainty, Proceedings of the International Conference “Informatics and Control”. St. Petersburg (Russia), pp. 808–816, 1997

RENEWABLE ENERGY IN ARMENIA: STATE-OF-THE-ART AND DEVELOPMENT STRATEGIES (HYDROPOWER)

SUREN GEVORGYAN
VARDAN SARGSYAN*
Armenian State University of Economics, Nalbandyan 128, Yerevan, 375025, Armenia

Abstract: Energy is a particularly strategic resource because it provides basic human services such as heat and light, and also because it enables all manner of other economically vital commercial and industrial activities. The ability of a country to safeguard its energy security depends on many factors and mainly energy resources. Armenia has no own fossil fuel resources and is completely dependant on supplies from outside. This fact makes the development of alternative energy resources vitally important for the country. At the same time Armenia has considerable renewable energy resources as hydro, solar, wind and geothermal. The potential of hydro energy capacity in Armenia is around 1,000 MW and formed 20–35% of total installed capacity. Part A of presented paper examined the current status of the Armenian energy system, the situation, importance and strategies for development of renewable, particularly hydro energy and the limitations of opportunities connected with environmental and other aspects.

Keywords: alternative energy, renewable energy, sustainable development, energy security, hydropower

1. Background

The lessons about the significance of energy security – the basis for sustainable social and economic development, have been practically learnt by

---

* To whom correspondence should be addressed. Vardan Sargsyan, Armenian State University of Economics, Nalbandyan 128, Yerevan, 375025, Armenia; e-mail: vsarg@freenet.am

J.W. Sheffield and Ç. Sheffield (eds.), Assessment of Hydrogen Energy for Sustainable Development, 211–216.

Armenia since the years of its national independence. Nowadays performing the most perspective trend, the renewable energy took the lead over the nuclear energy. In the world energy consumption the share of the renewable energy makes up 11.7% (without the large-scale HPPs), whereas the share of nuclear energy is 6.5% [1, 2]. The speeded-up growth of the renewable energy use complies with the Concept of sustainable development in the sustainable energy and greenhouse gas (GHG) mitigation, adopted at the World Summit and the United Nations Conference on Environment and Development in Rio de Janeiro in 1992, and the Kyoto Protocol recently ratified by Armenia. The role of the renewable energy is assumed as even of greater importance for the present Armenia, due to following circumstances: (1) absence of own fossil fuel resources, (2) geopolitical situation, (3) solar and wind resources, (4) environmental degradation, (5) necessity of stopping nuclear station.

Armenia has achieved remarkable results in reforming the power sector and improving its performance. The remaining challenge for the sector is to ensure sustainable and reliable power supply by shifting reliance from costly and polluting sources of energy to lower cost and environmentally friendly alternatives and increasing the energy diversification for a higher degree of energy security through indigenous renewable energy resources. While the overall legal and regulatory framework in Armenia is supportive to the development of renewable resources. The World Bank approved a Renewable Energy Project started in 2005 [3] for Armenia totaling US $25 million, including a US $5 million International Development Association (IDA) credit, and a US $3 million grant from the Global Environment Facility (GEF). The project is also supported by other sources, such as US $7 million from the government and local financial institutions. The Renewable Energy Project will provide assistance to remove the existing barriers and debt financing, as well as technical, legal, managerial and business support to a selected number of renewable projects. By the time of completion, the project is expected to contribute to the development of about 80 MW of additional renewable energy generation capacity, adding 200 GWh annual renewable generation to the electricity generation mix. In addition, CO_2 emissions are expected to be lowered by around 130,000 tons annually.

2. Armenian energy system: history, legislation, developments and problems

The Republic of Armenia has a population of approximately 3.2 million people and limited energy resources to satisfy its needs. The energy sector of Armenia has been one of the most developed parts of the economy. In the

1980s Armenia was a net exporter of electrical power. Armenia has no oil and natural gas reserves, and imports all its energy (oil or oil products from Iran, Russia and Europe; gas exclusively from Russia through Georgia; and nuclear fuel from Russia). The only main indigenous energy resource in Armenia is hydropower.

Electricity in Armenia is provided by three main sources – nuclear power plant, hydro cascades and thermal stations. The nuclear power plant provides 30–40%, hydroelectric plants (total installed capacity of approximately 1,000 MW) satisfy 20–35% of the country's needs depending on level of precipitation, which varies significantly. Besides, the hydropower generation is declining due to limitations associated with irrigation purposes of the hydro plants and environmental constraints. The remaining electricity demand is satisfied by thermal power plants with total installed capacity of 1,350 MW, which can burn either oil or natural gas. The share of the thermal plants in the generation mix of the country is on average 30–35%. Other sources such as wind power stations provided only 0.1–0.2% of total produced energy in Armenia. In summary, over 70% of the electricity demand in Armenia is satisfied through nuclear and thermal generation that relies entirely on imported energy. That is why the energy security of the country is a major concern for the government.

Armenia is particularly sensitive to its energy security because it faced a crippling energy crisis between 1992 and 1995 as a result of the collapse of former markets in the Soviet Union. The severity of the crisis was compounded by a decision in March of 1989 to shut down the Armenian nuclear power plant due to pressure from environmental groups and safety concerns following the 1988 earthquake. Instability in the power grid resulted in over utilization of hydro resources, particularly Lake Sevan.

During the 1990s, Armenia grappled with how to resolve its energy shortages. Since then, its nuclear power plant (NPP) has been restarted, financial and technical assistance has come from the international community, natural gas imports have increased and the energy crisis has been mitigated. NPP's installed capacity equals 815 MW and its annual average output amounts to 2.0 billion kWh of electric power per year. The main consumer of the electric power is the Armenian power market. As of today, one of two blocks of the plant is under operation (the operating capacity of the block is 375 MW and it generates more than 40% of the electric power produced in Armenia [4, 5]. To ensure further continuous and trouble-free operation of the Armenian NPP, on 18 September 2003, the Republic of Armenia and RAO UES of Russia subsidiary, CJSC "RAO UES INTERNATIONAL," signed a five-year contract on transfer of rights certified by 100% of Armenian nuclear power plant's shares into trust management. And the Armenian government remains the owner of JSC "Armenian NPP." Over the past few years there has been increased pressure from the European Community to shut the nuclear plant down. The Metsamor NPP has two reactors with projected useful lives that will expire in a decade. The most persuasive of these arguments is that the reactors sit in a seismically active zone near a densely populated area.

Armenia's energy strategy (Poverty Reduction Strategy Paper (PRSP)) prepared in 2003 clearly emphasizes (among others): "Maintaining and strengthening energy independence by developing indigenous and alternative energy sources and promoting energy efficiency. Regarding the development of indigenous resources, priority should be given to developing renewable energy production." Armenia's Energy Law, which was enacted in 1997 and revised by the national assembly in 2001 states among others (Article 5) that the main principles of the state policy in the energy sector are: efficient use of local energy resources and energy renewables, ensuring energy security, promotion of the energy independence of the republic and ensuring environmental security.

Armenia's commitment to promote renewable resources relates to its need to diversify its energy resource base and reduce energy imports. The country has taken concrete steps to make renewable energy development part of its energy law and energy strategy. On 9 November 2004 legislation was passed on the Law of the Republic of Armenia on Energy Saving and Renewable Energy. In 1996, government projected that alternative sources of energy might be developed.

Armenia's energy crisis has had at least one benefit. Its isolation and lack of hydrocarbon reserves has lead to some innovative ideas about alternative energy sources.

3. Hydro energy

Hydropower generates 20–35% of Armenia's energy needs. Although this form of power generation does not emit atmospheric pollution, there can be significant environmental impacts. The greatest impacts are on water quality and quantity of Lake Sevan, and changes to the surrounding environment. Sevan is the greatest lake of Transcaucasus region and one of the greatest freshwater high-mountain lakes of Eurasia. At present, the water level is lower almost on 20 m. Lake Sevan's waters have been used for decades to generate electricity, but at a cost to the lake's ecosystem. The increased outflow of the lake's water for use in hydroelectric generation has contributed to the lake's deterioration by reducing its volume by roughly 40%, increasing the water temperature and impacting environmental quality and fishing industry. The Sevan problem aroused from the beginning of current century. Primary the problem was how to use the natural resources of the site. High location of the lake compared to the fertile but arid Ararat Valley, luck of energy resources in the country attracted the engineers to find the methods to explore the water of the lake intensively for energy and irrigation. Hydroelectric system has been developed in the area on the River Hrazdan, which is the main outflow from the Lake [6].

3.1. CONDITIONS OF HYDROELECTRICITY GENERATION ON SEVAN–HRAZDAN CASCADE

Hydropower in Armenia is provided by the Sevan–Hrazdan and Vorotan cascades. The Sevan–Hrazdan cascade consists of six power plants with a total installed capacity of 535 MW, however due to age and deferred maintenance, the capacity of the cascade has been derated to 328 MW (TACIS 1999). The only pondage on the Sevan–Hrazdan cascade is Lake Sevan which was drawn down excessively during the energy crisis when hydro generation was the only source of power. Lack of storage greatly restricts the flexibility of use of this cascade since it must operate in a run-of-river regime. Because water release from Lake Sevan is seasonal and limited, the Sevan–Hrazdan cascade is best suited to provide daily peaking power [7].

In the winter, the capacity of the Sevan–Hrazdan hydro cascade is limited because of the need to increase the level of Lake Sevan conserving water for summer irrigation and the possibility of future energy crisis situations. The maximum acceptable level of winter discharge from Lake Sevan is a politically and scientifically contentious issue, but generation from the Sevan–Hrazdan cascade could be limited to as little as 60 MW during the winter peak demand period and total hydro generation to as little as 400 MW. At this time energy generation in Armenia is stabile. It is important to mention, that since 1997 Armenia has been exchanging electric power with Iran, supplying power in summer and receiving power during the winter. Some electric sales have been made to Georgia.

Question arises: Is it acceptable for Armenian economy and energetic security not to account on Sevan–Hrazdan Cascade and to generate hydropower from Sevan only during irrigation period? It appears that the Armenian electric power generation is able to meet the demands and conditions energy security and stability in Armenia. Taking into account also the plans of development of alternative (solar, wind and hydrogen) power systems it is obvious that Sevan–Hrazdan cascade could serve only during irrigation period and even not to generate energy in winter at all. According to various investigations and statements, from both, economical and environmental points of view it is not effective to charge water resources of Sevan for energy generation in non-critical situations. That is why during

1993–1997, rearrangements took place among three types of energy generation in Armenia. Reopening Armenian nuclear station in 1995 contributed to bringing down the part of hydropower in the energy balance of Armenia and thus maintaining of water resources of Sevan. Table 1 shows the shifting mix of power actually generated between 1992 and 1997.

TABLE 1. Energy generation mix during 1993–1997[†]

Type of generation	1993	1994	1995	1996	1997
Thermal	33%	38%	60%	37%	50%
Hydro	67%	62%	35%	26%	23%
Nuclear	0%	0%	5%	37%	27%

4. Conclusion

Armenia has hydro energy resources that can cover up to 35% of country's energy demand, but according to above mentioned, hydropower development has no much perspective in the country due to limitations of hydropower resources and this could result environmental degradation, particularly lose of environmental quality of the Lake Sevan. However, the system of small hydropower plants on mountainous rivers could be developed as a support to Armenian energy grid.

References

1. World Energy Assessment: Energy and the Challenge of Sustainability/UNDP, UN Department of Economic and Social Affairs, 2000.
2. IEA Energy Statistics of non-OECD Countries. 1998–1999, 2001 edition.
3. A.Marjanyan, N. Mirzoyan GEF/WB Grant Program for Renewable Energy Development in Armenia, Energy for Future, Yerevan 2005.
4. Contract IAEA TC-ARM/0/004 "Energy and Nuclear Power Planning Study for Armenia (covering the period 1999–2020)". Signed in 1998, IAEA, Vienna, Austria.
5. Source Book, 4th ed., Nuclear Energy Institute, 1996; Soviet-Designed Nuclear Power Plant Profiles, US Department of Energy, 1999.
6. Armenia, Lake Sevan, Action Program, Main Report, The International Bank of Reconstruction and Development, 1999.
7. The Scheme of Development Small HPP in Armenia, Arm hydroproject, Yerevan, 1997.

[†] Source: *Energy Sector Overview*, prepared by AID for Armenian Energy Sector Investment Conference in Fall 1998.

RENEWABLE ENERGY IN ARMENIA: STATE-OF-THE-ART AND DEVELOPMENT STRATEGIES (WIND, SOLAR, AND HYDROGEN ENERGY)

VARDAN SARGSYAN[*]
Armenian State University of Economics, Nalbandyan 128,
Yerevan, 375025, Armenia

SUREN GEVORGYAN

Abstract: Armenia has no own fossil fuel resources and is completely dependant on supplies from outside. Development of alternative energy resources is strategically important for the country. The inflow of solar energy per square unit of surface is higher for around 70% than in Europe, the assessed wind potential is 400–450 MW. There are definite shifts in hydrogen energy technologies. Some solar and hydrogen technologies are already commercialized. Definite progress is being made, with wind-, hydrogen-, and solar-generated projects. Part B of presented paper examined the current status and development paths of wind, solar, and hydrogen energy applications in Armenia. Following points, which presented specific interest, are in the focus: in what extent Armenia succeeded in keeping up the world tendencies of renewable energy, and what are the preconditions for the speeded-up development of renewable energy in Armenia?

Keywords: alternative energy, renewable energy, sustainable development, energy security, fuel cells

1. Wind energy

Armenia does not have a wind stream that is comparable to the Gulf Stream that exists in the USA, but there is nevertheless some wind potential. At

---

[*] To whom correspondence should be addressed. Vardan Sargsyan, Armenian State University of Economics, Nalbandyan 128, Yerevan, 375025, Armenia; e-mail: vsarg@freenet.am

J.W. Sheffield and Ç. Sheffield (eds.), Assessment of Hydrogen Energy for Sustainable Development, 217–223.

present, the economically viable capacity for wind energy is comparable with nuclear, but wind energy development in Armenia is in its infancy. If wind power proves to be feasible, then Armenia could add wind-generated electricity to its portfolio of energy sources. It is too costly to use one windmill to generate electricity for commercial purposes, but a single windmill could be used in places with extensive rural areas. Armenia has large tracts of rural areas, but one of the legacies of Soviet industrialization is, that nearly every place in Armenia has access to the electricity grid, so a remote location that might otherwise need to generate its own energy simply does not need to. The future for wind power in Armenia, therefore, is in large wind farms that generate electricity that is then added to the grid. Some studies [1] have identified a number of such prospective sites in Armenia where wind farms could be erected. The Armenian government hopes one day to be able to generate as much as 10% of its electricity in this way. Start-up costs for establishing wind as an alternative energy source would be insignificant compared to the cost of building a new nuclear power plant. Wind conditions vary strongly in Armenia. Average wind speeds are mostly rather low (<4 m/s), but much higher wind speeds (in excess of 8 m/s) have been reported in several specific locations [1]. At this wind velocity, wind turbines can generate electricity for as little as three cents per kilowatt-hour, which is quite inexpensive.

Some calculations show that in Armenia could be technically possible to get 1.6 billion KWh wind energy yearly [1, 2]. Monitoring of wind energetic potential in Armenia was started in 1999. This research was organized within governmental agreement between Armenia and the Netherland. “ArmNedWind” company have established five monitoring stations, 14 more were setup by “Solaren” company and together with US National renewable energy laboratory (NREL) was worked out the Atlas of Winds in Armenia. Based on the results of the study the assessed total wind energy potential in Armenia for wind farms is 4,550 MW [3] (Table 1). During next five years is planned to construct two wind power plants with 50 MW and 20 MW capacities. The identified sites in Eastern-Sevan Ridge have

TABLE 1. Calculated energy potential of wind power stations in Armenia

Wind speed m/s	Area sq.km	% from total area	Total installed capacity MW
7.5–8.1	451	1.6	2250
8.1–8.6	207	0.7	1050
8.6–9.5	169	0.6	850
>9.5	85	0.3	400
Total	**912**	**3.2**	**4550**

potential for wind farm development with capacity of 50 MW and with power output of 153,000 MWh/year that can reduce over 100,000 ton/year of greenhouse gas emissions.

Zod Wind Company is involved in a 25 million dollar project to build a set of wind turbines in the east of Armenia [3].

Conclusions

Armenia's wind potential is not on a high level, but there are some capabilities for development of wind energy. Wind energy development in Armenia is on initial phase. The future for wind power in Armenia is in large wind farms as Armenia inherited from USSR developed energy grid and it will be not economically effective to construct single windmills. Several prospective sites where wind farms could be erected are already defined. The part of wind energy in energetic balance in Armenia in future is estimated up to 10%.

2. Solar energy

Energy from the sun is typically more affordable than wind power for individual residences. Currently photo voltaic cells needed for solar power are far too costly to be used for the national electrical grid. Solar energy generation capacity in Armenia is currently around 650 MW, but estimates for future capacity are as high as 3,500 MW.

2.1. SUCCESSFUL EXPERIENCE

Limited practical applications of solar energy have proven cost-effective for American University of Armenia (AUA), however. This university is supplied with hot water and with heating and cooling by a project that its academic engineers from Engineering Research Center (ERC) are working on. At Engineering Research Center in American University of Armenia for years is being researched solar energy and its applications. For nearly a decade, ERC has been engaged in a variety of solar energy-related projects, such as Solar Monitoring Station (SMS) Project, "Design and Installation of a Solar Driven Desiccant Cooling Demonstration System" – (DESODEC) Project and "Solar Photovoltaic Power Station" Project.

SMS project has National significance. The station collects solar radiation data to assist with evaluating and developing solar energy devices. Based on SMS data, engineers have calculated that one square meter of land in Yerevan receives about 1,700 kWh of sun power annually (please see Table 2) [4, 5].

TABLE 2. Sun power on one square meter of land annually in different areas of Armenia

Stations	Sun power (kWh/sq.m)	Stations	Sun power (kWh/sq.m)
Yerevan	1674.2	Martuni	1740.0
Kalinino	1404.0	Jermuk	1682.0
Giumri	1624.0	Qochbeq	1786.4
Sevan	1670.0	Kapan	1647.2

Yerevan is sunny for 300 days each year. Additional solar data collectors are proposed for installation at several locations around the country to further research the applications of solar energy.

AUA is supplied with hot water and with heating and cooling by DESODEC project. The system provides the university with heat in the winter, and cooling in the summer. DESODEC is the first solar driven combined system in the former Soviet Union, and one of a handful in the world. Solar photovoltaic station installed on the roof, provides electricity to the system that makes the university building independent from the electricity grid, and which serves to back-up the university Internet servers.

Conclusions

Armenia has sufficient solar resources for development of solar energy. Particularly in Yerevan one square meter of land receives about 1,700 kWh of sun power annually, which is 70% more that in Europe, where weighable shifts for solar energy applications are going on. Installation of solar energy systems in American University of Armenia in is a successful case of solar energy application in former Soviet Union.

3. Hydrogen energy

Hydrogen could well become the major component of clean sustainable energy systems in the longer term. There are four major tracks in the development of use of hydrogen: production, transport, utilization, and storage. Hydrogen can provide storage options for intermittent renewable technologies such as solar and wind. Storage of hydrogen is an important area for international cooperative research and development, particularly when considering transportation as a major user and the need for efficient energy storage for intermittent renewable power systems. Armenia is in the stage of research in this field and these production technologies are being investigated, which have the potential to produce essentially unlimited quantities of hydrogen in a sustainable manner.

3.1. HYDROGEN FUEL CELLS: FIRST FIRM STEPS

Investigation of hydrogen energy applications in Armenia are being realized mainly by small companies, such as H_2 ECOnomy. Activities of this company mainly are focused on fuel cells. H_2 ECOnomy is a research and development company located in the Ararat valley, Armenia. Its expertise encompasses conductive composite materials, catalyst chemistry, polymer chemistry, electronic design, embedded systems and system integration [6]. Knowledge in these fields has led to the creation of fuel cells for the educational and demonstration markets, sold worldwide through distributors in the USA, Europe, and Asia. H_2 ECOnomy was set up in 2002. It currently employs about 30 experienced scientists. H_2 ECOnomy already manufactures several types of fuel cells and auxiliary products on a small scale, selling their samples to researchers around the world.

Activities of this company are under attention of international community. The US government provided a $500,000 scientific grant to this company for the development of fuel cells, a forward-looking technology to transform hydrogen and oxygen into electricity. The grant is part of the US Energy Department’s ongoing Initiatives for Proliferation Prevention (IPP) program.

The funding is allocated through a major research center of the U.S. Department of Energy (DOE). The two-year US grant is aimed at improving technical parameters and cost-effectiveness. US government funding is not only an opportunity to advance research but also a recognition of companies achievements. Officials from the US National Renewable Energy Laboratory (NREL), the DOE’s Colorado-based research arm also are supporting Armenian initiatives in hydrogen energy investigations.

The technological process of the environmentally friendly power generation is remarkably simple. But there is a catch. Extracting hydrogen from other substances such as hydrocarbons and water is itself a very costly and power-consuming chemical process. On the other hand, pressurized storage of the very light gas requires additional expenses.

Fuel cell experts believe that the search for a more cost-effective technology will intensify in the next few decades as the world gradually runs out of its oil and natural gas deposits. According to several estimations, transition to a hydrogen-based energy system can occur in the 20–40-years time frame if government will make a strong focused effort to bring it about. The problem is that none of the dozens of fuel cell companies around the world, many of them owned by multinational carmakers, is believed to be profitable yet. They still have a long way to go before making the technology, which can power anything.

For H_2 ECOnomy, a more realistic goal now is to become a big research center that would sell fuel cell know-how to foreign manufacturers. The company is already "well positioned" to achieve that. There are a number of markets today where H_2 ECOnomy's fuel cell products can compete with current technologies. These areas include reliable back-up power or UPS systems and remote applications in the telecommunications area. H_2 ECOnomy's latest product is a fuel cell-based UPS extender with a capacity of 1 kilowatt. It can simultaneously power three personal computers.

Conclusions

Hydrogen could become the major component of clean sustainable energy in Armenia. Armenia is in the stage of research in this field. Investigation of hydrogen energy applications in Armenia are being realized by small companies, based on outside financing and methodical support, as these activities could not be economically profitable. Particularly H_2 ECOnomy company worked out fuel cells and is planning to establish research center and to sell fuel cell know-how to foreign manufacturers. Government is not active yet in this field.

4. Concluding remarks

Alternative resources might not be exploitable today, but that it might become a better bargain when, or if, Armenia scraps nuclear power. Over time, hydrogen, wind and solar productions may attract more and more donor support from the government and from others.

In the case of sufficient financial and technical assistance it is quite realistic to develop capacity for generation of 1,595 million kWh hydro, wind, and solar energy annually in coming 10–20 years. This will substitute 518,000 ton of emissions. fossil fuel and, consequently, 802 ton of CO_2 emissions will be avoided (Table 3).

TABLE 3. Indicators of renewable energy utilization

Used energy type	Power production million kWh/year	Fuel substitute 1,000 ton	Prevention of CO_2 emission 1,000 ton
Hydropower	1,275	420.8	690
Wind energy	120	39.6	64.9
Solar energy	200	28.9	47.4
Total	1,595	489.3	802.3

With an appropriate and comprehensive strategy, Armenia has an opportunity to enter the international renewable energy market. In contrast to other established industrial markets, the renewable energy industry has not yet matured worldwide, which could provide an opportunity for Armenia's scientists, its manufacturing industry, and associated businesses.

References

1. Wind Energy Resource Assessment in Armenia, Marjanyan A.H., Caucasus Energy News, vol. 2(3), pp. 4–5, July–August 1995.
2. S. Adamian, L. Manukyan, A. Lalayan, E. Adilkhanyan, 10–20 MW Wind Farm development in Zod region, Armenia. WINDPOWER. Washington DC, 2001.
3. Wind Energy Resource Atlas of Armenia. July 2003, NREL-TP-500-33544.
4. A. Kocharyan, The Main Ways of Renewable Energy Development in Armenia, Renewable Energy in Armenia: Reality and Perspectives, Yerevan 2003.
5. K. Hakobyan, R. Davtyan, Perspectives of Solar Energy Utilization in Armenia Renewable Energy in Armenia: Reality and Perspectives, Yerevan 2003.
6. G. Qaramyan, V. Odabashyan, Fuel Cell Developments in Armenia, Renewable Energy in Armenia: Reality and Perspectives (conference proceedings) pp. 124–128, Yerevan 2003.

THERMODYNAMIC EFFICIENCY ANALYSIS OF A HYDROGEN PRODUCTION SYSTEM FUELED WITH HYDROCARBON FUELS FOR FUEL CELL APPLICATIONS

DR. ATILLA ERSÖZ*
TUBITAK Marmara Research Center
Energy Institute, Gebze Kocaeli, 41470, Turkey
ASSOC. PROF. DR. FEHMI AKGÜN
TUBITAK Marmara Research Center
Energy Institute, Gebze Kocaeli, 41470, Turkey
DR. EVREN GÜNEN
TUBITAK Marmara Research Center
Energy Institute, Gebze Kocaeli, 41470, Turkey

Abstract: In this paper, we discuss the results of a preliminary systematic process simulation study: the effect of operating parameters on the product distribution and conversion efficiency of hydrocarbon fuels in a reforming reactor. The ASPEN One HYSYS-2004 simulation software has been utilized for the simulations and calculations of the fuel-processing reactions. It is desired to produce hydrogen rich reformed gas with as low as possible carbon monoxide (CO) formation, which requires different combinations of reformer, steam to carbon and oxygen to carbon ratios. Fuel properties only slightly affect the general trends.

Keywords: hydrogen production, reformer, efficiency, process simulation, reactor

---

* Corresponding author: TUBITAK Marmara Research Center, Energy Institute, 41470, Gebze Kocaeli, Turkey. Phone: +90 262 6772707. Fax: +90 262 6412309. e-mail: Atilla.Ersoz@mam.gov.tr

J.W. Sheffield and Ç. Sheffield (eds.), Assessment of Hydrogen Energy for Sustainable Development, 225–241.

1.

PEM fuel cell systems are being developed for supplying primary power (heat and electricity) for residential applications. Residential fuel cell systems can be operated to provide primary or backup power for the home. They can run independently or in parallel to an existing power grid. There are several companies currently working on residential fuel cells. Several demonstration units are being tested by the fuel cell companies around the countries in cooperation with local governments and/or utilities. The precommercial units are expected to enter into the market in the 2005–2010 time frame. Many fuel cell manufacturers are considering the use of natural gas as a hydrogen-carrier fuel for rural and remote residential fuel cell applications.

Fuel cells combine hydrogen and oxygen without combustion to produce electricity. Water and heat are the only by-products of this reaction. The process combines oxygen from the air and hydrogen extracted from any one of a number of suitable hydrogen containing fuels. The result is DC electrical power produced with greater efficiency than most of the other conventional power generation methods, such as internal combustion engine generators. The net electric efficiency of low temperature fuel cell systems is approximately 35–45%. Proton exchange membrane (PEM) fuel cells generate electrical power from hydrogen or a hydrogen rich gas and air via electrochemical reactions (Ersoz et al., 2003; FC handbook, 2000; Doss et al., 2001; Moon et al., 2001; Pereira et al., 1999; Docter and Lamm, 1999). There is continuous interest in converting current hydrocarbon fuels such as natural gas, propane, gasoline, and diesel into hydrogen rich gases acceptable by PEM fuel cells (FC handbook, 2000; Doss et al., 2001; Moon et al., 2001; Megede, 2002; Pereira and Bae, 2000; Bernaya et al., 2002; Pettersson, 2001).

Fuel reforming systems can extract hydrogen from a variety of conventional fuel sources for the residential micro cogeneration application with fuel cell. Existing infrastructures such as natural gas pipelines and propane distribution systems can be used for these systems. Hydrogen rich gases can be produced via various fuel-processing technologies. Steam reforming, partial oxidation, and autothermal reforming (ATR) are the three major fuel-processing technologies (Pereira et al., 1999; Docter and Lamm, 1999; Megede, 2002; Pereira and Bae, 2000).

The use of chemical flow sheeting software has become an integral part of the evaluation of the performance of fuel cell systems (Petterson, 2001; Kivisaari et al., 2001). In this study, the Aspen-HYSYS 3.2 simulation software has been used to evaluate several fuel-reforming technologies for residential fuel cell micro cogeneration systems. This paper presents the results of a study for a 5 kW_e DC electrical power residential PEM fuel cell system utilizing several reforming technologies fed by natural gas fuel.

2. Methodology

The process simulation code "Aspen-HYSYS 3.2" has been used for residential PEM fuel cell system calculations. Natural gas has been simulated as three different sources for hydrogen production. The chemical compositions of the natural gas fuel are summarized in Table 1. The average molecular weight of natural gas is around 16.6 kg/kmol. All simulation studies are performed based on this composition.

TABLE 1. Natural gas composition

Component	Mass fractions (w%)	Molar fractions (mol%)
Methane	0.9693	0.9375
Ethane	0.0227	0.0412
Propane	0.0080	0.0212
Total	100	100

The simulated residential PEM fuel cell system consists of the following sections and their components:

- Fuel processing and cleanup section
- PEM fuel cell section
- Auxiliary units

The overall residential fuel cell micro cogeneration system can be seen in Figure 1. The fuel processing is one of the sections of this whole system.

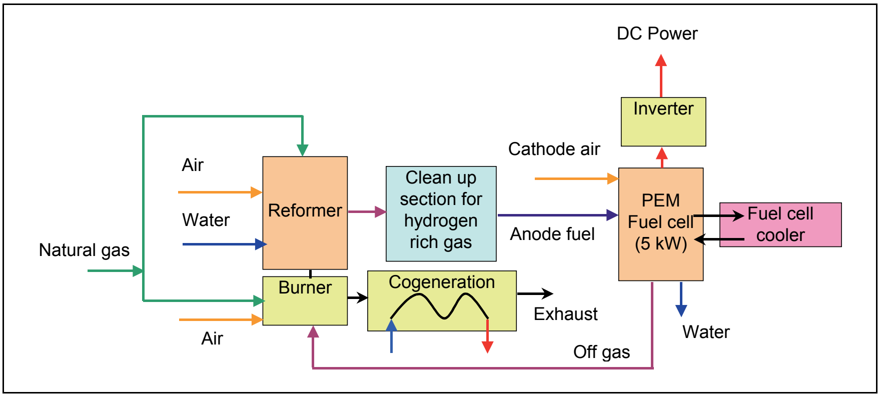


Figure 1. Schematic diagram of a residential fuel cell micro cogeneration system

Several fuel-processing steps such as reforming and clean up are figure out in Figure 2. The reforming section can contain the reforming reactors such as an autothermal reformer (ATR), a steam reformer (SREF), and a partial oxidation (POX) reactor. High and low temperature shift reactors (HTS and LTS) and the preferential oxidation (PROX) or a methanation reactor are the other units of the cleanup sections. PEM fuel cell and auxiliary units are the other sections of the whole CHP system. Auxiliary units comprise pumps, compressor, expander, heat exchangers, heaters coolers, and combustor. Also there are several unit controllers such as temperature, pressure, voltage, electric loads etc. within the system.

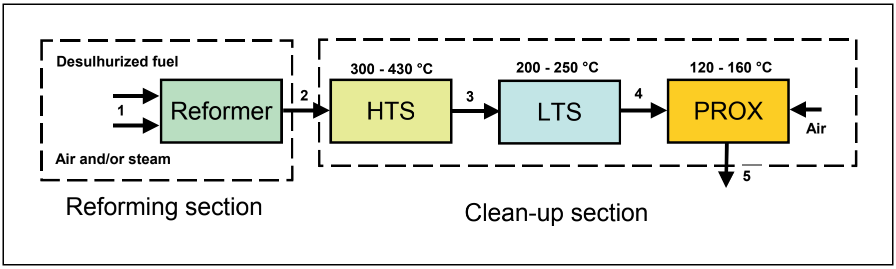


Figure 2. Schematic diagram of the fuel-reforming and cleanup sections

The aim of this study is to convert as much as the hydrogen in the fuel into hydrogen gas while decreasing CO and CH_4 formation. Process parameters of fuel preparation steps have been determined considering the limitations set by the catalysts and hydrocarbons involved. Lower S/C (steam to carbon) ratios favor soot and coke formation, which is not desired in catalytic steam and autothermal reforming processes. A considerably wide S/C ratio range has been selected to see the effect on hydrogen yield and CO formation.

The mole fractions of air have been simulated as 0.21 and 0.79 for O_2 and N_2 respectively. The two parameters, S/C, O/C (oxygen to carbon) ratios have been used to analyze the reforming reactors effectively. These two relationships can be written as follows:

$$O/C = 0.5 * (F_{O2} / F_{CH4})$$
$$S/C = F_{H2O\,(v)} / F_{CH4}$$

The catalytic properties limit applicable operational parameter ranges such as S/C, O/C, and operation temperatures and pressures. The durability of the reformer is governed by the thermal durability of the reforming catalysts by coke formation. In reality, a certain catalyst for a reforming system might be able to be used at higher temperatures, but most comercially available catalysts have been operated at less than 800°C to secure their thermal durability. Therefore, it is necessary to determine favorable operating conditions for each of the reforming reactors (Seo et al., 2002).

The thermodynamic equilibrium system calculations are based on minimizing the Gibbs free energy. The equilibrium temperature and outlet compositions of each reactor have been calculated with simulation studies. For all cases, reactor simulation calculations have been performed under adiabatic conditions keeping "$T_{reactor}$" almost constant taking reaction heats into account. Within this frame selected S/C and/or O/C ratio(s) are studied parametrically to achieve finally acceptable hydrogen production yield along with low CO formation. The ranges of operating conditions investigated in the simulation studies are given in Table 2.

TABLE 2. The investigated ranges of reformer operating conditions

Reforming reactor	Temperature (°C)	Pressure (bar)	S/C	O/C
SREF	700–850	3	2.0–3.5	–
ATR	400–800	3	0.3–3	0.35–0.6
POX	800–1,100	3	–	0.25–2.0

PEM fuel cell system has been simulated in the study for all reforming process options. PEM fuel cell system and the auxiliary units consist of the following components:

- PEM fuel cell section
- Fuel cell stack
- DC/AC converter

Some of the selected PEM fuel cell characteristics are presented in Table 3.

TABLE 3. The PEM fuel cell characteristics (e: Electron)

Anode reaction	$H_2 \rightarrow 2H^+ + 2e^-$
Cathode reaction	$\frac{1}{2} O_2 + 2H^+ + 2e^- \rightarrow H_2O$
Fuel utilization (%)	80
Fuel cell outlet temperature (°C)	80
Pressure (bar)	3
Average cell voltage (V)	0.722
Active area (m^2)	0.04
Stack cooling media	Water

Table 4 summarizes the data of different auxiliary system components utilized in the simulation studies while Table 5 presents the efficiency correlations used in the simulations for various components and subsystems.

TABLE 4. Auxiliary system component data

Component	Parameter	Value
Water pump	Adiabatic efficiency (%)	75
Cooling water pump	Adiabatic efficiency (%)	75
Compressor	Adiabatic efficiency (%)	75
Heat exchangers	Minimum temperature approach (°C)	25
Combustor	Outlet temperature (°C)	720
Chimney	Outlet temperature (°C)	90
DC/AC Converter	Conversion efficiency (%)	98

TABLE 5. Efficiency correlations used in the simulations

m i (kg/h)	$\eta_{stack\ voltage} = V_{cell} * 0.8$
$\eta_1 = (m_{103}*LHV_{103})/(m_F*LHV_F)$	$V_{cell} = f(I_{current})$
$\eta_{pre\text{-}SREF} = (m_{401}*LHV_{401})/(m_{400}*LHV_{400})$	$I_{current} = I_{calculated} / A_{active}$
$\eta_{SREF} = (m_{404}*LHV_{404})/(m_{402}*LHV_{402})$	A_{active} = Cell active area (m^2)
$\eta_{HTS} = (m_{406}*LHV_{406})/(m_{404}*LHV_{404})$	$I_{calculated} = H_{2\ consumed} *2/(1.04*10^{-8} * n_{cell} * 3600)$
$\eta_{LTS} = (m_{408}*LHV_{408})/(m_{406}*LHV_{406})$	$\eta_8 = \eta_6 * \eta_7 * \eta_{auxiliary} * \eta_{DC/AC}$
$\eta_{PROX} = (m_{410}*LHV_{410})/(m_{408}*LHV_{408})$	$P_{parasitic} = (P_{P1} + P_{P2} + P_{P3} + P_C) / \eta_{motor}$
$\eta_2 = \eta_1 * \eta_{pre\text{-}SREF}$	$\eta_{auxiliary} = 1 + (P_E - P_{parasitic}) / P_{PEM\ AC}$
$\eta_3 = \eta_2 * \eta_{SREF}$	$\eta_{motor} = 0.90$
$\eta_4 = \eta_3 * \eta_{HTS}$	$\eta_{DC/AC} = 0.98$
$\eta_5 = \eta_4 * \eta_{LTS}$	$P_{PEM\ DC} = 100$ kW
$\eta_6 = \eta_5 * \eta_{PROX}$	$P_{PEM\ AC} = P_{PEM\ DC} * \eta_{DC/AC}$
$\eta_7 = \eta_{stack\ voltage} * 0.8$	$U_{H2} = 0.80$

Fuel processing (η_{FP}), PEM fuel cell (η_{FC}), and overall system efficiencies ($\eta_{net.el}$) are calculated as follows:

$$\eta_{FP} = \eta_6$$

$$\eta_{FC} = (U_{H2}) \times (\eta_{stack\ voltage}) \times (\eta_{DC/AC})$$

$$\eta_{net.el} = \eta_8 = \eta_{FP} \times \eta_{FC} \times \eta_{aux.}$$

3. Results and discussion

3.1. REACTOR EQUILIBRIUM CALCULATION AND RESULTS

Fuel processing and overall system efficiencies of natural gas for the investigated fuel-reforming options are presented in Table 6. The simulation results

(Table 6) indicate that the fuel-processing efficiencies decrease in the order of steam reforming > autothermal reforming > partial oxidation for both gasoline and diesel fuels.

The promising and efficient reforming options are the steam reforming and autothermal reforming processes, as can be seen in Table 6. We can compare these two efficient systems in order to observe the equilibrium behavior in the reforming section of the whole micro CHP system. Here, the results of the most efficient options, namely natural gas with steam reforming and autothermal reforming.

TABLE 6. Fuel processing and overall system efficiencies of natural gas fuel

Parameter	Natural gas		
	SREF	ATR	POX
P (bar)	3	3	3
T (°C)	750	750	750
η_{FP}	98	93	76
$\eta_{net.el}$	48	42	31

3.1.1. Steam reforming process

Steam reforming appears as the most promising fuel-reforming option based on fuel processing efficiencies (Ersoz et al., 2003; FC Handbook, 2000; 1, 2).

Natural gas shows higher fuel-processing efficiencies then the liquid fuels, hence, also higher overall system efficiencies. The highest fuel-processing efficiency is achieved for the steam reforming of natural gas, namely 98%. The same option gives a maximum net electrical efficiency at 48%. Hence, the natural gas with steam reforming is about 14% more efficient than its liquid fuel counterparts based on steam reforming (Tables 7 and 8).

TABLE 7. Fuel processor and overall fuel-processing efficiency for natural gas

Efficiency	NG-SREF
η_{FP}	98
$\eta_{net.el}$	48

The major units of the Aspen-HYSYS simulation for natural gas steam reforming based fuel cell system are presented in Figure 3.

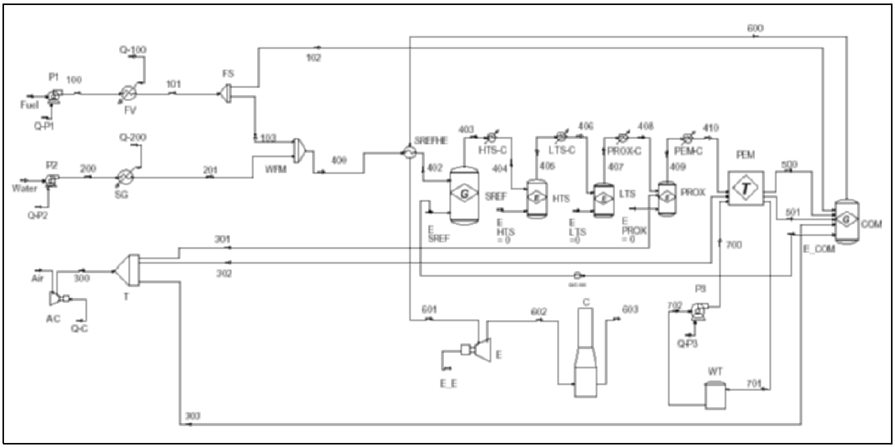


Figure 3. Major fuel cell system units of the Aspen-HYSYS simulation for natural gas with steam reforming

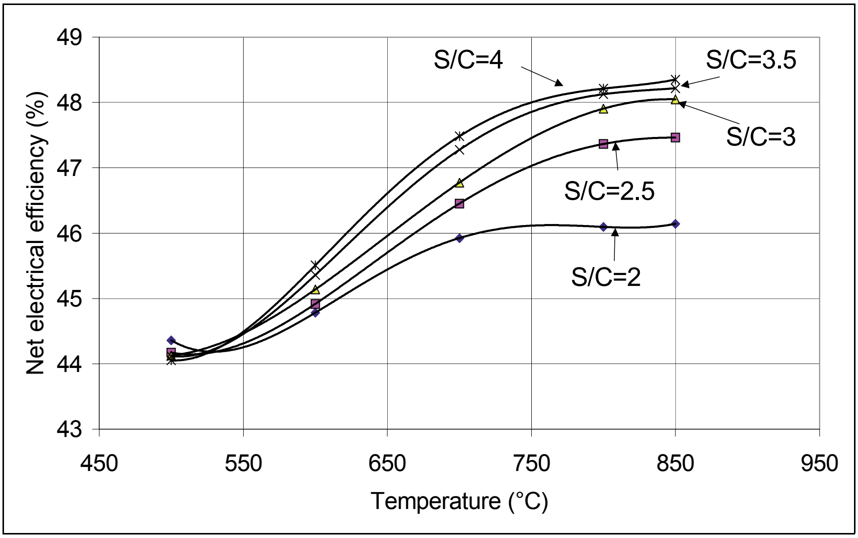


Figure 4. Effect of the S/C ratio on overall system efficiency

The operation parameters of the SREF are of utmost importance to achieve the desired high hydrogen and low CO content product gases along with acceptable fuel conversion efficiency levels. The steam to carbon ratio range studied is between 2 and 4 while the operating temperature has been changed between 500°C and 850°C (Figures 4 and 5). The S/C ratio at 3.5 appears to fulfill the requirements for temperatures around 800°C. A decrease of the S/C ratio decreases both the efficiency as well as the quality of the product gases. The operation parameters of the SREF are selected as

800°C and S/C = 3.5. The product compositions for all the other fuel-processing reactors following the steam reformer are presented in Figure 6.

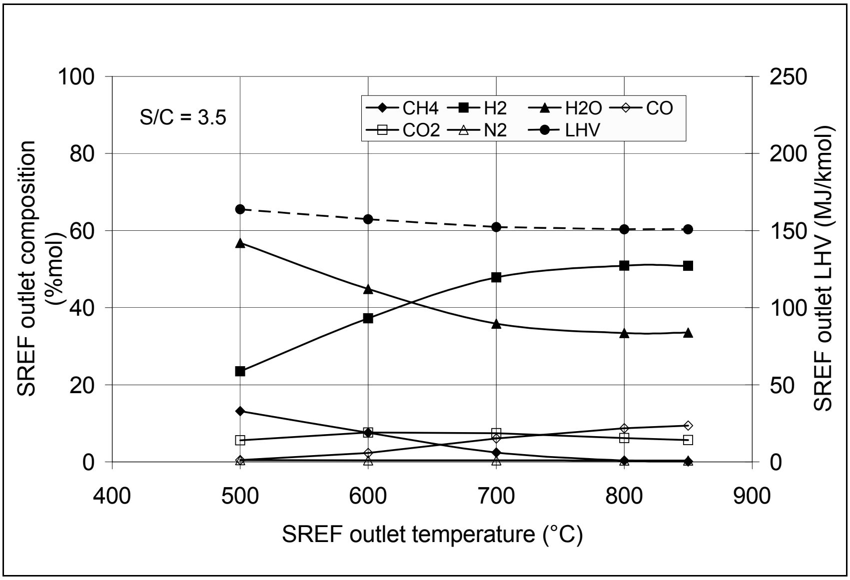


Figure 5. The molar compositions and LHV values of the steam reformer products

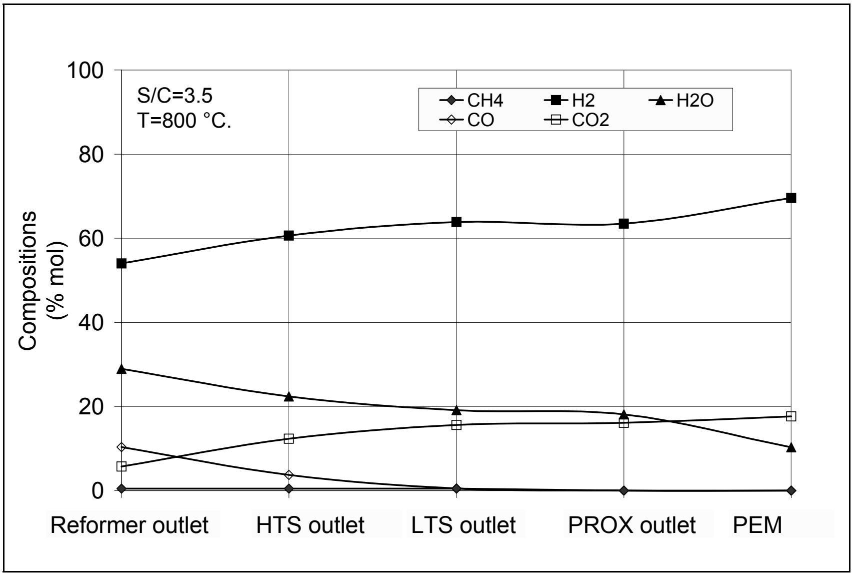


Figure 6. Product compositions of fuel preparation reactors

The SREF based fuel-processing, fuel cell, auxiliary, and overall system efficiencies of the investigated fuels are presented in Table 8. The values indicate that natural gas is the best option while there are only minor differences regarding the investigated liquid fuels. The slight differences observed between gasoline and diesel options are primarily due to the better heat integration of the latter.

TABLE 8. SREF-based fuel-processing, fuel cell, auxiliary, and overall system efficiencies

Fuel	η_{FP}	η_{FC}	$\eta_{Aux.}$	$\eta_{net.el.}$
Natural Gas	98.1	50.6	97.0	48.2
Gasoline	85.5	50.6	95.1	41.1
Diesel	86.3	50.6	97.1	42.4

3.1.2. Autothermal reforming process

Autothermal reforming reactor (ATR) is maintained under adiabatic conditions. There is no heat transfer from or to the reactor section during the reaction. The effect of S/C and O/C ratios on the net electric efficiency of the system with fuel cell has been calculated. The results are illustrated for different inlet temperatures (700° and 400°C) in Figures 7 and 8. A decrease of the S/C ratio decreases the efficiency. On the other hand, an

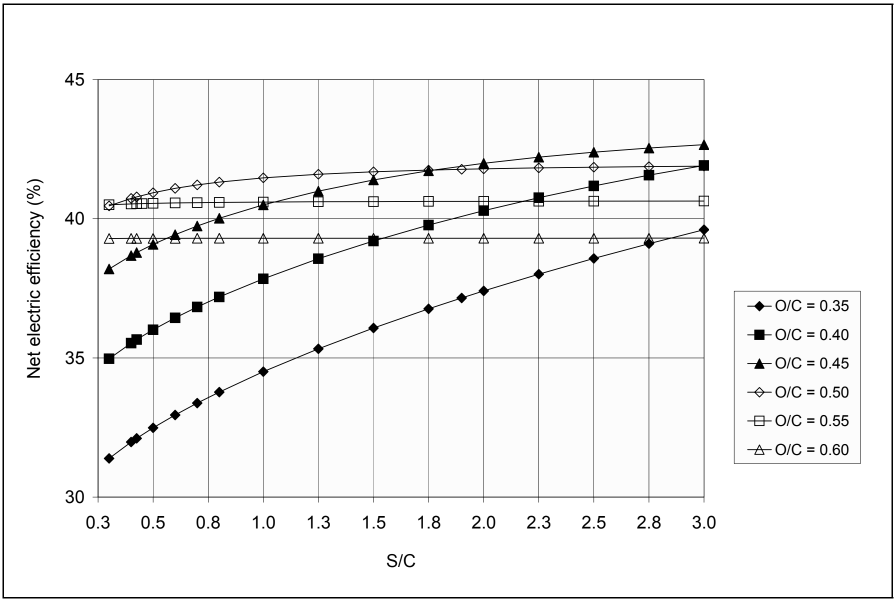


Figure 7. S/C effect on the net electric efficiency with different O/C (T_{ATR} inlet = 700°C)

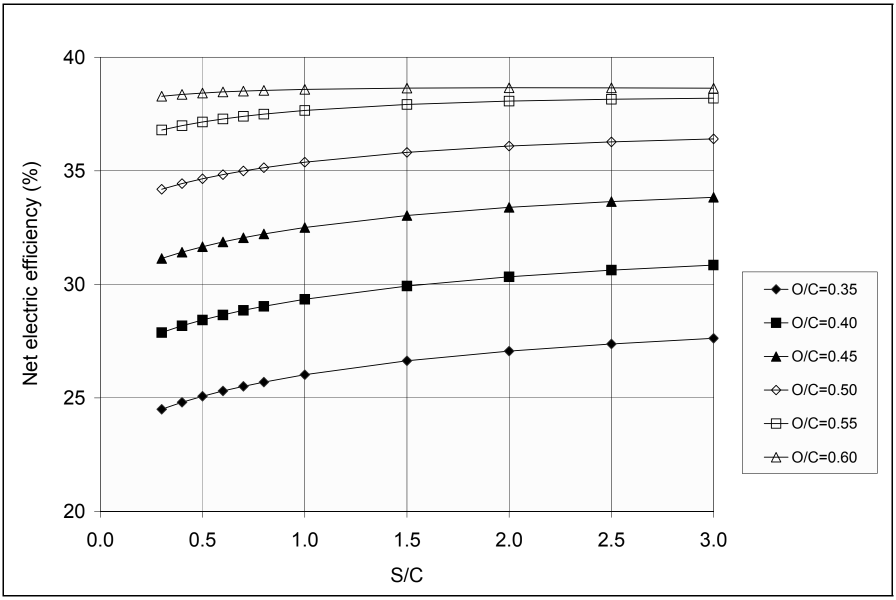


Figure 8. S/C effect on the net electric efficiency with different O/C (T_{ATR} inlet = 400°C)

increase of the O/C ratio increases the efficiency in general. The operating parameters of the ATR reactor are selected as the inlet temperature of 800°C, S/C = 1.5, and O/C = 0.45 within the optimum efficiency range.

The evaluation of the effect for different S/C and O/C ratios on the temperature difference between the reactor inlet and the outlet has been shown in Figures 9 and 10. The O/C ratio significantly affects the delta T as seen in related figures. The S/C ratio also affects the temperature difference. A decrease of the S/C increases the difference between inlet and outlet reactor temperatures. Higher S/C means lower delta T. The most promising inlet reactor temperature is selected as 700°C according to the catalysts thermal durability limitations. The value of the delta T is between 50°C and 100°C with selected O/C = 0.45. The optimum operating value is calculated as around 60°C (outlet temperature is around 760°C) for S/C = 1.5 and O/C = 0.45.

The outlet concentrations and the net electrical efficiency of the system have been similarly observed for the different reactor inlet temperatures for the selected operating parameters (S/C = 1.5 and O/C = 0.45) (Figures 11 and 12). The net electric efficiency value is around 41% for the selected inlet temperature (700°C). The outlet molar flow of hydrogen and CO are 0.12 and 0.034 kmol/h respectively. The mole fraction of hydrogen decreases after O/C = 0.45 as seen in Figure 12. The mole fraction of CO increases with increasing O/C ratios at selected S/C ratio of 1.5. Methane, carbon dioxide, and water concentrations are also decreasing with increasing O/C ratios.

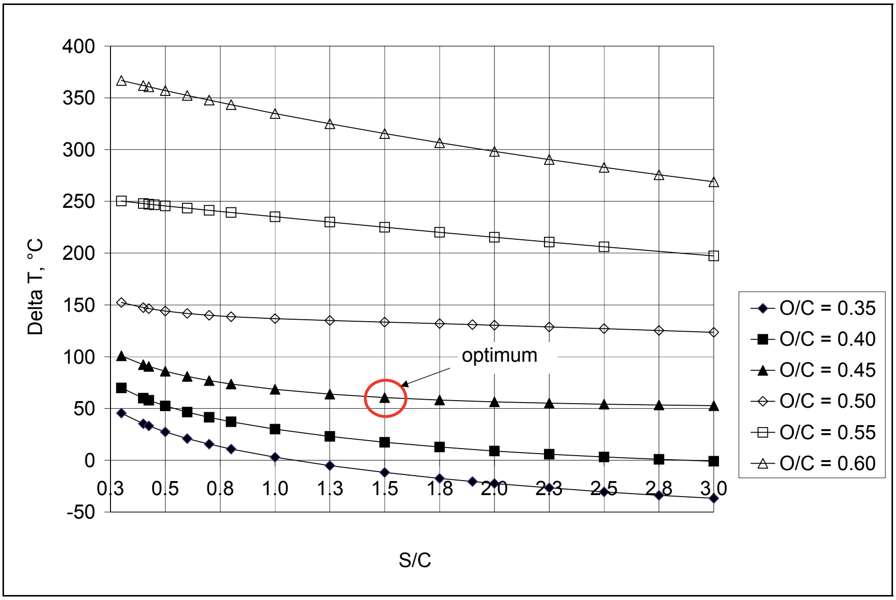


Figure 9. S/C effect on Delta T ($T_{ATR\ out}-T_{ATR\ in}$) with different O/C (T_{ATR} inlet = 700°C)

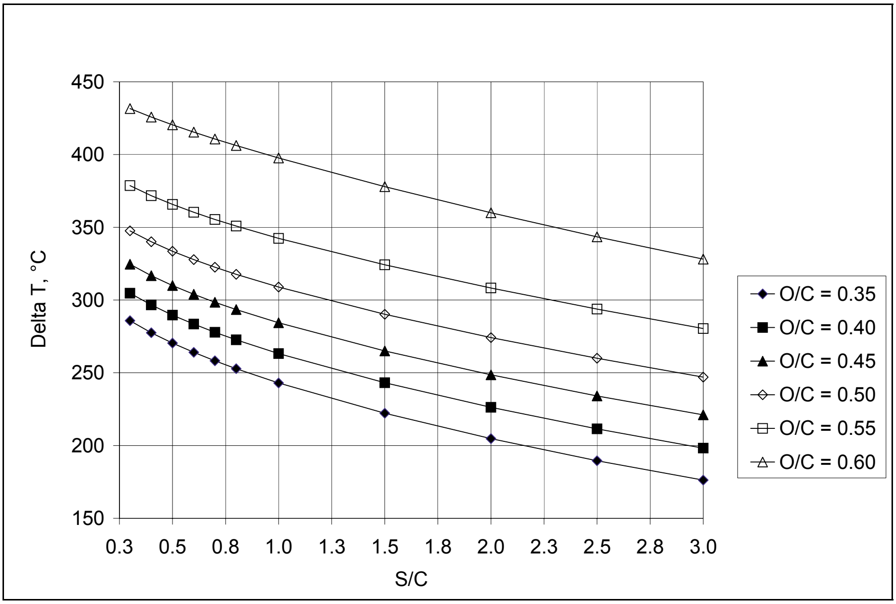


Figure 10. S/C effect on Delta T ($T_{ATR\ out}-T_{ATR\ in}$) with different O/C (T_{ATR} inlet = 400°C)

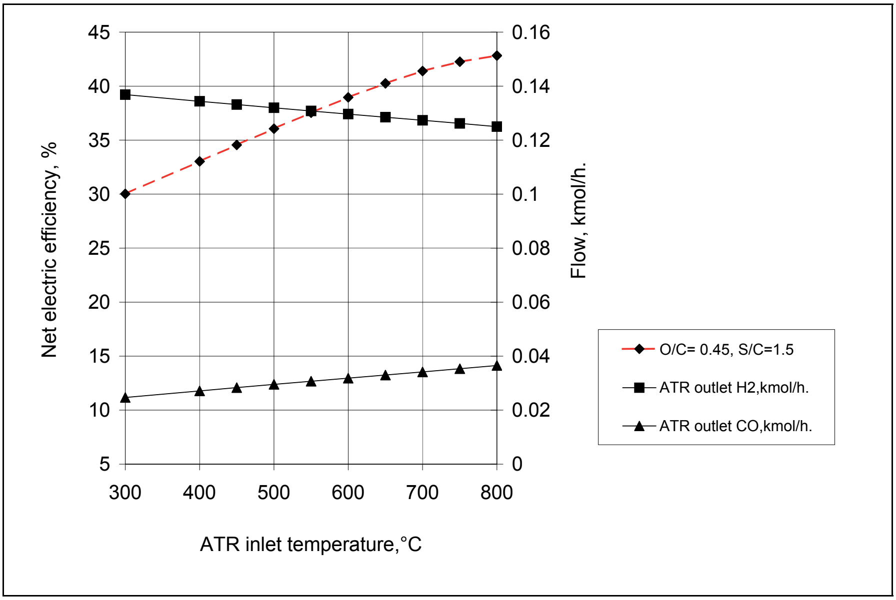


Figure 11. ATR inlet temperature effect on the net electric efficiency with selected O/C and S/C

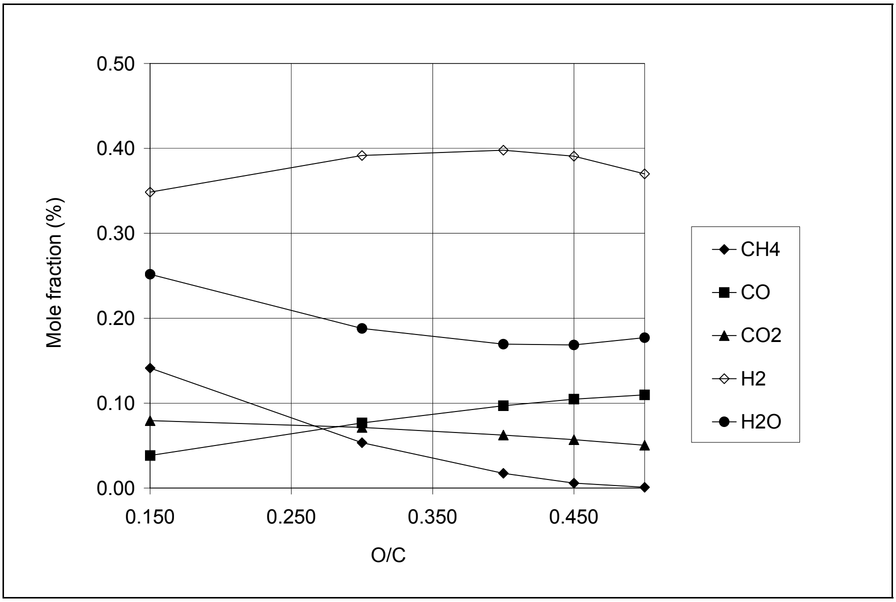


Figure 12. O/C versus Comp. mol fractions at S/C = 1.5 (T_{ATR} inlet = 700°C)

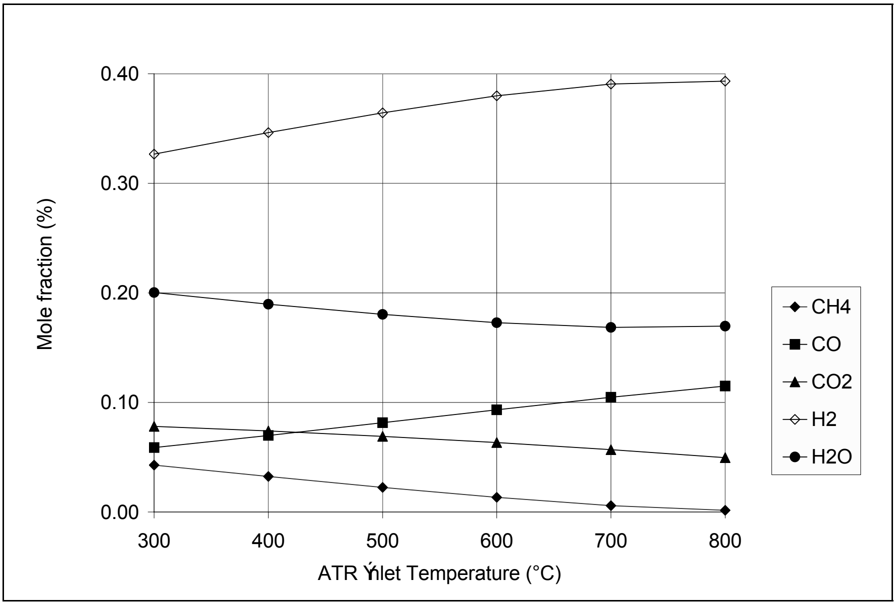


Figure 13. Effect of ATR inlet temperature on ATR outlet compositions at S/C = 1.5, O/C = 0.45

The effect of ATR inlet temperature on the outlet reactor compositions for the selected operating conditions (S/C = 1.5, O/C = 0.45) is given in Figure 13. The maximum hydrogen yield can be observed with the selected inlet reactor temperature of 700°C. The value is hydrogen mole fraction is 0.39 for this operating condition.

4. Concluding remarks

The thermodynamic characteristics of the several reforming options: steam reforming, autothermal reforming, and partial oxidation. All these reforming process options have been investigated with appropriate simulation conditions for 5 kW PEM fuel cell power. The most promising operating conditions have been selected for each process. The material and energy balance calculations have also been performed by using ASPEN-HYSYS simulation code.

Natural gas appears as the best fuel for hydrogen rich gas production due to its favorable composition from lower molecular weight compounds. Steam reforming and autothermal reforming appear as the most competitive fuel-processing options in terms of fuel-processing efficiencies. POX shows the lowest fuel-processing efficiency level. Among the options studied the highest fuel-processing efficiency is achieved with natural gas steam reforming at about 98%.

Several operating conditions have been found which satisfy the requirements for no coke formation. The optimum S/C ratio at 3.5 appears to fulfill the requirements for temperatures around 800°C for steam reforming process. The optimum O/C and S/C ratios are found 0.45 and 1.5 respectively for ATR reactor simulations at the inlet temperature of 700°C.

High system efficiency levels can be achieved only with intensive heat integration within the fuel cell micro CHP systems. Hence, heat integration system studies are of utmost importance along with the development of novel reforming catalysts, cleanup systems, and PEM fuel cell components if on-site hydrogen production is desired for micro CHP applications.

5. Nomenclature

AC	Air compressor
SREF-HE	SREF heat exchanger
ATR	Autothermal reformer
C	Chimney
COM	Combustor
E	Expander
E-i	Energy of unit i
F_{O2}	Oxygen flow rate, kmol/h
$F_{H2O\ (v)}$	Steam flow rate, kmol/h
F_{CH4}	Natural gas flow rate, kmol/h
FC	Fuel cell
FS	Fuel splitter
FV	Fuel vaporizer
HTS	High temperature shift reactor
HTS-C	HTS cooler
LHV	Lower heating value (MJ/kmol)
LTS	Low temperature shift reactor
LTS-C	LTS cooler
m i	Mass flow rate (kg/h)
P	Power [W or kW]
PC	Power (Compressor), kW

PE	Power (Expander), kW
PEMFC	Polymer electrolyte membrane FC
PEM-C	PEM FC cooler
PEMAC	AC Power (PEM Fuel cell), kW
POX	Partial oxidation reactor
PROX	Preferential oxidation reactor
PROX-C	PROX cooler
P1	Fuel pump
P2	Water pump
P3	Cooling water pump
SG	Steam generator
SREF	Steam reformer
T	Splitter or temperature [C]
V	Voltage [V]
WFM	Water fuel mixer
WT	Water tank
1	SREF inlet
2	SREF exit
3	HTS exit
4	LTS exit
5	PROX exit
η	Efficiency

References

Anonymous. Fuel Cell Handbook (Fifth Edition), By EG&G Services Parsons, Inc. Science Applications International Corporation, U.S. Department of Energy. Office of Fossil Energy National Energy Technology Laboratory. October (2000).

Bernaya, C.; Marchanda, M.; Cassir, M. Prospects of different fuel cell technologies for vehicle applications. Journal of Power Sources, **108**, (2002), 139–152.

Danial Doss, E.; Kumar, R.; Ahluwalia, R. K.; Krumpelt, M. Fuel processor for automotive fuel cell system: a parametric analysis. Journal of Power Sources **102**, (2001), 1–15.

Docter, A.; Lamm, A. Gasoline fuel cell systems. Journal of Power Sources, **84**, (1999), 194–200.

Dong Ju Moon; Sreekumar, K.; Lee, S. D.; Gwon, B.; Kim, H. S. Studies on gasoline fuel processor for fuel cell powered vehicle application. Applied Catalyst, **215**, (2001), 1–9.

Ersoz, A.; Olgun, H.; Ozdogan, S.; Gungor, C.; Akgun, F.; Tiris, M. Autothermal reforming as a hydrocarbon fuel processing option for PEM fuel cell. Journal of Power Sources, **118**, (2003), (1–2), 384–392.

Kivisaari, T.; Van der Laag, P. C.; Ramsköld, A. Benchmarking of chemical flow sheeting software in fuel cell application, Journal of Power Sources, **94**, (2001), 112–121.

Megede D. zur. Fuel processors for fuel cell vehicles. Journal of Power Sources, **106**, (2002), 35–41.

Pereira, C.; Wilkenhoener, R.; Ahmed, S.; Krumpelt, M. Liquid Fuel Reformer Development. Electrochemical Technology Program Chemical Technology Division, Argonne National Laboratory, Illinois, USA, July 2, (1999).

Pereira, C.; Bae, J-M.; Ahmed, S.; Krumpelt, M. Liquid Fuel Reformer Development: Autothermal Reforming of Diesel Fuel. Electrochemical Technology Program Chemical Technology Division Argonne National Laboratory U.S. Department of Energy, (2000) Hydrogen Program Technical Review San Ramon, California, USA.

Pettersson, L. J.; Westerholm, R. State of the art of multi-fuel reformers for fuel cell vehicles: problem identification and research needs. International Journal of Hydrogen Energy, **26**, (2001), 243–264.

Seo, Y. S.; Shirley, A.; Kolaczkowski, S. T. Evaluation of thermodynamically favourable operating conditions for production of hydrogen in three different reforming technologies. Journal of Power Sources, **108**, (2002), 213–225.

DEVELOPMENT OF ECOLOGICALLY FRIENDLY TECHNOLOGY FOR GASIFICATION OF MUNICIPAL SOLID WASTES

MAXIM SLENKIN*
Institute of Engineering Thermophysics of NASU, 2a,
Zheliabova St., Kiev, 03057, Ukraine
GEORGIY GELETUKHA
Institute of Engineering Thermophysics of NASU, 2a,
Zheliabova St, Kiev, 03057, Ukraine

Abstract: Ukraine as well as other countries all over the world has a problem of municipal solid waste utilization. One of the most popular technologies is combustion of MSW. However, MSW combustion cannot provide permissible level of harmful matters emission without very difficult and expensive gas cleaning systems. Especially it applies to polychlorinated dibenzo-(p)-dioxins and furans – global superecotoxicants, which have strong mutagenic, immunosuppressive, carcinogenic, teratogenic, and embryotoxic activity. Dioxins are always generated with presence of oxygen, chlorine, and organic compounds at high temperature (above 300°C). In the waste chlorine is mainly present in such compounds as kitchen salt and polyvinyl chloride. Existing technologies of MSW combustion do not decrease dioxin emissions with 100% effectiveness. The most powerful method of dioxin formation suppression is based on deactivating potential of its formation precursors, such as: chlorine, oxygen, and catalysts. One of possible technological approaches is gasification of chlorine-containing fuels or wastes: absence of oxygen effectively blocks dioxin formation routes. Product gas cleaning from ashes and halogens eliminates dioxin reformation after combustion. In the Institute of Technical Thermophysics the experimental fluidized bed installation for chlorine containing waste gasification is under development.

Keywords: gasification, MSW, gasifier, producer gas, dioxins

---

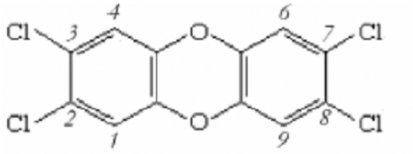
* To whom correspondence should be addressed. Maxim Slenkin, Institute of Engineering Thermophysics of NASU, 2a, Zheliabova str., Kiev, 03057, Ukraine; e-mail: maxst@biomass.kiev.ua

J.W. Sheffield and Ç. Sheffield (eds.), Assessment of Hydrogen Energy for Sustainable Development, 243–247.

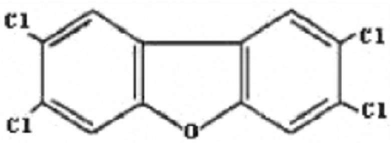
1. Dioxins and furans

Dioxins – global superecotoxicants, which have strong mutagenic, immunosuppressive, carcinogenic, teratogenic, and embryotoxic activity.

- They are crystal substances with high melting temperature (200–400°C).
- They are easily solved in organic solvents, fats, not in distilled water.
- They have strong adhesion properties.
- The period of degradation in soil is 10–20 years, in water up to two years.
- They have high thermal resistance. Thermal degradation under temperature less than 1,250°C is reversible.



Dioxin
2,3,7,8 tetrachloro dibenzo - p- dioxin



Furan
2,3,7,8 tetrachloro dibenzo - p- furan

The causes of decreasing of dioxins and furans emission by gasification process:

In case of combustion dioxins are always generated with presence of oxygen, chlorine, and organic compounds at high temperature (above 300°C).

Decon reaction is one of the main stages in the process of dioxins generation:

$$2HCl+1/2O_2 \Leftrightarrow Cl_2 + H_2O$$

Reaction goes with presence of Cu, Pb, Sn catalysts, and Cl_2 formation.

$$Cl_2+O_2+C_xH_y + \text{time and } 250\text{–}350°C = \text{DIOXINS/FURANS}$$

The main idea of dioxin formation suppression is based on deactivating potential of its formation precursors, such as: Cl_2, O_2, or catalysts.

Gasification of chlorine-containing fuels or wastes in reduction atmosphere leads to forming HCl. Product gas cleaning from ashes and HCl eliminates dioxin reformation after combustion.

2. Gasification unit with two fluid bed reactors

The basic idea of the gasifier concept is to divide the fluidized bed into two zones: a gasification zone and a combustion zone. Between these two zones a circulation loop of bed material is created but the gases should remain separated. The circulating bed material acts as heat carrier from the combustion to the gasification zone. The principle is shown graphically in Figure 1.

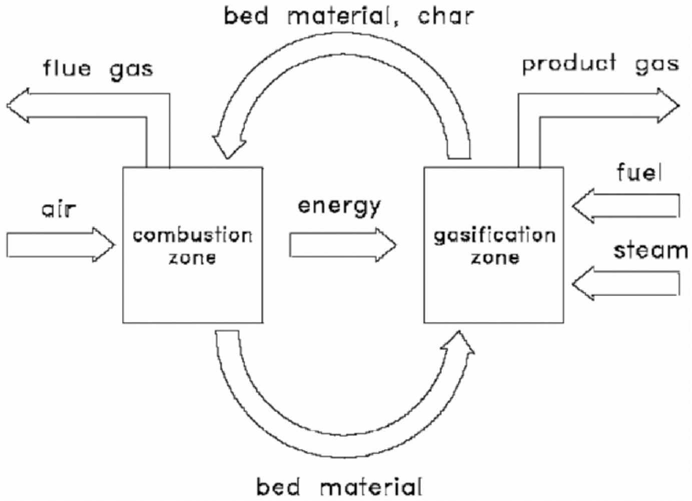


Figure 1. The principle of the gasifier concept

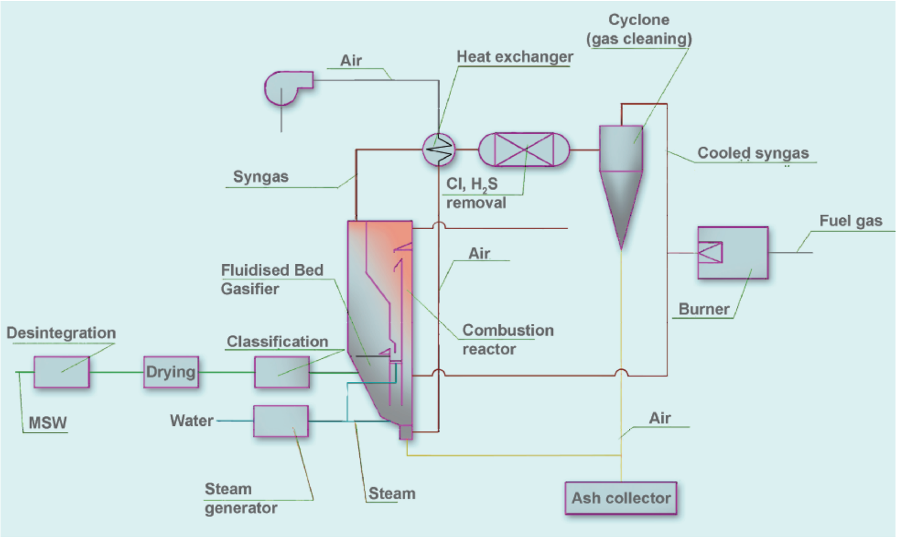


Figure 2. General flowchart of two fluid bed gasification unit

3. General description of the unit

Municipal solid wastes (MSW) gasification unit which is under development in the project consists of two fluid bed reactors (Figure 2). The first reactor is a gasifier, the second reactor is a combustion chamber for charcoal. To obtain producer gas of middle calorific value water steam is applied as a blowing. Fluid bed is organized by supplying water steam to gasifier (inert material is sand) and air to combustion chamber. The installation is equipped with all necessary devices to measure rate, temperature, and pressure.

4. Features of the experimental unit

Heat capacity	50 kW	
Gasifier chamber:		
height	1,500 mm	
diameter	300 mm	
Combustion chamber:		
height	3,800 mm	
diameter	70 mm	
Work temperature:		
камера газификации	800°C	
камера сжигания	900°C	
Bed material	Silica sand	
Bed weight	20 kg	
Mean diameter of bed solid particles	0.3–0.7 mm	
Fuel	biomass, model fuel, separated MSW	
Fuel input	19 kg/h	
Air input in combustion chamber	35 m^3/h	
Steam input in gasification chamber	12 kg/h	
Expected product gas composition:	Dry	Wet
H_2	37.7%	25.7%
CO	29.1%	19.8%
CO_2	25.3%	17.2%
CH_4	6.9%	4.7%
Cl	1%	0.8%
H_2O		31.8%

5. Information about project

Authors: Institute of Engineering Thermophysics, SEC “Biomass”.
Patent: under preparation.
Present status: detail design is developed.
Support of Science and Technology Centre in Ukraine (Project Agreement N 3036, $118,830).
October 2004–September 2006
Collaborators: Pacific Northwest National Laboratory (USA); Biomass Technology Group BV (The Netherlands).
Field of application: utilization of MSW in urban and rural areas.
Further steps: manufacture of production prototype; scaling-up.

PROSPECTS FOR SUSTAINABLE DEVELOPMENT OF UKRAINIAN ENERGY SECTOR

OLEG UDOVYK*
National Institute for Strategic Studies
Kyiv, Ukraine
OKSANA UDOVYK
2Ukrainian Nongovernmental Environmental Organization
"MAMA-86", Kyiv, Ukraine

Abstract: This paper describes the estimation of prospects for sustainable development of Ukrainian energy sector. It is being built upon the report of the INFORSE and incorporates results from more resent our research. For the analysis we used existing prognoses for the development of Ukraine's economy and data from the Energy strategy of Ukraine for the period till 2030. The second part of the paper highlights Ukrainian's legislation in energy field.

Keywords: renewable energy, legislation, Ukraine

1. Introduction

To estimate possibility for the transition to sustainable development in energy field, the international network for sustainable energy (INFORSE) worked out scenarios for the development of energy sector in different countries – "Vision 2050". The scenarios are based on prognosed data of the world development.

Predicting further development of economy and energetic on the basis of modern and the most effective technologies, experts came to a conclusion

---

* To whom correspondence should be addressed. Oleg Udovyk, National Institute for Strategic Studies, Kiev, Ukraine; e-mail: oleg_udovyk@hotmail.com

J.W. Sheffield and Ç. Sheffield (eds.), Assessment of Hydrogen Energy for Sustainable Development, 249–256.

about possibility to replace nuclear and fossil fuel (totally or partly depending on a region) by renewable energy sources.

For example, scenario worked out for Denmark demonstrates that transition to sustainable energy system will not exceed expenditures necessary for supporting traditional energetic, at least during the nearest 30 years. At the same time emission of CO_2 can be reduced by 70%.

Will Ukraine's energetic be able to develop in accordance with a similar scenario? This paper describes such an estimation. For the analysis we used existing prognoses for the development of Ukraine's economy and data from the last draft Energy strategy of Ukraine for the period till 2030.

2. Renewable energy sources in Ukraine

2.1. WIND ENERGY

Ukraine has favorable conditions for the development of wind energy. In many regions average annual wind velocity is 5–5.5 m/sec at a standardized height of 10 m above ground level.

It is considered that installed capacity of wind power plant (WPP) that can be achieved as a part of centralized energy system of Ukraine may come up to 16,000 MW, and power generation may come up to 25–30 TWh/year. This figure is often accepted as a potential of wind power. The area necessary for the construction of such a WPP capacity is 2,500–3,000 km^2 that is quite real taking into account shoal of the Azov Sea and the Black Sea. According to other estimations 7,000 km^2 of Ukraine's territory can be used for the construction of WPP of 35,000 MW total capacity.

It is accepted that WPP of 16,000 MW total capacity can be potentially built in Ukraine. Accepted capacity factor is 30% (2,630 h/year) that may be quite achieved in Ukraine's climatic conditions when using modern wind turbines. With such assumptions the potential of wind energy is 42 TWh/year.

Currently total capacity of WPP is 50 MWe. For the period till 2030 it is predicted the construction of WPP of 11,290 MW total capacity with annual power generation of nearly 25 TWh/year. Prognosis for increasing capacity of WPP for the period till 2030 is accepted with slowing down rate in 2030–2050. Based on these prerequisites power generation by WPP may come to 42 TWh by 2050.

2.2. SOLAR ENERGY

Period of sun shining at the territory of Ukraine is 1,900–2,400 h/year, and total average annual solar radiation varies from 1,070 kWh/m^2 in northern part of Ukraine to 1,400 kWh/m^2 in southern part.

Existing programmers for energy development envisages increasing use of solar energy mainly for local hot water supply in summer season. Potential of solar energy for heat production is estimated at about 32 TWh.

Climatic conditions of Ukraine allow also the use of solar energy for the heating of buildings, creation of year-round centralized district heating systems with seasonal heat storage. Such technical solutions have been already realized in many countries located much more to the North than Ukraine. When using solar collectors (counting 3.9 m^2/capita) and 400 kWh annual heat production by 1 m^2 of solar collector, potential of solar energy for heat production is almost 75 TWh/year.

The rate for the installation of solar collectors for the period till 2030 is accepted in accordance with [1] with accelerating rate in 2030–2050. It may be assumed that by 2050 solar collectors will produce about 23 TWhth/year.

In Ukraine technical potential of solar energy for power production is estimated at about 16 TWh/yr that makes up in average about 3.3 m^2 of PV batteries per capita with the production of about 100 kWh/m^2/year. Provided that a dwelling is equipped with modern and promising energy saving household appliances, indicated volume of power production could satisfy necessary household needs. It is assumed for year 2030 the PV-power generation makes 2 TWh/year, and that for 2050 makes 9 TWh/year.

2.3. THE USE OF FIREWOOD AND WOOD RESIDUES

In Ukraine forests cover only 15.6% of the territory, at that nearly half of them have environmental value. The country lacks for merchantable wood that is why timber is imported. The main forest areas are located in the Carpathians and Polissia (Forest Land) were more than 90% of wood is harvested. Wood potentially available for energy production makes up 1.6 mill m^3/year of felling residues, 2.1 mill m^3/year of wood processing waste, 3.8 mill m^3/year of firewood that in sum is equivalent to 16 TWh/year.

In 2005 consumption of wood and wood waste for energy production amounted to about 5.8 TWh. Consumption of wood and wood waste for energy production will be about 13 TWh in 2030 and may achieve 16.3 TWh/year in 2040.

Further development of energy utilization of wood can be also expected under reorganization of forestry and intensive development of forestry. At present there are workable propositions aimed to raise productivity of Ukraine's forests to the level of neighboring countries and achieve wood logging of 30 mill m^3/year and then 60 mill m^3/year without any harm to nature. So, prognosis on energy utilization of wood in 2050 may be 25 TWh/year.

2.4. THE USE OF AGRICULTURE RESIDUES

Ukraine has good prospects to revive highly efficient agriculture, which is able to satisfy domestic needs in foodstuff and feedstock and also produce products for export. The big part of the territory is steppe. It is characterized by low atmospheric precipitation, frequent draughts, and other unfavorable phenomena. Due to that yields of the main crops are not stable. Potential yield of straw and stems may come to 35 mill t/year. Demand of agriculture is 13 mill t of straw a year, the surplus – about 20 mill t/year that is equivalent to 82 TWh – can be used for other purposes including energy production.

In Ukraine some people have doubts as to possibility to use straw and stems for energy purposes. It can be explained by insufficient productivity of agriculture, big losses, and burning of straw on fields, absence of stems storing.

Projects realized in Ukraine under support of European countries demonstrated technical possibility and economic expediency of straw application for energy production. At present amount of straw used for energy production in Ukraine is equivalent only to 2 GWh/year.

In accordance with the prognosis for the development of bioenergy in Ukraine the use of straw and stems for energy purposes will be equivalent to 23 TWh in 2030. Further increase to 50 TWh/year in 2050 may be assumed that will require up to 60% of technically available potential.

2.5. THE USE OF BIOGAS

Technical potential of biogas available for energy production consists of the biogas from manure (animal husbandry and poultry farming) – 2308 mill m^3, the biogas from sewage sludge – 334 mill m^3, and landfill gas – 2300 mill m^3. In sum it is equivalent to 28.2 TWh.

Formerly in Ukraine biogas was widely produced at wastewater treatment plants, total volume of installed digesters was 162,000 m^3. Now biogas production in many cases is stopped because of bad technical condition of digesters, and because the state does not stimulate this activity. In 2005 the use of biogas was equivalent to 0.02 TWh.

A number of biogas plants for dung and manure processing are out of operation. Now in Dnepropetrovsk oblast a modern biogas plant is under construction that is supported by Dutch government. There was realized a demonstration project on the extraction and utilization of biogas on Lugansk landfill.

The use of landfill gas and biogas from sewage sludge will develop dynamically in the nearest years. After 2010 it is expected the increase in biogas production from animal husbandry waste. In 2030 total utilization of biogas will amount to 10.2 TWh, and by 2050 it will achieve 17.4 TWh/year.

2.6. GEOTHERMAL ENERGY

Ukraine has a big potential of geothermal energy. According to official data of the Ministry of Ecology and Natural Resources reserves of thermal waters are 27.3 mill m^3/day. Technical potential of geothermal resources is 97.7 TWh/year. In 2005 geothermal energy utilization amounted to 0.1 TWh. It is expected that total capacity of constructed geothermal district heating systems will be 9,000 MWth and that of geothermal power plants will be 400 MWe in 2030. That will ensure production of 42 TWh, and in 2050 the production will come to 57 TWh.

Such degree of geothermal energy use seems to be too optimistic. Geothermal energy is renewable only in geological scale of time. Promising under geological conditions of Ukraine geo-circulating systems will exhaust aquifer resource during 20–30 years, and their renewing will take thousands of years. It means necessity to move geothermal energy extraction to other sites every 20–30 years. It is assumed that amount of utilized geothermal energy will be 8 TWh/year in 2030 and 14 TWh/year in 2050 that is equivalent to present use of geothermal energy in the whole Europe.

2.7. HYDRO ENERGY

Among all renewable energy sources hydro energy is known as technically proven technology for energy production. Seven large hydroelectric plants and one hydro accumulating plant of 3,907 MW total capacity and 10–12 TWh average annual power generation were built on the Dnepr River.

The Dniestr hydroelectric plant of 702 MW capacity with 1 TWh average annual power generation was put into operation on Dniestr river. The Dniestr hydro power cascade will include the biggest in Europe Dniestr hydro accumulating plant of 2,268 MW capacity and buffer hydroelectric plant. Fifty small hydroelectric plants of about 100 MW total capacity with 0.25 TWh annual power production are exploited in Ukraine.

In Ukraine technically available potential of hydro energy is 81 TWh/year. As for large hydroelectric plants and small hydro energy, total economically expedient unused potential is 17–19 TWh and up to 3.7 TWh correspondingly. Then total economically expedient potential of hydro energy amounts to about 33 TWh/year.

In Ukraine's conditions the development of hydro energy is real with the construction of hydroelectric plants of relatively high capacity (20–50 MW). Among priority measures is reconstruction of the hydroelectric plants of Dnepr cascade that will give 300 MW of additional capacity and increase in power production by 290 mill kWh.

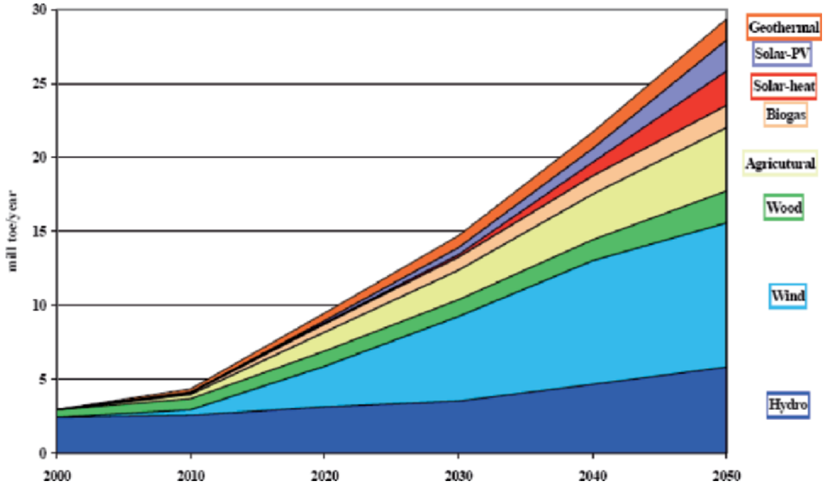
Priority measure may be also the construction of hydroelectric plants on the section of the Tisa river from Burshtyn to Vilki of 220 MW total capacity.

Priority measure is considered the reconstruction of operating small hydroelectric plants and restoration of existing small hydroelectric plants, which are the most suitable for further exploitation. When constructing small hydroelectric plants priority will be given to plants, which protect neighbor territories from flood. There may be considered construction of small hydroelectric plants on existing water bodies, for energy utilization in main canals, technical water supply systems and water drain.

In 2030 power production by hydroelectric plants may come to 15.1 TWh/year. Further increase in power production up to 25 TWh in 2050 may be expected.

2.8. REPLACEMENT TRADITIONAL AND RENEWABLE ENERGY SOURCES

It should be marked that value of individual RES also depends on the amount of fossil fuel that can be replaced by them. Power produced by hydroelectric plants, WPPs, PV units replaces almost three times bigger amount of fossil energy necessary for the generation of the same amount of power. In 2030



replacement of fossil fuel and nuclear energy by RES may be carried to 14 mill toe/year, and in 2050 – to 30 mill toe/year (see diagram).

3. Ukraine's legislation on renewable energy

Governmental organizations responsible for RE issues in Ukraine are Ministry of Fuel and Energy and State Committee for Energy Conservation. Lately profile energy committee of Ukrainian Parliament has undertaken coordination in preparation of "Energy strategy of Ukraine for the period till 2030 and future perspective" including the section on RE.

A few Laws of Ukraine on renewable energy sources and cogeneration have been recently developed/accepted in Ukraine.

Law of Ukraine "On power energy" with amendments envisages finance stimulus for wind power plant construction due to state budget expense. There are profitable tariffs for electricity generated at WPP. Really Ukrainian government gives such a support only for state owned wind power plants.

Law of Ukraine "On corrective action to the Law of Ukraine "On power energy" has been developed and approved by the Cabinet of Ministers and has been submitted to the Verkhovna Rada. This Law was developed according the schedule of works on adaptation of Ukrainian legislation to legislation of EU. The subject of legislative regulation is improvement of relations on the power market, guaranty of power quality, in the sphere of construction of new generating capacities, and free access to the power grids, stimulation of power production from renewable energy sources.

According to this Law power supply companies must guarantee access to the power grids to small hydropower stations, and power stations producing power from renewable energy sources. New chapter IV "Stimulation of power production from renewable energy" is included in the Law. This stimulation includes:

- Purchase on the whole sale market of Ukraine power produced from RES
- Guarantee access to the power grids for producers of power from RES
- Installation of special tariff for the transportation of power from RES in the grids
- Providing to RES power generating companies by subsidies, grants, tax, credit, and other concessions

The Law of Ukraine "On alternative sources of energy" was accepted by Verkhovna Rada in 2003. It is framework Law, which defines legislative, economic, ecological, and organizational basis for the utilization of alternative sources of energy and promotion for their use in fuel-energy complex. According this Law term "alternative sources of energy" is equalized to “renewable energy sources”. This Law does not propose any financial stimuli and support mechanisms for producers and consumers of renewable energy sources. In any case this Law has progressive significance such as indicated increase of renewable energy production and utilization as a main principle of State policy in this field.

The Law of Ukraine “On combined heat and power production (co-generation) and utilization of dump energy potential” was accepted “in the first reading/or as a base” by Verkhovna Rada. This Law regulates relations between State, producers of power, which use cogeneration technologies, dump energy potential of technological processes, and energy supply companies. This Law acts for qualified CHP plants, which started exploitation after January 1, 2003. It is proposed stimulation of construction and utilization of such CHP plants.

National Commission on Regulation of Power Sector of Ukraine has to use profit norm of 22% for calculation and approval of sale tariffs for RES power. This figure is calculated from the condition that payback period for investments in such CHP plants will be less than 4.5 years. It is maximal payback period, which is still interesting for investors in Ukrainian conditions.

The “Energy Strategy of Ukraine till 2030” is under development by a group of Ukrainian energy experts on the decree of President of Ukraine. According to draft version targeted utilization of RES is 6.6 Mtoe (4.7% of Primary Energy Consumption (PEC)) in 2010 and 21.8 Mtoe (17% of PEC) in 2030.

4. Conclusion

Will Ukraine choose the way for sustainable development in energy sector? Draft “Energy strategy of Ukraine for the period till 2030 and further prospect” is being developed with big difficulties. Proposals to use RES envisaged rather moderate, but a number of leading specialists do not want to take them into account properly. Nevertheless development of RE has legislative basis in Ukraine.

References

Project «Energy strategy of Ukraine for the period till 2030 and further prospect (general provisions)/The Ministry of Fuel and Energy of Ukraine, the National Academy of Sciences of Ukraine, (2006).

THE LATEST ACTIVITIES OF INTERNATIONAL ECOENERGY ACADEMY ON RENEWABLE ENERGY DEVELOPMENT IN AZERBAIJAN

PROF. F. G. ALIYEV
F. F. ALIYEV
International Ecoenergy Academy,
Baku, Azerbaijan

1. Azerbaijan republic

Azerbaijan is one of the oldest oil-producing countries of the world. By the end of 1900s it was the world's biggest oil-producing province. During the Soviet period, Azerbaijan held a leading oil production role among the other USSR republics.

The end of the 20th century is famous with political and economical processes that led to fundamental changes. Azerbaijan people achieved independence and government sovereignty.

A strong oil industry infrastructure meeting all international standards has been created in Azerbaijan over the last years. 50 million tons of oil will be produced in the republic by 2010. However, as the number of oil contracts increases, so increases the concern about environmental protection.

Today, Azerbaijan Republic is characterized by acute environmental situation and increased anthropogenic impact on the environment. According to the BP company's forecast, the production of oil and gas condensate from Azeri–Chirag–Guneshli–Shahdeniz fields will result in the emission of 51 million tons of GHG during 2002–2014 years.

Calculations have shown that, as a result of future developments the amount of hydrocarbons emitted by oil–gas sector will amount 80–85% of total emissions in the republic. It is expected that compared to 1990 in 2025 the level of hydrocarbon emissions only will be 1.8–2.0 times higher (see Fig. 1 and Fig. 2). As a result of combustion of a huge amount of fossil fuels the annual air temperature on the geographical zones of Azerbaijan has increased by 0.5–0.8°C during the second half of the 20th century.

J.W. Sheffield and Ç. Sheffield (eds.), Assessment of Hydrogen Energy for Sustainable Development, 257–268.

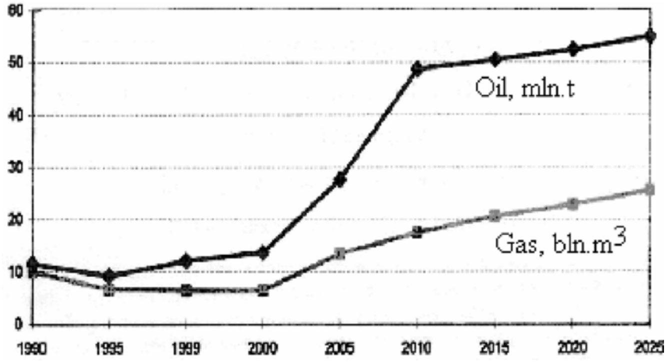


Figure 1. Hydrocarbon production

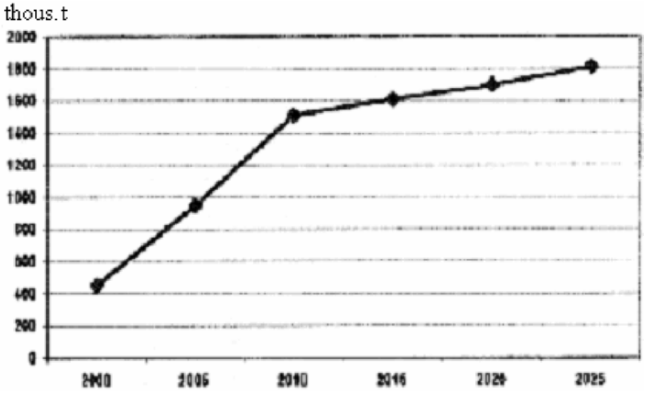


Figure 2. Methane emission

In 2003 in the republic the amount of GHG emissions was 6 tons/capita. According to forecasts it will amount to 8 tons/capita up to 2010–2020 years due to the increase of consumption of fossil fuels, particularly oil and gas by 40–50% and 15–20%, respectively.

Transport is one of the main sources of GHG emissions. In Azerbaijan, regularly updated National Inventory is the base for estimation of possibility of activity conducting on mitigation of anthropogenic influence to climate. Full inventory was conducted for 2003 year and partly for 1990–2003 years. Trend was defined for 1990–2003. CO_2 emissions from fuel combustion in transport are shown in the following figure 3 and figure 4.

Due to the commence of Baku–Tbilisi–Ceyhan pipeline and the Great Silk Route the amount of GHG emissions is expected to increase in the future years.

Analysis of the present situation shows that in order to reduce GHG emissions and to control climate changes we must use alternative, carbon-free energy sources.

There are many different sources of renewable energy in Azerbaijan. Among those sources are solar, wind, biomass, and hydro energy.

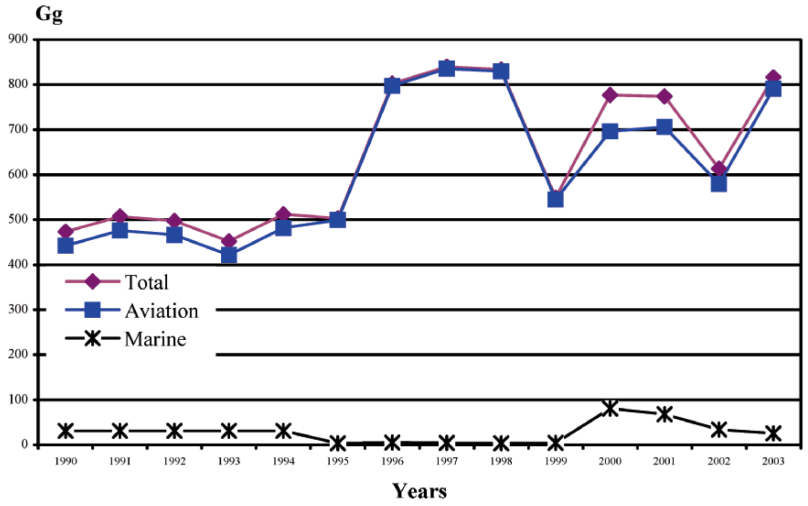


Figure 3. Total CO_2 emissions from international bunkers

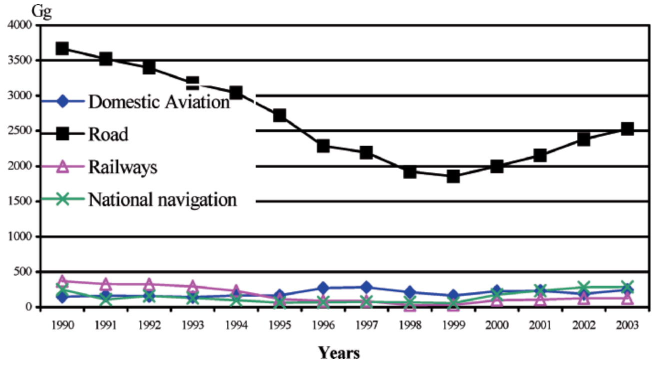


Figure 4. CO_2 emissions from fuel combustion in transport sector

According to the report prepared for the European Bank for Reconstruction and Development by Black & Veatch International (BVI), there is wind energy resource potential of 110 × 10 kWh/year in Azerbaijan. Potential of wind energy resources allows to produce 4 billion kWt.h electrical energy. It allows to economize 1 billion kWt.h conditional fuel, while reducing 3.7 million tons of CO_2 per year.

Most prospective areas are :

1. The territory of Absheron peninsula including the towns of Baku and Sumgait and adjoining islands. Wind regime here is exception.
2. Ally intensive with estimated potential of 1,500 MW.

3. Caspian Sea zone and the Kura River lower reaches – 500 MW from the Kura spit in the South to the border with Dagestan in the North.
4. Nakhichevan Autonomous Republic (70 MW), which includes separate localities on the Zangezur ridge.

Potential of wind energy resources allows to produce 4 billion kWt.h electrical energy. It allows to economize 1 billion kWt.h conditional fuel, while reducing 3.7 million tons of CO_2 per year.

Evaluations have shown that Azerbaijan's hydropower potential amounts to 16 billion kWt.h including 5 milliard kWt.h of small hydropower potential. Utilization of this potential will allow to save annually 500 thousand tons of conditional fuel that will result in reducing the amount of CO_2 emissions by 1.5 million tons/year.

Average annual hydropower generation in Azerbaijan amounts to 1.5 billion kWh, meeting 15% of energy demand of the power system. Hydro installed capacity totals 0.9 million kWh.

At present, small hydropower development is most promising in power sector. The largest small hydro potential is concentrated in multiple tributaries of the Kura and the Aras rivers and a group of creeks inflowing into the Caspian Sea.

First Priority Potential Medium-Size Hydro Power Projects are Poilinsk HPP in the cascade of the Kura River and Gudialchay HPP at the irrigation project in Gudialchay River, which installed capacity are of 90 MW.

The area of forests in Republic is 14,400 km from the overall territory. Republic occupies the first place among Republics of the former USSR and the fourth place in the world in production of raw cotton. The population of Azerbaijan is using the waste of cultivating cotton and cereal crops as a fuel in private household equipment.

Table shows the overall biomass resource data for Azerbaijan:

Several measures have been implemented by Azerbaijan Government for encouraging the use of alternative energy resources. The State Program "On the use of alternative and renewable energy resources in Azerbaijan Republic" was adopted by the Decree of the Azerbaijan Republic President dated October 21, 2004.

We do not now have all conditions to apply renewable energy technologies in the republic at the required scale. But we need to determine appropriate technologies today.

The main direction of our International Ecoenergy Academy's (IEA) activity is environment protection and replacing fossil fuels with renewable energy technologies.

TABLE 1. Azerbaijan Biomass Resource Data (FAO 2002a, b)

Biomass resource type	Total production	Production density
Primary crop production (ton)	(avg. 1999–2001, ton)	(ton/1,000 ha)
Total primary crops (rank among CO_2)	7,806,794 (18)	901 (19)
Top primary crops		
Mixed grasses, legumes	2,600,000	300
Maize for forage & silage	1,200,000	139
Wheat	1,189,327	137
Potatoes	479,325	55
Tomatoes	370,678	43
Apples	281,767	33
Watermelons	252,579	29
Vegetables and roots, fodder	231,667	27
Barley	208,967	24
Vegetables fresh (misc)	133,000	15
Animal units, number	(number)	(number/1,000 ha)
Cattle	1,933,270	223
Poultry	12,972,000	1.498
Pigs	22,900	3
Equivalent animal units	2,072,150	239
Forest products, cubic meters	(avg. 1999–2000, cubic meters)	(cubic meters/1,000 ha)
Wood fuel and charcoal	6,300	1
Wood residues	NA	NA

Since its foundation (1994), the Academy has involved Azerbaijan and foreign specialists in carrying out scientific investigations and projects in the mentioned areas. In cooperation with the Trento University of Italy a project of “Feasibility study of wind-electric conversion systems for offshore oil platforms in Azerbaijan” has been carried out.

Platforms for crude oil extraction are widely employed in the Caspian Sea, at tens and hundreds kilometers offshore.

For the human living they are provided with autonomous electric delivery systems and usually diesel-generator sets are used for this. However, the diesel generation is expensive because of the fuel consumption, moreover, as the fuel has to be carried on the platforms by boat from the coast. The more suitable solution to produce really autonomous electric energy on oil platforms is to convert locally the wind energy by means of a wind generator set up on the platform itself.

Although the capital cost of a Wind-Electric Conversion System (WECS) is higher than that of a Diesel-Electric Conversion System (DECS), owing to fuel saving in few years the WECS generation becomes cheaper that the DECS. Moreover, the WECS should give a real autonomy to the electric supply. On the basis of these considerations an evaluation of the feasibility of a pilot set of WECS for oil-platforms on Caspian Sea has been carried out. In order to study the feasibility of some pilot systems, we considered a small size platform. The suitability of a WECS strictly depends on the amount and the distribution of the wind energy resource. Evaluations were based on wind data measured at 20 m of elevation on a platform at Neft Dashlari (Oily Rocks) during one year (see Table 2 and Fig. 5).

TABLE 2. Mean wind data at 20 m of height, Neft Dashlari

Annual mean wind speed	8.4 m/s
Annual cubic mean wind speed	9 m/s
Monthly mean wind speed:	
Minimum (April)	7.1 m/s
Maximum (November)	9.4 m/s
Monthly cubic mean wind speed:	7.6 m/s
Minimum (April)	9.7 m/s
Maximum (November)	
Annual available specific energy	3900 kWh/m^2
Weibull parameters	K= 4.5; c = 9.2

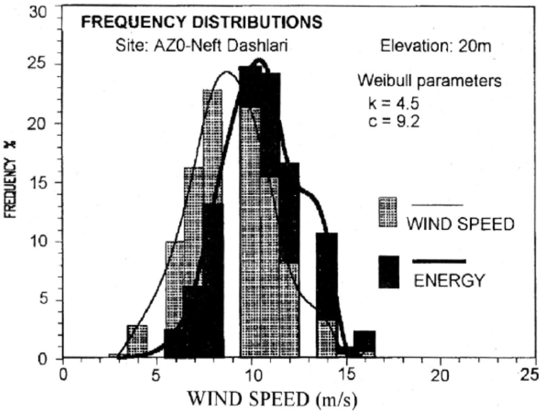


Figure 5. The frequency distribution of wind speed and the available energy

2. The frequency distribution of wind speed and the available energy

These data show that the wind energy resource is quite rich. Assuming a precautionary value of 20% for the overall system efficiency, in a year a

WECS should supply 780 kWh/m^2 of the turbine disk area. A 6 m diameter turbine would supply 22,000 kWh/year, that is enough to answer the annual energy needs. There will be shorter or longer (up to several days) calm periods. Therefore, it is assumed that the calms are to be covered by a standby diesel-generator set (DECS).

Based on the studies three pilot plants are proposed and analyzed for three oil platforms at Neft Dashlari. All plants are integrated system with three main components: (1) a wind generator (8 m diameter wind turbines) to produce primary energy, (2) a standby diesel-electric set, to cover the lack of energy during calm periods, and (3) a storage battery bank to cover daily imbalances between power production and power load during the day.

The benefit analysis shows that the proposed three pilot wind-power generation plants become economically profitable as regards diesel-electric generation after several years.

Solar energy potential in Azerbaijan is very high due to the favorable climatic conditions. Annual total solar radiation in many regions is up to 4.7 kWh/m^2/day and about 5,000–6,500 MJ/m^2/year. The highest solar insolation areas are Absheron peninsula and Nakhichevan region. Solar energy can be used for heating and electricity generation purposes. Calculations have shown that through applying solar collectors using the potential of a total 10,000 m^2 area, 13,000 tons of conditional fuel can be saved and 23,000 tons of CO_2 can be reduced annually. Semiconductor solar photocells can produce in average 200–540 W hour electric power per day.

In the recent years, solar power plants have been applied worldwide due to the falling of photoelectric transformation price (see Fig. 6). It means that solar power can compete with other electric power sources in the near future.

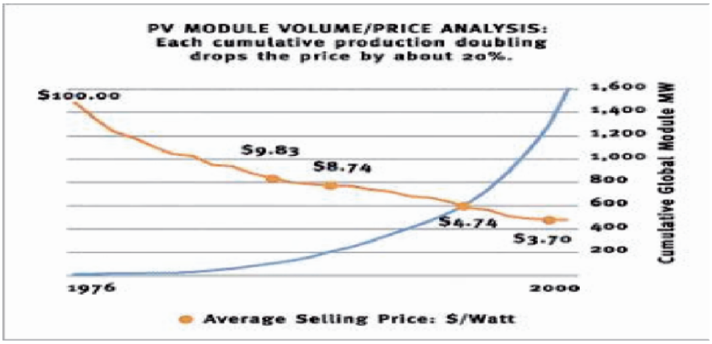


Figure 6. PV volume/module price analysis

Extensive studies have been conducted in IEA on the use of solar energy. Most part of Azerbaijan: Nakhichevan AR, Absheron peninsula, Canja–Gazakh plain, Alazan–Agrichay valley, and Samur–Divichi lowland are rich in solar energy resources. Duration of solar radiation varies from 1,900 to 2,800 h on different regions including high-mountain zones of the Great and Small Caucasus. Practical use of solar installations is depending on the characteristics of solar radiation of individual regions. On the basis of 12 years (1991–2003) studies IEA, in cooperation with the scientists of the Institute of Radiation Problems, developed a solar cadastre of Absheron peninsula (the Caspian coast).

Actinometrical measurements were carried out at the Pirallahi weather station of the Ministry of Ecology and Natural Resources. The data derived from investigations give us great opportunity for the use of solar energy in this region allowing to define the type of solar installation. For the elaboration of the elements of solar cadastre we have calculated $S^{\perp}$, D, and R (in conformity with straight, diffusive, and reflected radiation from the earth in W/m^2). The results of calculations are shown in Fig. 7.

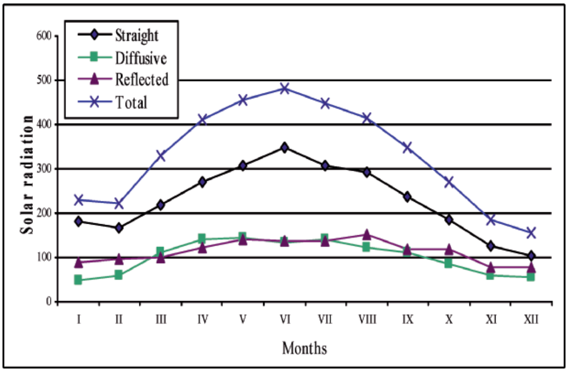


Figure 7. Results of calculations per one year

Analysis of calculations has shown that the maximal efficiency of solar installation is characteristic for the period from April to October.

Besides, possibilities of the use of solar energy for heating and energy supply purposes have been studied for the regions of Mil–Mugan lowland and southern territory of the republic (see Fig. 8).

One of the projects developed in IEA is intended for the use of hybrid solar–biomass plants in the country's mountain regions. The work of such a hybrid system is based on the principle of obtaining the optimal temperature needed for biomass fermentation by using solar collectors or photovoltaic modules. The biogas obtained through this process may be used as fuel in domestic appliances and also for agricultural purposes. Since the residual biomass are used to produce odourless organic fertilizers, development and introduction of solar–biomass hybrid systems allows resolving not only energy but also environmental problems.

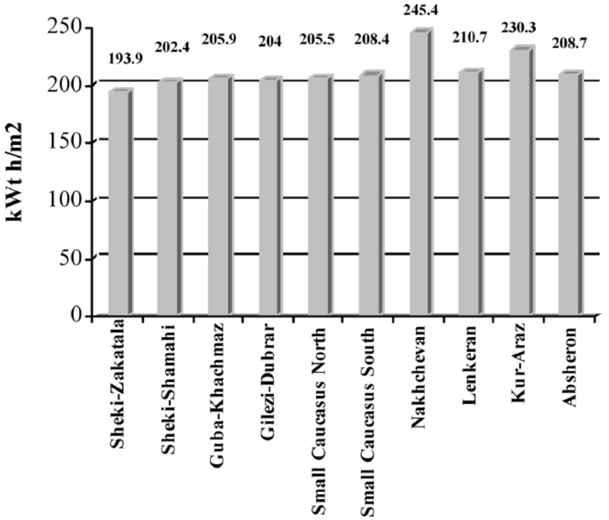


Figure 8. Annual energy production of solar photoelectric modules on the climatic zones of Azerbaijan Republic

On the basis of biomass utilization it is possible in average to produce 7.5 million m^3 biogas that is equivalent to 5,000 tons of conditional fuel.

IEA in cooperation with “KiSKA” Technical Construction Company of Turkey has constructed and installed seven individual biogas plants in five districts of the republic.

Lately, Azerbaijan government has expressed interest in the prospects of the use of Small Hydro Power Plants in rural regions. Creation of agrarian complexes on the bases of Small Hydropower Plants will allow preventing disasters of season floods. At the same time, these complexes will help solve a range of social, economic, and environmental problems. Development of agricultural sector, tourist, and recreation zones while providing local population with large employment opportunities will play an important role in: protection of biospecies, rehabilitation of forests, and preventing the migration of rural population to large cities.

With the purpose of complex approach to solving the above mentioned problems IEA is developing projects for wide-scale introduction of Small Hydropower Plants.

“Hydro-Hydrogen Pilot Project” developed on the basis of cooperation with UNIDO-ICHET is one of the important steps of IEA towards alternative energy development.

The main purpose of this project is to demonstrate perspectives of using the energy generated by intermittent renewable sources such as hydropower. Two hydropower stations each 1 MW are planned in Niyazoba village in the Kuba–Khachmas region of Azerbaijan Republic due to the difficulties of matching energy generation with local electricity demand. 1,500 kWt will be enough to meet local requirements. The excess of energy produced at hydropower plants – 500 kWt will be stored for the production of hydrogen by electrolysis for later use. The long-term goal of the project is to demonstrate the compatibility of hydrogen technologies with renewable energy generation, and act as a model for further cogeneration plants.

The project will be implemented in three stages:

- Construction of two hydropower stations in Niyazoba village in the Kuba–Khachmas region, Azerbaijan Republic to produce electricity.
- Using an excess of energy (500 kWt) generated by hydropower for the production of hydrogen through electrolysis of water.
- Storage and distribution of hydrogen (and oxygen) produced at Niyazoba plant.

Water electrolysis is one of the important methods for hydrogen production at present. There is particular interest in using water as a hydro source, because it is clean and abundant.

Electrolysis of water is an electrochemical process during which water dissociates to oxygen and hydrogen in the presence of electric current and electrolyte on the following chemical equation:

$$2\,H_2O + \text{Energy} \rightarrow 2H_2 + O_2$$

Electrolysis from renewable energy would give a significant environmental advantage to the method.

However, this method is not economically feasible for all applications due to power requirements. Electrolysis has been used for long wherever electric power is available cheap or pure hydrogen was needed or where there is a renewable energy source available.

For setting up SHP location is a prime factor. The proposed SHP will be located in Niyazoba village of Kuba–Khachmas region due to the existing energy shortages and abundant hydro-resources of this area.

An economic analysis of hydrogen production costs indicates that in comparison with hydrogen produced in USA, hydrogen generation in Niyazoba will be much cheaper, particularly if the electricity is supplied at zero cost to the electrolizer plant. In this case, the usage of hydrogen as a fuel in automobiles will be significantly increased because of its low cost and environmental friendly nature.

Kuba-Khachmas region is situated in the Northern part of Azerbaijan bordering with Russian Federation. This is one of the large agricultural regions and recreation centers of the republic in the Caspian coast. According to newly adopted governmental program on the development of tourism and recreation zones, one of the five tourist routes is situated in this region.

Based on the above mentioned, we can say that significant demand will be for hydrogen in Kuba–Khachmas zone in the future.

There are a number of industrial and agricultural enterprises in Kuba–Khachmas territory.

Therefore, the hydrogen produced in Niyazoba may be used for many commercial purposes including: commercial fixation of nitrogen from the air to produce ammonia for fertilizer; methanol production, hydrodealkylation, hydrocracking, hydrodesulphyrization, metallic ore reduction and superconductivity study, etc.

The main advantage derivable from the project is that hydro-electric plants do not emit any of the standard atmospheric pollutants such as CO_2 produced by fossil fuel power plants.

Hydrogen is clean and renewable energy source. It can promote a healthy environment by eliminating harmful pollutants.

According to the data of World Health Organization (WHO), 68% of diseases are caused by polluted air. Greenhouse gases (GHG), especially CO_2 remain in atmosphere over a long time, up to 100 years and they influence radiation effect for long time, accordingly. As a result of these changes additional thermal effect and increase of atmosphere temperature happen. During the second half of the 20th century the average annual temperature in the Kuba–Khachmas region has increased by 0.6°C.

Hydrogen produced at the Niyazoba site will displace significant GHG emissions.

It is anticipated that 500 households (6,000 people) will benefit from the Niyazoba plant.

At the same time, the project complies with important international conventions on environment protection (climate change, desertification, protection of ozone layer, etc.) ratified by Azerbaijan, such as:

- Protocol on Substandces that Deplete the Ozone Layer. 1987, Montreal Protocol (ratified in June 18, 2000)
- Convention on Environmental Impact Assessment in a Transboundary Context. 1991, ESPO Convention (ratified in February 1, 1999)
- UN Framework Convention about Climate Changes, 1992, Kyoto Protocol to this Convention (July 18, 2000)

Therefore, it is anticipated that this initial project will lead to broader social and environmental advances and act as a model for further cogeneration plants. Conversion of hydro, wind and, solar energy to electricity and to hydrogen will open a new venue for the efficient utilization of renewable energy resources in Azerbaijan.

I should note that all projects will be implemented with close cooperation of the experienced foreign specialists using modern environmental friendly technologies.

References

1. Aliyev F.G., Pallabazer R. Feasibility study on wind electric-conversion systems for offshore oil platforms in Azerbaijan. Proceedings of the Fourth Baku International Congress "Energy, Ecology, Economy", September 1997 Baku pp. 9–20.
2. Aliyev I., Tagiyeva U. New technologies and possible ways of reducing gas wastes causing greenhouse gas emission. Proceedings of the Eighth Baku International Congress "Energy, Ecology, Economy", June 2005 Baku pp. 400–402.
3. Mahmudov H.M. The forecast of methane emission in oil-gas sector of Azerbaijan. Proceedings of the Eighth Baku International Congress "Energy, Ecology, Economy", June 2005 Baku pp. 548–549.
4. National Inventory Report for Transport Sector in Azerbaijan, 2005.
5. Rzayev R.F., Movsumov E.N., Abasova F.A., et al. Solar cadastre and its practical use. Proceedings of the Eighth Baku International Congress "Energy, Ecology, Economy", June 2005 Baku pp. 99–101.
6. State Program "*On the use of alternative and renewable energy resources in Azerbaijan Republic*" adopted by the Decree of the Azerbaijan Republic President from October 21, 2004.

THE HYDRIDE SYSTEMS AND PECULIARITIES OF HYDROGEN SOLUBILITY IN THESE STRUCTURES

SVETLANA YU. ZAGINAICHENKO*,
DMITRY V. SCHUR
Institute for Problems of Materials Science of NAS of Ukraine,
3 Krzhyzhanovsky St., Kyiv, 03142, Ukraine
ZINAIDA A. MATYSINA
Dnepropetrovsk National University,
Nauchnaya St., 13, Dnepropetrovsk, 49050, Ukraine

Abstract: Theoretical investigation on the solubility of C-impurity in AB and AB_3 alloys with hexagonal close-packed lattices of different structures has been carried out by the method of configurations in approaching the pair interaction of the nearest atoms. It is supposed that impurity atoms are located in octahedral and tetrahedral interstitial sites. The solubility dependence on alloy composition, temperature and order parameter has been defined. Comparison of the theoretical results with experimental data on the concentration and temperature dependence of hydrogen solubility shows good agreement between theory and experiment for PdPt–H, FeV–H, PdNi–H, Ni3Fe–H alloys. The theoretical calculation of hydrogen solubility in ordering bcc and fcc crystals of fullerites has been performed by the method of average energies and configuration method, i.e., taking into consideration the possibility of realization of different configurations of C_{60}, C_{70} fullerenes around interstitial sites of various types, under the assumption of geometrical ideality of crystal lattices, with regard to the ordering of C_{60}, C_{70} fullerenes on lattice sites and hydrogen atoms arrangement in interstitial sites of different types. The equilibrium concentrations of hydrogen atoms in interstices of all types and then the total solubilities of hydrogen in bcc and fcc fullerites

---

[*] To whom correspondence should be addressed. Svetlana Yu. Zaginaichenko, Institute for Problems of Materials Science of NAS of Ukraine, 3 Krzhyzhanovsky str., Kyiv, 03142 Ukraine; e-mail: shurzag@materials.kiev.ua

J.W. Sheffield and Ç. Sheffield (eds.), Assessment of Hydrogen Energy for Sustainable Development, 269–310.

have been found from conditions of free energies minimization. The dependences of hydrogen solubilities in bcc and fcc fullerites on temperature, fullerite composition, long-range order, hydrogen atoms activity, and energetic constants have been ascertained.

Keywords: statistico-thermodynamic theory, hydrogen solubility, hydride, fullerite, degree of order, temperature

1. Introduction

Solubility is one of the important properties of an alloy. Interstitial impurities (for example, hydrogen, oxygen, carbon, boron, and other chemical elements) in metals and alloys change considerably their physical properties [1–18].

The solubility of interstitial atoms depends on the structure and type of solvent, on the dimension of interstitial atoms, on the type of interstitial sites, on composition and long-range order of the solvent, and on temperature and pressure.

The present paper is concerned with hydrogen storage in different crystalline solids. Such solids can be metal hydrides, carbon-based materials, and microporous materials.

The essential requirements for hydrogen storage in solids are that it be: (a) high H-mass density; (b) high H-volume density; (c) appropriate pressure, temperature stability; (d) reversible absorption/desorption. The results of research in the field of hydrogen solubility in the metal-hydrogen systems and carbon nanostructures are presented in this paper.

The hydrogen density in different phase states and compounds is given at the Figure 1. As obvious from this figure, the hydrogen density in all aggregation states substantially ranks below its density in compounds. Among compounds the metal-hydrogen systems have the highest density in hydrogen. The density of hydrogen atoms in vanadium hydride is in three times greater than in liquid hydrogen and is two times more than in solid hydrogen (at the temperature of 1.5 K). For this reason, particular attention should be given to the metal-hydrogen systems.

At present metal hydrides, owing to their unique properties, find applications (Figure 2) in many fields of science and technology, associated with hydrogen storage, thermal compression, separation, electrochemistry, switchable mirror, etc.

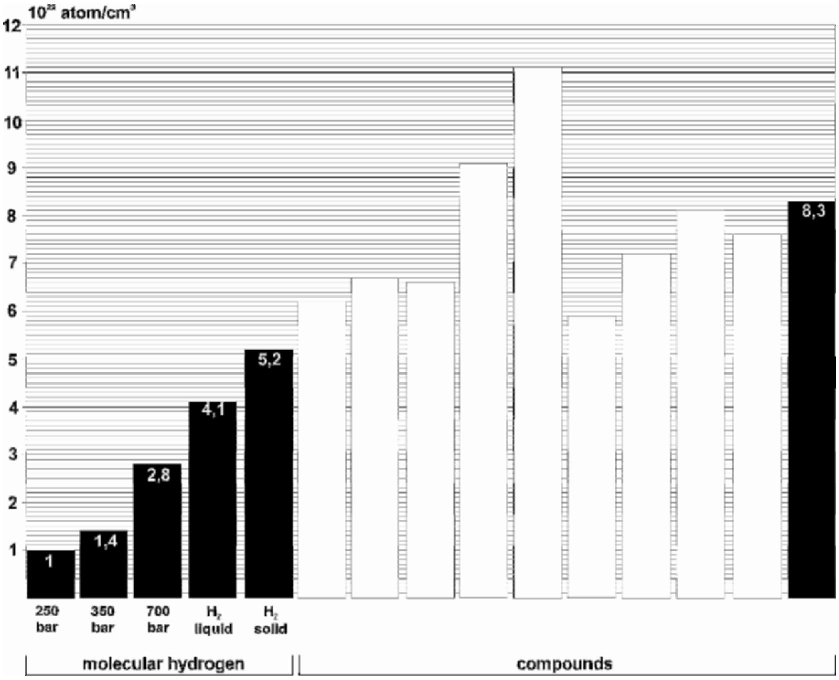


Figure 1. The density of hydrogen atoms in different phases and compounds.

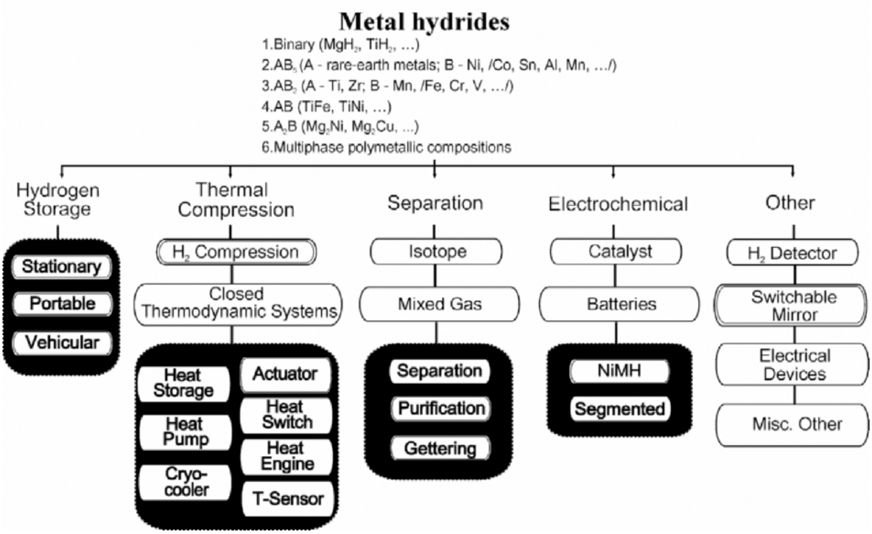


Figure 2. Family of hydride applications

All physicochemical properties of hydrides in use depend on electronic structure of metals and consequently on geometrical structure of lattice (Figure 3) that is defined by interaction of nearest metal atoms, metals interaction with H atoms, and also interaction between H atoms (Me–Me, Me–H, and H–H). The solid solutions (mono-, di-, and trihydrides) are formed according to these conditions.

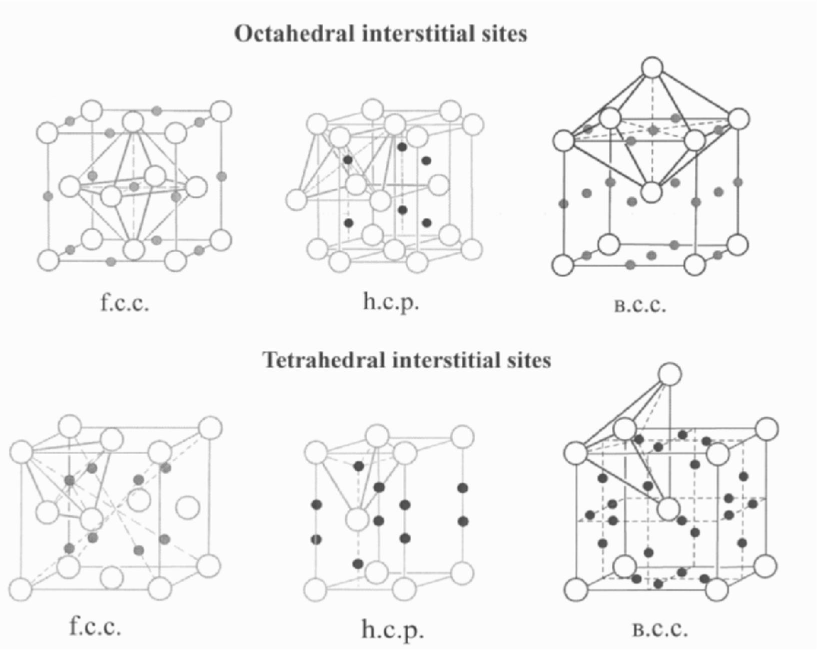


Figure 3. Positions occupied by hydrogen atoms in metallic lattices

As this takes place, hydrogen atoms can occupy quite definite positions in the lattice of metal (octahedral, tetrahedral, or both octa- and tetrahedral interstitial sites).

The ordering of atoms of metallic lattice, containing hydrogen atoms, brings into existence of hydrogen sublattice in the metal volume. In some cases it turns out that metallic atoms in this sublattice are packed closely together 2–3 times closer than hydrogen atoms in solid state. The reason is that the solid hydrogen is molecular crystal.

The solubility of hydrogen atoms in metallic lattice is a rather complicated physicochemical process.

This process has been proposed to your notice in the first part of paper by the example of hexagonal close-packed structures. Many of hydride-forming metals and alloys have such crystal lattices.

2. Hydrogen solubility in metal structures with hexagonal lattices

Theoretical investigation has been carried out on interstitial H atom solubility in ordering alloys with various hexagonal structures, having two types of interstitial sites: octahedral and tetrahedral. Figure 4 demonstrates all possible hexagonal superstructures of binary ordering alloys AB and AB_3. All lattice sites of first and second types are occupied by A and B atoms; the process of atomic ordering occurs at these lattice sites. These lattice sites are nonequivalent from the point of view of the crystal lattice structure, i.e., they have different types of surroundings with neighboring lattice sites. Interstitial sites are occupied by H atoms or vacant. Each of such crystals has both octahedral and tetrahedral interstitial sites of one, two, and even three types depending on their surroundings by the nearest A and B atoms. Types of interstitial sites in different hexagonal lattices are given in Figure 5 and Table 1.

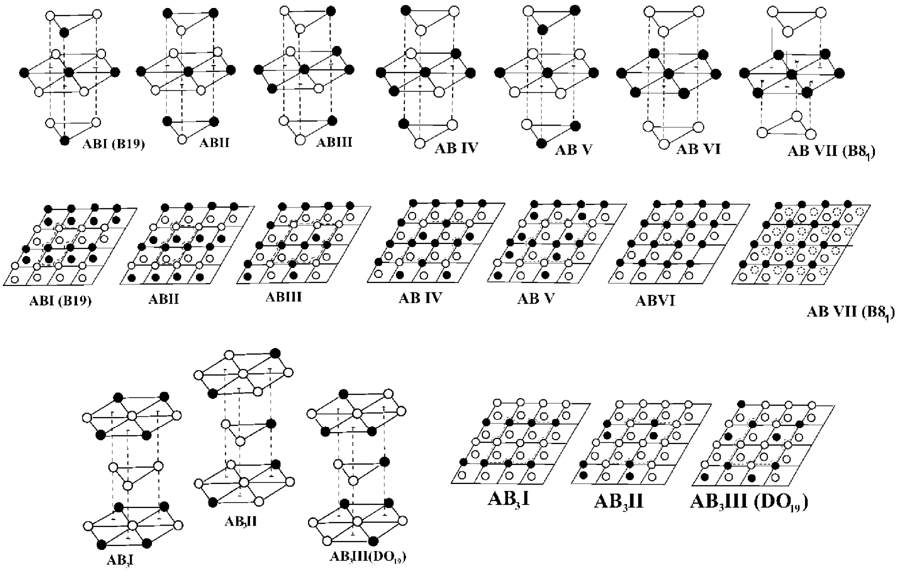


Figure 4. Hexagonal superstructures of AB and AB_3 alloys (B19, $B8_1$, DO_{19}, and other structures) in three-dimensional presentation and in projection on the equatorial plane. The sites of elementary cell are indicated by dotted lines

● – sites of first type corresponding to A atoms
○ – sites of second type corresponding to B atoms

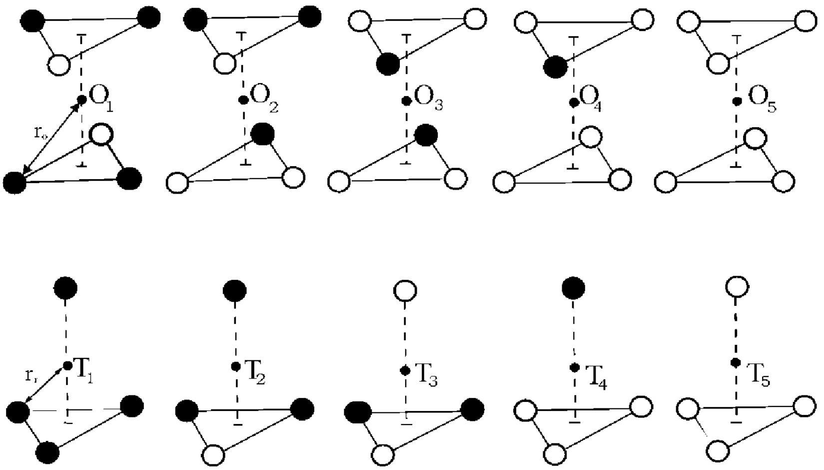


Figure 5. Types of octahedral and tetrahedral interstitial sites in different hexagonal lattices

TABLE 1. The values of structural coefficients m, m_1, m_2, m_3, z, l_1, l_2, l_3 of AB and AB_3

Superstructures	Interstitial sites	m	m_1	m_2	m_3	z	l_1	l_2	l_3
AB – $C_{int.}$									
I	O_1, O_3 T_3	4 8	2 8	2 0	0 0	6 4	4 2	2 –	– –
II, VI, VII	O_2, T_2, T_4	4 8	4 4	0 4	0 0	6 4	3 3	– 1	– –
III	O_2, T_1, T_4, T_5	8 16	8 2	0 12	0 2	6 4	3 4	– 2	– –
IV, V	O_1,O_2, O_3 T_2, T_3, T_5	8 16	2 4	4 8	2 4	6 4	4 3	3 2	2 1
AB_3 – $C_{int.}$									
I	O_3, O_5 T_4	8 16	6 16	2 0	0 0	6 4	2 1	0 –	– –
II, III	O_3, O_4 T_3, T_4, T_5	8 16	4 4	4 8	0 4	6 4	2 2	1 1	– 0

2.1. HYDROGEN SOLUBILITY ALLOYS OF $B8_1$ STRUCTURE

This paper presents the theoretical investigation and determination of interstitial component solubility in AB VII ($B8_1$) alloy and then the derivation of overall formula of interstitial component solubility for all hexagonal structures.

2.1.1. Free energy of alloy

The solution of these problems has been performed by calculation and analysis of crystal free energy (1). The alloy free energy has been found by the configurational method within the approximation of the pair interaction of nearest atoms without considering geometric distortion of lattice. This structure $B8_1$ has two types of tetrahedral T_2, T_4 interstitial sites, defined by different type site surroundings, and one type of octahedral O_2 interstitial site

$$F = E - kT\ln W \tag{1}$$

where k is the Boltzmann constant, T is the absolute temperature. The configurational part of the free energy E and the thermodynamic probability W can be written in the form:

$$E = -\sum_{i=0}^{6} N_0^{(i)}\upsilon_i - \sum_{i=0}^{4}(N_{T_1}^{(i)} + N_{T_2}^{(i)})\upsilon_i' \,, \tag{2}$$

$$W = \prod_{i=0}^{6}\frac{Q_0^{(i)}!}{N_0^{(i)}!(Q_0^{(i)} - N_0^{(i)})!}\cdot\prod_{i=0}^{4}\frac{Q_{T_1}^{(i)}!}{N_{T_1}^{(i)}!(Q_{T_1}^{(i)} - N_{T_1}^{i})!}\cdot\prod_{i=0}^{4}\frac{Q_{T_2}^{(i)}!}{N_{T_2}^{(i)}!(Q_{T_2}^{(i)} - N_{T_2}^{(i)})!}, \tag{3}$$

where $N_0^{(i)}, N_{T_1}^{(i)}, N_{T_2}^{(i)}$ are the numbers of H atoms in O, T_1, T_2 interstitial sites with *i*-configuration, $Q_0^{(i)}, Q_{T_1}^{(i)}, Q_{T_2}^{(i)}$ are the numbers of possible A, B atoms configurations around O, T_1, T_2 interstitial sites for each *i* value, υ_i, υ_i' are the H atoms energies in the octahedral and tetrahedral interstitial sites with the A, B atoms in *i*-configuration in nearest sites.

$$\upsilon_I = i\alpha + (6 - i)\beta, \tag{4}$$

$$\upsilon_i' = i\alpha' + (4 - i)\beta' \,, \tag{5}$$

$\alpha = \upsilon_{AC}$, $\beta = \upsilon_{BC}$, $\alpha' = \upsilon_{AC}'$, $\beta' = \upsilon_{BC}'$ are the interaction energies for the indicated atom pairs, taken with the opposite sign. The *i*-configuration means that the A atoms are present in the *i* nearest sites and the B atoms in the other sites.

The $Q_0^{(i)}, Q_{T_1}^{(i)}, Q_{T_2}^{(i)}$ numbers are determined by

$$\begin{aligned}
Q_0^{(i)} &= N\frac{3!}{l!(3-l)!}P_A^{(1)^l}P_B^{(1)^{(3-l)}}\ \frac{3!}{j!(3-j)!}P_A^{(2)^j}P_B^{(2)^{(3-j)}}, \\
Q_{T_1}^{(i)} &= N\frac{3!}{l!(3-l)!}P_A^{(1)^l}P_B^{(1)^{(3-l)}}\ \frac{1!}{j!(1-j)!}P_A^{(2)^j}P_B^{(2)^{(1-j)}}, \\
Q_{T_2}^{(i)} &= N\frac{1!}{l!(1-l)!}P_A^{(1)^l}P_B^{(1)^{(1-l)}}\ \frac{3!}{j!(3-j)!}P_A^{(2)^j}P_B^{(2)^{(3-j)}},
\end{aligned} \tag{6}$$

where N is the number of interstitial sites corresponding to the O, T_1, T_2 type, $P_A^{(1)}, P_A^{(2)}, P_B^{(1)}, P_B^{(2)}$ are the a priori probabilities of first and second type sites substitution by A, B atoms. These are determined by the *a*, *b* alloy composition ($a + b = 1$) and the long-range order η:

$$P_A^{(1)} = a + \frac{1}{2}\eta, \quad P_B^{(1)} = b - \frac{1}{2}\eta, \quad P_A^{(2)} = a - \frac{1}{2}\eta, \quad P_B^{(2)} = b + \frac{1}{2}\eta. \tag{7}$$

In Eq. (6) $i = j + l$, where l is the number of first type nearest sites and j is the number of second type nearest sites around the present interstitial site, occupied by an A atom.

The calculation of free energy (1) gives the following formula:

$$\begin{aligned} F = {} & \sum_{i=0}^{6} N_0^{(i)} \upsilon_i - \sum_{i=0}^{4} \left(N_{T_1}^{(i)} + N_{T_2}^{(i)}\right) \upsilon_i' - kT \Bigg[\sum_{i=0}^{6} Q_0^{(i)} \ln Q_0^{(i)} + \sum_{i=0}^{4} Q_{T_1}^{(i)} \ln Q_{T_1}^{(i)} \\ & + \sum_{i=0}^{4} Q_{T_2}^{(i)} \ln Q_{T_2}^{(i)} - \sum_{i=0}^{6} N_0^{(i)} \ln N_0^{(i)} - \sum_{i=0}^{4} N_{T_1}^{(i)} \ln N_{T_1}^{(i)} - \sum_{i=0}^{4} N_{T_2}^{(i)} \ln N_{T_2}^{(i)} \\ & - \sum_{i=0}^{6} \left(Q_0^{(i)} - N_0^{(i)}\right) \ln \left(Q_0^{(i)} - N_0^{(i)}\right) - \sum_{i=0}^{4} \left(Q_{T_1}^{(i)} - N_{T_1}^{(i)}\right) \ln \left(Q_{T_1}^{(i)} - N_{T_1}^{(i)}\right) \\ & - \sum_{i=0}^{4} \left(Q_{T_2}^{(i)} - N_{T_2}^{(i)}\right) \ln \left(Q_{T_2}^{(i)} - N_{T_2}^{(i)}\right) \Bigg]. \end{aligned} \tag{8}$$

2.1.2. *Solubility of hydrogen*

The $N_0^{(i)}, N_{T_1}^{(i)}, N_{T_2}^{(i)}$ numbers are constrained by the relation

$$\varphi \equiv \sum_{i=0}^{6} N_0^{(i)} + \sum_{i=0}^{4} (N_{T_1}^{(i)} + N_{T_2}^{(i)}) - N_c = 0, \tag{9}$$

where N_c is the number of C atoms in the alloy.

The free energy minimum conditions

$$\frac{\partial F}{\partial N_0^{(i)}} + \lambda \frac{\partial \varphi}{\partial N_0^{(i)}} = 0, \quad \frac{\partial F}{\partial N_{T_1}^{(i)}} + \lambda \frac{\partial \varphi}{\partial N_{T_1}^{(i)}} = 0, \quad \frac{\partial F}{\partial N_{T_2}^{(i)}} + \lambda \frac{\partial \varphi}{\partial N_{T_2}^{(i)}} = 0, \tag{10}$$

where λ is the Lagrange factor, at $N_c \ll N$ reduce to the solution

$$N_0^{(i)} = DQ_0^{(i)} \exp\frac{\upsilon_i}{kT}, \quad N_{T_1}^{(i)} = DQ_{T_1}^{(i)} \exp\frac{\upsilon_i'}{kT}, \quad N_{T_2}^{(i)} = DQ_{T_2}^{(i)} \exp\frac{\upsilon_i'}{kT}, \tag{11}$$

where $D = \exp(-\lambda/kT)$ is the factor by which the system state function is increased for each additional impurity atom introduced from the external medium.

Summing $N_0^{(i)}, N_{T_1}^{(i)}, N_{T_2}^{(i)}$ (11) over all *i* configurations with taking account of Eq. (6), we find the number of C atoms in O, T_1, T_2 interstitial sites as:

$$N_c^{(0)} = \sum_{i=0}^{6} N_0^{(i)} = DNK_1^3K_2^3, \quad N_c^{(T_1)} = \sum_{i=0}^{4} N_{T_1}^{(i)} = DNK_1'^3K_2', \quad N_c^{(T_2)} = \sum_{i=0}^{4} N_{T_2}^{(i)} = DNK_1' \; K_2'^3, \tag{12}$$

where

$$K_1 = P_A^{(1)} \exp\frac{\alpha}{kT} + P_B^{(1)} \exp\frac{\beta}{kT}, \; K_1' = P_A^{(1)} \exp\frac{\alpha'}{kT} + P_B^{(1)} \exp\frac{\beta'}{kT}, \quad K_2 = P_A^{(2)} \exp\frac{\alpha}{kT} + P_B^{(2)} \exp\frac{\beta}{kT}, \; K_2' = P_A^{(2)} \exp\frac{\alpha'}{kT} + P_B^{(2)} \exp\frac{\beta'}{kT}. \tag{13}$$

The solubility of the interstitial impurity in the $B8_1$ alloy is determined by the C atom concentration, which is obtained by summing Eq. (12) as:

$$S = \frac{1}{3N}\left(N_c^{(0)} + N_c^{(T_1)} + N_c^{(T_2)}\right) = \frac{1}{3}D\left[K_1^3K_2^3 + K_1'K_2'(K_1'^2 + K_2'^2)\right], \tag{14}$$

where 3N is the total number of interstitial sites in the alloy.

The derived formula (14) in view of Eqs. (13) and (7) determines the C atom solubility dependence on the alloy composition *a*, *b*, the temperature T, and the order parameter η.

2.1.3. Concentration dependence of impurity solubility in disordered alloy

In the case of disordered alloy (η = 0)

$$K = K_1 = K_2 = a\exp\frac{\alpha}{KT} + b\exp\frac{\beta}{KT}, \quad K_1' = K_2' = K' = a\exp\frac{\alpha'}{KT} + b\exp\frac{\beta'}{KT} \tag{15}$$

and the formula for the solubility becomes

$$S^0 = S^0(a,T) = \frac{1}{3}D\left(K^6 + 2K'^4\right) = \frac{1}{3}D\left[\left(a\exp\frac{\alpha}{kT} + b\exp\frac{\beta}{kT}\right)^6 + 2\left(a\exp\frac{\alpha'}{kT} + b\exp\frac{\beta'}{kT}\right)^4\right]. \tag{16}$$

The dependence of the solubility on the concentration *a*, *b* is determined also by the relation between the energy parameters α, β, α′, β′. In this case an extremal dependence of the solubility on composition may occur. The plot that demonstrate the $S^0(a)$ as a function of composition *a* is shown by full line in Figure 6.

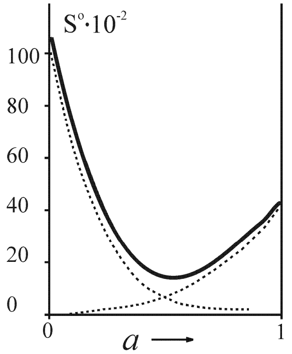


Figure 6. The concentration dependence of solubility of interstitial impurity in alloy of NiAs type

$$\exp\frac{\alpha}{kT} = 0{,}25, \quad \exp\frac{\beta}{kT} = 1, \quad \exp\frac{\alpha'}{kT} = 0{,}8, \quad \exp\frac{\beta'}{kT} = 0{,}2$$

$$(\alpha < \beta, \qquad \alpha' > \beta')$$

In the case when C atoms are located in octahedral or only in tetrahedral interstitial sites the solubility will be determined by the following Eq. (17) for ordered alloy and by Eq. (18) for disordered alloy (η = 0) that give a monotonic dependences (dotted lines) on the composition *a* (as was shown in Figure 6) for ordered alloy.

$$S_0 = \frac{N_c^{(0)}}{N} = DK_1^3K_2^3, \qquad S_T = \frac{N_c^{(T_1)} + N_c^{(T_2)}}{2N} = \frac{1}{2}DK_1'K_2'\left(K_1'^2 + K_2'^2\right), \tag{17}$$

for disordered alloy (η = 0)

$$S_0^0 = D\left(a\exp\frac{\alpha}{kT} + b\exp\frac{\beta}{kT}\right)^6, \qquad S_T^0 = D\left(a\exp\frac{\alpha'}{kT} + b\exp\frac{\beta'}{kT}\right)^4. \tag{18}$$

2.1.4. Temperature dependence of impurity solubility in disordered alloy

The dependence of the solubility on the temperature S_O^0 (T) or S_T^0 (T) shows that these functions may have a minimum under the condition

$$-\frac{\alpha}{\beta}=\frac{b}{a}\exp\frac{\beta-\alpha}{kT_m} \tag{19}$$

for the octahedral interstitial site and

$$-\frac{\alpha'}{\beta'}=\frac{b}{a}\exp\frac{\beta'-\alpha'}{kT_m} \tag{20}$$

for the tetrahedral interstitial site, T_m is the temperature at the solubility minimum. From Eqs. (19) and (20) it follows that in this case the energy parameters α and β or α' and β' have different signs. The plot of temperature dependence of solubility is shown in Figure 7.

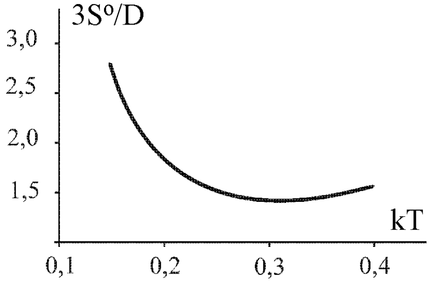


Figure 7. The temperature dependence of the solubility of interstitial impurity in alloy of NiAs type

2.1.5. Influence of atomic order on the solubility of an impurity in the alloy

The influence of long-range order η on the solubility of interstitial atoms when they occupy octahedral or tetrahedral interstitial sites is conveniently calculated for their relative values by

$$f_0=\frac{S_o}{S_0^o}=(1-\text{æ}_1^2)^3, \qquad f_T=\frac{S_T}{S_T^o}=1-\text{æ}_2^4, \tag{21}$$

where

$$\text{æ}_1=\frac{1}{2}\eta\frac{\exp\frac{\alpha}{kT}-\exp\frac{\beta}{kT}}{a\exp\frac{\alpha}{kT}+b\exp\frac{\beta}{kT}}; \qquad \text{æ}_2=\frac{1}{2}\eta\frac{\exp\frac{\alpha'}{kT}-\exp\frac{\beta'}{kT}}{a\exp\frac{\alpha'}{kT}+b\exp\frac{\beta'}{kT}}. \tag{22}$$

From Eqs. (21) and (22) it follows that the atomic order η decreases the solubility of the interstitial impurity in alloys with the examined structure, as illustrated in Figure 8, and it being found that the influence of order on the solubility is stronger in the case of the octahedral interstitial site occupation by the interstitial atoms. If interstitial atoms fill simultaneously all positions, the solubility dependence on order parameter will be displayed graphically as some intervening line between lines, shown in Figure 8. From the dependence of the solubility at atomic ordering it is possible to conclude in which interstitial sites of the alloy the interstitial atom is located and this may allow one to predetermine the physical properties of the alloys.

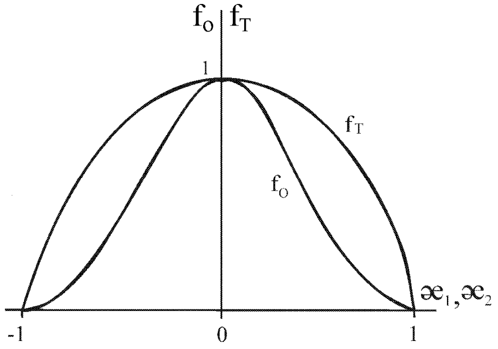


Figure 8. The relative solubility of interstitial impurity in octa- and tetrahedral interstitial sites of alloys of NiAs type in dependence on parameters æ_1, æ_2, proportional to long-range order parameter

2.1.6. Solubility of hydrogen in alloys of B19 and DO$_{19}$ structures

The analogous calculation of the solubility of the interstitial impurity as a function of the H atom concentration, temperature, long-range order have been carried out for AB and AB$_3$ alloys of other hexagonal structures. The results of such calculations are listed below [19–22].

For alloys with the B8$_1$ structure (NiAs type):

$$\left.\begin{aligned}
&S=\frac{1}{3}D\left[K_1^3K_2^3+K_1'K_2'(K_1'^2+K_2'^2)\right],\\
&S^0=\frac{1}{3}D\left(K^6+2K'^4\right),\\
&S_0=\frac{N_c^{(0)}}{N}=DK_1^3K_2^3\,,\quad S_T=\frac{N_c^{(T_1)}+N_c^{(T_2)}}{2N}=\frac{1}{2}DK_1'K_2'\left(K_1'^2+K_2'^2\right),\\
&S_0^o=DK^6,\quad S_T^o=DK'^4,\\
&f_0=S_o/S_0^o=(1-\text{æ}_1^2)^3,\quad f_T=S_T/S_T^o=1-\text{æ}_2^4,\\
&\text{æ}_1=\frac{1}{2}\eta\frac{\exp\frac{\alpha}{kT}-\exp\frac{\beta}{kT}}{a\exp\frac{\alpha}{kT}+b\exp\frac{\beta}{kT}};\qquad \text{æ}_2=\frac{1}{2}\eta\frac{\exp\frac{\alpha'}{kT}-\exp\frac{\beta'}{kT}}{a\exp\frac{\alpha'}{kT}+b\exp\frac{\beta'}{kT}}.
\end{aligned}\right\}\quad(23)$$

For alloys with the B19 structure (MgCd type):

$$\left.\begin{aligned}
&S=\frac{N_0+N_T}{3N}=\frac{1}{6}D\left[K_1^2K_2^2\left(K_1^2+K_2^2\right)+4K_1'^2K_2'^2\right],\\
&S^0=\frac{1}{3}D(K^6+2K'^4),\\
&S_0=\frac{N_C^{(0_1)}+N_C^{(0_2)}}{N}=\frac{1}{2}DK_1^2K_2^2\left(K_1^2+K_2^2\right),\ S_T=\frac{N_C^{(T)}}{2N}=DK_1'^2K_2'^2,\\
&S_0^o=DK^6,\ \ S_T^o=DK'^4,\\
&f_0=S_0/(S_0)_{\eta=0}=(1-\ae_1^2)(1-\ae_1^4),\quad f_T=S_T/(S_T)_{\eta=0}=(1-\ae_2^2)^2
\end{aligned}\right\}\qquad(24)$$

For alloys with the DO_{19} structure (Ni_3Sn type):

$$\left.\begin{aligned}
&S_0=N_C^{(0)}/N=\frac{1}{4}DK_2^4(3K_1^2+K_2^2),\quad S_T=N_C^{(T)}/2N=DK_1'K_2'^3,\\
&f_0=\frac{1}{4}(1-\ae_1)^4[(1-\ae_1)^2+3(1+3\ae_1)^2],\quad f_T=(1+3\ae_2)(1-\ae_2)^3,\\
&\ae_1=\frac{1}{4}\eta\frac{\exp\frac{\alpha}{kT}-\exp\frac{\beta}{kT}}{a\exp\frac{\alpha}{kT}+b\exp\frac{\beta}{kT}};\quad \ae_2=\frac{1}{4}\eta\frac{\exp\frac{\alpha'}{kT}-\exp\frac{\beta'}{kT}}{a\exp\frac{\alpha'}{kT}+b\exp\frac{\beta'}{kT}}.
\end{aligned}\right\}\qquad(25)$$

The Eqs. (23)–(25) permit for each concrete alloy to define the dependence character of solubility of interstitial impurity of definite kind on concentration *a*, temperature T, degree of long-range order η, if energetic parameters α, α′, β, β′ are known.

Figures 9 and 10 illustrate the plots of dependences of relative solubilities on order parameters $f_0(\ae_1)$, $f_T(\ae_2)$, $f(\ae)$ for considered structures B19, $B8_1$, and DO_{19}. As shown by these figures, the long-range order decreases the solubility of interstitial impurity. At the arrangement of interstitial atoms in tetrahedral interstitial sites the influence of long-range on the solubility will be more considerable for structure B19 and more weak for structure $B8_1$.

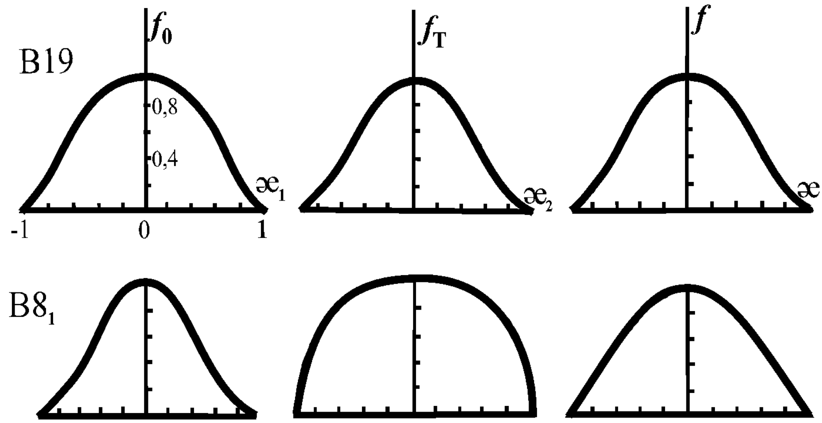


Figure 9. The relative solubilities f_0, f_T, f in dependence on the parameters $\ae_1$, $\ae_2$, $\ae$, proportional to η, for the AB alloys of B19 and $B8_1$ structures

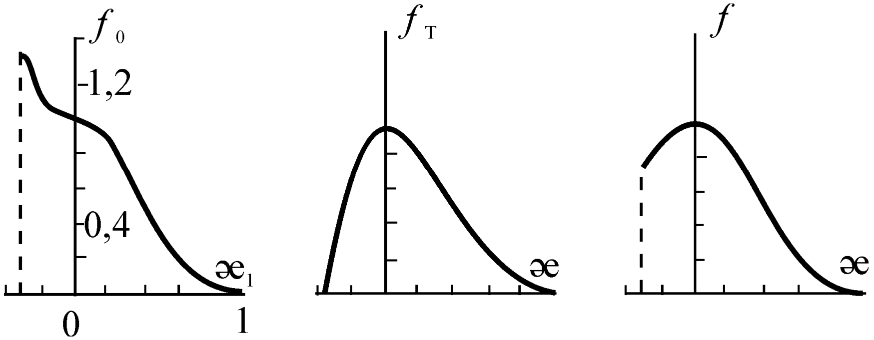


Figure 10. The relative solubilities f_0, f_T, f in dependence on the parameters $\ae_1$, $\ae_2$, $\ae$, proportional to η, for the AB_3 alloys of DO_{19} structures

The ordering of atoms on the sites of AB_3 alloys of DO_{19} structure increases the solubility of interstitial impurity, if C atoms are distributed over the octahedral interstitial sites and $\ae$ parameter is negative ($\beta < \alpha$). In the rest cases the atomic order prevents the dissolution of interstitial impurity. At the boundary values of order parameter $\ae = -1/3$ and $+1$ the concentration of interstitial atoms in T positions reduces to zero.

However it should be pointed out that parameter $\ae$, determined by long-range order η, concentrations a, b, and energetic parameters α, β, will be dissimilar for octa- and tetrahedral interstitial sites, because energies α and β of interatomic interaction depend on the distance between atoms and it will be different for pairs AH, BH, when H atom will be in octa- O or tetrahedral T interstitial site, i.e., it is necessary to consider the f value as a function of $\ae_1, \ae_2$ parameters. Graphically the relative solubility f will be the some curve on the surface f $(\ae_1, \ae_2)$ given in Figure 11. The ordinates of this curve for crude estimate are presented by the semi-sum of values f_0 and f_T.

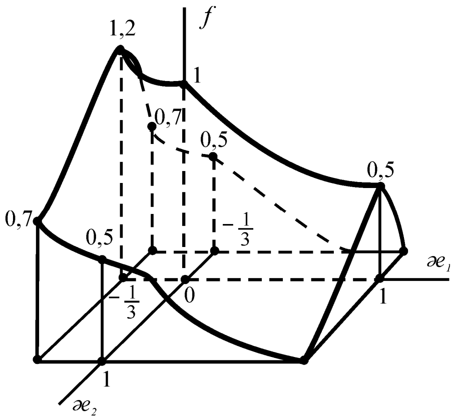


Figure 11. The surface on which the plot of relative solubility f( ) of C impurity in the AB_3 alloy is arranged

2.2. GENERAL FORMULA FOR HYDROGEN SOLUBILITY IN ALLOYS OF HEXAGONAL STRUCTURES

In the closing of this section we have derived the general formulas that determine the solubility of interstitial impurity in alloys of different hexagonal structures, occurring in nature. Figure 4 shows all possible, realized, and hypothetical, hexagonal superstructures of binary ordering alloys AB and AB_3 and types of interstitial sites in these hexagonal lattices are given in Figure 5 and Table 1. The theory proposes that impurity atoms C are introduced only in octa-, or only in tetrahedral interstitial sites, assuming that concentration of interstitial impurity is small ($N_C << N$).

The appearance impurity atom C in alloy increases its configurational energy E_C by the value μ (chemical potential) and energy E_T of thermal fluctuations by the value ν (phonon potential). We shall examine the distribution of C atoms in potential field, determined by energy $u_{ij} - \mu - \nu$, where u_{ij} is the energy of C atom in interstitial site ij. Numbers i, j indicate the number of A atoms in the sites nearest to interstitial site correspondingly of first and second type.

According to Boltzmann distribution the number of C atoms in interstitial ij is equal to:

$$N_{ij} = Q_{ij}\exp\left(-\frac{u_{ij}-\mu-\nu}{kT}\right), \tag{26}$$

where Q_{ij} is the number of interstitial sites of ij type determined by the number of configurations of A, B atoms of alloy around the interstitial site:

$$\begin{aligned} Q_{ij} = \frac{N}{m}[& \frac{l_1!}{i!(l_1-i)!}\cdot\frac{(z-l_1)!}{j!(z-l_1-j)!} m_1 P_A^{(1)^i} P_B^{(1)^{(l_1-i)}} P_A^{(2)^j} P_B^{(2)^{(z-l_1-j)}} \\ & + \frac{l_2!}{i!(l_2-i)!}\cdot\frac{(z-l_2)!}{j!(z-l_2-j)!} m_2 P_A^{(1)^i} P_B^{(1)^{(l_2-j)}} P_A^{(2)^j} P_B^{(2)^{(z-l_2-j)}} \\ & + \frac{l_3!}{i!(l_3-i)!}\cdot\frac{(z-l_3)!}{j!(z-l_3-j)!} m_3 P_A^{(1)^i} P_B^{(1)^{(l_3-i)}} P_A^{(2)^j} P_B^{(2)^{(z-l_3-j)}}], \end{aligned} \tag{27}$$

where $m = m_1 + m_2 + m_3$ is the number of interstitial sites in the lattice cell; m_1 is the number of interstitial sites of first type having the greater amount of neighboring sites of first type legal for A atoms; m_2, m_3 are the numbers of interstitial sites of second and third type; l_1, l_2, l_3 are the numbers of sites of first type nearest to interstitial site correspondingly for interstitial sites of first, second, and third type; z number determines the coordination of interstitial site. From z neighboring sites for each interstitial site l is the number of nearest sites of first type and $(z-l)$ is the number of nearest sites of second type. The values of these structural coefficients m, m_1, m_2, m_3, l_1, l_2, l_3, z for investigated superstructures are given in Table 1.

Summing the N_{ij} numbers (26) over the i and j, we find the full number of C atoms, introducing in octa- and tetrahedral interstitial sites:

$$N_c = \lambda\upsilon \sum_{i=0}^{\ell_1}\sum_{i=0}^{\ell_2}\sum_{i=0}^{\ell_3}\sum_{j=0}^{z-\ell_1}\sum_{j=0}^{z-\ell_2}\sum_{j=0}^{z-\ell_3} Q_{ij}\exp\frac{-u_{ij}}{kT}, \tag{28}$$

where $\lambda = \exp\frac{\mu}{kT}$; $\upsilon = \exp\frac{\nu}{kT}$.

Substituting here the value of energy u_{ij}

$$u_{ij} = (i+j)\alpha + (z-i-j)\beta, \qquad \alpha = -\upsilon_{AC}, \;\; \beta = -\upsilon_{BC} \tag{29}$$

and the Eq. (27), we receive the equation:

$$N_c = \frac{N\lambda\upsilon}{m}\left(m_1 K_1^{\ell_1} K_2^{z-\ell_1} + m_2 K_1^{\ell_2} K_2^{z-\ell_2} + m_3 K_1^{\ell_3} K_2^{z-\ell_3}\right),$$
$$K_1 = P_A^{(1)} \exp\frac{\alpha}{kT} + P_B^{(1)} \exp\frac{\beta}{kT}, \quad K_2 = P_A^{(2)} \exp\frac{\alpha}{kT} + P_B^{(2)} \exp\frac{\beta}{kT}. \tag{30}$$

The relative concentrations of interstitial atoms for octa- and tetrahedral interstitial sites are determined by the relations

$$f_0 = N_c/N, \qquad f_T = N_c/2N. \tag{31}$$

Substituting into the formula (30) the numbers m, m_1, m_2, m_3, l_1, l_2, l_3 from Table 1 and known formulae for probabilities (7), we find the solubility of interstitial impurity in alloy of each structure correspondingly for octa- and tetrahedral interstitial sites in dependence on alloy composition, temperature and degree of long-range order.

2.3. COMPARISON OF THE THEORY WITH EXPERIMENTAL DATA

Now we shall fulfill the comparison of the results of theoretical calculations with experimental data on investigation of the solubility of interstitial impurities.

For the theoretical plots we use the dissolution heat values λ (A, C) of the interstitial impurity C (H, C, N, O) in the pure A or B metal which in units of $J \cdot mol^{-1}$ are listed in Table 2.

The dissolution heats are related to the energetic parameters α, β (or α′, β) by the relation

$$-zR\,(\alpha - \beta) = k\,[\lambda(A, C) - \lambda(B, C)] \tag{32}$$

where R is the gas constant; z = 6 for octahedral interstitial sites and z = 4 for tetrahedral interstitial sites, k is the Boltzmann constant.

The D factor in the theoretical Eqs. (23)–(25) is determined from the experimental plots.

Experimental investigations of concentration and temperature dependences of interstitial impurity solubility show that they can be both monotonic and external [8, 12, 23–26]. In Figures 12 and 13 the experimental data for concentration and temperature dependences of hydrogen solubility in Pd–Pt, Fe–V, Pd–Ni, Fe–Ni alloys, carbon in Fe–Ni alloy, nitrogen in Fe–Co, Fe–Mn, Fe–Si alloys, oxygen in Ag–Au alloy are shown by the points; the theoretical curves are shown by continuous lines on these figures. As is evident from Figures 12 and 13 in the majority of cases the good agreement between theory and experimental data is observed.

TABLE 2. The dissolution heat λ (A, C) of the interstitial impurity C (H, C, N, O) the pure metal A (or B) [23–27]

#	Atoms of interstitial Impurity	Metal A (or B)	Dissolution heat of impurity, $\text{J} \cdot \text{mol}^{-1}$
1	H	Fe	13,300
2	H	Ni	18,163
3	H	Pd	–8,370
4	H	Pt	148,149
5	H	V	–32,225
6	C	Fe	43,524
7	C	Ni	36,200
8	N	Co	73,000
9	N	Fe	–12,560
10	N	Mn	–87,000
11	N	Ni	47,300
12	N	Si	15,320
13	N	V	–428,000
14	O	Ag	39,000
15	O	Au	10,2000

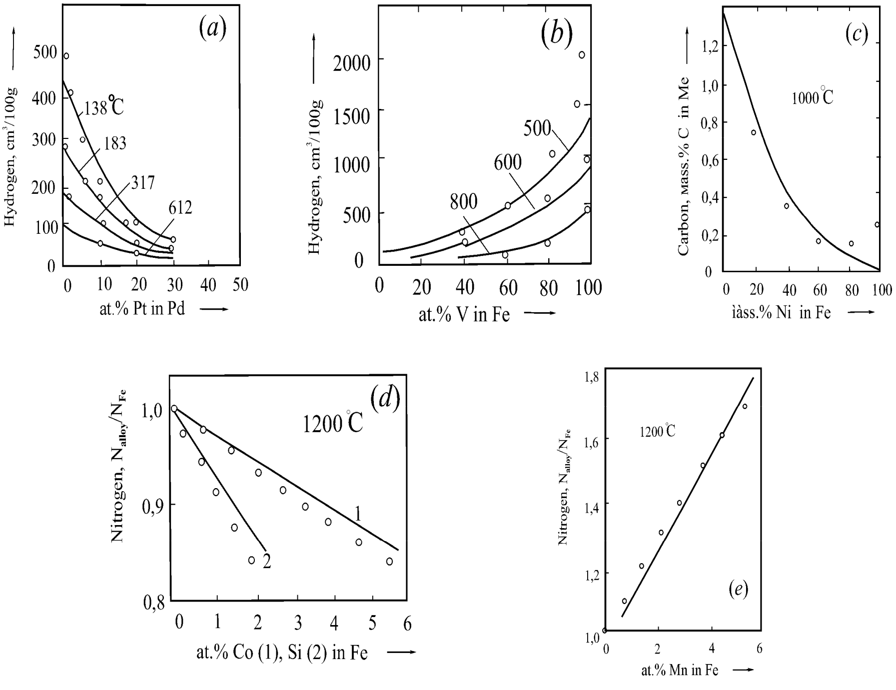


Figure 12. The concentration dependences of hydrogen solubility in Pd–Pt (a), Fe–V (b) alloys, carbon solubility in Fe–Ni (c) and nitrogen solubility in Fe–Co, Fe–Mn (d, e) alloys

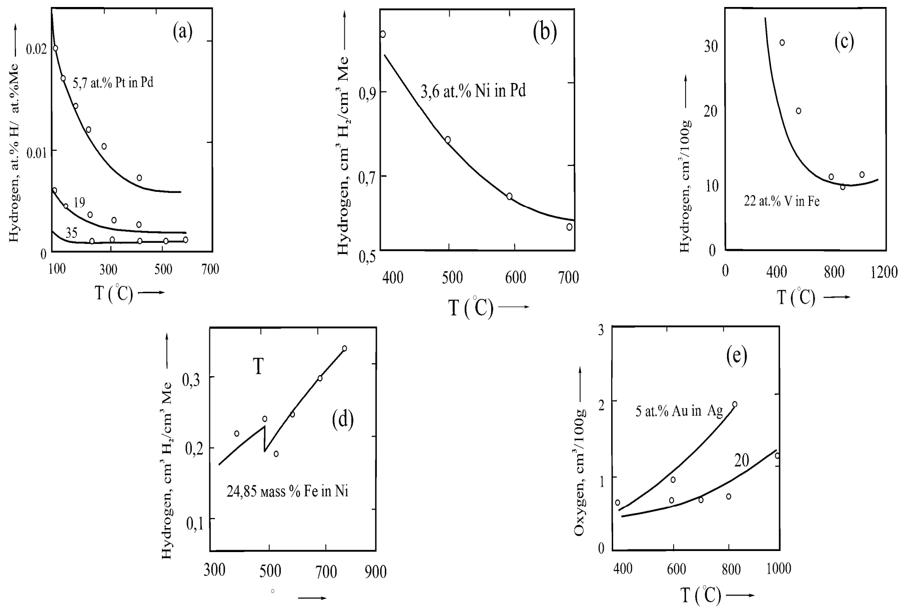


Figure 13. The temperature dependences of hydrogen solubility in Pd–Pt (a), Pd–Ni (b), Fe–V (c), Fe–Ni (d) and oxygen solubility in Ag–Au (e) alloys. The theoretical curves are shown by continuous lines; the points correspond to the experimental data

There is a minimum in the experimental temperature dependence of hydrogen solubility in the FeV–H alloy [28]. For this alloy the condition

$$-\frac{\alpha}{\beta} = \frac{a}{b} \exp \frac{\beta-\alpha}{kT} \tag{33}$$

must be satisfied and the dissolution heats λ (Fe, H) and λ (V, H) must have unlike signs (necessary condition). As seen from Table 2, these values unlike signs. But for the FeV–H alloy, tests of condition (33) show that the right side of Eq. (33) is approximately 3.5 times larger than the left hand side.

In the case of the $FeNi_3$–H alloy at temperature $T_\eta \approx 500^\circ C$ the atomic order–disorder phase transition takes place. In this alloy in accordance with Eq. (25) for f_0 with the value of dissolution heat (see Table 2), the atomic order must increase the hydrogen solubility. This theoretical conclusion is also in accordance with the experimental data.

3. Hydrogen in fullerites

3.1. INTRODUCTION

The discovery of fullerenes [29–34] and features of their formation, structure, and physical and chemical properties are of great scientific interest. Fullerenes have made investigators pay attention to their unusual hydrogen-sorbing properties [35–48]. Under certain conditions fullerenes can accept and donate hydrogen atoms [49–51]. The research into the processes of their reversible reaction with hydrogen is of interest in connection with the development of systems for hydrogen accumulation and storage [52–54].

Theoretically, the hydrogen storage capacity prospects for new materials seem rather optimistic. When one hydrogen atom is joined to each carbon atom (what is quite probable), there appears a possibility for producing a sorbing matrix based on these materials. It allows storage of up to 7.7 wt.% H_2.

Before considering the features of hydrofullerite formation, one should note that hydrogen forming these fullerenes exists in the lattice in different energy states and geometric positions. At least, two hydrogen states are known in the hydrofullerene: lattice and fullerenated hydrogen. Lattice hydrogen is hydrogen existing in solid solution and distributed in interstitial sites of the lattice. Its state is defined by the energy of interatomic interaction and also with fullerene molecules. The content of hydrogen corresponds to the $C_{60}H_x$ compound, where x is an integer (<6) depending on the crystal structure. Fullerenated hydrogen is hydrogen whose atoms are chemically bound with carbon atoms that form the fullerene cage. This hydrogen can be also in two exo- and endostates. Hydrogen is a component of the product formed by direct hydrogenation of the fullerene molecules, presented in lattice sites. Thus, the hydrogenated molecules of fullerene are located in the sites of the crystal lattice and make the simplest particles of hydrofullerites. This type of hydrogen is formed in the fcc lattice of $C_{60}H_x$ hydrofullerite at $x > 2$, and in the bcc lattice it is formed at $x > 6$. It has been found that formation of lattice hydrogen is more energetically favorable in comparison to fullerenated hydrogen [55].

By direct noncatalytic hydrogenation of fullerite in solid phase [56–58] the simplest fullerene hydrides are formed at the high enough temperature and high pressure of hydrogen atmosphere. They are mono-, di-, triango-, or tetra-hydrofullerenes ΦH, ΦH_2, ΦH_3, ΦH_4 [59], where $\Phi = C_{60}, C_{70}, C_{76}, C_{78}, C_{84}$ is one of the called fullerenes, which by mass makes up respectively 83% C_{60}, 15% C_{70}, and 2% of the all rest high fullerenes. As found out experimentally, the pure fullerite has simple cubic lattice (scl) and at temperature above 260 K the hydrogenous solid-phase fullerites have both body-centered cubic lattice (bccl) [39, 60, 61] and face-centered cubic lattice (fccl) [62, 63], depending on production method.

The aim of present work is theoretical study of hydrogen solubility in ordering bcc and fcc crystals of fullerites on the assumption that hydrogen atoms are distributed over interstitial sites of different types: (a) octahedral, tetrahedral in bcc lattice; (b) octahedral, tetrahedral, trigonal, and bigonal in fcc lattice, i.e., the lattice distribution of hydrogen atoms has been considered.

Such distribution of lattice hydrogen over interstitial sites of different types allows an explanation for high solubility of hydrogen in fullerite with production of hydrofullerenes (deuterofullerenes) ΦH_x (ΦD_x), where x is integer depending on the crystal structure within the range $0 < x < 18$ [64, 65], Φ is fullerene $\Phi_1 = C_{60}$, $\Phi_2 = C_{70}$, or a combination of both. It is assumed that only C_{60} and C_{70} fullerenes enter into the composition of fullerite, because concentration of higher fullerenes is small. Two-component fullerite from $\Phi_1 = C_{60}$ and $\Phi_2 = C_{70}$ will be studied. The solid-phasefullerite Φ_1–Φ_2 of any composition was produced experimentally in [66–69]. As it was substantiated in [66], due to the entropy term the Φ_1–Φ_2 fullerite crystal is more stable thermodynamically compared to the pure fullerene components or their mixture. Their molecular concentrations are equal to $c_1 = 0.85$ and $c_2 = 0.15$ respectively. We consider that crystal lattices of fullerite of sc phase as well as with hydrogen of bcc and fcc phases are geometrically ideal.

To solve these problems the free energies of crystals have been calculated on the basis of molecular-kinetic concept, taking in the account the interaction of nearest fullerenes $\Phi_1\Phi_1$, $\Phi_2\Phi_2$, $\Phi_1\Phi_2$, as well as fullerenes interaction with hydrogen atoms Φ_1H, Φ_2H and also interaction between hydrogen atoms HH.

3.2. HYDROGEN SOLUBILITY IN BCC FULLERITE

The free energy F_1 of bcc phase (Figure 14) is calculated by the method of average energies by the formula

$$F_1 = E_1 - kT\ln W_1 - kTN_H\ln\lambda, \tag{34}$$

where E_1 is the configuration internal energy, W_1 is the thermodynamical probability, k is Boltzmanns constant, T is the absolute temperature, N_H is the number of hydrogen atoms, λ is hydrogen activity. We also introduce the following symbols:

N is the number of lattice sites (fullerenes),

N_1, N_2 are the numbers of Φ_1, Φ_2 fullerenes,

N_{11}, N_{22}, N_{12} are the numbers of the nearest pairs of $\Phi_1\Phi_1$, $\Phi_2\Phi_2$, $\Phi_1\Phi_2$ molecules,

$c_1 = N_1/N$, $c_2 = N_2/N$ are molecular concentrations of Φ_1, Φ_2 fullerenes,

$c_1 + c_2 = 1$,

$\upsilon_{11} = \upsilon_{11}\left(d_1/\sqrt{2}\right)$, $\upsilon_{22} = \upsilon_{22}\left(d_1/\sqrt{2}\right)$, $\upsilon_{12} = \upsilon_{12}\left(d_1/\sqrt{2}\right)$ are energies with opposite sign for interaction of $\Phi_1\Phi_1$, $\Phi_2\Phi_2$, $\Phi_1\Phi_2$ fullerene pairs,

$\upsilon_{H1} = \upsilon_{H1}\ d_1\sqrt{5}/4$, $\upsilon_{H2} = \upsilon_{H2}\ d_1\sqrt{5}/4$ are energies with opposite sign for interaction of Φ_1H, Φ_2H pairs,

$\upsilon_{HH} = \upsilon_{HH}\left(d_1/2\sqrt{2}\right)$, $\upsilon'_{HH} = \upsilon'_{HH}(d_1/2)$ are interaction energies between hydrogen atoms, d_1 is bcc lattice parameter.

Using the taken symbols, we get the formulae for configuration energy E_1 and thermodynamic probability W_1:

$$E_1 = -N_{11}\upsilon_{11} - N_{22}\upsilon_{22} - N_{12}\ln N_{12} - N_{H1}\upsilon_{H1} - N_{H2}\upsilon_{H2} - N_{HH}\upsilon_{HH} - N'_{HH}\upsilon'_{HH}, \tag{35}$$

$$\ln W_1 = N\ln N - N_1\ln N_1 - N_2\ln N_2 + 6N\ln 6N - N_H\ln N_H - (6N - N_H)\ln(6N - N_H). \tag{36}$$

The numbers of pairs can be expressed by concentrations c_1, c_2, c_H for bcc phase by formulae:

$$\begin{aligned} &N_{11} = 4Nc_1^2,\ N_{22} = 4Nc_2^2,\ N_{12} = 8Nc_1c_2, \\ &N_{H1} = 4Nc_1c_H,\ N_{H2} = 4Nc_2c_H,\ N_{HH} = \frac{1}{3}Nc_H^2,\ N'_{HH} = \frac{1}{6}Nc_H^2, \end{aligned} \tag{37}$$

where $c_H = N_H/N$ is the hydrogen concentration in relation to the fullerenes number.

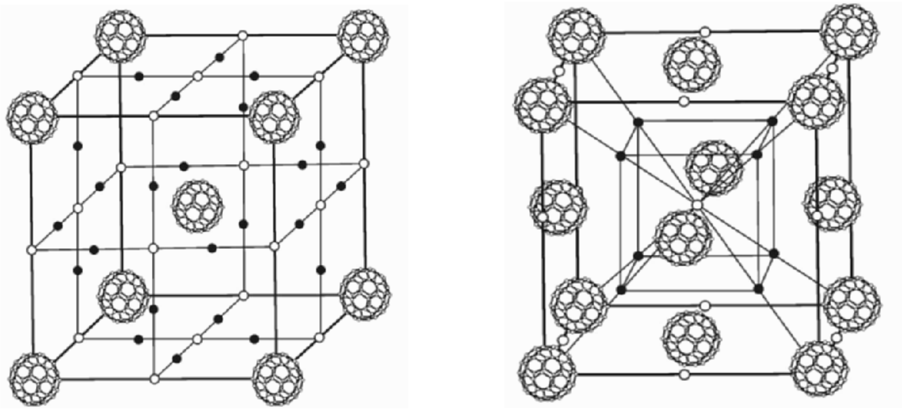


Figure 14. Unit cells of fullerite with bcc (a) and fcc (b) structures with lattice hydrogen only. (Shaded circle) Sites of crystalline lattices, in which fullerenes molecules are distributed; (•) octahedral (O) interstitial sites; (o) tetrahedral

Substituting values of E_1 (35) and W_1 (36) in Eq. (34) we calculate the free energy of bcc phase per one fullerene molecule

$$f_1 = \frac{F_1}{N} = -V_1(c_1) - V_2(c_1)c_H - V_H c_H^2 + kT(c_1 \ln c_1 + c_2 \ln c_2) + kT\left[c_H \ln\frac{c_H}{6} + (6 - c_H)\ln\frac{6 - c_H}{6}\right] - kTc_H \ln\lambda \ , \tag{38}$$

where

$$V_1 = 4\left(c_1^2\upsilon_{11} + c_2^2\upsilon_{22} + 2c_1c_2\upsilon_{12}\right), \ V_2 = 4(c_1\upsilon_{H1} + c_2\upsilon_{H2}), \ V_H = \frac{1}{3}\left(\upsilon_{HH} + \frac{1}{2}\upsilon'_{HH}\right) \tag{39}$$

are energetic parameters of the system, which are determined by the interaction energies, taken with opposite sign, of the nearest pairs and by fullerene concentrations c_1, c_2.

The derived formula (38) determines the dependence of free energy of bcc fullerite on temperature, fullerene concentrations, hydrogen content, its activity, and energetic constants.

The hydrogen solubility is determined by its equilibrium concentration in the lattice and is found from the condition $\partial F_1/\partial c_H = 0$, that gives equation

$$\left(V_2 + 2V_H c_H^o\right)\Big/ \ln\frac{c_H^o}{\lambda\left(6 - c_H^o\right)} = kT \ . \tag{40}$$

The Eq. (40) gives the relation defining the equilibrium value of hydrogen concentration c_H^o in bcc fullerite depending on temperature.

It is easy to verify that function $c_H^o(T)$ is monotonic and concentration c_H^o vary over a range

$$\begin{gathered} 3 \le c_H^o \le 6, \ \text{if} \ \ \lambda = 1 \ \ \text{and} \ \ V_2 > 0, \ V_H > 0, \\ 0 \le c_H^o \le 3, \ \text{if} \ \ \lambda = 1 \ \ \text{and} \ \ V_2 < 0, \ V_H < 0, \\ 0 \leftarrow \frac{6\lambda}{1+\lambda} = c_H^{\min} \le c_H^o \le 6, \ \text{if} \ \lambda << 1 \ \text{and} \ V_2 > 0, \ V_H > 0, \\ 0 \le c_H^o \le c_H^{\max} = \frac{6\lambda}{1+\lambda} \to 6, \ \text{if} \ \lambda >> 1 \ \text{and} \ V_2 < 0, \ V_H < 0 \end{gathered} \tag{41}$$

taking on the minimum or maximum value in the extreme points of interval of c_H values.

Figure 15 shows the plots of temperature dependence of hydrogen solubility in bcc phase, constructed for fullerenes concentrations $c_1 = 0{,}85$, $c_2 = 0{,}15$ and for the different values of activity and energetic parameters.

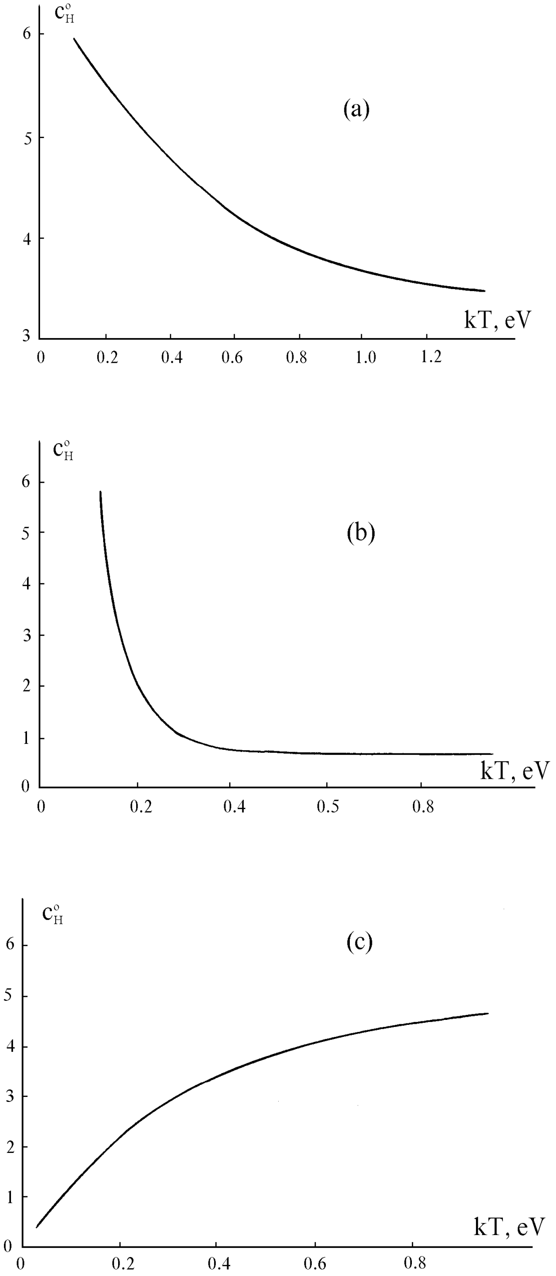


Figure 15. The plots of temperature dependence of hydrogen solubility in bcc phase for fullerenes concentrations and for different values of activity and energetic parameters

$$(a)\ \lambda = 1,\quad V_{\Phi H} = 0{,}1\,eV,\ V_H = 0{,}05\,eV,$$
$$(b)\ \lambda = 0{,}1,\quad V_{\Phi H} = 0{,}1\,eV,\ V_H = 0{,}05\,eV,$$
$$(c)\ \lambda = 10,\quad V_{\Phi H} = -0{,}1\,eV,\ V_H = -0{,}1\,eV.$$

As can be seen from Figure 15(a), (b), (c), the regularities of temperature dependence of hydrogen solubility mentioned below in Eq. (41) manifest themselves. The solubility decreases with increase in temperature when V_2, V_H energies take positive values, i.e., $\Phi H, HH$ pairs interactions have the attraction character. The hydrogen solubility in fullerite increases with a rise in temperature when interaction of $\Phi H, HH$ pairs have the repulsion character (as mentioned in [39] for HH pairs), i.e., for negative V_2 and V_H energies. This is in full accordance with experimental data. The high hydrogen solubility $c_H^o \to 6$ is reached owing to great activity of hydrogen atoms. The hydrogen atoms activity depends on experimental conditions, the procedure of hydrogenation and availability of catalysts.

It might be well to point out also that at sufficiently low temperatures the curves of $c_H^o(T)$ dependences are more steep, but their slope decreases with increase in temperature and $c_H^o(T)$ curves become comparatively flat. By this is meant that at rather high temperatures, when the $c_H^o(T)$ dependence is more low, the fullerenated hydrogen may appear, i.e., a set of hydrofullerenes with different hydrogen content is formed, as revealed also experimentally [39].

3.3. HYDROGEN SOLUBILITY IN FCC FULLERITE

In this paper the hydrogen solubility in the fcc phase (Figure 16) is studied on the assumption that hydrogen atoms are placed in octahedral O, tetrahedral Θ, trigonal Q, and bigonal D interstices. As it was found out experimentally [62, 64], hydrogen sorption did not change the fcc structure of fullerite but only increased the lattice constant d_2 from 1.417 nm at x = 0–1,448 nm at x = 18.

The calculations of free energy of fcc fullerite is carried out by the configuration method, i.e., taking into account the possibility of formation of different configurations of Φ_1–Φ_2 fullerenes around hydrogen atoms. This approach is more successive compared to the method of average energies and makes possible to have more correct information on the functional dependences of hydrogen solubility in fullerite.

We assume that the crystal lattice of fullerite in its ordered state is the one of the Ll_o type (Figure 16). In this lattice the sites of the first and the second types valid for Φ_1 and Φ_2 fullerenes, respectively, alternate in layers. In this case O, Θ, Q, D interstices, depending on their surrounding by the lattice sites of first and second types, are divided into O_1, O_2 Θ, Q_1, Q_2, D_1, D_2, D_3 interstitial sites, respectively.

The distances between hydrogen atoms and the nearest fullerenes for O, Θ, Q, D interstitial sites are equal to:

$$r_O = 0{,}5d_2,\ r_Q = d_2/\sqrt{6} \approx 0{,}408d_2,\ r_\Theta = d_2\sqrt{3}/4 \approx 0{,}433d_2,\ r_D = d_2/2\sqrt{2} \approx 0{,}354d_2.$$

The free energy of the crystal of fcc phase is calculated by the formula:

$$F = E - kT\ln W, \qquad (42)$$

where E is the configuration internal energy, W is the thermodynamical probability, k is Boltzmanns constant, T is absolute temperature. Also we introduce the following symbols:

N is the number of lattice sites (fullerenes) in the crystal,

N, 2N, 8N, 7N are numbers of O, Θ, Q, D interstitial sites, respectively,

$N_O^{(l)}, N_\Theta^{(l)}, N_Q^{(l)}, N_D^{(l)}$ are the numbers of hydrogen atoms in O, Θ, Q, D interstitial sites with *l*th configuration of Φ_1, Φ_2 fullerenes. In this case some of interstitial sites can not be occupied by hydrogen atoms;

$G_O^{(l)}, G_\Theta^{(l)}, G_Q^{(l)}, G_D^{(l)}$ are numbers of O, Θ, Q, D interstices, respectively, with *l*th configuration of fullerenes,

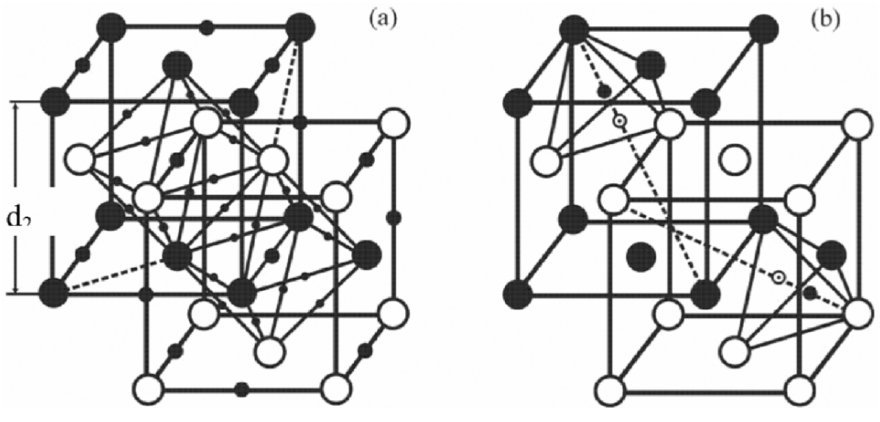


Figure 16. Ll_o crystal lattice of hydrofullerite

●○ lattice sites of the first and the second types occupied mainly by Φ1, Φ2 fullerenes, respectively. Interstitial sites: ● – octahedral O (a), ● – tetrahedral Θ (b), ⊙ – trigonal Q (b), • – bigonal D (a)

$$N_{H\to O} = \sum_l N_O^{(l)},\ N_{H\to\Theta} = \sum_l N_\Theta^{(l)},\ N_{H\to Q} = \sum_l N_Q^{(l)},\ N_{H\to D} = \sum_l N_D^{(l)} \qquad (43)$$

are the numbers of hydrogen atoms in O, Θ, Q, D positions with any configuration,

$$N_H = N_{H\to O} + N_{H\to\Theta} + N_{H\to Q} + N_{H\to D} \tag{44}$$

is the total number of hydrogen atoms,

$$c_O = N_{H\to O}/N, \quad c_\Theta = N_{H\to\Theta}/N, \quad c_Q = N_{H\to Q}/N, \quad c_D = N_{H\to D}/N \tag{45}$$

are hydrogen atoms concentrations in O, Θ, Q, D interstices in relation to the number of lattice sites (fullerenes) of the crystal,

$$c = c_O + c_\Theta + c_Q + c_D \tag{46}$$

is the total hydrogen concentration determining its solubility,

c_1, c_2 ($c_1+c_2 = 1$) are Φ_1, Φ_2 fullerenes concentrations,

$$P_{\Phi_1}^{(1)} = c_1 + \frac{1}{2}\eta, \quad P_{\Phi_1}^{(2)} = c_1 - \frac{1}{2}\eta, \quad P_{\Phi_2}^{(1)} = c_2 - \frac{1}{2}\eta, \quad P_{\Phi_2}^{(2)} = c_2 + \frac{1}{2}\eta \tag{47}$$

are the a priori probabilities of the substitution of the lattice sites of the first and second types with Φ_1, Φ_2 fullerenes, η is the order parameter in fullerenes distribution in the lattice sites of the crystal. $\upsilon_O^{(l)}, \upsilon_\Theta^{(l)}, \upsilon_Q^{(l)}, \upsilon_D^{(l)}$ are energies with the opposite sign for interaction of hydrogen atoms in O, Θ, Q, D interstices with the nearest fullerenes in the case of fullerenes with *l*th configuration around these interstices.

Each O, Θ, Q, D interstitial site in its nearest surrounding has 6, 4, 3, and 2 fullerenes, respectively. The *l*th configuration of fullerenes around the interstitial site points to the number of Φ_1 fullerenes around the hydrogen atom. The rest of Φ_2 fullerenes around the hydrogen atom will be: 6–*l* for O, 4–*l* for Θ, 3–*l* for Q, and 2–*l* for D interstitial sites. Then the hydrogen atoms energies in each interstitial site, determined by the sum of interaction energies with the nearest fullerenes, will be equal to, respectively:

$$\begin{aligned} \upsilon_O^{(l)} &= l\alpha_1 + (6-l)\alpha_2, \quad \upsilon_\Theta^{(l)} = l\beta_1 + (4-l)\beta_2, \\ \upsilon_Q^{(l)} &= l\gamma_1 + (3-l)\gamma_2, \quad \upsilon_D^{(l)} = l\delta_1 + (2-l)\delta_2, \end{aligned} \tag{48}$$

where α_i, β_i, γ_i, δ_i (i = 1; 2) are interaction energies between hydrogen atoms and Φ_1, Φ_2 fullerenes, respectively.

Using the taken symbols and the Stirling formula lnX! = X(lnX–1) for large X numbers, we find the free energy of fcc phase as follows:

$$
\begin{aligned}
F = &-\sum_{l=0}^{6}(N_{O_1}^{(l)}+N_{O_2}^{(l)})\upsilon_{O}^{(l)}-\sum_{l=0}^{6}N_{\Theta}^{(l)}\upsilon_{\Theta}^{(l)}-\sum_{l=0}^{3}(N_{Q_1}^{(l)}+N_{Q_2}^{(l)})\upsilon_{Q}^{(l)}-\sum_{l=0}^{2}(N_{D_1}^{(l)}+N_{D_2}^{(l)}+N_{D_3}^{(l)})\upsilon_{D}^{(l)}\\
&+kT\Bigg\{\sum_{l=0}^{6}(G_{O_1}^{(l)}\ln G_{O_1}^{(l)}+G_{O_2}^{(l)}\ln G_{O_2}^{(l)})+\sum_{l=0}^{4}G_{\Theta}^{(l)}\ln G_{\Theta}^{(l)}+\sum_{l=0}^{3}(G_{Q_1}^{(l)}\ln G_{Q_1}^{(l)}+G_{Q_2}^{(l)}\ln G_{Q_2}^{(l)})\\
&+\sum_{l=0}^{2}(G_{D_1}^{(l)}\ln G_{D_1}^{(l)}+G_{D_2}^{(l)}\ln G_{D_2}^{(l)}+G_{D_3}^{(l)}\ln G_{D_3}^{(l)})\\
&-\sum_{l=0}^{6}(N_{O_1}^{(l)}\ln N_{O_1}^{(l)}+N_{O_2}^{(l)}\ln N_{O_2}^{(l)})-\sum_{l=0}^{4}N_{\Theta}^{(l)}\ln N_{\Theta}^{(l)}-\sum_{l=0}^{3}(N_{Q_1}^{(l)}\ln N_{Q_1}^{(l)}+N_{Q_2}^{(l)}\ln N_{Q_2}^{(l)})\\
&-\sum_{l=0}^{2}(N_{D_1}^{(l)}\ln N_{D_1}^{(l)}+N_{D_2}^{(l)}\ln N_{D_2}^{(l)}+N_{D_3}^{(l)}\ln N_{D_3}^{(l)})\\
&-\sum_{l=0}^{6}[(G_{O_1}^{(l)}-N_{O_1}^{(l)})\ln(G_{O_1}^{(l)}-N_{O_1}^{(l)})+(G_{O_2}^{(l)}-N_{O_2}^{(l)})\ln(G_{O_2}^{(l)}-N_{O_2}^{(l)})]-\sum_{l=0}^{4}(G_{\Theta}^{(l)}-N_{\Theta}^{(l)})\ln(G_{\Theta}^{(l)}-N_{\Theta}^{(l)})\\
&-\sum_{l=0}^{3}[(G_{Q_1}^{(l)}-N_{Q_1}^{(l)})\ln(G_{Q_1}^{(l)}-N_{Q_1}^{(l)})+(G_{Q_2}^{(l)}-N_{Q_2}^{(l)})\ln(G_{Q_2}^{(l)}-N_{Q_2}^{(l)})]\\
&-\sum_{l=0}^{3}[(G_{D_1}^{(l)}-N_{D_1}^{(l)})\ln(G_{D_1}^{(l)}-N_{D_1}^{(l)})+(G_{D_2}^{(l)}-N_{D_2}^{(l)})\ln(G_{D_2}^{(l)}-N_{D_2}^{(l)})+(G_{D_3}^{(l)}-N_{D_3}^{(l)})\ln(G_{D_3}^{(l)}-N_{D_3}^{(l)})]\Bigg\}.
\end{aligned}
\tag{49}
$$

The equilibrium state of fullerite is determined from the conditions for minimum of free energy, that are easily found by the method of the indeterminate Lagrange factor λ. Factor λ is correlated with the equation of the relation between numbers $N_{s}^{(l)}(s=O_1,O_2,\Theta,Q_1,Q_2,D_1,D_2,D_3)$. After substitution of free energy F into the conditions for free energy minimum, we find equations whereby the numbers $N_S^{(l)}$ of hydrogen atoms in the interstitial sites s = O_1, O_2, Θ, Q_1, Q_2, D_1, D_2, D_3 with *l*th configuration of Φ_1, Φ_2 fullerenes are evaluated

$$
\begin{aligned}
&N_{O_1}^{(l)}=A\,G_{O_1}^{(l)}\exp\frac{\upsilon_{O}^{(l)}}{kT}/(1+A\exp\frac{\upsilon_{O}^{(l)}}{kT}),\quad N_{O_2}^{(l)}=A\,G_{O_2}^{(l)}\exp\frac{\upsilon_{O}^{(l)}}{kT}/(1+A\exp\frac{\upsilon_{O}^{(l)}}{kT}),\\
&N_{\Theta}^{(l)}=A\,G_{\Theta}^{(l)}\exp\frac{\upsilon_{\Theta}^{(l)}}{kT}/(1+A\exp\frac{\upsilon_{\Theta}^{(l)}}{kT}),\\
&N_{Q_1}^{(l)}=A\,G_{Q_1}^{(l)}\exp\frac{\upsilon_{Q}^{(l)}}{kT}/(1+A\exp\frac{\upsilon_{Q}^{(l)}}{kT}),\quad N_{Q_2}^{(l)}=A\,G_{Q_2}^{(l)}\exp\frac{\upsilon_{Q}^{(l)}}{kT}/(1+A\exp\frac{\upsilon_{Q}^{(l)}}{kT}),\\
&N_{D_1}^{(l)}=A\,G_{D_1}^{(l)}\exp\frac{\upsilon_{D}^{(l)}}{kT}/(1+A\exp\frac{\upsilon_{D}^{(l)}}{kT}),\quad N_{D_2}^{(l)}=A\,G_{D_2}^{(l)}\exp\frac{\upsilon_{D}^{(l)}}{kT}/(1+A\exp\frac{\upsilon_{D}^{(l)}}{kT}),\\
&N_{D_3}^{(l)}=A\,G_{D_3}^{(l)}\exp\frac{\upsilon_{D}^{(l)}}{kT}/(1+A\exp\frac{\upsilon_{D}^{(l)}}{kT}),
\end{aligned}
\tag{50}
$$

where $A=\exp\frac{\lambda}{kT}$ is chemical potential defined the hydrogen atoms activity, i.e., the increase in the state function of crystal due to each additional hydrogen atom appeared from surroundings and dissolved in this crystal.

Summing up the attained numbers (50) for all configurations *l*, we can find the total number N_H of hydrogen atoms in the crystal or the hydrogen solubility in fullerite by Eqs. (45) and (46).

We shall examined special cases of hydrogen solubility in fcc fullerite.

Let fullerene of one sort (C_{60} or C_{70}) be contained in the crystal. Then we shall have only four types of O, Θ, Q, D interstitial sites. Each O, Θ, Q, D interstice has the only configuration: surrounding by the nearest Φ fullerenes.

Instead of eight equations (50) for the $N_s^{(l)}$ numbers of hydrogen atoms in the interstices s = O, Θ, Q, D, we shall have four

$$\begin{aligned} N_0 &= 2N(1+\frac{1}{A}\exp\frac{-6\alpha}{kT})^{-1}, & N_\Theta &= 2N(1+\frac{1}{A}\exp\frac{-4\beta}{kT})^{-1}, \\ N_Q &= 8N(1+\frac{1}{A}\exp\frac{-3\gamma}{kT})^{-1}, & N_D &= 7N(1+\frac{1}{A}\exp\frac{-2\delta}{kT})^{-1}, \end{aligned} \tag{51}$$

and the hydrogen concentration in the fullerite interstices will be equal to

$$\begin{aligned} c_0 &= 1/(1+\frac{1}{A}\exp\frac{-6\alpha}{kT}), & c_\Theta &= 2/(1+\frac{1}{A}\exp\frac{-4\beta}{kT}), \\ c_Q &= 8/(1+\frac{1}{A}\exp\frac{-3\gamma}{kT}), & c_D &= 7/(1+\frac{1}{A}\exp\frac{-2\delta}{kT}). \end{aligned} \tag{52}$$

Each individual formula from (52) determines the hydrogen solubility in fullerite for hydrogen atoms distribution only in O, Θ, Q or D interstitial sites, respectively.

When hydrogen atoms are arranged in all interstitial sites, hydrogen solubility will be determined by the sum of c_O, c_Θ, c_Q, c_D concentrations according to Eq. (46).

Eqs. (51) and (52) show that at the infinitely low temperature T→0 there exists possibility of maximum hydrogen solubility in fullerite, determined by the sum of interstitial sites when all interstices are occupied with hydrogen atoms. The maximum hydrogen solubility is equal to

$$c_m = c_O+c_\Theta+c_Q+c_D = (G_O+G_\Theta+G_Q+G_D)/N = 18. \tag{53}$$

This case corresponds to the formation of ΦH_{18} fullerite.

However, by virtue of the large differences in the distances between hydrogen atoms and fullerenes, as it was noted above, hydrogen atoms can be arranged in the interstitial sites of two or three types. We shall consider these cases below.

In the case, when hydrogen atoms are distributed in octahedral and tetrahedral interstitial sites of single-component fullerite, the maximum possible concentration of hydrogen atoms in fullerite at T→0 is defined by the relative number of interstitial sites and equals

$$c_m = (G_O + G_\Theta)/N = 1+2 = 3.$$

At any temperatures the hydrogen atoms concentration in O, Θ interstitial sites and the total concentration are determined by the following equations

$$c_0 = (1 + \frac{1}{A}\exp\frac{-6\alpha}{kT})^{-1}, \quad c_\Theta = (1 + \frac{1}{A}\exp\frac{-4\beta}{kT})^{-1}, \quad c = c_0 + c_\Theta. \qquad (54)$$

Using these equations, we find

$$c_0 = \{c(1-\varepsilon_1) - 2 - \varepsilon_1 + \sqrt{[c(1-\varepsilon_1) - 2 - \varepsilon_1]^2 + 4c\varepsilon_1(1-\varepsilon_1)}\ \}/2(1-\varepsilon_1), \quad c_\Theta = c - c_0, \qquad (55)$$

$$\varepsilon_1 = \exp\frac{6\alpha - 4\beta}{kT},$$

The Formula (55) allows us to evaluate the hydrogen atoms distribution over O and Θ interstitial sites that are determined by temperature, the relation between α and β energy parameters and the total concentration of hydrogen atoms. Based on the relations (55), in the range $0 \le c \le 3$ the dependences for hydrogen atoms distribution in O and Θ interstitial sites are shown in the Figure 17.

The maximum hydrogen concentration $c_m = 3$ corresponds to the formation of ΦH_3 hydrofullerite, i.e., in this case atomic hydrogen concentration in reference to the number of fullerenes cannot exceed x = 3.

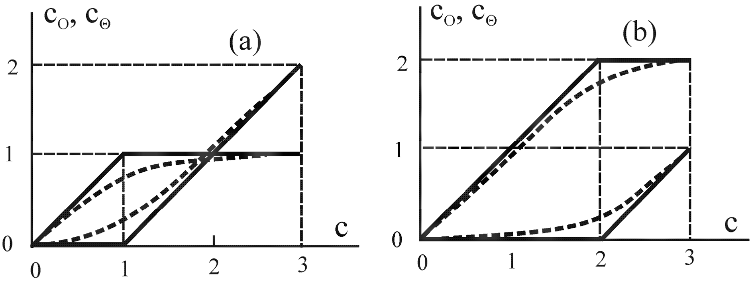


Figure 17. The hydrogen atoms distribution in octahedral O and tetrahedral Θ interstitial sites at $6\alpha - 4\beta > 0$ (a) and $6\alpha - 4\beta < 0$ (b)

The solid broken lines correspond to T→0, the dotted lines correspond to the temperature $T \neq 0$.

Note that in virtue of small radii of hydrogen atoms and large volumes of interstitial sites in fullerite, hydrogen atoms distribution in trigonal Q and bigonal D interstitial sites can appear more probable. Let us consider this case.

The hydrogen atoms concentration in Q and D interstitial sites and the total concentration are determined by the following equations

$$c_Q = 8(1+\frac{1}{A}\exp\frac{-3\gamma}{kT})^{-1}, \quad c_D = 7(1+\frac{1}{A}\exp\frac{-2\delta}{kT})^{-1}, \quad c = c_Q + c_D, \tag{56}$$

and the maximum hydrogen concentration in fullerite can be equal to the number of Q and D interstitial sites, i.e.,

$$c_m=(G_Q+G_D)/N=7+8=15. \tag{57}$$

Using Eq. (56), we easily find the following relations

$$\begin{gathered} c_Q = \{c(1-\varepsilon_2)-7-8\varepsilon_2+\sqrt{[c(1-\varepsilon_2)-7-8\varepsilon_2]^2+32c\varepsilon_2(1-\varepsilon_2)}\}/2(1-\varepsilon_2), \\ c_D = c - c_Q, \ \varepsilon_2 = \exp\frac{3\gamma-2\delta}{kT}. \end{gathered} \tag{58}$$

The Eq. (58) defines the character of hydrogen atoms distribution in Q and D interstitial sites depending on the temperature, the total hydrogen concentration *c* and the relation between γ and δ energetic constants.

The hydrogen atoms distributions over Q and D interstitial sites are shown in Figure 18.

When hydrogen atoms are arranged in Q and D interstices, there exists possibility to form ΦH_{15} hydrofullerite in which the number of hydrogen atoms is x = 15 times as great as the number of fullerenes.

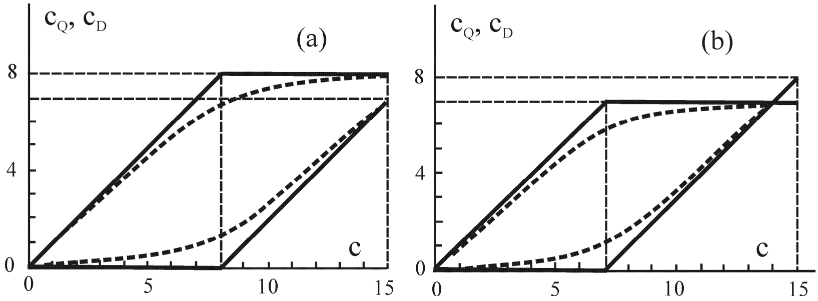


Figure 18. The hydrogen atoms distribution in trigonal Q and bigonal D interstitial sites at $3\gamma - 2\delta > 0$ (a) and $3\gamma-2\delta < 0$ (b). The solid broken lines correspond to the infinitely low temperature T→0, the dotted lines correspond to $T \neq 0$

Now let us elucidate the functional dependences of hydrogen solubility in Φ_1–Φ_2 combined fcc fullerite at the low concentration of hydrogen atoms when $N_H \le N$. In this case Eq. (50) is simplified and have the form

$$\left.\begin{aligned}
&N_{O_1}^{(l)} = AG_{O_1}^{(l)} \exp\frac{\upsilon_O^{(l)}}{kT}, \quad N_{O_2}^{(l)} = AG_{O_2}^{(l)} \exp\frac{\upsilon_O^{(l)}}{kT}, \quad l = 0,\dots,6,\\
&N_{\Theta}^{(l)} = AG_{\Theta}^{(l)} \exp\frac{\upsilon_\Theta^{(l)}}{kT}, \quad l = 0,\dots,4,\\
&N_{Q_1}^{(l)} = AG_{Q_1}^{(l)} \exp\frac{\upsilon_Q^{(l)}}{kT}, \quad N_{Q_2}^{(l)} = AG_{Q_2}^{(l)} \exp\frac{\upsilon_Q^{(l)}}{kT}, \quad l = 0,\dots,3,\\
&N_{D_1}^{(l)} = AG_{D_1}^{(l)} \exp\frac{\upsilon_D^{(l)}}{kT}, \quad N_{D_2}^{(l)} = AG_{D_2}^{(l)} \exp\frac{\upsilon_D^{(l)}}{kT}, \quad l = 0,1,2,\\
&N_{D_3}^{(l)} = AG_{D_3}^{(l)} \exp\frac{\upsilon_D^{(l)}}{kT}, \quad l = 0,1,2.
\end{aligned}\right\} \qquad (59)$$

In the ordered fullerite the *l*th configuration of Φ_1, Φ_2 fullerenes is defined by the configuration of fullerenes in the lattice sites of the first and second type, respectively, i.e., the *l* value is determined by the sum $l = i + j$, where i is the number of Φ_1 fullerenes in the lattice sites of the first type, and j is the number of the same Φ_1 fullerenes in the lattice sites of the second type around each interstitial sites.

Substituting the calculated $G_s^{(l)}$ numbers and $\upsilon_s^{(l)}$ energies into Eq. (59) and summing up the $N_s^{(l)}$ numbers for all the configurations $l = i + j$, we find the number of hydrogen atoms in the interstitial sites s = O_1, O_2, Θ, Q_1, Q_2, D_1, D_2, D_3.

In summation we use Newton binomial find the hydrogen concentration in O, Θ, Q, D interstices, respectively

$$\begin{aligned}
&c_O = (N_{H\to O_1} + N_{H\to O_2})/N = \frac{1}{2}AK_1^{(O)^2}K_2^{(O)^2}(K_1^{(O)^2} + K_2^{(O)^2}),\\
&c_\Theta = N_{H\to\Theta}/N = 2AK_1^{(\Theta)^2}K_2^{(\Theta)^2},\\
&c_Q = (N_{H\to Q_1} + N_{H\to Q_2})/N = 4AK_1^{(Q)}K_2^{(Q)}(K_1^{(Q)} + K_2^{(Q)}),\\
&c_D = (N_{H\to D_1} + N_{H\to D_2} + N_{H\to D_3})/N = A(4K_1^{(D)}K_2^{(D)} + \frac{3}{2}K_1^{(D)^2} + \frac{3}{2}K_2^{(D)^2}).
\end{aligned} \qquad (60)$$

where

$$K_1^{(s)} = P_{\Phi_1}^{(1)} \exp\frac{\omega_1^{(s)}}{kT} + P_{\Phi_2}^{(1)} \exp\frac{\omega_2^{(s)}}{kT}, \quad K_2^{(s)} = P_{\Phi_1}^{(2)} \exp\frac{\omega_1^{(s)}}{kT} + P_{\Phi_2}^{(2)} \exp\frac{\omega_2^{(s)}}{kT}, \qquad (61)$$

$$\omega_1^{(s)} = \alpha_1,\ \beta_1,\ \gamma_1,\ \delta_1,\quad \omega_2^{(s)} = \alpha_2,\ \beta_2,\ \gamma_2,\ \delta_2 \tag{62}$$

for s = O, Θ, Q, D, respectively.

The derived Eq. (60) determines the hydrogen solubility, if hydrogen atoms are distributed in one type of O, Θ, Q, D interstitial sites.

When hydrogen atoms are distributed in all interstitial sites, the hydrogen solubility is defined by the sum of concentrations (60) and will be equal to

$$\begin{aligned} c = c_O + c_\Theta + c_Q + c_D = A[\frac{1}{2}K_1^{(0)^2}K_2^{(0)^2}(K_1^{(0)^2} + K_2^{(0)^2}) + 2K_1^{(\Theta)^2}K_2^{(\Theta)^2} \\ + 4K_1^{(Q)}K_2^{(Q)}(K_1^{(Q)} + K_2^{(Q)}) + 4K_1^{(D)}K_2^{(D)} + \frac{3}{2}K_1^{(D)^2} + \frac{3}{2}K_2^{(D)^2}]. \end{aligned} \tag{63}$$

Formulae (60) and (63) with regard to the relations (61) and (47) determine the corresponding hydrogen solubilities in dependence on the fullerite composition (c_1, c_2 concentrations), temperature, degree of the long-range order in the fullerenes distribution over the lattice sites, and the energetic constants.

In the absence of atomic order in the crystal sites we have

$$K^{(s)} = K_1^{(s)} = K_2^{(s)} = c_1 \exp\frac{\omega_1^{(s)}}{kT} + c_2 \exp\frac{\omega_2^{(s)}}{kT}, \tag{64}$$

and the hydrogen solubilities, according to Eqs. (60) and (63), will be equal to

$$\left.\begin{aligned} c_O^o = (c_O)_{\eta=0} = AK^{(O)^6}, \quad c_\Theta^o = (c_\Theta)_{\eta=0} = 2AK^{(\Theta)^4}, \\ c_Q^o = (c_Q)_{\eta=0} = 8AK^{(Q)^3}, \quad c_D^o = (c_D)_{\eta=0} = 7AK^{(D)^2}, \end{aligned}\right\} \tag{65}$$

$$\begin{aligned} c^o = c_{\eta=0} = A[(c_1 \exp\frac{\alpha_1}{kT} + c_2 \exp\frac{\alpha_2}{kT})^6 + 2(c_1 \exp\frac{\beta_1}{kT} + c_2 \exp\frac{\beta_2}{kT})^4 \\ + 8(c_1 \exp\frac{\gamma_1}{kT} + c_2 \exp\frac{\gamma_2}{kT})^3 + 7(c_1 \exp\frac{\delta_1}{kT} + c_2 \exp\frac{\delta_2}{kT})^2]. \end{aligned} \tag{66}$$

Eqs. (65) and (66) define the temperature and concentration dependence of hydrogen solubility, the character of which depends to a large extent on the relations between $\omega_1^{(s)}$ and $\omega_2^{(s)}$ energetic parameters (62).

The dependence of hydrogen solubility on the degree of fullerite ordering is easily found out for the relative values

$$\varphi_0 = c_0 / c_0^0, \quad \varphi_\Theta = c_\Theta / c_\Theta^0, \quad \varphi_Q = c_Q / c_Q^0, \quad \varphi_D = c_D / c_D^0. \tag{67}$$

Let us introduce and consider the following parameters

$$æ_s = \frac{1}{2}\eta \frac{\exp\frac{\omega_1^{(s)}}{kT} - \exp\frac{\omega_2^{(s)}}{kT}}{c_1 \exp\frac{\omega_1^{(s)}}{kT} + c_2 \exp\frac{\omega_2^{(s)}}{kT}}, \quad s = \mathrm{O}, \Theta, \mathrm{Q}, \mathrm{D}. \tag{68}$$

The range for possible values of $æ_S$ parameters is easily evaluated by Eq. (68). In fact, the order parameter has the maximum possible value $|\eta| = 1$. For crystals with the stoichiometric composition, when $c_1 = c_2 = 0.5$, and for slightly differed energetic constants, when $\omega^{(S)} \approx \omega_1^{(S)} \approx \omega_2^{(S)}$, the $æ_S$ parameters can change in the range from -1 to $+1$, i.e., $-1 \leq æ_S \leq 1$.

It is easy to see that the ratios between values of $K_1^{(S)}$, $K_2^{(S)}$ (61), and $K^{(S)}$ (64) are equal to:

$$K_1^{(S)} / K^{(S)} = 1 + æ_S, \qquad K_2^{(S)} / K^{(S)} = 1 - æ_S, \tag{69}$$

and according to Eqs. (60) and (65), the relative solubilities φ_O, φ_Θ, φ_Q, φ_D will be determined by the following equations

$$\varphi_0 = (1 - æ_0^4)(1 - æ_0^2), \;\; \varphi_\Theta = (1 - æ_0^2)^2, \;\; \varphi_Q = 1 - æ_Q^2, \;\; \varphi_D = 1 - \frac{1}{7} æ_D^2. \tag{70}$$

The dependence of φ_O, φ_Θ, φ_Q, φ_D values on the corresponding $æ_S$ parameters, which are proportional to the degree of the long-range order according to Eq. (68), defines the character of the atomic order effect during Φ_1, Φ_2 fullerenes distribution over the fullerite lattice sites on the hydrogen solubility when hydrogen atoms are arranged in the interstitial site of any one type s = O, Θ, Q, D. The plots of these dependences are shown in Figure 19.

As Figure 19 shows, the atomic order decreases the hydrogen solubility in fullerite. In this case for the low value of $æ_S$, which is proportional to the order parameter η, the hydrogen solubility slightly depends on the degree of the long-range order. However, with increasing $æ_S$ parameters, effect of the long-range order on the hydrogen solubility during hydrogen atoms distribution over O, Θ, Q interstitial sites can be significant. At hydrogen atoms arrangement in D interstitial sites, the order has a weak effect on hydrogen solubility in the whole range of $æ_D$ values.

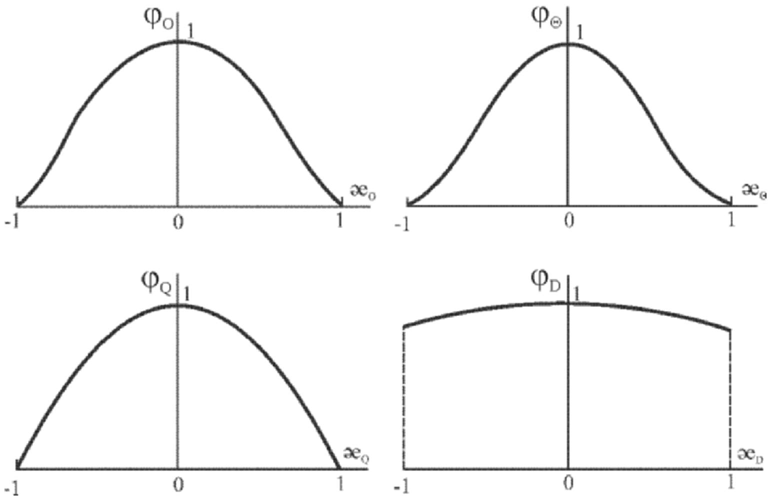


Figure 19. The curves for relative hydrogen solubility in fullerite in dependce on the parameter $æ_S$ (s = O, Θ, Q, D), which is proportional to the degree of the long-range order, for octahedral O, tetrahedral Θ, trigonal Q, and bigonal D interstitial sites

Below we shall find out the dependence of hydrogen solubility on fullerite composition and temperature at hydrogen atoms distribution in tetrahedral, trigonal, and bigonal interstitial sites.

The nearest distance between hydrogen atoms and fullerenes for octa-interstices significantly exceed such distances for tetrahedral, trigonal, and bigonal interstitial sites while these distances for the latter differ from one another slightly. Therefore, one can suppose that hydrogen atoms in fullerite are arranged in Θ, Q, D positions. In this case in the absence of ordering ($\eta = 0$) the solubility is defined by the function

$$c^0 = A[2(c_1 \exp\frac{\beta_1}{kT} + c_2 \exp\frac{\beta_2}{kT})^4 + 8(c_1 \exp\frac{\gamma_1}{kT} + c_2 \exp\frac{\gamma_2}{kT})^3 + 7(c_1 \exp\frac{\delta_1}{kT} + c_2 \exp\frac{\delta_2}{kT})^2]. \tag{71}$$

Each term in Eq. (71) gives the monotonous dependence on c_1 concentration, the first two terms in (71) will give the increasing curves with c_1 concentration and the third term will give the descending curve with increasing c_1. The resulting curve $c^o = c^o(c_1)$ can be extreme. This case, as an example, is given in Figure 20 when

$$\begin{array}{ll} \exp\dfrac{4\beta_1}{kT} = 0{,}875, & \exp\dfrac{4\beta_2}{kT} = 0{,}25, \\ \exp\dfrac{3\gamma_1}{kT} = 0{,}5, & \exp\dfrac{3\gamma_2}{kT} = 0{,}795, \\ \exp\dfrac{2\delta_1}{kT} = 0{,}143, & \exp\dfrac{2\delta_2}{kT} = 0{,}857. \end{array} \tag{72}$$

The study of $c^o = c^o(T)$ functions (71) has shown that the extremum can appear on the case of change of interaction character between H–Ф pairs. In this case, with changing distance r from r_D to r_Θ, interaction in this pair will change from attraction to repulsion or inversely what is highly improbable. Therefore, one can suppose that the temperature dependence of hydrogen solubility in the disordered fullerite must be monotonous.

The interaction character between H–Ф pairs is repulsive what corresponds to the negative values of β_1, β_2, γ_1, γ_2, δ_1, δ_2 energies. For this case, as an example, Figure 21 shows the plots for $c^o = c^o(T)$ dependence for fullerite crystals of the stoichiometric composition ($c_1 = c_2 = 0.5$) and for the energies defined at $kT = 0.86 \cdot 10^{-1}$ eV by relations

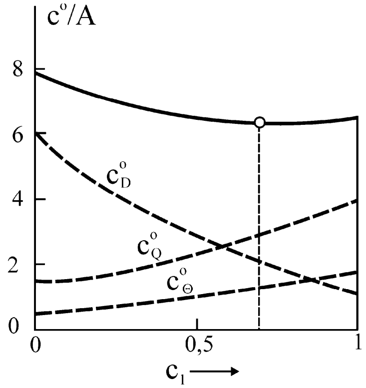


Figure 20. The concentrational dependence of hydrogen solubility in the disordered fcc fullerite (the solid curve). The circle marks the minimum hydrogen solubility at $c_l = 0.7$. The dotted curves correspond to hydrogen solubility when hydrogen atoms are ar

$$\begin{array}{ll} \exp\dfrac{\beta_1}{kT} = 0{,}967, & \exp\dfrac{\beta_2}{kT} = 0{,}707, \\ \exp\dfrac{\gamma_1}{kT} = 0{,}795, & \exp\dfrac{\gamma_2}{kT} = 0{,}572, \\ \exp\dfrac{\delta_1}{kT} = 0{,}378, & \exp\dfrac{\delta_2}{kT} = 0{,}926. \end{array} \tag{73}$$

It is seen from Figure 21 that hydrogen solubility $c^o = c^o(T)$ in fullerite (as well as terms $c^o_\Theta(T)$, $c^o_Q(T)$, $c^o_D(T)$) is increased with temperature rise. At low temperatures the solubility is sharply increased with increasing temperature, and further the growth of solubility is determined by the flattened plot.

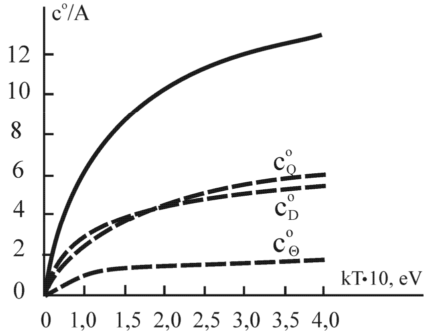


Figure 21. The temperature dependence of hydrogen solubility in the disordered fullerite (the solid curve). The dotted curves correspond to hydrogen solubility when hydrogen atoms are arranged only in tetrahedral Θ, only in trigonal Q, or bigonal D inters

Hence the statistical and thermodynamical theory of the lattice hydrogen solubility in fcc fullerite with consideration for the hydrogen atoms distribution over the interstitial sites of different types has allowed us to explain and justify the formation of ΦH_x hydrofullerites with high hydrogen concentration when $0 \leq x \leq 18$. It has been found that hydrogen solubility depends on the fullerite composition, its temperature, the order parameter in $\Phi_1 = C_{60}$, $\Phi_2 = C_{70}$ fullerenes distribution over the lattice sites, the energetic constants characterizing the interaction between H–Φ pairs at the different distances.

The specific cases have been studied. The character of hydrogen atoms distribution in the interstitial sites of different types has been studied at the infinitely low temperature $T \to 0$ and at $T \neq 0$.

The possibility of appearing extremum in the concentrational dependence of hydrogen solubility has been established. It has been shown that the temperature dependence of hydrogen solubility is the function monotonically increasing with temperature rise. It has been elucidated that the order in Φ_1, Φ_2 fullerenes distribution in the lattice sites decreases hydrogen solubility for each type of interstitial sites. In this case the low degree of ordering is scarcely affected by solubility, however, the large values of the order parameter, depending on the type of interstitital sites in which hydrogen atoms are arranged, can decrease the hydrogen solubility down to zero.

4. Conclusions

The received formulae for the number of hydrogen atoms in interstitial sites of different types permit us to ascertain the character of hydrogen atoms distribution in the systems being studied, to explain the character of the possible functional dependencies (on alloy composition, temperature, and degree of long-range order) of hydrogen solubility at different energies of interatomic interaction and to determine the causes responsible for these dependencies.

They also permit forecasting of the mutual influence of processes of atomic ordering and impurity solubility for each concrete hydride system in the presence of energetic parameters known from independent experiments.

The carried out calculations also give the grounds of possibility of hydrofullerenes formation in their simplest forms at the solid-phase hydrogenation.

It is pertinent to note that experimental construction of phase diagram and determination of temperature dependence of hydrogen solubility in fullerite make it possible with the use of derived equations to estimate numerically the energetic parameters of fullerenes interaction between themselves and with hydrogen atoms. This in its turn makes possible the definition of binding energies of ΦH, HH pairs in solid solutions, their strength and reactivity, their amplification or reduction, and lastly to compare the results of evaluation of binding energies of CH and CC pairs with calculation and experimental data available in literature [39, 49, 55, 70, 71].

The comparison of working characteristics (Table 3) of metal-hydrides, hydrocarbons, and fullerenes shows that fullerenes are one of the most promising materials for hydrogen storage.

The research into the processes of their reversible reaction with hydrogen is of interest in connection with the development of systems for hydrogen accumulation and storage. The high potential for practical applications of fullerenes will promote the progress in this field of studies. This will inevitably result in the development of materials of new types and generations.

In summary it should be noted that the pursued investigations can be refined due to taking into account: the volume effects induced by hydrogen atoms, local distortions of the crystal lattice around the hydrogen atoms (deformation effects), the interaction between H–Me and H–Φ pairs in the next coordination spheres, the fullerenes ordering and formation of four sublattices [45], the change of the phase states in the hydrogen atoms system (possible isotopic ordering), the effect of external pressure of gas from which the hydrogen atoms go in fullerite, the electron properties of hydrogen solvent, possible presence of fullerenated hydrogen in hydrofullerite.

TABLE 3. Metallic and organic hydrides as hydrogen accumulators

Reactions	Volume of reversible hydrogen, (at H/cm^3) 10^{-22}	Weight content of reversible H_2, %	Electrochemical capacity, MAh/g
$Pd + 1/2H_2 \leftrightarrow PdH_{\sim 0.8}$	5.30	0.75	200
$V + H_2 \leftrightarrow VH_2$	10.50	3.75	990
$Ti + H_2 \leftrightarrow TiH_2$	9.05	4.00	1050
$Mg + H_2 \leftrightarrow MgH_2$	6.60	7.60	2000
$CeCo_3 + 2H_2 \leftrightarrow CeCo_3H_4$	4.10	1.25	330
$LaNi_5 + 3H_2 \leftrightarrow LaNi_5H_6$	4.30	1.40	360
$TiFe + H_2 \leftrightarrow TiFeH_2$	5.90	1.90	500
$Mg_2Ni + 2H_2 \leftrightarrow Mg_2NiH_4$	8.0	3.60	950
$C_6H_6 + 3H_2 \leftrightarrow C_6H_{12}$	3.35	7.15	1,880
$C_7H_8 + 3H_2 \leftrightarrow C_7H_{14}$	2.85	6.15	1,620
$C_{10}H_8 + 5H_2 \leftrightarrow C_{10}H_{18}$	4.50	7.25	1,900
$C_{60} + 30H_2 \leftrightarrow C_{60}H_{60}$	8.25	7.70	2,000
$C_{70} + 35H_2 \leftrightarrow C_{70}H_{70}$	8.25	7.70	2,000
$C_{60} + 18H_2 \leftrightarrow C_{60}H_{36}$	5.40	4.50	1,250

References

1. N.S. Kurnakov, *Introduction of physico-chemical analysis* (in Russian). (Izv. Akad. Nauk S.S.S.R., Moscow, 1940).
2. L.S. Darken and R.W. Gurry, *Physical chemistry of metals* (McGraw-Hill, New York, 1953).
3. M.S. Vrevskii, *Works on theory of solutions* (in Russian). (Izv. Akad. Nauk S.S.S.R., Moscow, 1953).
4. D.A. Petrov, *Ternary systems* (in Russian). (Izv. Akad. Nauk S.S.S.R., Moscow, 1953).
5. J.M. Sivertsen and M.E. Nicholson, *The structure and properties of solid solution* (Pergamon Press, Oxford, 1962).
6. O. Kubaschewskii and B.E. Hopkins, *Oxidation of metals and Alloys* (2nd edn. Butterworths, London, 1962).
7. B.K. Vulf, *Ternary metallic phases in alloys* (in Russian). (Izd. Metallurgiya, Moscow, 1964).
8. J.D. Fast, *Interaction of metals and gases* (Philips Technical Library, Eindhoven, 1965).
9. H.J. Goldschmidt, *Interstitial alloys* (Butterworths, London, 1967).
10. W.M. Mueller, S.P. Blackledge, and G.G. Libowitz, *Metal hydrides* (Academic Press, New York, 1968).

11. O. Kubaschewskii, A. Cibula and C. Moore, *Gases and metals* (Iliffe, London, 1970).
12. E. Fromm and E. Gebhardt, *Gases und Kohlenstoff in Metallen* (Springer, Berlin, 1976).
13. C.J. Smithells (Ed.), *Metals reference book* (Butterworths, London, Boston, 1976).
14. R.A. Andrievskii and Ya.S. Umanskii, *Introduction phases* (in Russian). (Izd. Nauka, Moscow, 1977).
15. G. Alefeld and J. Völkl, *Hydrogen in metals*, 1, 426; 2, 378. (Springer, Berlin, 1978).
16. Z.A. Matysina, *Theory of impurities solubility in ordering phases* (in Russian). (Izd. DGU, Dnepropetrovsk, 1991).
17. Z.A. Matysina and D.V. Schur, *Hydrogen and solid phase transformations in metals, alloys and fullerites* (in Russian). (Izd. Nauka i obrazovanie, Dnepropetrovsk, 2002).
18. Z.A. Matysina, S.Yu. Zaginaichenko, and D.V. Schur, *Solubility of impurities in metals, alloys, intermetallic compounds and fullerites* (in Russian). (Izd. Nauka i obrazovanie, Dnepropetrovsk, 2006).
19. M.A. Krivoglaz, Solubility in ordering alloys (in Russian), *Zhurn. Techn. Fiz.* 24, 1077–1089 (1954).
20. S.Yu. Zaginaichenko, O.L. Kurbatova and Z.A. Matysina, Interstitial impurity in alloys of $B8_1$ and B31 structure (in Russian), *Fiz. Metal. Mettalov* 54(4), 636–643 (1982).
21. S.Yu. Zaginaichenko, O.L. Kurbatova, and Z.A. Matysina, Solubility and correlation in alloys of B19 structure (in Russian), *Izv. VUZ. S.S.S.R. Fiz.* 1, 17–24 (1982).
22. Z.A. Matysina, M.I. Milyan, and S.Yu. Zaginaichenko, The solubility of interstitial impurities in ordering phases, *Phys. Status Solidi* (a) 95, K9–K14 (1986).
23. C.J. Smithells, *Gases and metals* (in Russian). (Izd. Metallurgiya, Moscow, 1940).
24. S. Dushman, *Scientific foundation of vacuum technique* (Wiley, New York, 1962).
25. V.B. Vykhodets, V.B. Dyomin, P.V. Geld, A.N. Men, A.YA. Fishman, and G.I. Chufarov, The solubility of hydrogen in metals with fcc lattice (in Russian), *Izv. Akad. Nauk S.S.S.R.*, *Metal* 6, 71–77 (1971).
26. P.V. Geld and R. Ryabov, *Hydrogen in metals and alloys* (in Russian). (Izd. Metallurgiya, Moscow, 1974).
27. V.N. Lnyanoi, Up to the determination of surface energy of graphite (in Russian), *Izv. Akad. Nauk S.S.S.R., Metal* 5, 59 (1976).
28. S.Yu. Zaginaichenko, V.N. Lnyanoi, Z.A. Matysina, and V.I. Ryzhkov, Temperature redistribution of interstitial atoms on the surface and in the volume of crystal (in Russian), *Izv. VUZ. S.S.S.R., Fizika* 7, 119 (1987); Internal Rep. VINITI, № 8892–B866 1–30 (1986).
29. H.W. Kroto, J.R. Heath, S.C. O'Brien, and R.E. Smalley, C_{60}: Buckminsterfullerene, *Nature* 318, 162 (1985).
30. R.E. Smalley, Discovering fullerenes (in Russian), *Usp. fiz. nauk* 168(3), 323–330 (1988).
31. R.F. Kerl, Sources of fullerenes discovery: experiment and hypothesis (in Russian), *Usp. fiz, nauk* 168(3), 331–342 (1988).
32. G. Kroto, Symmetry, outer space, stars and C_{60}, *Usp. fiz. nauk* 168(3), 343–344 (1988).
33. E. Osawa, Superaromaticity (in Japanese), *Kagaku (Chemistry)* 25, 854 (1970).
34. E. Osawa, The evolution of football structure for the C_{60} molecule: a retrospective. *Philos. Trans. R. Soc. London Ser. A – Phys. Sci. Eng.* 343, 1 (1993).
35. K. Shigematsu, K. Abe, M. Mitani, and K. Tanaka, Catalytic hydrogenation of fullerene C_{60}, *Chem. Express* 7(12), 37–40 (1992).
36. A.H. Hirsch, *The chemistry of the fullerenes* (Georg. Thieme Verlag, Stuttgart, 1994).
37. A. Drelinkiewicz, P. Byszewski, and A. Bielanski, Catalytic hydrogenation of C_{60} fullerene, *React. Kinet. Catal. Lett.* 59(1), 19–27 (1996).

38. R. Nozu and O. Matsumoto, Hydrogenation of C_{60} by electrolysis of KOH-H_2O solution, *J. Electrochem. Soc.* 143(6), 1919–1923 (1996).
39. N.F. Goldshleger and A.P. Moravsky (in Russian), Hydrides of fullerenes, *Uspekhi khimii* 66(4), 353–375 (1997).
40. B.P. Tarasov, V.N. Fokin, A.P. Moravsky, Yu.M. Shul'ga, and V.A. Yartys', Hydrogenation of fullerenes C_{60} and C_{70} in the presence of hydride-forming metals and intermetallic compounds, *J. Alloys Comp.* 25, 253–254 (1997).
41. B.P. Tarasov, V.N. Fokin, A.P. Moravsky, Yu.M. Shul'ga, V.A. Yartys', and D.V. Schur, Promotion of fullerene hydride synthesis by intermetallic compounds, *Proc. of 12th World Hydrogen Energy Conference*, Buenos Aires, Argentina 2, 1221–1230 (1998).
42. B.P. Tarasov, Mechanism of hydrogenation of fullerite-metallic compositions (in Russian), *Zhurn. Obschchei khimii* 68, 1245–1248 (1998).
43. B.P. Tarasov, V.N. Fokin, A.P. Moravsky, and Yu.M. Shul'ga, Synthesis and properties of crystalline fullerene hydrides, *Izv. RAN.*, *Ser. khim.* 10, 2093–2096 (1998).
44. M.S. Dresselhaus, K.A. Williams, and P.C. Eklund, Hydrogen absorption in carbon materials, *MRS Bulletin* 24(11), 45–50 (1999).
45. A. Hirsch, Fullerenes and related structures. In: *Topics in Current Chemistry*, edited by A. Hirsch (Springer, Berlin, 1999).
46. Yu.M. Shul'ga, B.P. Tarasov, V.N. Fokin, N.Yu. Shul'ga, and V.N. Vasilets, Deuteride of fullerene $C_{60}D_{24}$: investigation by spectral methods (in Russian), *Fizika tverdogo tela* 41(8), 1520–1526 (1999).
47. M.Yu. Kornilov, T.V. Ljubchuk, S.D. Isaev, H. Panasyuk, V.B. Chernogorenko, and D.V. Schur, Perhydrofullerenes as accumulators of hydrogen, *Molecular Materials* 13, 285–290 (2000).
48. B.P. Tarasov, N.F. Goldshleger, and A.P. Moravsky, Hydrogen-containing compounds of carbon nanostructures (in Russian), *Usp. khimii* 70(2), 149–166 (2001).
49. P.J. Fagan, P.J. Krusic, D.H. Evans, S.A. Lerke, et al., Synthesis, chemistry and properties of monarylkylayted buckminsterfulleren derivative, t-BuC_{60} anion, J *Am. Chem. Soc.* 114, 9697–9699 (1992).
50. M.I. Attalla, A.M. Vassallo, B.N. Tattam, and J.V. Hanna, Preparation of hydrofullerenes by hydrogen radical induced hydrogenation, *J. Phys. Chem.* 97, 6329–6331 (1993).
51. C.C. Henderson, and P.A. Cahill, Synthesis of the simplest C_{60} hydrocarbon derivative, *Science* 259, 1885–1887(1993).
52. A. Hirsch, Chemistry of fullerenes, *Chemie in unserer Zeit* 28, 79–87 (1994).
53. A.G. Avent, A.D. Darwish, D.K. Heimbach, H.W. Kroto, M.F. Meidine, J.P. Parsons, et al., Formation of hydrides in fullerene-C_{60} and fullerene-C_{70}, *J. Chem. Soc. Perkin Trans.* 2, 15–22 (1994).
54. A.S. Lobach, A.A. Perov, A.I. Rebrov, O.S. Roschupkina, V.A. Tkacheva, and A.N. Stepanov, Production and investigation of C_{60} and C_{70} fullerenes hydrides (in Russian), *Izv. RAN. Ser. khimii* 671–678 (1997).
55. L.I. Tkachenko, A.S. Lobach, and V.V. Strelets, Redox- stimulated transfer of hydrogen from hydrofullerene $C_{60}H_{36}$ to fullerene C_{60} (in Russian), *Izv. RAN. Ser. khim.* 6, 1136–1139 (1988).
56. J.A. Howard, EPR, FTIR and FAB mass spectrometric investigation of reaction of H atoms with C_{60} in a cyclohexane matrix, *Chem. Phys. Lett.* 203, 540–544 (1993).
57. P.A. Bruhwiller, S. Andersson, M. Dippel, N. Martensson, P.A. Demirev, et al., Hydrogenation of solid C_{60} by atomic hydrogen, *Chem. Phys. Lett.* 214, 45–49 (1993).

58. C. Jin, R. Hettich, R. Compton, D. Compton, D. Jouce, et al., Direct solid-phase hydrogenation of fullerenes, *J. Phys. Chem.* 98, 4215 (1994).
59. C.C. Henderson, C.M. Rohlfing, K.T. Gillen, and P.A. Cahill, Synthesis, Isolation and equilibration of 1,9 – and 7,8-$C_{70}H_2$, *Science* 264, 397–399 (1994).
60. L.E. Hall, D.R. McKenzie, M.J. Attalla, A.M. Vassallo, R.L. Davis, et al., The structure of $C_{60}H_{36}$, *J. Phys. Chem.* 97, 5741–5744 (1993).
61. A.I. Kolesnikov, Antonov V.E., Bashkin I.O., Grosse G., Moravsky A.P., et al., Neutron spectroscopy of C_{60} fullerene hydrogenated, *J. Phys. Condens. Matter.* 9, 2831 (1997).
62. V.I. Trefilov, D.V. Schur, B.P. Tarasov, Yu.M. Shulga, A.V. Chernogorenko, and S.Yu. Zaginaichenko, *Fullerenes as a basis for materials of the future* (in Russian). (ADEF, Kiev, 2001).
63. Z.A. Matysina and D.V. Schur, *Hydrogen and solid-phase transformations in metals, alloys and fullerites* (in Russian). (Nauka i obrazovanie, Dnepropetrovsk, 2002).
64. V.N. Bezmelnitsyn, V.B. Glazkov, V.P. Zhukov, V.A. Somenkov, and S.Sh. Shilshtein, Neutron diffraction study of structure of the deuterated fullerenes, *Abstr. 4th Biennial Int. Workshop in Russia "Fullerene and Atomic Clusters". St. Petersburg*, 70 (1999).
65. V.P. Glazkov, V.P. Zhukov, V.A. Somenkov, and T.N. Ivanova, Interaction of palladium doped fullerene with hydrogen, *Ibid.*, 71, (1999).
66. M.S. Boba, T.S.L., and R. Bolasubramajan, Studies on the thermodynamics of C_{60}–C_{70} binary system, *J. Phys. Chem.* 98, 1333–1340 (1994).
67. K. Kniaz, J.E. Fisher, and L.A. Girifalco, Fullerene alloys, *Sol. State Comm.* 96, 739–743 (1995).
68. D. Havlik, W. Schranz, M. Haluska, H. Kuzmany, and P. Rogl, Thermal expansion measurements of C_{60}–C_{70} mized crystals, *Sol. State Comm.* 104, 775–779 (1997).
69. V.N. Bezmelnitsin, A.V. Eletskiy, and M.V. Okun, Fullerenes in solutions (in Russian), *Uspehi fizicheskih nauk* 168, 1195–1221 (1995).
70. A. Rathna and J. Chandrasekhar, Theoretical study of hydrogenated Buckminsterfullerene derivatives with benzenoid rings, $C_{60}H_{60-6n}$ (n = 1–8), *Chem. Phys. Lett.* 206, 217–223 (1993).
71. K. Shigematsu, K. Abe, M. Mitani, and K. Tanaka, Catalytic hydrogenation of fullerene C_{70}, *Chem. Express* 8, 957–960 (1993).

AUTHOR INDEX

SUBJECT INDEX