Progress in Hydrogen Energy

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edited by

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TO

MY PARENTS

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PREFACE

Hydrogen has been recognised as a universal, clean fuel which is expected to provide energy to our homes, industry and automobiles in the future. It is considered as one of the most interesting alternatives to petroleum fuels. A considerable amount of research and development work on production, storage and transportation, and utilisation of hydrogen is in progress all over the world. In India, several institutions have been working on the various aspects of the hydrogen considering it as an energy vector. A three-day National Workshop on Hydrogen Energy was organised at Indian Institute of Technology (IIT) Delhi to focus attention on developments in hydrogen energy at national and international levels and to provide a forum to coordinate contemporary research trends in the country in this field. The presentations made at the Workshop covered the topics which are considered to be of significance to work out the perspective, problems and promises for the future for transition to hydrogen energy.

The proceedings of the Workshop are reported in this book, which include the inaugural address, description of the national research and development programme in the field of hydrogen energy, papers presented on production, storage and transportation, and utilisation of hydrogen and the panel report.

In the inaugural address, emphasis is laid on the need for a transition from the presently used fuels to the newer ones, preferably to those which are renewable and non-polluting such as hydrogen. However, future developments for the application of hydrogen will depend significantly on the success achieved in improving production (especially using renewable sources), storage and transportation, and utilisation.

Hydrogen production based on electrolysis, photoelectrolysis, ocean thermal power and micro-organisms is discussed in four papers which also include advanced technologies being pursued in the respective fields. In the paper on electrolytic hydrogen production, besides the conventional method, solid polymer electrolyte (SPE) electrolysis, high temperature water vapour electrolysis and other advanced technologies and developments are covered. Details of an advanced high temperature and high pressure electrolyser of 1.5 $m^3h^{-1}H_2$ capacity developed by Bhabha Atomic Research Centre, Bombay, are presented. Salient features of the processes are reviewed in the paper on hydrogen production through photoelectrolysis. The basic characteristics of the photoelectrothermal processes leading to photoelectrolysis, employing two important semiconducting photoelectrodes, namely n-TiO_2 and n-WSe_2, are described in detail. The importance of the results obtained with these materials with regard to hydrogen production through photoelectrolysis is highlighted. Ocean thermal power for hydrogen production is the topic for another paper. Hydrogen can provide a highly efficient carrier for transferring very large chunks of OTEC power from mid-ocean sites to the mainland. In principle, liquid hydrogen, liquid ammonia and methanol produced at an OTEC plant can help conservation of terrestrial fossil fuel resources. A variety of micro-organisms belonging to morphological and physiological groups have the ability to evolve hydrogen. The paper on hydrogen production by micro-organisms discusses these groups and it explains that the biological system has the ability to use wide range of visible light spectrum to catalytically split water to H_2 and O_2.

On the storage side, presentations are made on solid state storage and cryogenic storage mode of hydrogen. Experiments conducted by synthesising amorphous phases of $RNi_5(LaNi_5,MmNi_5)$ materials are discussed which demonstrate that this phase has a higher hydrogen storage capacity. Comparison is made between bulk and thin film hydrogen storage systems. The discussions on cryogenic storate of hydrogen covers the why and how of hydrogen liquefaction. Ortho-para conversion is taken into account while working out the energy requirement for liquefaction of hydrogen. It is specified that liquid hydrogen can be stored in insulated walled containers having either liquid nitrogen or hard vacuum in the interspace of the walls.

The potential of hydrogen as a fuel is discussed in six papers which cover a wide variety of its applications for ground, air and naval vehicles; for domestic, commercial and industrial purposes; and for electrical power generation through fuel cells and MHD power generators. The benefits and limitations of gaseous hydrogen are clearly brought out for spark ignition (S.I.) and compression ignition (C.I.) engines. On the basis of results presented it is concluded that a hydrogen fuelled S.I. engine would be a feasible proposition. However, for hydrogen fuelled C.I. engine dual fuel operation is considered preferable in which the intake system should be modified enabling induction of a hydrogen gas-air mixture during the suction stroke and injection of appropriate diesel charge near the end of the compression stroke in the usual manner. It is brought out in the paper on the use of liquid hydrogen that three candidate fuels could be seriously considered as alternatives for the future transport aircrafts, viz. liquid hydrogen, synthetic jet fuel and liquid methane. The liquid hydrogen fuelled aircraft is shown to be superior in many respects when compared with the conventionally fuelled transport aircraft. It would be lighter, use smaller engines, have a smaller wing (but a longer fuselage) and would operate using short runways. Use of liquid hydrogen fuel for both subsonic and supersonic aircrafts is discussed. To establish the point, reference is made to the test flight made by Lewis Research Centre with a modified B-57 aircraft in which engines are converted to accept H_2 as fuel. It is also pointed out that liquid hydrogen can not only replace fossil fuels but can also supplement nuclear power systems in ships and submarines.

The use of hydrogen for domestic, commercial and industrial purposes, requiring only minimal modifications to the existing furnaces and cumbustors, could significantly implement the hydrogen economy, even with the level of technology available. The flameless catalytic combustion of hydrogen could be used in domestic appliances as there would be no pollutants. These aspects are covered in a paper. Two routes for generating electricity from hydrogen are discussed in the papers on this topic - fuel cells and MHD power generation. Hydrogenase, the enzyme that catalyses the oxidation of hydrogen, seems to be an ideal candidate for most hydrogen-oxygen type fuel cells. It is pointed out in the papers on the fuel cell that glucose oxides systems could be useful for bringing down the operating temperature and pressure of the fuel cells. Feasibility studies carried out on the use of hydrogen in portable as well as steam-bottomed MHD power generators are presented. The analytical investigations have been shown to give overall efficiencies of steam-bottomed MHD generators of up to 50 per cent for optimal design parameters.

While discussing the case for hydrogen using input-output structures for energy technology characterisation and assessing the impact hydrogen energy could make, it is realised that there is a paucity of data regarding hydrogen as input to various sectors of the economy and inputs from various sectors of economy to hydrogen in monetary terms. However, the model presented in the paper is limited in the sense that it does not include the clean fuel concept (environmental aspect) of hydrogen.

The recommendations made by a panel, on the basis of the deliberations of the Workshop, are listed in the Panel Report.

R.P. Dahiya
Coordinator of the Workshop and
Editor of the Proceedings

New Delhi, 1986

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The Secretary, Department of Non-Conventional Energy Sources, Government of India, Shri Maheshwar Dayal, has been supporting whole-heartedly the area of hydrogen energy in India. His support and encouragement for organising the National Workshop on Hydrogen Energy is gratefully acknowledged. The Workshop has been fully sponsored by the Department of Non-Conventional Energy Sources, New Delhi.

We are grateful to Prof. N.M. Swani, Director, Prof. M.K. Jain, Deputy Director (Administration) and Prof. R.C.Malhotra, Deputy Director (Faculty), Indian Institute of Technology Delhi, for providing the facilities to organise the Workshop at IIT Delhi. A special debt of gratitude is owed to Prof. P.D. Grover, Head, and Prof. K.L. Chopra, Ex-Head,Centre of Energy Studies, Prof. M.S. Sodha and Prof. H.B. Mathur for their constant support.

The idea of organising the National Workshop on Hydrogen Energy has been pursued vigorously by Dr. J. Gururaja, Adviser, Dr. E.V.R. Sastry and Dr. Ved Mitra, Department of Non-Conventional Energy Sources. My special thanks are to them. Shri J.R. Meena is thanked for his cooperation and untiring efforts to make the Workshop a success.

Thanks are due to the speakers who not only shared their views with the participants of the Workshop but also made available their manuscripts for publication in the present Proceedings. The members of the Panel are specially thanked for their deliberations during the Panel discussion.

The efforts of many other individuals were essential in planning and organising the Workshop. While it is difficult to acknowledge each person individually, I would like to mention Dr. Ami Chand who greatly contributed to the success of the Workshop. The assistance of Shri M.P. Joseph for a neat and painstaking typing of the manuscript, and of Shri Kirpal Singh for his skilled art work is duly acknowledged.

I must also acknowledge with appreciation the publishers, D. Reidel Publishing Company, Holland, for undertaking the publication of the Proceedings.

It would not have been possible for me to organise this Workshop and bring out its proceedings without the patience and cooperation of my wife Chandrawati Dahiya, and our sons Rajeev and Manish. I express my appreciation to them.

R.P. Dahiya
Coordinator of the Workshop and
Editor of the Proceedings

New Delhi, 1986

Inaugural address by Shri Maheshwar Dayal, Secretary, Department of Non-Conventional Energy Sources (DNES), Government of India.
Seated (from left to right): Dr. R.P. Dahiya, Coordinator of the Workshop, IIT Delhi; Prof. M.K. Jain, Deputy Director (Administration), IIT Delhi; Prof. K.L. Chopra, Dean, IRD, IIT Delhi; Dr. J. Gururaja, Adviser, DNES, New Delhi; Prof. H.B. Mathur, IIT Delhi.

INAUGURAL ADDRESS

Maheshwar Dayal
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Prof. Jain, Prof. Chopra, Prof. Mathur, Dr. Gururaja, Dr. Dahiya and distinguished colleagues from various parts of the country,

I am very happy to be here with you this morning in connection with this National Workshop on Hydrogen Energy. The longer term energy problems that we are likely to face have been discussed on several previous occasions. I have also written and spoken extensively about the overall energy problems and their solutions; in summary, it should be clear to all that we have to move to an energy transition away from the present sources of fuel on to newer systems and preferably those systems which are renewable in nature, which nature itself replenishes in a reasonable period of time and which are non-polluting. Use of renewable energy sources also preserves the ecological balance and the environment. Energy and environment are, I think, the two most crucial issues facing the whole world society today. We have now clearly understood the limitations of oil as a source of fuel. From time to time there are certain fluctuations in the availability and the price of oil. But the basic fact which cannot be in any way contradicted is that the total resource of oil on our planet earth is limited. It is a finite source and though we might stretch the period for exhaustion of this source by a few years here and there due to various measures, sooner or later it will be exhausted. In India, this has been a matter of some discussion and controversy from time to time. But I was interested to see only last week a statement reported in the papers by my colleague, the Petroleum Secretary. He is reported to have said that perhaps within the next 15 years, i.e. by the turn of this century, we we may be facing a gap of almost 50 million tonnes per year between our demand and the supply of indigenous oil. This is in spite of the fact that we have made commendable strides in the production of oil from indigenous sources.

In this type of situation no delay should be made in considering alternatives, and one of the most interesting alternatives that we can consider as a replacement for petroleum based fuels is Hydrogen. This has been talked about by scientists from time to time; indeed the possibility of a "hydrogen economy" has been raised. Hydrogen is a fuel which should excite great interest for the simple reason that it is

R. P. Dahiya (ed.), Progress in Hydrogen Energy, 1–8.

abundantly available - everybody knows that all water consists of hydrogen and oxygen. But what is also elegant about hydrogen as a fuel is that when it is burnt, you get back water. Therefore, it is a practically perennial source of energy because if you can get hydrogen and use it through the oxygen route for combustion, you get back water, which is clean, and in the process energy will be generated due to the exothermic nature of the reaction. Of course, we are also aware of another route through which hydrogen can be used for energy, and that is using the nuclear properties of hydrogen. I am talking here of nuclear fusion. We have already the example of the hydrogen bomb which liberates enormous amount of energy in a short period of time and that is what gives it its explosive character. Controlled fusion of hydrogen nuclei or its isotopes, if developed commercially, could provide enormous amounts of energy. I will not go into the aspect of fusion in greater detail today, but deal more with the methods by which we can derive energy from hydrogen as a fuel through the combustion route or through other ways of combination with oxygen.

It is interesting to note that on combustion hydrogen gives one of the best heat values per unit weight amongst many possible fuels. For example, hydrogen gives about 52,000 Btu per pound as compared to methane which gives about 21,500, gasoline which gives only 19,100, ethanol about 11,600, methanol about 8,700 and ammonia about 8,000. So if we take the relative weight of fuel required to equal the hydrogen heat value we find that with hydrogen as 1, ammonia is about 6 times, methane 2.4 times, methanol 6 times, ethanol 4.4 times, gasoline 2.7 times, and avaiation fuels 2.8 times. The combustion and other characteristics of hydrogen can well be compared with the fossil fuels. A comparison of some of the properties of hydrogen with methane and aviation fuel JP_4 is made in Table I and Table II respectively.

TABLE I - Comparison of Hydrogen and Methane Fuel Characteristics

	H_2	CH_4
Liquid density at normal boiling point kg/m^3	425	71
Net calorific value for gas k cal/mole	57.8	21.3
Flammability limits volume per cent	4-74	5-15
Ignition energy for stoichiometric fuel-air mixture millijoule	0.019	0.29
Maximum burning velocity for fuel-air mixtures at NTP m/s	3	0.4
Adiabatic flame temperature for stoichiometric combustion with air K	2400	2200

TABLE II - Physical and Thermochemical Data for JP_4 and H_2

Property	JP_4	H_2
Heat of combustion, k cal/gm	10.40	28.65
Spontaneous ignition temperature, °C	250	571
Specific gravity	0.78	0.0705(LH_2)
Fuel for maximum flame speed (% stoich)	107	171

In addition, hydrogen is capable of being stored and transported. It can be used also as a feedstock for fertilizers, and for metallurgical, petrochemical, semiconductor and pharmaceutical industries. It has possibilities of inter-convertibility to various forms of energy and it has a potential of being a means for harnessing solar energy.

One of the main problems that has been arising in hydrogen development is the energy input needed in its production. Research has, therefore, to be concentrated on trying to find ways of reducing this energy input, and for using renewable sourcesof energy for this production. Solar energy offers a very exciting field for possible application in the production of hydrogen. If we can develop economic ways of applying solar energy for the production of hydrogen through photolysis or other methods, then we shall have taken a very long step towards the practical application of hydrogen on a large scale.

The potential for hydrogen, therefore, taking all these possible advantages is very great and various estimates have been made of this potential. According to an estimate made recently at the Third World Hydrogen Energy Conference, in the United States alone it would be possible by the year 2005 to have an application of hydrogen for both non-energy and energy uses of more than 7000×10^{15} joules per year. The future development for the application of hydrogen will depend significantly on the success achieved in improving its production, transportation and use. It is difficult to forecast exactly the time when this may take place because of several unknown factors. However, it is quite clear that hydrogen will play an important role in future, particularly in what is called the post oil era or the post fossil fuel era, and therefore our research and development programme must provide the necessary knowhow in time. As a matter of fact, I think this is a very interesting example of what we can do here in India in a field which is developing all over the world. It is not something which has achieved a real breakthrough in economic and practical terms in other countries also and, therefore, here is a field in which there is every chance for India, by putting adequate research and development efforts, to be abreast or even ahead of the most advanced industrial and scientific nations. This, I think, is the sort of thing we should look at when we are talking about our entry into the 21st century, i.e. frontier area technologies and frontier area science as a possible path for application of our own scientific efforts.

The range of subjects to be covered under the research and development programmes can be broadly classified as the production, storage, transportation and utilization. The various routes of production are either electrolysis or photolysis of water or production through chemical or thermochemical methods from fossil fuels. In the broad category of storage and transportation is included work on hydrides, gaseous storage and liquid storage. The area of utilization includes some applications which have already started such as launch vehicles for satellites, and other possible applications such as for aircrafts, surface vehicles and stationary engines. We have a very interesting engine which is already developed and is working right here in the Indian Institute of Technology Delhi. This could be an interesting application for both vehicles and stationary uses of hydrogen as a fuel. Then we come to the use of hydrogen through fuel cells and its application in chemical and metallurgical industries. One area of research and development which obviously must receive a lot of attention is safety and health hazards because of the potentially explosive nature of hydrogen above the flash point. This is one of the aspects that has deterred many people from considering hydrogen applications. But I am sure it can be handled with proper research and development concentration on this area. Finally, we have to do more and more research and development work in materials which are involved in the whole chain of production, storage, transportation and utilization of hydrogen.

As far as production from coal and fossil fuels is concerned, this has often been translated into a need for development of the catalysts to push reaction rates of the water gas reaction namely carbon plus water giving carbon monoxide and hydrogen. As the sulphur present in coal fastens the catalyst, new catalysts based on sulphur compounds are also being investigated. So far as water electrolysis is concerned, this is a well known technique for production, which is presently being employed for chemical purposes largely. With increasing demand for hydrogen, research programmes have been undertaken to increase the efficiency and decrease the unit cost of electrolyser. In the United States, the Department of Energy has sponsored the development of advanced technology for the production of hydrogen with industrial contractors like the General Electrical Company, the Teledyne Energy Systems and Life Systems Inc. The necessary supporting fundamental research has been entrusted to several universities. Two major methods of electrolysis are the alkaline water electrolysis as being attempted at Teledyne Energy Systems and Life Systems Inc. and the solid polymer electrolyser being followed by the General Electric Research Group. The Teledyne programme has been supported by the US Department of Energy from the 60's onwards and concentrates on three vital areas for improving the efficiency of the existing alkaline technology. The areas in which improvements are sought are: firstly, operating temperature of the electrolysis to be 125°C or more to improve the voltage efficiency; secondly, improvement in the catalyst and electrode structure; and thirdly, development of a stable electrode separator which can withstand high temperatures and alkaline environment. Teledyne has completed the identification of candidate components after elaborate screening. These components will be assembled into a working system to obtain life and performance data. Future phases of work would address to scale up of manufacturing engineering, evaluating performance in terms of industrial application and other similar related activities. The work at Life Systems Inc. started only in 1980 and their technology is based on the static feed concept wherein the water feed is supplied to the cell as a vapour after passing through an asbestos matrix and being driven by the difference in water vapour partial pressure across the matrix. They have demonstrated certain cells containing super electrolyte, and single cells of more than a square foot have also been fabricated and tested at varying current density. General Electric Company technology is based on the use of a solid polymer electrolyte cation exchange membrane and catalytic electrode technology originally developed for fuel cells in 60's. By 1982 a 2.5 sq.ft. cell of 200 kW capacity had been developed at a cell efficiency which they quoted as 83 per cent and ran for more than 700 hours. The cell efficiency has been reported to have gone up to something 80 per cent or more by reducing the thickness of the membrane and by lowering the current collector resistance. The work has been progressing from there onwards to try and improve the cell efficiency to 90 per cent and the life to more than 40,000 hours. There is also a lot of work going on in other countries on electrolytic hydrogen production. Belgium for instance has reported success in the use of polyantymonic acid membrane in alkaline electrolytic systems. Large size membranes up to 30-50 cm are being presently manufactured. The Canadian programme is mainly on the non-noble metal catalysts. They are also concentrating on the organic polymer for high temperature advanced electrolysis. A long term test facility for separator and electro-catalyst has been constructed in Canada. The French programme concentrates on making the fabric suitable for use as diaphragm in alkaline electrolysis at 200°C. In Italy efforts are under way on deposition techniques of electrocatalyst as the SPE material for alkaline electrolysis. Japan has demonstrated an advanced alkaline electrolysis pilot plant operating at an efficiency of 90 per cent at 1.54 volts. A 60 kW plant is also expected to be in regular operation. At the Brown Boveri Research Centre, Switzerland, the work on SPE electrolysis is in progress. The concentration is mainly on the electrocatalyst and the current collector development programme.

Thermochemical methods leading to water splitting offer a promising route. Five thermochemical water splitting cycles have been extensively studied. They all have in common sulphurdioxide and sulphuric acid as part of the cycle with acid concentration ranging from 50 to 60 per cent. Laboratory scale units have been assembled and operated at ambient pressure. The five cycles are: the General Atomic Sulphur Iodine cycle, the ISPRA Mark XVI cycle, the Westinghouse Sulphuric Acid cycle, the ISPRA Mark XI cycle and the ISPRA Mark XIII Bromine Hydride cycle. In Italy, the decomposition of sulphuric acid by the Pristine process has been studied to supplement the data required for the thermochemical cycles which require hydrogen sulphate decomposition. Experimental work relating to hybrid thermochemical cycle involving bismuth trisulphate and/or bismuth oxysulphate and zinc sulphate have also been attempted. A three step thermo electrochemical water splitting cycle produces hydrogen by an electrochemical reaction of water with cadmium anode. Japan under the Sunshine project has studied iron floride and cadmium iodide based cycles. In Germany a number of research groups are working on hybrid processes like electrolytic oxidation of sulphur dioxide in aqueous solutions with simultaneous production of hydrogen. Another process of interest is the formation of metal hydride in an electrolytic step followed by thermochemical step to generate hydrogen.

The one area which to my mind is extremely interesting for our work in India is the possibility of a photolytic process for production of hydrogen through solar energy. Research in this area includes many elements including photocatalysis, solar electrolysis, basic investigations of photosynthesis and its processes, photochemical and photoelectrochemical processes. Two recyclable photocatalysts are being investigated in detail, one inorganic and another mixture of organic and inorganic. Research in biophotolysis is another very interesting area which should be expanded further. This involves an understanding of low micro-organism and how they produce, transfer and use hydrogen through investigation of genetics and biochemistry of photosynthetic apparatus, electron transport and enzyme systems. The absorption characteristics of electrode materials and reduction in the required electrical potential are also being investigated. Photoelectrochemical properties of chlorophyl as a photocatalyst in water splitting programmes is also being investigated and is another very promising possibility. I will not go into all of these in detail. But I hope I have given some idea of the broad range of activities that are being attempted in many parts of the world including India in regard to the production of hydrogen.

Coming to storage and transportation, hydrogen can be stored and transported either in the form of a gas, a liquid, or a solid compound. Gaseous hydrogen has been transported efficiently through underground pipelines using systems similar to natural gas and transmission networks based on gas. According to some studies hydrogen may work out as a cheaper source for transmitting over distances beyond 300-500 miles through pipelines as compared to the transmission of electrical energy through overhead lines. This is another aspect that has to be kept in mind in the potential of hydrogen. However, economical hydrogen storage and transportation presents many technological challenges which have attracted considerable research. Storage as liquid in cryogenic tanks is feasible and has been developed. However, liquefaction and transportation presents many problems, particularly the economic penalties. The possibility of storing hydrogen underground just as helium is being explored. A promising storage concept, of course, is the metal hydride. For the transportation sector, it would be possible to consider having a tank which consists of basically a solid hydride and when the accelerator is pressed a little more hydrogen can be made to come out of the hydride and go into the engine to get extra power for the vehicle.
A novel method for storage and transportation of hydrogen being worked out is the reversible catalytic hydrogenation of a liquid hydride which has been demonstrated to an efficiency of 98 per cent. The liquid

hydride in the presence of proper catalyst gives benzene and hydrogen. In essence, hydrogen at source is made to react with benzene in an adiabatic reactor, with the production of cyclohexance which can be transported easily.

Finally, the general sector of hydrogen utilization. In the area of launch vehicles, aircrafts, turbines etc., the high heating value of hydrogen has already enabled this to be used as propulsive energy. The major drawback todate for its use in civilian aircraft or other aircrafts is the cost. However, with improved production methods, hydrogen could well be the fuel for tomorrow's aircraft. In fact, hydrogen fuelled aircrafts have been test-flighted by NASA Lewis Research Center. Hydrogen converted Boeing 747 will have 25 per cent reduction in the take-off gross weight and is being attempted by the Company. Launch vehicles and space shuttles are already using liquid H_2-O_2 systems, for putting satellites in geostationary orbits, either in booster or in upper stages because of their high specific impulse. India and Japan are joining in this task by initiating work on cryogenic systems. Coming to surface vehicles, hydrogen driven engines have been known for quite some time. A number of hydrogen fuelled automobile projects are under way in many countries. A major difficulty faced by hydrogen fuelled automobiles is that of on-board fuel supply. Also assuming acceptable means of transporting hydrogen can be developed, there is a general problem of servicing the vehicles fuelled with hydrogen. Tanking of hydrogen gas calls for heavy walled tanks, while liquid hydrogen calls for expensive dewar type vessels. Japan, incidentally, has been working on and has developed a "Musashi-4" car in 1980 on which a two stroke engine of 1100 cc and 3 cylinders was installed. The main objective of this programme is to convert the existing spark ignition engine for operation with hydrogen. Regarding hydrogen for trucks and utility vehicles there are not very significant problems to preclude its introduction, and this will perhaps come earlier than its use in passenger cars. The concept of cryohydrogen driven rails, trucks and the substitution of the diesel engine are also being tried.

There are also other routes to hydrogen use such as fuel cells and the chemical, metallurgical and fuel industries. And finally, as I mentioned earlier, the whole question of safety and health hazards and also that of materials, needs a major effort from all our research and development programmes. All this should receive attention from our research and development workers,preferably in an interdisciplinary manner, to achieve results in a time bound fashion. We should have certain targets for our programmes in this area and see how we can best meet them. There is always the question of funding, which is one of the commodities that seems to be in the shortest supply. I think finally we will resolve our energy shortages, but we may never solve our money shortages - that is something we have to simply live with. But we will have to make the best of what we have and see how to utilize it in the most optimum way.

Considering all that I have tried to survey in the brief time at my disposal today, it is very timely that this 'National Workshop on Hydrogen Energy' is being organised at IIT Delhi. I hope that the deliberations of the Workshop will lead to the formulation of a coordinated, integrated and time-bound programme and specific recommendations in this area. You must be aware that so far five World Hydrogen Energy Conferences have been held, starting from 1976. The fifth one was held last year at Toronto and I think some of you present here must have participated in that. Coordinated international activities in hydrogen energy were also started around the mid 70's as a result of which the International Association for Hydrogen Energy has been founded and the International Journal for Hydrogen Energy has also been inaugurated by Pergamon Press. It is heartening to note that our scientists and engineers have been publishing papers in the international journal and also participated in the World Hydrogen Energy Conferences. Also we have made some very interesting progress about which I am sure papers will be presented during this Workshop. A Hydrogen Energy Task Force has also been constituted to look into the various implications of hydrogen and the possible work that could be done in India. The Department of Non-conventional Energy Sources (DNES) has been promoting research and development efforts relating to hydrogen energy to the best of our ability considering the financial constraints. The DNES has set up a Technical Advisory Committee on Hydrogen Energy to review the progress and programmes in the area and to evaluate new proposals. It is on the recommendations of this Committee that this National Workshop has been sponsored by the DNES.

More than 10 research projects have been funded by the DNES on the various aspects of hydrogen energy technology. We would like to expand activities in this area by taking up additional projects to the extent feasible. Among the principal activities of DNES during 1984-85 are: a status report on studies relating to hydrogen storage has been completed; work on the project for the production of hydrogen by photo-assisted electrolysis of water utilizing solar energy continued during the year; a project for optimization of hydrogen production by blue green algae has been sanctioned; more research groups have been entrusted the task to investigate hydrogen storage in metals, alloys and other solid state materials; and interesting results have been obtained from the experiments conducted with hydrogen as a fuel for engines. Leading research institutions such as IITs, universities and national laboratories are involved in the research and development activities on hydrogen energy. In addition to the DNES sponsored projects, work related to hydrogen energy is underway at BARC Bombay, VSSC Trivandrum, TIFR Bombay, CFRI Dhanbad, NPL New Delhi, IIT Kharagpur, etc.

I hope that this National Workshop will become a regular feature and will be held from time to time to take stock of progress in this field and to make recommendations for the future. In a separate lecture my colleague, Dr. Gururaja, I am sure will give you more details about the various research and development programmes sponsored by the DNES. Therefore, without taking more of your time, I would like to conclude by congratulating the IIT Delhi, the Coordinator of the Workshop Dr. R.P. Dahiya and all other scientists who have taken initiative to organise this National Workshop and to participate in it, and I have great pleasure in inaugurating this National Workshop.

Thank you.

NATIONAL RESEARCH AND DEVELOPMENT PROGRAMME IN THE FIELD OF HYDROGEN ENERGY

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1. INTRODUCTION

Hydrogen is a versatile energy carrier and can be used in a variety of ways. Hydrogen can be obtained from any primary energy source including solar, nuclear or geothermal resources. Today, the hydrogen is mostly produced from hydrocarbons, but in future, hydrogen could be obtained from new and renewable sources of energy and could potentially replace petroleum products in the long term.

One of the most attractive features of hydrogen as fuel is that its primary resource is water. Thus if it is produced from water using solar energy, it can be considered as a primary source even though it does not occur in nature. A great deal of scientific research and technological developments will be required to realize the potential of hydrogen as an energy vector.

With these considerations, the Department of Non-conventional Energy Sources (DNES) has been supporting projects relating to hydrogen energy technology at various institutions in the country. A Technical Advisory Committee on Hydrogen Energy has been constituted to monitor the on-going projects and to identify and recommend thrust areas for intensive research and development. The programme in hydrogen energy area is being expanded substantially during seventh plan period.

2. HYDROGEN AS A FUEL

The utilization of hydrogen as energy source on a sizeable scale involves the following five basic issues:

- Production
- Storage and transport
- Application
- Safety
- Economy.

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2.1 Production

It is estimated that the current annual production of hydrogen for various applications world-wide is of the order of 25 million tonnes based on conventional energy. In the longer term, production processes that are of interest are:

(a) Solar Energy - thermal dissociation of water, electrochemical dissociation of water, photocatalysis, photobiological catalysis, photosynthesis, etc.
(b) Conventional electric power - electrolysis of water
(c) Geothermal energy - electrochemical dissociation of water
(d) Wave and tidal energy - electrochemical dissociation
(e) Coal - coal gasification
(f) OTEC - electrochemical dissociation of water
(f) Hydropower - electrochemical dissociation of water.

Among the various processes, the ones that are based on renewable energies are of direct interest to us. Photoelectrochemical splitting of water is considered to be the most potential futuristic technology for hydrogen production.

Another approach is the development of photochemical cells for the production of hydrogen by water cleavage, which differs from photoelectrochemical cells principally in that, in the former, light absorption takes place in a solution while in the latter, a solid is the light absorber. Recently, some Swiss experts are reported to have demonstrated that hydrogen and oxygen can be produced in small quantities from photochemical cells using heterojunction catalysts. In this technique, the light is absorbed by the transition-metal complex ruthenium tris (bipyridine) which then transfers an electron to a relay compound, methylviologen (also called as paraquat). In presence of a platinum catalyst, the latter compound generates hydrogen.

Another possibility is to use materials (algae, bacteria) which themselves contain enzymes which are capable of decomposing water to form hydrogen under the influence of sunlight. The production of hydrogen using thermochemical cycles which is a newer concept than the electrolytic production is also being studied in many countries of the world.

2.2 Storage and Transport

One of the concerns about the successful harnessing of hydrogen as energy source is generally associated with its storage and transportation. These problems are more or less related to the lightness and chemical activity of free hydrogen. Though hydrogen is light and more chemically active than natural gas, the former could be transported and stored on a large scale in the same way the latter is transported and stored, with some modifcation.

As regards storage, hydrogen can be stored for use as energy source, in the following ways:

- Gaseous storage
- Liquid storage
- Metal hydride storage

- Microballoon storage
- Underground storage

The storage of hydrogen in gaseous form requires large volumes. Even under compression, the volume-storage efficiency of gaseous storage is not as high as liquid hydrogen and the weight of the storage cylinders poses a major difficulty. Storage in the form of liquid hydrogen is certainly better because the volume storage efficiency is improved. The liquefied hydrogen can be transported over long distances without much problems. However, the necessity for super-insulated containers makes this mode of storage very expensive. Research and development efforts need to be pursued to solve these and other related issues.

An alternative and promising means of storing hydrogen is in hydride compounds. Certain metals and their alloys, namely, magnesium-nickel, magnesium-copper, and iron-titanium are capable of absorbing hydrogen gas to form chemical compounds referred to as hydrides. When heated, these compounds release the hydrogen again to be used as fuel. This particular method avoids having to contain large volumes of hydrogen as gas or to maintain special pressures and temperatures needed for storing hydrogen as a compressed gas or as a liquid. Research and development efforts are still required to investigate lighter hydrides or hydrides with even larger storage capacities which could lead to convenient use of hydrogen for vehicular and other applications.

Hydrogen as a gas could be stored underground in large amounts. The empty or abandoned wells of petroleum or natural gas are considered to be ideally suited for this type of hydrogen storage.

The microballoon storage of hydrogen may be desirable and advantageous for certain small applications. However, one has to maintain special pressures and take due safety measures in handling balloons filled with hydrogen gas.

Small quantities of hydrogen in liquid or gaseous form can be transported on land or water in special storage vessels. In the U.S.A. and a few other countries, small amounts of liquid or gaseous hydrogen are now being transported routinely, using the above modes of transportation. Liquid hydrogen is being transported on rail and road for over a decade in the U.S.A. But the large quantities of hydrogen can possibly be transported by pipelines or ocean tankers only. For transportation of gaseous hydrogen in pipelines, inexpensive, embrittlement resistant materials, or new techniques for designing pipelines with existing materials will have to be developed. Adding certain impurities or inhibitors to hydrogen could eliminate embrittlement. In case of liquid hydrogen, the problem to be faced relates to the proper insulation of pipes, if liquid hydrogen is to be transported through pipelines. This is an area where research efforts need to be pursued rigorously in India.

2.3. Utilization

Hydrogen is a versatile fuel and can be used for automobiles, spacecrafts, aeroplanes, helicopters, engines and in fuel cells. Hydrogen-driven scooters, buses, cars and aircrafts have already been developed and tested in U.S.A., U.K., Japan etc. However, among the major difficulties faced in this regard relate to the problem of on-board fuel supply, the servicing of hydrogen fueled vehicles, and the additional safety measures. If these problems are solved, it is considered that transport sector will be a large scale consumer of hydrogen.

Hydrogen can be used for indoor utilities, e.g. as a cooking fuel, for space heating and cooling, etc. Using hydrogen for load levelling in coal-fired, nuclear and solar power plants might become a possibility in future. The surplus electric power from the power plants could be used to generate hydrogen, then reconvert the hydrogen, in fuel cell or gas-turbine-driven generators, to electricity for use during off-peak hours. The supplementing power plant generating capacity with such hydrogen-based peak-power systems could save a considerable amount of fossil fuels, besides reducing the environmental pollution.

Hydrogen can also be used to produce electric power in fuel cells either in a centralised or a decentralised manner, depending upon the conditions of use. For example, for small villages, it could be advantageous to set up small fuel-cell substations for a few hundred households rather than for each household. This way, it could be easy to install, operate and maintain the systems in village environment in the country.

Hydrogen can be used to run pumps for drinking water supply and irrigation purposes in rural and remote locations, hilly regions, semi-arid and arid areas, where the supply of water is a chronic problem and where the supply of fossil fuels is difficult.

2.4. Safety

The utilization of hydrogen requires specific handling procedures to ensure safety. It may be noted that when hydrogen burns, the combustion proceeds very rapidly. The more rapid combustion of hydrogen and its low fuel-to-air combustion ratio make it more susceptible to explosive combustion in a closed space. Also, the low ignition energy of hydrogen makes it necessary to assure that it is adequately contained and protected from electrical discharge and catalytic agents which might cause combusion. It is necessary that hydrogen be kept under adequate pressure at all times during transportation and storage in order to ensure proper safety. The hydrogen driven vehicles will also call for addditional safety measures than the conventional ones.

2.5. Economy

Hydrogen offers manifold energy options. Hydrogen is a clean fuel and no major pollution problems are associated with the production and utilization of hydrogen as a fuel. Hydrogen has reasonable compatibility with fossil fuels technology, excellent interfacing with the future energy technologies and an optimal character in respect of the lack of pollution as stated above. However, the economy of hydrogen as energy source would depend upon a number of factors relating to production, storage and utilization. At present, detailed economic evaluation for energy purposes are still not available.

3. RESEARCH PROGRAMMES

The Department of Non-conventional Energy Sources has been promoting research and development activities in the field of hydrogen energy in the country. As mentioned earlier, the Department has also constituted a Technical Advisory Committee on Hydrogen Energy which reviews the progress of projects funded by DNES and scrutinises new proposals submitted by various institutions engaged in hydrogen energy programmes, for financial support. It identifies and recommends thrust areas for further research and development.

Considering the role hydrogen is expected to play in future, the Department has so far funded about 10 projects on different aspects of hydrogen energy technology, at research institutions, IITs, universities and national laboratories. These projects broadly include the preparation of status report on different topics of hydrogen energy technology, production, storage and utilization of hydrogen as fuel, including fuel-cell. A status report on studies concerning hydrogen storage has also been prepared. A project supported by DNES at IIT Madras, regarding the use of hydrogen as fuel for diesel engines has been completed recently. The study suggested that the addition of diluents and reducing the compression ratio enables higher quantities of hydrogen to be used in a dual-fuel engine. Another useful suggestion related to mixing of an optimum percentage of carbondioxide with hydrogen even at the bottling stage, so that one can achieve the maximum substitution of diesel oil used in I.C. engines.

Good progress has been reported in a project being supported at IIT Delhi, for the utilization of hydrogen as a substitute fuel for S.I. engines. Extensive experiments have been carried out to assess exaust NO_x emission from hydrogen driven engine under various operation conditions. The results achieved so far indicate that a hydrogen-fueled S.I. engine is a feasible proposition. In a similar project at BHU, Varanasi, a Kirloskar 5 BHP, single cylinder, 4 stroke C.I. engine has been converted to dual fuel engine to run on hydrogen. A 3 BHP petrol engine has also been modified to operate solely on hydrogen. The use of hydrogen in different engines is expected to save considerable amount of oil, besides solving pollution problems. Research and development efforts still need to be pursued vigorously in order to solve many technical problems.

In addition to projects being supported by DNES, a considerable amount of work relating to hydrogen energy is being carried out by BARC, VSSC, ISRO, TIFR, CFRI, IACS, NCL, NPL etc. in the country. The CFRI has designed, fabricated and installed a pilot plant for the production of hydrogen (designed capacity 35 Nm^3/hour), at a pressure of 21.1 kg/cm^2 by shift conversion of K-T gas/water gas. The objective was to meet the demand of hydrogen of the tar hydrogenation plant and test the catalysts developed by CFRI. The purity of hydrogen in washed gas has been reported to be 94%.

BARC has conceived and developed an advanced high pressure electrolysis system a decade ago and has the expertise to scale to commercial size plants. Possibility of setting up a hydrogen generation plant based on high efficiency, advanced type pressure electrolysis, is also being explored. If installed, this plant is expected to ensure smooth and continuous supply of hydrogen to operate a fleet of buses on hydrogen fuel.

The VSSC/ISRO have envinced keen interest in liquid hydrogen for its future space programmes. The liquid hydrogen has been considered to be one of the best fuels for subsonic and supersonic aircrafts worldwide in the years to come.

Work relating to fuel-cell energy systems is being carried out at TIFR. It is proposed to intensify research efforts in this area which has tremendous potential as reliable power source in rural areas of the country. A few pilot plants are proposed to be set up based on hydrogen-oxygen fuel-cell systems.

Research work relating to the development of suitable technology for the liquefaction of hydrogen fuel for various applications is being carried out at NPL and IIT Kharagpur.

4. FUTURE PROGRAMME

It is proposed to intensify research and development work in the area of hydrogen energy during Seventh Five Year Plan period. Projects relating to production of hydrogen (thermochemical system, electrolysis and photoelectrolysis of water, biological production etc.); hydrogen storage techniques, unitilization of hydrogen for different applications, including in fuel cells, will be supported. Various demonstration programmes for hydrogen-driven vehicles etc. will also be taken up during the Seventh Plan. Studies concerning safety and economics of hydrogen energy will be carried out.

The Sub-Group on Hydrogen Energy set up in connection with the preparation of proposals for the Seventh Plan in this area has proposed the setting up of centralised research centre where facilities would be available at the national level, for activities concerning theoretical studies, practical applications, testing and eventually certification of hydrogen energy systems. As regards programmes for 1985-86, a provision of Rs 40 lakhs has been made by DNES in order to support the on-going projects and new projects in the field of hydrogen energy during 1985-86.

ACKNOWLEDGEMENT

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ELECTROLYTIC HYDROGEN PRODUCTION

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1. INTRODUCTION

It is an accepted fact that the world's energy needs will increase greatly and the present so called cheap fossil energy sources will, slowly but surely, vanish within the next few decades. This growing awareness of the rapid depletion of our fossil fuel reserves, on the one hand, and the environmental damage caused by prolonged consumption of these fuels on the other, have led us to a vigorous search for non-fossil energy sources to meet our ever increasing energy demand. Fortunately, a variety of non-fossil energy sources are available and are in various stages of development and exploitation. The most prominent among these, drawing worldwide attention and developed to the stage of commercial feasibility is of course nuclear energy. Other potential but not yet proven sources are renewable sources like solar, wind, tidal, geothermal and ocean thermal energy.

However, all these energy sources are handicapped by their not being portable, and by not offering the logistic convenience and facility of oil. A primary energy source like nuclear energy has to be suitably transformed and distributed to the consumer in a usable form. Electricity has been the natural choice. The main difficulty with electricity is that it cannot be stored on a large scale. The power plant output must be perpetually adjusted so that it meets the varying demands of the consumers; thereby the average load-factor of the power plant is considerably reduced sometimes even to about 50 per cent or lower. Electricity is also not the most economical form of transportable energy for all domestic and industrial applications. The cost of transmission and distribution to the residential consumer is more than 50 per cent of the total cost at the point of end use. The cost of underground transmission and distribution will be even more.

We must, therefore, look out for a new energy carrier, the concept of hydrogen as a secondary energy carrier is under serious consideration around the world. The hydrogen produced by splitting water, fulfils all the requirements of versatile secondary energy carrier and ideally complements electricity in the energy economy of a post-fossil fuel era.

R. P. Dahiya (ed.), Progress in Hydrogen Energy, 15–29.

2. NUCLEAR POWER TO HYDROGEN

Nuclear heat can be converted into hydrogen either directly via thermal splitting of water or via electricity through the water electrolysis route. Thermochemical splitting requires temperatures of the order of 1100°K. High Temperature Gas Cooled Reactors (HTGR) have been suggested and even used as demonstration plants. However, due to technological problems these concepts have not been vigorously pursued. Further, so long as electricity continues as an important energy carrier, nuclear power generation will be practised and conversion of electricity into hydrogen will be more relevant.

3. ELECTROLYTIC HYDROGEN

This technology has been used for industrial production of hydrogen for more than eight decades. A number of different electrolysers were developed in the 1920 and 1930s, primarily for the ammonia fertilizer production based on low-cost hydroelectricity. However, during the time of Second World War, the adoption of this process has not found much favour due to the massive availability of low cost hydrocarbons as an alternative to electricity-based hydrogen.

Serious development efforts are being made all over the world to improve the efficiency of water electrolysis and to reduce the capital costs of electrolysis plants. One way to achieve these is to increase simultaneously the current density and temperature of the electrolysis cells. High temperature operation involves an increase in the overall system pressure also. By this the partial pressure of water vapour can be made small with respect to the product gas pressures, i.e. hydrogen and oxygen.

Generally, the aim is to achieve maximum efficiency, the efficiency being defined as the ratio between the water splitting energy, H, and the electrical energy input, E, to the electrolysis cells.

The theoretical energy requirement for the electrolytic decomposition of water at 25°C

$$2\ H_2O\ (1) \rightleftharpoons 2\ H_2 + O_2$$

is the negative of the heat of combusion of hydrogen.

$$\Delta H = -\Delta H = 286.25\ \text{KJ/gm mole}\quad (68.317\ \text{KCal/gm mole})$$

$$= 3.54\ \text{KWH/M}^3\ H_2$$

This energy is related to the decomposition voltage by the equation

$$\Delta H = -nFE$$

where n = number of electrons transferred per mole of water,
F = Faradays Constant 96,500 coulombs, and
E = electrolysis voltage.

Thus the energy required for electrolysis of water can be supplied by the application of 1.48 volts at 25°C.

However, the minimum electrical energy required is governed by the Gibbs free energy, ΔG, for water at 25°C.

ΔG = +237.53 KJ/gm mole which is equivalent to 1.23 volts. The remaining energy $T\Delta S$ can in principle be supplied by ambient heat. In other words, the electrical energy required for the process is only 83.7 per cent of the combustion energy of the hydrogen produced, the other 16.3 per cent is supplied as heat (i.e. the fuel value of hydrogen produced is 120 per cent of the heating value of the electrical energy input). Since electrical energy is increasingly a premium energy source from the view point of both availability and cost, it is advantageous to substitute heat for electrical work whenever possible.

In practical electrolysers, there is usually an efficiency loss that is greater than the difference between the free energy voltage and the enthalpy voltages. In other words, industrial cells usually operate at voltages greater than 1.48 volts and liberate heat because of a variety of efficiency losses occurring within the cells. As is well known to electrochemists the difference between the actual and theoretical electrolysis voltage is known as over-voltage (also called polarisation or over-potential). The basic reasons for the overvoltages are mainly due to the limited rate of reactions that occur at the electrode surfaces, blockages of the electrodes by gases, ohmic resistance of the electrolyte/separator interface which keeps the product gases from intermixing and also due to the localised increase in electrical resistance due to concentration gradient of the electrolyte at the electrodes.

The electrolysis voltage, E, or the "reversible voltage" as it is called decreases with increasing temperature (Figure 1) according to Gibbs Helmholtz equation:

$$\frac{dE}{dT} = \frac{E}{T} + \frac{\Delta H}{nFT}$$

a decrease of 8 mV for every 10°C rise in operating temperature. However, it may be noted from Nernst equation

$$\Delta E^o = - \frac{RT}{nF} \ln \frac{P^2H_2PO_2}{P^2H_2O}$$

or $\Delta E^o = 0.0295 \log P$

(where P is in atmospheres and E^o is in volts)

that increase in operating pressure increases the electrolysis voltage only marginally. The voltage increases only logrithamically with pressure and the electrolysis voltage at 1000 psi is about 0.54 volts higher than the voltage at normal atmospheric pressure. The energy required for this additional voltage is exactly equal to the potential energy contained in the high pressure hydrogen.

In practice, electrolyser cells operate slightly closer to the ideal at higher pressure than they do at atmospheric pressure, that is

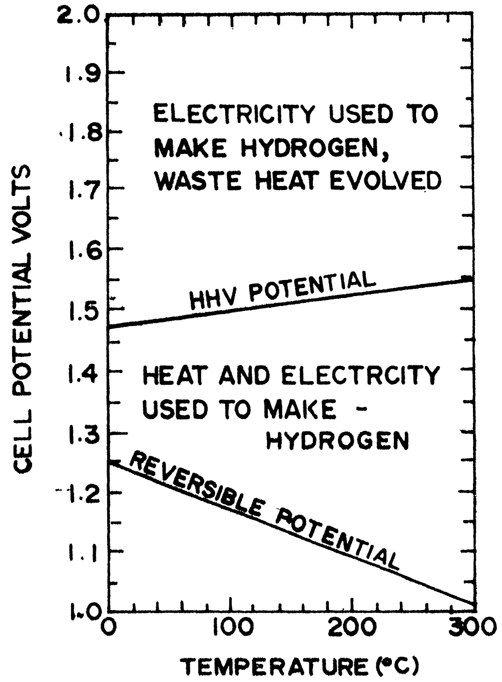


Figure 1. The cell potential for water electrolysis as a function of temperature. The thermoneutral potential is based on the higher heating value (HHV) of hydrogen while the reversible potential is based on the free energy change for the reaction.

to say, that efficiency losses are less at higher pressures. One of the reasons for this high efficiency is that the gas bubbles evolved are smaller at high pressures and offer less resistance to the passage of ionic current across the cell.

At pressures up to 30 atmospheres, the energy saved due to increased efficiency is greater than the extra energy that has to be exerted to overcome the theoretical voltage. Thus pressurised operation of the electrolysis cell in effect, improves the efficiency of generating hydrogen and moderate pressures can be developed at "apparent" pumping efficiencies more than 100 per cent.

4. PRESENT STATE OF THE ART OF WATER ELECTROLYSIS TECHNOLOGY

Presently the use of electrolytic hydrogen is restricted to special applications (Table I) (Hammerli, 1984) where high purity hydrogen is

TABLE I : Present uses of Electrolytic Hydrogen

(A) 2.5 kW to 5 MW Plants

1. Electricity generator cooling
2. Hydrogenation of foods
3. Hydrogenation of industrial chemicals
4. As a chemical reducing agent in:
    (a) Powdered metals production
    (b) Metallurgical processing
    (c) Electronic components manufacture
    (d) Production of float glass
5. Filling weather balloons
6. Bottled hydrogen for miscellaneous uses

(B) 100 MW Plants

1. Ammonia production
2. Heavy water recovery as a by-product

required or in areas that are too large to use bottled hydrogen economically but too small for on-site production based on fossil fuels. Generally hydrogen plants based on electrolysis are of capacities in the range of 15 m^3/d to about 30,000 m^3/day which corresponds to a power input of 2.5 KW to 5 MW. It may be noted that a 600 tonnes per day ammonia plant will require about 50,000 m^3/hr of hydrogen or a 240 MW electrolyser plant.

Only very few electrolytic hydrogen plants in the range of 100 MW exist. They are in Nangal in India, Ryukan in Norway and at Aswan Dam in Egypt. All of them are fertilizer plants generating hydrogen for ammonia synthesis using their cheap hydroelectricity put up long time ago.

There are two different types of electrolysis cell designs, namely the unipolar (tank type) and the bipolar (filter press type). Of the four very large electrolytic hydrogen manufacturing plants that are in operation now, only one (Trail Canada) is equipped with unipolar cells. In this "tank type" of design, each electrode has the same polarity on both sides. A single cell contains a number of electrodes with all the electrodes of the same polarity being connected electrically in parallel. A number of such cells are connected electrically in series by copper bus bar to match the output voltage of the rectifier system. This type of cell is considered outdated since it has a lower efficiency and requires more space than the bipolar type. Another disadvantage of these types of cells is they require relatively high current and low voltage rectifiers and are often costly. In bipolar electrolysers, a single module or assembly consists of a large number of electrodes each of which is cathodic on one side and anodic on the other. The module is held in place by a number of tie rods similar to that of a plate and frame filterpress. Each pair of electrodes with separating diaphragm forms an individual cell. Each bipolar electrode is insulated (at the metallic contact) from and is electrically in series with its neighbour. The current flows from one end of the module to the other. A module may thus contain several hundred individual cells in series arranged depending on the required output capacity.

Several international manufacturers offer commercial water electrolysers and these are listed in Table II (Hammerli, 1982).

TABLE II : List of Commercial Water Electrolyser Manufacturers

	Company	Type	Pressure	Status
1.	Brown, Boveri & Cie	Bipolar Alkaline	Atmospheric	Mature Technology
2.	Constructors John Brown (CJB) Development Ltd.	Bipolar Alkaline	Atmospheric	Mature Technology
3.	Denora S.P.A.	Bipolar Alkaline	Atmospheric	Mature Technology
4.	General Electric Co.	Bipolar	0.4 - 3 MPa	Commercial Prototype Stage (50 KW - 200 KW)
5.	Krebskosao (Formerly Demag)	Bipolar Alkaline	Atmospheric	Mature Technology
6.	Lurgi Apparate Technik GmbH	Bipolar Alkaline	3 MPa	Mature Technology
7.	Moritz Chemicals Engineering Co. Ltd.	Bipolar Alkaline	Atmospheric	Mature Technology
8.	Norsk Hydro A.S.	Bipolar Alkaline	Atmospheric	Mature Technology
9.	Pintsch Bamag A.G.	Bipolar Alkaline	Atmospheric	Mature Technology
10.	Teledyne Energy Systems	Bipolar Alkaline	0.7 MPa	Mature on Small Scale
11.	The Electrolyser Corpn. Ltd.	Unipolar Alkaline	Atmospheric	Mature Technology
12.	BARC	Bipolar Alkaline	2 MPa	Knowhow Transferred to M/s.GMM.Prototype under installation

It is seen that most of the large scale commercially available electrolysers operate at atmospheric pressures. Major objective of today's development programme is to design and develop high pressure electrolysers. Only Lurgi is the major manufacturer offering large-scale commercial electrolysers operating at high pressure. The pressure electrolysers that are marketed by the other two companies are still of small scale and in the prototype stage only. Table III (Hammerli, 1982) shows some of the large commercial water electrolysis plants that are in operation today.

TABLE III : List of Some Large Commercial Water Electrolysis Plants

	Plant Location	Electrolyser Manufacturer	Capacity (Nm^3H_2/h)
1.	Aswan, Egypt	Brown Boveri	33,000
2.	Nangal, India	DeNora	30,000
3.	Ryukan, Norway	Norsk Hydro	27,900
4.	Ghornfjord, Norway	Norsk Hydro	27,100
5.	Cuzco, Peru	Lurgi	4,500
6.	Huntsville, Alabama	The Electrolyser Corporation	535

5. ADVANCED TECHNOLOGIES AND DEVELOPMENTS

As has been described earlier, this almost a century old water electrolysis technology needs improvement. The bipolar alkaline electrolyser design remains principally unchanged except for the extension to high pressure operation. The main research and development efforts should be directed to improve the efficiency, i.e. development of temperature compatible materials and electrocatalysts. Material problems are abundant when the temperature of the caustic electrolyte is increased. Asbestos plaques which are used as diaphragms in the cell are found to be stable up to 100°C only and it is liable to be attacked by hot concentrated alkali at higher temperatures. Reliable materials are being searched as a substitute to asbestos for high temperature operation. Among the new materials, chemically resistant ion exchange membranes of Nafion (R) type and potassium titanate appear promising. Advances have been made in Europe, the United States, Japan and India in developing the components necessary for an advanced type of electrolyser operating at high temperature and pressures. At the Centre d'Etude Nucteaire in Mol, Belgium, a polyantimonic acid membrane of low resistivity is being developed as a substitute for asbestos diaphragm (Vandenborre, 1982).

The programmes financed by the Commission of European Communities have focused attention on the development of anodic and cathodic electrocatalysts to reduce the activation overpotentials (Imarisio, 1981). Novel engineering concepts have been developed using modified electrode configurations. An interesting concept being developed by Electricitie de France is shown in Figure 2 (Electricite de France, 1978). This electrolyser module of 75 MW capacity is part of a 444 MW capacity plant. Each lectrolyser has 540 unit cells with current loading capacity of 34 KA. The unit is proposed to be operated at a current density of 10 KAm^{-2} at a temperature of 160°C and pressure of 3.0 MPa. A notable feature is the use of containment pressurisation, which eliminates the necessity of the electrolysers themselves to withstand high pressure differentials. It may be noted here, that France (Aureille and Pottier, 1984) which has very low fossil fuel resources, has developed a large nuclear programme which results in both a low cost nuclear base electricity and availability of off-peak nuclear electricity within 6-8 years. It appears that the situation there is quite favourable for off-peak nuclear electricity for water electrolysis and hydrogen production. Since 1975, the country has embarked a research and development programme on advanced alkaline electrolysis system with the objective of some improvement in process efficiency and a decrease in capital investment. It is expected that their first demonstration unit (2 MW) will be in operation by about 1988 utilizing the off-peak power to take advantage of the favourable electricity rates.

In the United States, Teledyne Energy Systems have introduced advanced catalyst materials into their bipolar designs to improve the efficiency of the system (Murray, 1982). They are planning to put up a 2.5 MW unit.

In India, Desalination Division, Bhabha Atomic Research Centre (BARC), Bombay, has developed and operated an advanced high temperature and high pressure electrolyser of 1.5 nM^3/hr of hydrogen capacity. The electrolyser comprises advanced cell modules based on bipolar filter-press type configuration, incorporating high performance porous nickel electrodes. These cells operate at high current densities with lower energy consumption, resulting in a compact and economic hydrogen/oxygen generator.

The overall arrangement of the electrolyser is illustrated in Figure 3 along with the associated process equipment.

The module can operate up to 10,000 ASM without undue rise in cell voltage as compared with commercial cell modules, which do not go beyond 2000 ASM.

The cell module assembly consists of many cell blocks stacked in series. In each cell block, two porous nickel electrodes fit snugly within the countersunk cavities of the central bipolar plate. Two porous nickel electrodes from adjacent cell blocks, separated by a thin asbestos diaphragm soaked in 6 N.KOM solution constitute the working cell. The porous electrode is mounted between two closely fitting stainless steel rings which give the necessary mechanical support to the porous plates. The bipolar plate acts as the main electrode and houses the auxiliary porous electrodes. The bipolar plate incorporates provisions for electrolyte inlet, gas outlet manifolds, inlet and outlet

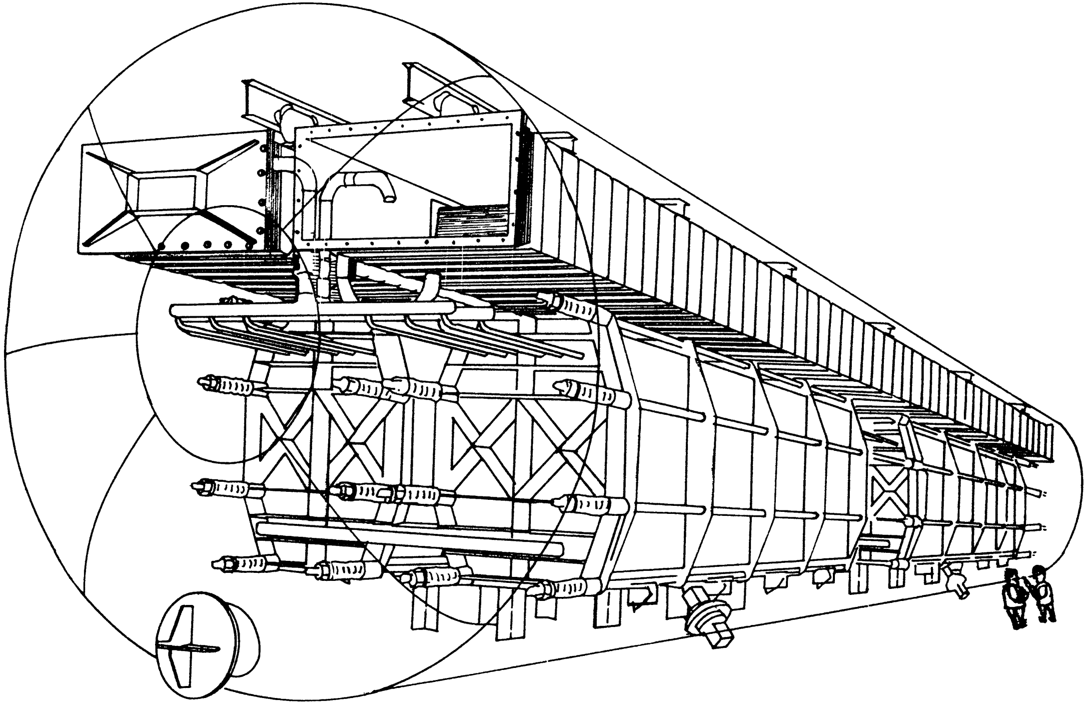


Figure 2. Artist's view of the 75-MW electrolyser module proposed by Electricite de France. The module contains four 34-kA filter-press units inside a vessel which is pressurized to 3.0 MPa.

LEGEND

M-1 }
M-2 } ELECTROLYSIS CELL MODULES
E-1 ELECTROLYTE MIXING TANK
S-1 HYDROGEN SEPARATOR TANK
S-2 OXYGEN SEPARATOR TANK
C-1 HYDROGEN COOLER
C-2 OXYGEN COOLER
C-3 ELECTROLYTE COOLER
P-1 ELECTROLYTE CIRCULATING PUMP
P-2 WATER MAKE-UP PUMP
ES-1 ENTRAINMENT SEPARATOR H_2 SIDE
ES-2 ENTRAINMENT SEPARATOR O_2 SIDE

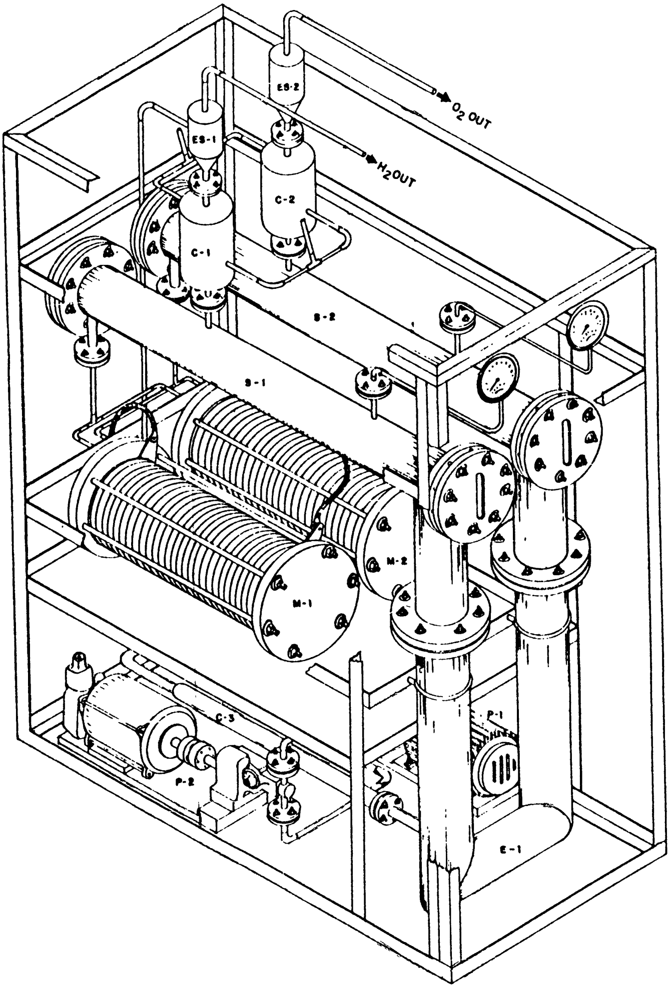
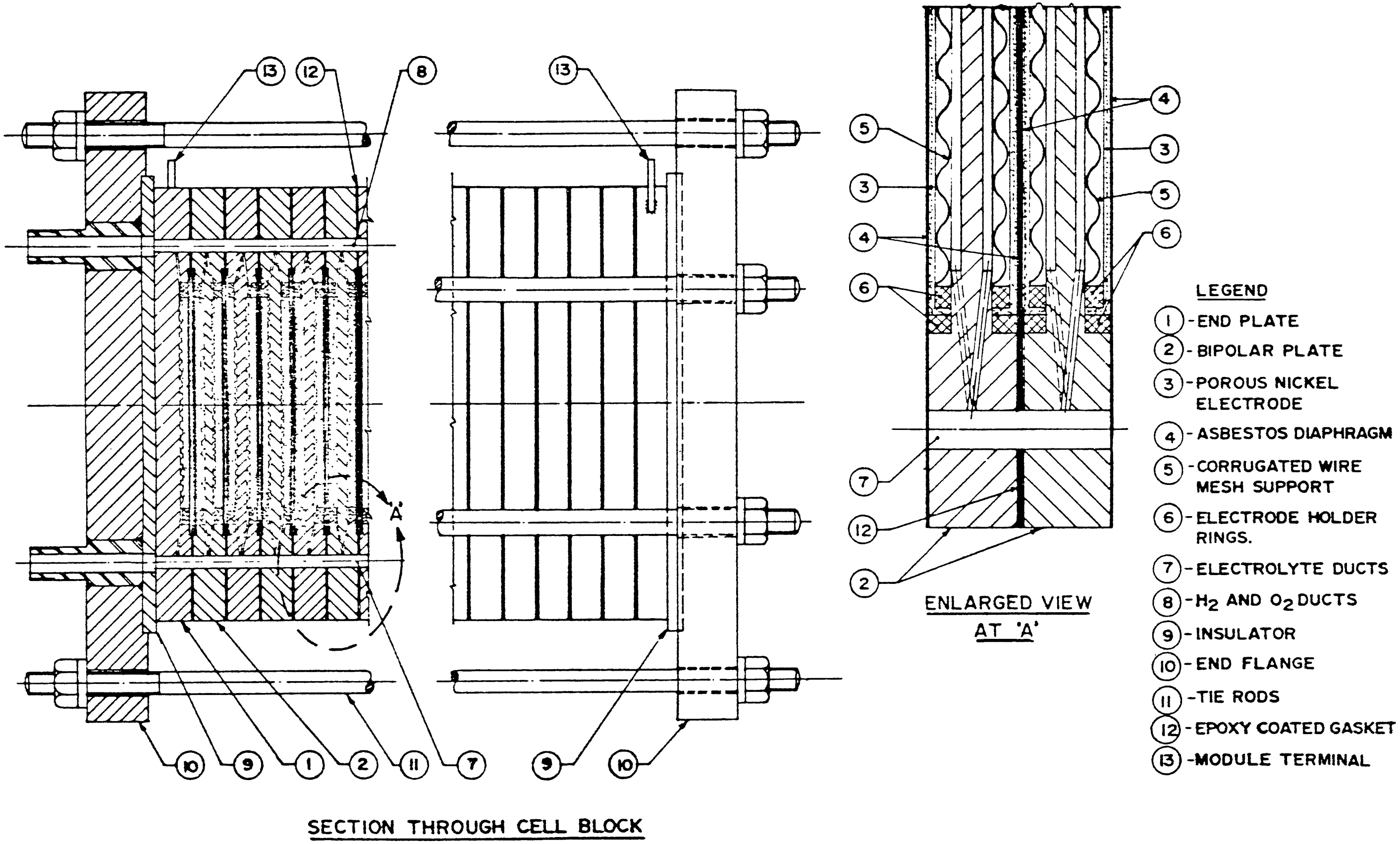


Figure 3. The overall arrangement of electrolyser.



SECTION THROUGH CELL BLOCK

ENLARGED VIEW AT 'A'

Figure 4. Sectional view of the cell module.

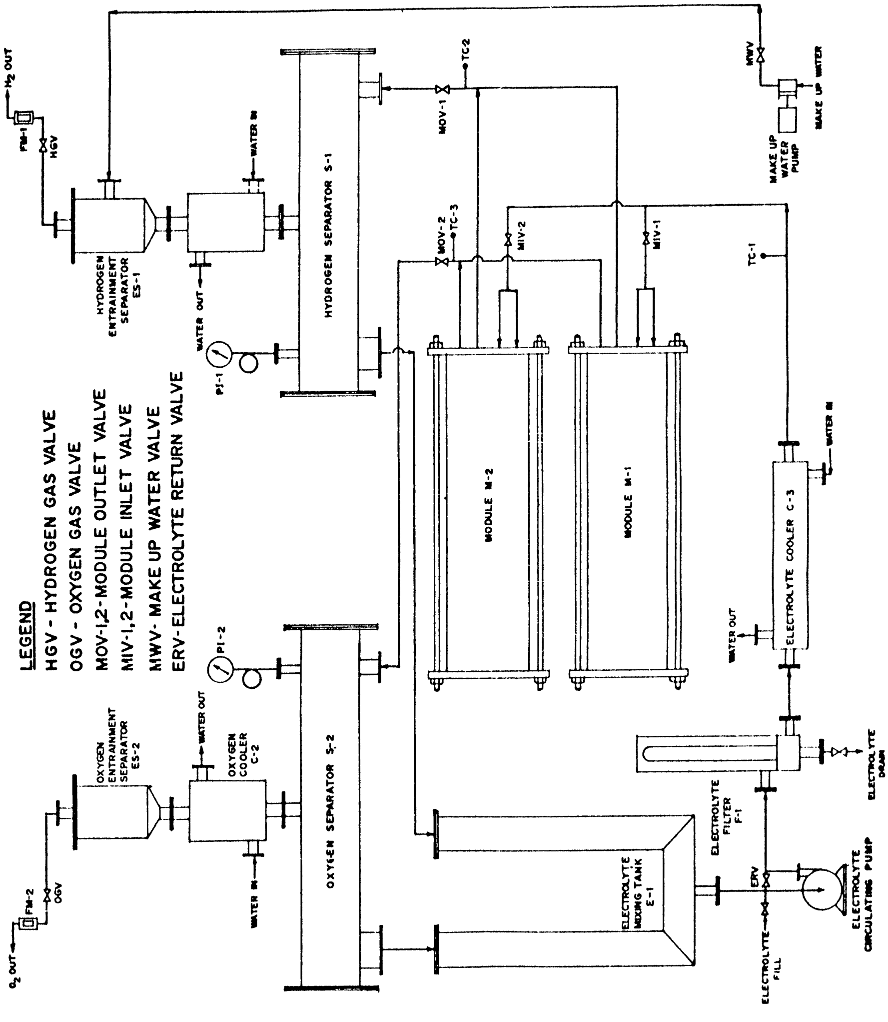


Figure 5. Flow schematic of electrolysis system.

channels. The space formed between the bipolar plate and electrodes constitute the cathode and anode chambers. The bipolar plate is so constructed that each outlet manifold carries only one product gas.

The individual cell components are tightly held together in pressure frames.

A sectional view of the cell module incorporating the above features is shown in Figure 4.

The flow schematic of the electrolysis system developed at BARC is shown in Figure 5 and an exploded view of the cell module is shown in Figure 6.

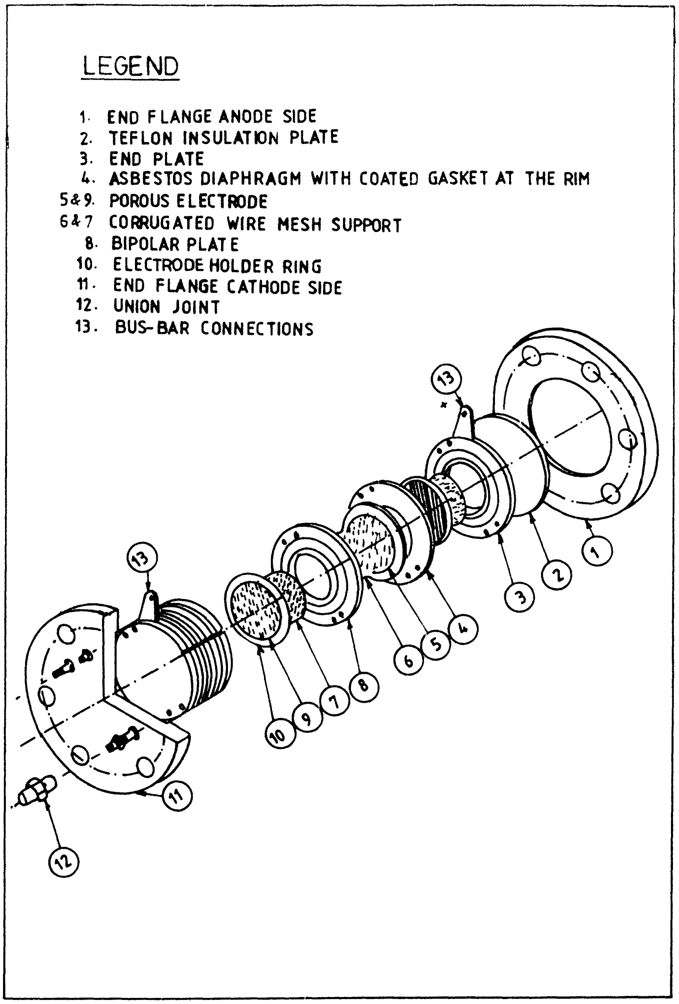


Figure 6. Exploded view of the advanced electrolysis cell module.

The improved features allow the operation of the cell at higher current densities without the excessive power losses usually associated with increase of current densities in the present day commercial cells.

6. SOLID POLYMER ELECTROLYTE (SPE) ELECTROLYSIS

A promising water electrolysis technology is being developed by the General Electric Co. of the United States for the past two decades (Nuttal and Russel, 1980). It is based on solid polymer electrolyte membranes - a hydrocarbon based material commercially available under the trade name Nafion - which serves as an electrolyte capable of conducting hydrogen ions when wet. Teflon bonded catalysts are attached mechanically on to the surface of the membrane on either side to generate electrode - electrolyte contact. Unfortunately, this solid polymer Nafion is highly acidic and corrosive to materials with which it is in direct contact. Thus expensive current collectors and electrode materials mostly noble metals are required. This together with the high cost of the membrane itself (about Rs.2000/m^2) amounts to a high capital cost per unit cell. However, this handicap is overcome to some extent by the high current density capability and high energy efficiency of the system. The SPE system has a dimensionally stable solid electrolyte and only feed water needs be circulated. It is ideally suited to be built into a high pressure system operating even up to 150°C. If the material problems can be solved economically, the SPE system has the potential of becoming a new technology.

7. HIGH TEMPERATURE WATER-VAPOUR ELECTROLYSIS

The possibility of electrolysing steam (water vapour) at high temperature shows that hydrogen can be produced below the enthalpic voltage. Thus a heat source can be directly used to produce hydrogen (chemical energy) with greater efficiency than electrical energy.

The water-vapour electrolysis concept has been developed by several groups, the most prominent among them perhaps is the Dornier Systems of Germany (Doenitz and Schmidberger, 1982). The technology is based on stabilized Zirconia as oxygen ion conducting electrolyte at high temperature. From thermodynamic angle, high temperature (above 1000°C) electrolysis seems to be advantageous due to the following reasons:

(a) the theoretical energy requirements are less than in conventional cells by about 25 per cent,

(b) activation overpotential losses at higher temperature are very low and hence the cell operation can be performed at high current densities, and

(c) the heat energy required for the cell operation can be supplied through ohmic heat losses or alternatively from a high temperature heat source.

However, this technology is still in the laboratory development stage and there are many problems to be solved before this system can be realised in practice. The major bottlenecks are the material problems associated with the development of ceramic base for the bigger cells and their electric interconnection. Experimental data so far obtained indicate that even at 1000°C it has been found difficult to operate the cell below 1.3 V at economic current densities of 4 to 5 kAm^{-2}. The cause of this high voltage is attributed to the presence of hydrogen in the reagent water, high contact resistances at the interelectrodes and also due to resistances of the solid oxide separator itself. In short, the outlook for this technology is bleak for commercial realization until the beginning of the next century.

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HYDROGEN PRODUCTION THROUGH PHOTOELECTROLYSIS

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Because of being a perfect substitute for the fossil fuel 'oil' and the added advantage of nearly zero pollution, 'Hydrogen' is of strategic significance on the renewable non-conventional energy scenario. Unfortunately, however, the present day methods of hydrogen production are based on fossil fuel based energy input for splitting of water. Apparently long term 'Hydrogen' production methods will have to be based on renewable sources of energy. Solar energy is the most attractive option and hydrogen production employing solar energy through the process of photoelectrolysis is thought to be the most viable process for hydrogen production. At present the photoelectrochemical (PEC) process leading to hydrogen production is plagued by materials problem. The semiconducting photoelectrode material should be optimised with respect to three different parameters - the band gap, the flat band potential and the stability. The present paper first reviews the salient features of the 'photoelectrolysis' process. The basic characteristics of the PEC process leading to photoelectrolysis employing two important semiconducting photoelectrodes namely n-TiO_2 and n-WSe_2 have been described in some detail. New results encountered with these materials have been highlighted. The importance of these results in regard to 'Hydrogen' production through 'photoelectrolysis' have been outlined.

1. INTRODUCTION

Out of the various possible non-conventional renewable energy sources, 'hydrogen' is of paramount importance. This is so since a large fraction ($\sim$60%) of our daily energy requirement is met by chemical energy sources at present mostly by oil (petroleum, gasoline) whose reserve stocks are dwindling fast and which may have to be abandoned earlier than the stipulated period for environmental considerations (green house effect, air pollution, acid rains). Hydrogen, which is the perfect substitute of oil with the added advantage of nearly zero pollution, is available in plenty in the universe. It should be mentioned that besides the zero pollution factor, hydrogen tops the list of possible fuels since its energy content is very high. One kilogram of

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hydrogen carries an enormous energy content of 33,000 Whr. The whole of planet Jupiter is made up of liquid and solid hydrogen. Even the intersteller space contains about one hydrogen molecule per cubic centimeter. However, on our planet hydrogen although found in abundance is not freely available. It forms only 0.2 per cent of the atmosphere. This is rather too small a quantity when looked from the point of view of world's fuel needs. Therefore, other sources of hydrogen will have to be considered. It is linked with oxygen in the most common substance known to mankind - the water. It is thus imperative that hydrogen will have to be procured from water from some input energy which can split it to produce hydrogen. The most attractive energy would of course be solar energy, which through the process of 'Photoelectrolysis' is capable of producing hydrogen from water. It is interesting to note that solar energy which is itself produced through fusion of hydrogen atoms/nuclei, only after 10 minutes of its release from the sun is again involved in 'photosynthesis' process involving hydrogen production from water. The photosynthetic process sustains the very life on earth. It is thus apparent that solar light induced hydrogen production from water is already going on in nature and the man-made efforts at hydrogen production through photoelectrolysis is at best efforts to mimic a part of the complex process inherent in nature.

Before coming to describe the details of the photoelectrolysis process, it will be worthwhile to recapitulate the various possible processes through which hydrogen can be produced. Some of the important processes leading to production of hydrogen are outlined in the following.

(A) Conventional Processes

(i) Manufacture of hydrogen by steam reformation of natural gas/naptha

$$C_nH_{2m} + nH_2O \longrightarrow nCO + (n+m)H_2$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2$$

(ii) Thermochemical processes for the production of hydrogen from water

$$6MnCl_2 + 8H_2O \longrightarrow 2Mn_3O_4 + 12HCl + 2H_2 \quad (700^\circ C)$$

$$3Mn_3O_4 + 12HCl \longrightarrow 6MnCl_2 + 3MnO_2 + 6H_2O \quad (100^\circ C)$$

$$3MnO_2 \longrightarrow Mn_3O_4 + O_2 \quad (900^\circ C)$$

(iii) Coal-based processes for hydrogen production

(a) Complete gasification of coal and CO shift conversion.

(b) Steam iron process by reduction of iron ore with producer

gas either in fixed bed or in fludised bed at atmospheric or elevated pressure.
    - (c) Hydrogen production from coal using Nuclear Heat source.

- (iv) Production of hydrogen by electrolysis of water (on hand technology)
    - (a) Conventional electrolytic methods.
    - (b) Advanced water electrolysis cells -
        1. Solid polymer electrolytic cells.
        2. New bipolar electrolyser of Allis-Chalmers.
        3. Electrolysers with valve electrodes and Eloflux arrangement.

(B) Light Induced Processes

- (i) Hydrogen production through 'photoelectrolysis', photoelectrochemical decomposition of water using 'Sun Light' (most promising process-futuristic technology).
- (ii) Hybrid water-splitting systems involving photochemical and thermoelectric utilisation of 'Solar Energy'.
- (iii) Biological production of hydrogen
    - (a) Water splitting through photosynthetic marine organism.
    - (b) Biochemical production of hydrogen by bacteria.
    - (c) Hydrogen production through blue-green algae.
- (iv) Photochemical cleavage with a metal complex (Ruthenium Complex and particulate semiconductor systems).
- (v) Hydrogen production through Ocean Thermal Energy Conversion (OTEC).
- (vi) Plasma induced photolysis.
- (vii) Photovoltaic electrolysis.

At present large scale hydrogen production is carried out by following the processes under (A), in particular naptha reforming and electrolysis form the on hand technology for hydrogen production. In view of the limited availability of fossil energy sources and the limitations of the conventional power, the long term process for hydrogen production will have to be any of the methods listed under (B). In view of the huge amount of available solar light with its inexhaustible supply, the long term and the eventual process will have to be based on the solar energy. Out of the various possible processes capable of producing hydrogen with input energy being solar light, photoelectrolysis which usually implies solar photon induced electrolysis of water is the most attractive one. It is also possible to produce hydrogen from solar light induced photoelectrochemical dissociation of hydrogen rich fluids like HI, HB_r. In the following we proceed to discuss the basic processes involved in photoelectrochemical and photoelectrolysis devices which when operated from solar photons are known photoelectrochemical and photoelectrolysis solar cells. The basic emphasis of our discussion would be on solar photon induced hydrogen production.

2. BASIC CHARACTERISTICS OF PHOTOELECTROCHEMICAL/PHOTOELECTROLYSIS CELLS

The devices embodying wet photovoltaic systems (semiconductor liquid junctions) are known as photoelectrochemical solar cells. The photoelectrochemical cells can be broadly classified as two types based on the net free energy changes accompanied in the overall cell reaction. In the liquid junction photovoltaic cell (or regenerative type) the aim is the production of an electrical current flow without net changes occurring either in the electrolyte solution or in the electrode materials. These cells, which are the photoelectrochemical equivalent of solid state solar cells utilise a single redox couple. The photodriven oxidations ($D + h^+ \rightarrow D^+$) occurs at n-type semiconductor electrode while the reduction ($D^+ + e^- \rightarrow D$) occurs at the counter electrode leading to the zero free energy change (see Figure 1). However, the choice of the redox couple is often of crucial importance since it fixes the operating voltage and stabilizes the semiconductor from photocorrosion processes. More interesting are the cells in which there is a net chemical reaction as a result of finite free energy change. These are the photoelectrosynthetic cells. If the change in free energy is positive ($\Delta G > 0$), the light energy is stored as chemical energy in the products as a result of photoelectrolysis. The cells embodying this process are known as photoelectrolysis cells. On the other hand, if the free energy change is

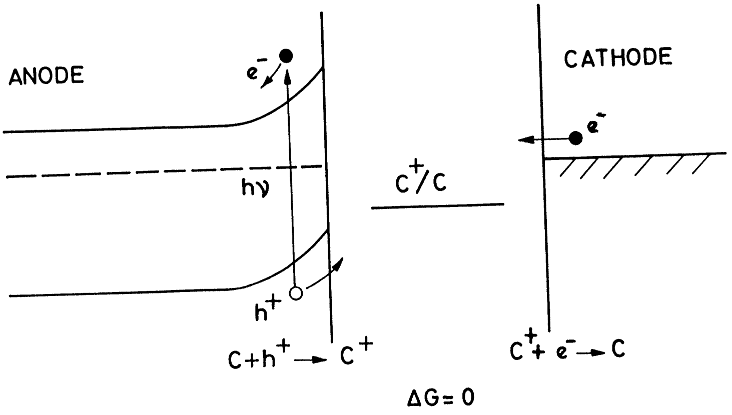

Figure 1. Energy level diagram for electrochemical photovoltaic cells. Notice that the free energy of the cell reaction (ΔG) is zero.

negative ($\Delta G < 0$), the optical energy provides the activation energy for the reaction and this is called the photocatalysis process - the cells based on this are known as photoelectrocatalytic cells (Gerischer, 1981).

In the photoelectrolysis cells ($\Delta G > 0$), the anodic reaction has a more positive redox potential than the cathodic reaction. Again, two types of photoelectrolysis cells can be visualised depending upon the kind of electrode system employed. The commonest of these two possess a semiconductor electrode and a metal counter electrode. In the second type, one electrode is an n-type semiconductor and the second a p-type semiconductor electrode. The latter type is a dual semiconductor electrode two-photon PEC cell intended for special purposes. In the photoelectrolysis of water to hydrogen and oxygen, the former type of cells incorporating one semiconductor (n-type) are widely used. A simple consideration of energetics of this type of cells may be put forward. The minimum thermodynamic free energy to cause the splitting of water ($H_2O \longrightarrow H_2 + \frac{1}{2}O_2$) at standard temperature and pressure is 2.46 eV per water molecule (56.7 KCal/mole) or 1.23 eV per electron transfer. Therefore, the Fermi level of the counter electrode which will accept an electron generated in the reaction

$$H_2O \longrightarrow 2H^+ + 2e^- + \tfrac{1}{2}O_2$$

must be at least 1.23 volts positive with respect to NHE. Since in aqueous electrolyte there are two redox couples (H^+/H_2 and O_2/H_2O) whose energy difference is about 1.23 eV, a part of this energy can be supplied from solar energy and the rest is to be given by anodic bias. Upon immersion of semiconductor (SC) electrode into the electrolyte, the Fermi level of SC equilibrates with the electrolyte Fermi level, producing a band bending V_b in accordance with

$$V_b = U_e - U_{fb} \qquad (1)$$

where U_e is the Fermi level of the semiconductor and U_{fb} the flat band potential. Under illumination, the Fermi level in the semiconductor rises toward the U_{fb} producing a photopotential, V_{ph}. With the electrodes shortened together, the maximum Fermi level position possible is the flat-band potential. If the flat-band potential (U_{FB}) is below the H^+/H_2 potential, even upon intense illumination, hydrogen cannot be evolved at the counter electrode. In order to raise the Fermi level in the counter electrode above the H^+/H_2 potential, an external anodic bias (E_b) must be applied (see Figure 2). The larger the difference between U_{FB} and H^+/H_2 redox potential the greater is the bias to be applied (Nozik, 1981).

It is possible to optimise the cell characteristics using the energy balance equation for photoelectrolysis using n-type semiconductor.

$$E_{BG} - V_B - (E_{CB} - E_F) = \left[\frac{\Delta G}{nF} + \eta_a + \eta_c + IR + V_H\right] q \qquad (2)$$

The left hand side of this equation describes the energy that can be used to drive a reaction of free energy, ΔG. E_{BG} is the semiconductor

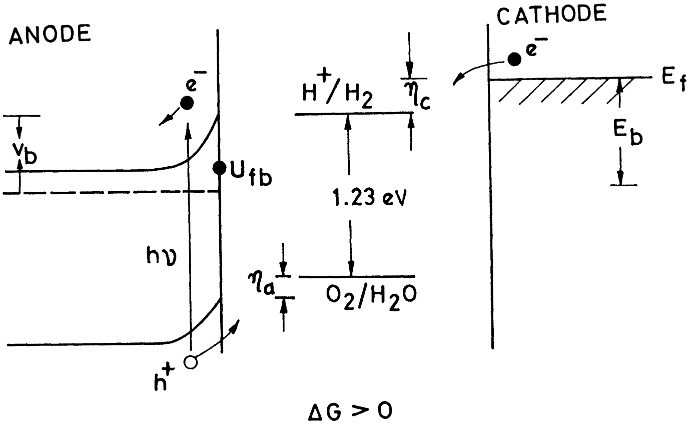

Figure 2. Energy level diagram of photoelectrosynthetic cells. Notice that free energy of the reaction is positive ($\Delta G > 0$) and an external bias, E_b is necessary to produce hydrogen.

band gap and precludes the use of light with lesser energy than E_{BG} itself. V_B is the magnitude of band bending found in the semiconductor upon immersion into a redox electrolyte. Bending of conduction and valence bands is essential to prevent the recombination of photogenerated holes and electrons in the space charge layer. E_{CB} is the conduction band edge, and E_F is the Fermi level - a thermodynamic quantity that describes the average energy of mobile electrons in the semiconductor.

The right hand side of the above equation (2) consists of the free energy change for electrolysis, ΔG and some other parameters adding to the barrier height. Terms adding to ΔG should be minimized. η_a and η_c are overpotentials for the reactions occurring at anode and cathode respectively. These overpotentials are related to the kinetic processes leading to the oxygen and hydrogen evaluation at anode and cathode respectively. IR is the ohmic potential drop, which occurs due to likely significant resistance of electrolyte between semiconductor surface and the Luggin capillary attached to calomel electrode. V_H is the Helmholtz potential, and q is the electronic charge. The reaction overpotentials η_a and η_c can be reduced by incorporation of catalysts (Au, Pd, Pt etc.) on the semiconductor electrode surface and ohmic loss can be minimized by choosing a high conducting electrolyte as well as lowering the distance between Luggin capillary and semiconductor surface. Therefore for good performance, the photoanode must have minimal polarisation losses and good catalytic activity for oxygen evolution. It is implicit in the above treatment that the modifications in the parameters on either side of equation, in the positive sense, would improve the power characteristics.

3. BASIC MATERIALS FOR PHOTOELECTROLYSIS - WIDE BAND GAP OXIDE SEMICONDUCTOR

The photolysis of water occurs at the event of absorption of light by semiconducting materials. Among the several semiconductors used, titanium dioxide (n-TiO_2) and titanates especially strontium titanate ($SrTiO_3$) have been of crucial importance, since they exhibit greater stability against the photocorrosion reactions. Ever since the Fujishima and Honda's (1972) work on n-TiO_2 photoelectrode based water photoelectrolysis, efforts have been made to produce stable semiconductor materials of suitable band gap ($\sim$2 eV) capable of carrying out unassisted photoelectrolysis with sun light. A critical problem here is to simultaneously minimize the band gap, maximize the stability and optimize the flat-band potential of the semiconductor electrode. Stability is a crucial problem for most semiconductors since under PEC conditions the photon generated holes/electrons in the semiconductor which oxidise/reduce the electrolyte are also capable of oxidizing/reducing the semiconducting material itself. As for example, for a n-type semiconductor electrode the photon generated minority carriers - the holes which travel to the surface of the semiconductor electrode can pass on the electrolyte to oxidise it but the same holes can also oxidise the semiconductor surface and thus the semiconductor gets degraded through corrosion. The non-oxidic semiconductors (e.g. CdS, CdTe, GaAs etc.) are more susceptible to corrosion than the oxidic ones like TiO_2 and $SrTiO_3$. However, the latter are wide band gap materials (TiO_2, E_G = 3.01 eV; $SrTiO_3$, E_G = 3.2 eV) and hence respond only in the ultraviolet portion of the solar spectrum. The corrosion problem on the other hand precludes the use of non-oxidic semiconductors which are low band gap materials (1-2 eV) in photoelectrochemical/photoelectrolysis solar cells. No semiconductor material has been found to date in which all the three parameters (the band gap, the stability and the flat band potential) are optimised. Research is in progress to improve the power characteristics by electronic modifications, surface modifications and electrolyte modifications. However, the photoelectrochemical parameters, viz. the photopotential and photocurrent, are strongly influenced by photoelectronic characteristics like the nature of intrinsic and extrinsic defects, light absorption coefficient etc. The present study is aimed to bring out some correlation between photoelectrochemical parameters and the homogeneity and morphology of the surface of the semiconductor electrode (n-TiO_2) examining the I-V characteristics.

3.1. Experimental - Preparation and PEC Behaviour of TiO_2 Films

The titanium dioxide semiconducting surface is prepared employing two different methods, namely flame oxidation and anodization using suitable electrolyte. Titanium sheets, 2 cm^2 in geometric area, and thickness ranging between 1-10 μ, were machined from high purity titanium metal and were mounted on a perspex holder. The mounted pieces of titanium in conjunction with a steel counter electrode were exposed to 1 M NaOH (pH:13) and were anodized at 30 V for about 20 hours current. The pieces were removed from mounts and washed thoroughly in flowing water and distilled water and were made ready for photoelectrochemical study. In the second method similar area titanium plates were exposed to air in a furnace at a temperature of 600°C for 1 hour. The semiconductor electrodes thus prepared were used in a conventional three-electrode assembly. Counter electrode was a 1 cm^2 platinum sheet. Reference electrode was a saturated calomel electrode. Only 1 cm^2 area of the semiconducting electrode was exposed to the light and the rest of the surface was properly sealed from illumination. The electrolyte in the cell was 0·1 M NaOH, its pH being adjusted to 4.7 using potassium hydrogen pthalate buffer. A Princeton Applied Research (PAR) 175 universal programmer, a PAR 173 potentiostat/galvanostat and a PAR 176 I/E converter have been used to control the potential at the semiconductor electrode and the currents were recorded on a Houston Model 2000 X-Y recorder. Some modifications in the scanning mode and cell conditions were carried out to acquire additional information.

3.2 Results and Discussion

In a photoelectrochemical cell, irradiation of the semiconducting electrode in contact with an appropriate electrolyte produces a change in the electrode potential (open-circuit conditions) or produces a change in the current flowing in the cell (closed-circuit conditions). These variations reflecting the progress of reaction can be examined by obtaining I-V characteristics. Typical I-V characteristics for n-TiO_2 (flame oxidized) are shown in Figure 3. Scan rate, temperature etc., at which these are obtained are incorporated in the body of the figure.

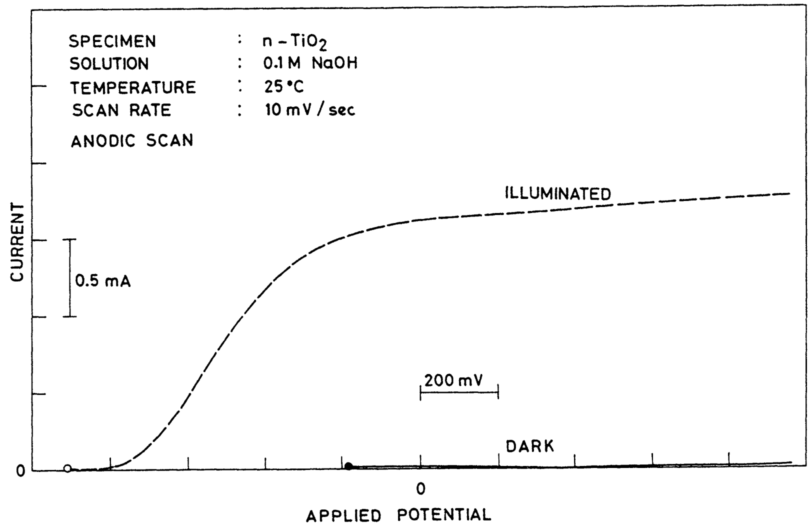

Figure 3. Anodic response of n-TiO_2 (The specimen was prepared through oxidation) under illuminated and dark conditions. Notice that the photovoltage is 720 mV and saturation current is equal to ~1.5 mA.

The figure contains the curves both under dark and illumination conditions. As can be examined from the figure, the open-circuit potential in the dark (V_{oc}, dark) was -180 mV. This potential has made a shift towards more negative potential and stabilized at -900 mV, upon illumination. Thus, the photovoltage comes out to be 720 mV. Without illumination, the anodic current remained very small when the n-TiO_2 was anodically biased. On illumination of TiO_2, large anodic currents passed at potentials positive of -800 mV vs. SCe. These anodic currents are photocurrents which obtained saturation at potentials beyond -200 mV/SCe. The anodic photocurrent corresponds to oxygen evolution at TiO_2 electrode surface, which may be expected to take place with the involvement of holes and water molecules:

$$2h^+ + H_2O \longrightarrow \tfrac{1}{2}O_2 + 2H^+$$

In the present case saturation of photocurrents occurred at 1.5 mA.

A similar study of I-V characteristics performed this time with anodized TiO_2 semiconductor electrode exhibited different magnitudes of photoelectrochemical parameters (Figure 4). With n-TiO_2 of $1cm^2$ area,

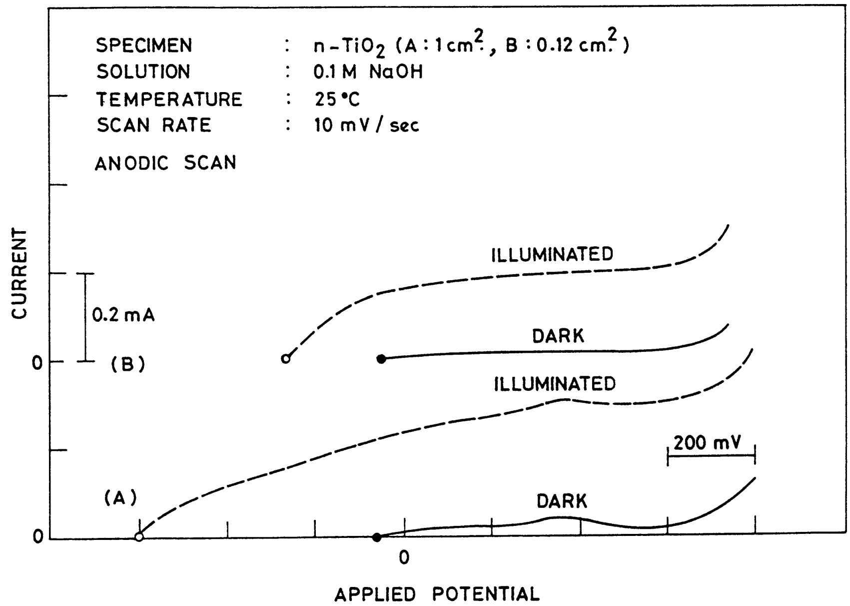

Figure 4. Anodic response of n-TiO_2 (prepared through anodization) against the variation of illuminated area. Notice that the photovoltage is 520 mV for large area sample (A) and 250 mV for small area sample (B). Saturation currents are 300 μA and 200 μA for A and B respectively.

the photopotential was only 520 mV and the photocurrents increased rather with low gradient and attained saturation with a characteristic current value equal to 300μA. This value is one-fifths of the saturation current value of flame-oxidized sample. Further, saturation on the anodized sample is noticed to occur at more positive potentials with respect to SCE, than that observed with flame-oxidized sample. All these parameters suggest that the photoelectrochemical performance of flame-oxidized sample is much better than that of the anodized samples.

The maximum photocurrent in a photoelectrochemical cell is the saturation current. It was mentioned earlier that oxygen evolution occurs on the semiconductor electrode under illumination coupled with anodic bias. Further increase in the bias potential increases the rate of evolution of oxygen and eventually a stage arrives at which the rate of formation of oxygen equals the rate of desorptions of oxygen from the semiconducting electrode surface. This leads to the fact that the semiconductor electrode is covered, with a phalanx of oxygen molecules at any instance. The constant rate of oxygen evolution leads to the attainment of saturation. If the foregoing description is true, experiments carried out with vigorous stirring of electrolyte should lead to increased saturation currents. The results obtained in the experiments carried out with this interest are shown in Figures 5 and 6 which depict the voltammetric response. The saturation current in the unstirred use is close to 1.5 mA (Figure 5). However, when stirring is imposed (Figure 6), the saturation current has increased to 2.5 mA. This rise in the saturation current upon stirring indicates that the photoelectrochemical process is

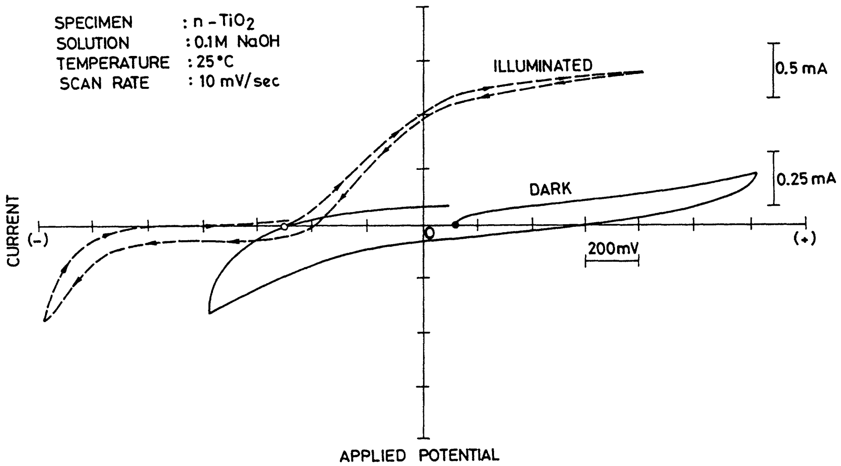

Figure 5. Voltammetric response of n-TiO$_2$ (prepared by flame-oxidization). Notice that photovoltage is 620 mV and saturation current is 1.3 mA.

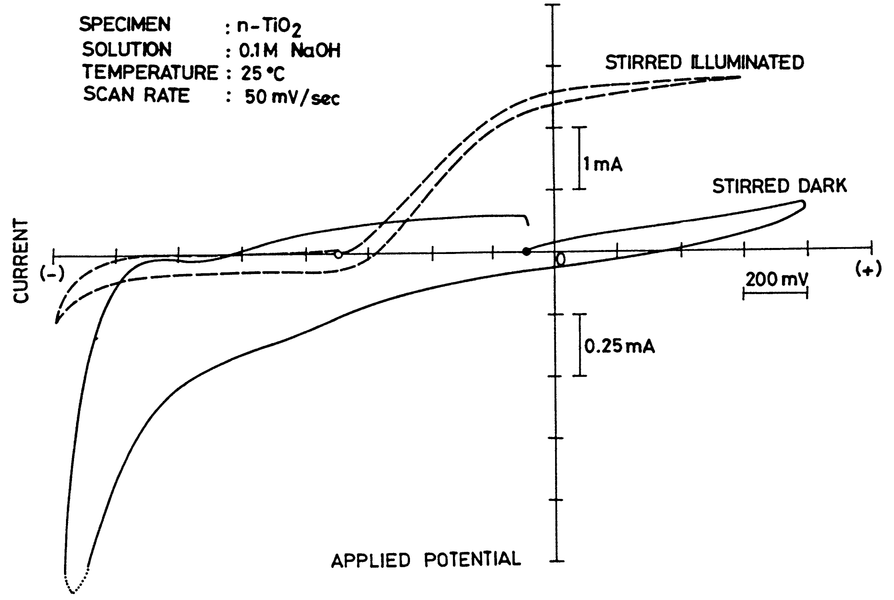

Figure 6. Effect of stirring on the voltammetric response of n-TiO_2 (flame oxidized). Notice that photovoltage is 600 mV and saturation current raised to 2.5 mA (see Figure 5 for comparison).

mass transfer controlled and stirring of electrolyte actually improves the performance. Stirring of the liquid around the electrode removes the gas bubbles clogged on the surface and results in the rise of saturation currents. Further, the anodic current in dark is not influenced by stirring indicating the absence of any mass-producing reaction in the dark.

3.3. Further Work on PEC Production of Hydrogen Based on TiO_2 Photoelectrodes

The PEC characteristics described in section 3.2 reveal clearly that TiO_2 photoelectrodes are typically suited for splitting of water through PEC process (photoelectrolysis). In our cyclic voltammetry experiments under suitable bias we have noted copious hydrogen production. Since in PEC devices employing n-TiO_2 photoanodes in aqueous solution, the Fermi energy of the electrons ends up below the H^+/H_2 redox potential, external bias becomes essential for hydrogen production. However, as long as this bias is less than about 1.23 volts, the process is still solar driven. A major problem connected with TiO_2 (EG $\simeq$ 3.01 eV) is the poor matching with solar spectrum, since it responds only to a small part of the spectrum (ultraviolet region). A broadening of the absorption spectrum of TiO_2 towards the viable region has been demonstrated to take place through doping (Ghosh and Maruska, 1977). This leads to only small increase in the spectral response. Another possibility for increasing the response is to synthesise TiO_{2-x} starting from TiO_2. The TiO_2 photoelectrodes with moderate values of x($\sim 4\times10^{-4}$) may correspond to high PEC efficiency for hydrogen production by virtue of the creation of acceptor level near the valence band from where the hole remains available for the OH/H_2O oxidation process (Subbarao et al., 1978; Gautron et al., 1980). Efforts are under way in our laboratory to prepare well characterised TiO_{2-x} photoelectrodes for better spectral response. It is also planned to prepare photoelectrodes with configurations $TiO_2/TiO_{2-x}$and TiO_{2-x_1}/TiO_{2-x_2}. These configurations are likely to produce tandemization effect leading to better spectral response and hence higher PEC efficiencies, through the creation of n/n solid state homojunction (Weber and Dignam, 1984). Since TiO_2 is a stable photoelectrode under PEC conditions leading to hydrogen production, improvement in the spectral response may make TiO_2 as the ideal semiconducting material for photoelectrolysis of water.

4. BASIC MATERIAL FOR PHOTOELECTROLYSIS - LOW BAND GAP d-d TRANSITION MX_2 TYPE SEMICONDUCTORS

The low band gap ($1 \lesssim EG \lesssim 2$ eV) semiconductors in sharp contrast to the wide band gap oxide semiconductors like TiO_2, have much better solar spectral response. But for the corrosion problem, the low band gap materials (mostly chalcogenides like CdS, CdTe, etc.) would have been ideal PEC photoelectrodes. Recently a new type of low band gap chalcogenides like WSe_2, WS_2 etc. have been explored for PEC conversions. These are thought to be corrosion resistant due to their special d-d transition band structure. In the following we proceed to discuss the MX_2 type d-d transition semiconductors in relation to the growth, structure and the PEC conversion characteristics.

4.1. Introduction

Layered type transition metal dichalcogenides have a typical structure in which the transition metal atoms form closely packed monolayers sandwiched between two parallel closely packed monolayers of chalcogenide atoms. The sandwiches are stacked one over the other and held together by weak van der Waals forces, whereas inside the sandwiches there are strong covalent bonds. The surface parallel to the plane of the layers ($\perp$ to C-axis) is called van der Waals surface. Tributsch (1977) showed that the layered type materials belonging to groups IV, V, VI and VII of periodic system are of potential interest in photoelectrochemistry. Depending on transition group, there are some differences in electronic structure and occupation of energy bands. Basically there are two different types of symmetries representing transition metal dichalcogenides - one is octahedral and another is trigonal prismatic (Figure 7). In case of group VI dichalcogenides (e.g. WSe_2; $EG \simeq 1.7$ eV) is splitting of energy band into a lower d_z2 energy band and higher

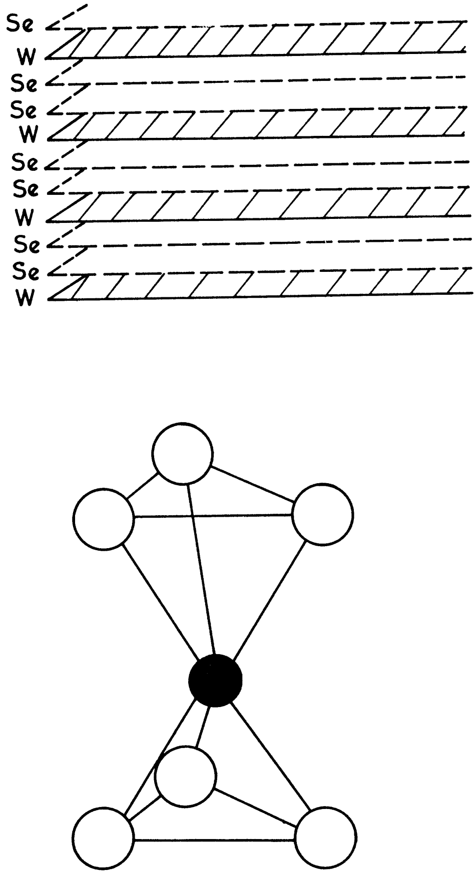

Figure 7. Structure and crystal symmetry (trigonal prismatic) of WSe_2.

d-band (derived from d_{xy} and $d_{x^2-y^2}$ states of the metal atom) separated by a hybridization gap. The lower d_{z^2} energy band is full in WSe_2, while the higher band is empty. The schematic transitions which occur in these materials are shown in Figure 8. Due to d-d type phototransition where both the levels belong to the transition metal atoms, a weakening of cation-anion bonding does not take place on photoexcitation. Hence they are corrosion resistant and form novel low band gap ($\lesssim 2$ eV) i.e. high solar response semiconductor photoelectrodes for PEC solar cells.

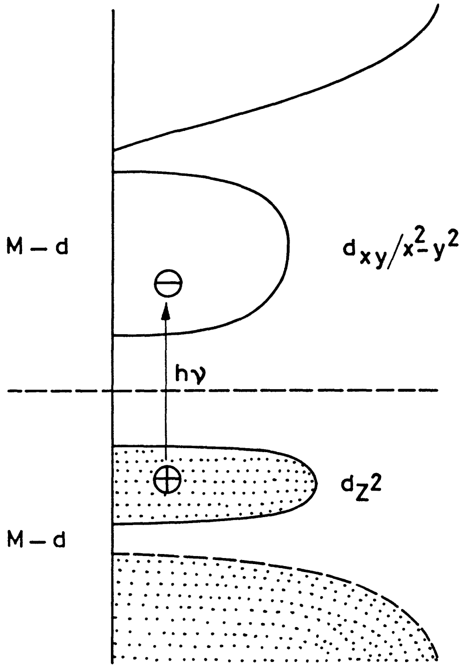

Figure 8. Energetic distribution of electronic d states of the transition metal in WSe_2. Notice that transition is from lower d_{z^2} orbital to higher d_{xy/x^2-y^2} orbital.

4.2. Synthesis and Growth of WSe_2 Single Crystals

Stoichiometric amounts of tungsten and selenium powders were introduced in a silica tube of internal diameter 2.25 cm (Al-Hilli et al., 1972). The ampoule was then evacuated to a pressure less than 10^{-5} torr, and sealed. The ampoule was then introduced in a two-zone furnace, whose temperature was increased in steps of 50°C from room temperature to final temperature which is 700°C. This slow heating was necessary to avoid any possible explosion due to the strongly exothermic reaction between two elements. The ampoule was maintained at this final temperature up to 24 hours and then removed from furnace and allowed to cool. This homogenisation treatment led to the synthesis of WSe_2 powder. X-ray diffraction Guinier patterns confirmed this.

Large single crystals of WSe_2 were prepared by chemical vapour transport technique, by using Br or Cl (for n type) or I_2 (for p-type) as transporting agent. In the present study $TeCl_4$ was used as transporting agent to make n-type WSe_2 crystals. A measured weight of powdered compound prepared earlier was introduced in a fresh silica tube of length about 20 cm. $TeCl_4$ was added as per volume of tube in a concentration of 0.05 mg/cc. A three-zone furnace having auxillary heater was found suitable for good crystal growth (Kershaw et al., 1967). In such a furnace the growth zone temperature is constant up to 3 inches and gradually increases towards tip of tube due to auxillary heater. This profile causes the coolest part of the tube, where the crystals grow to be near the centre rather than towards the end. The crystals are therefore spread out and well formed, instead of being crowded at the tip of tube. At the beginning of temperature run, the charge end was kept at room temperature, and the other end was maintained at 1100^oC. This causes the minimization of nuclei numbers in growth zone. After 24 hours the charge zone was raised to 1100^oC and growth (centre) zone was programmed to 1050^oC, in a regular interval of increase in temperature. Transport was allowed to continue for 5 days. All the heaters were then shut off and the tube was allowed to cool to room temperature. Crystals were then removed from the tube and washed with dilute hot HCl to remove excess chlorine.

4.3. PEC Behaviour of WSe_2 Single Crystals

The layered compounds provide a very useful model for the chemical nature of semiconductor surface states. The van der Waals surface composed of close-packed selenium atoms has no dangling bonds as do the surface of materials with three dimensional order and thus could be expected to be rather free of surface states within the band gap. However, the edges of crystal would be expected to be rich in surface states, because of termination of the lattice which results in coordinatively unsaturated transition metal sites. The photoelectrochemical behaviour of transition metal dichalcogenides has been systematically studied by Tributsch (1980) in various redox couples. In comparison with other redox systems, best results were obtained with I^-/I_3^- redox couple, as both photocurrent and flat band potentials were observed to be shifted towards more negative potential values.

It was found in the study of n-WSe_2 using aqueous I^-/I_3^- redox system, photogenerated holes are consumed by two competing reaction channels, i.e. oxidation of donor iodide and surface recombination. The surface recombination process is very fast and can only be surpassed by a large iodide concentration. Small amount of iodine can react with surface states and deactivate them. On the other hand, presence of large amounts of iodine can react with smooth surface of electrode also and thus can generate new surface states. This causes large potential drop in Helmholtz double layer. Hence solar energy conversion efficiency depends upon concentration of iodine in I^-/I_3^- redox system (Peraldo Bicelli, 1984).

4.4. Results and Discussion

The PEC behaviour of n-WSe_2 crystals has been extensively studied by us. The voltammetric response of as-grown n-WSe_2 crystals in iodide/iodine redox couple prepared in acidic electrolyte (0.5 M H_2SO_4) obtained(Fig.9).

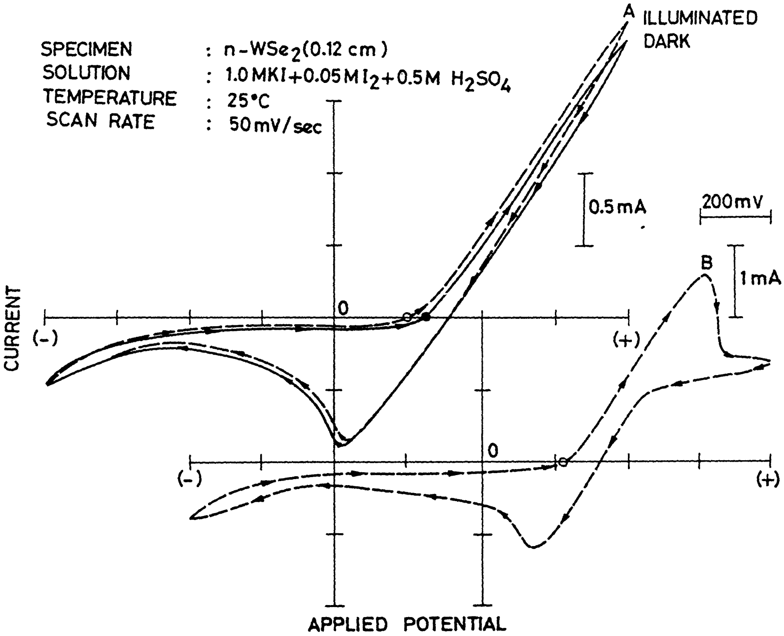

Figure 9. Voltammetric response of n-WSe_2. It may be seen that the photovoltage and photocurrents are small. Two hours of illumination resulted in the abrupt decrease of current (Curve'B').

The open-circuit potential in the dark is about +240 mV, which is close to the redox potential of I^-/I_2 against SCE. Upon illumination the change in the potential was minimal amounting to a photovoltage ranging between 40-100 mV. As can be seen from the figure, the magnitude of photocurrents is not significant ($\sim 150\,\mu A$). The currents in the dark are significant (~ 1.5 mA) at the positive extremum of bias potential (+800 mV). The semiconductor electrode, when illuminated for an extended period of time (2 hrs), exhibited reduction in the current which was rather sudden in the anodic branch. This behaviour may be correlated to the formation of non-conducting layer on the surface of the electrode, a behaviour usually exhibited by active-passive metals in electrochemistry. Surprisingly, when the sample is replaced after repeated washing with distilled water, it showed a voltammetric response (Figure 10), which is much the same as the original response (Figure 9). This points out to the fact that extended periods of illumination leads to some drastic variation in the surface chemistry, but original behaviour may be restored when washed with water - a physical process. This suggests that the semiconductor physics is unaltered but changes are found at interface only.

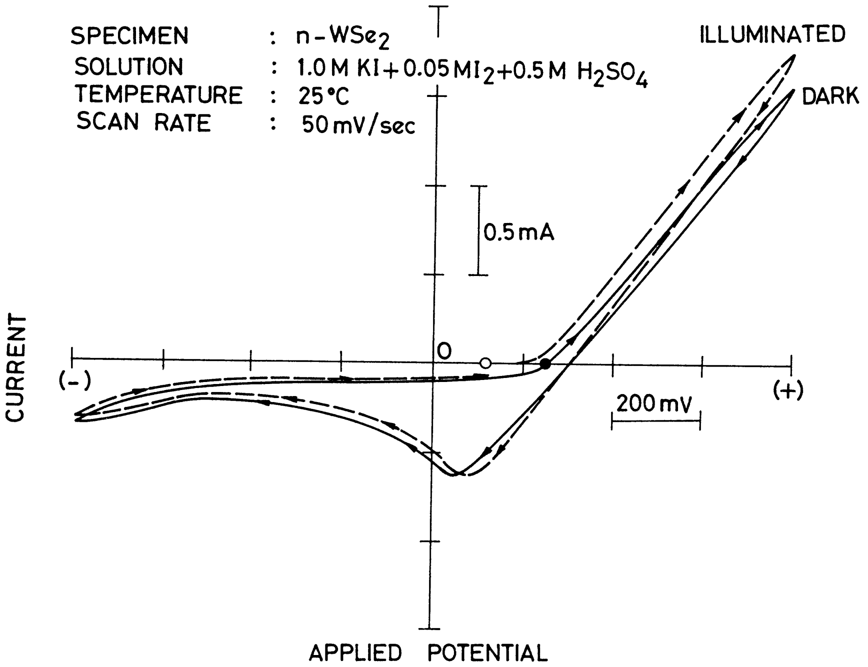

Figure 10. Voltammetric response of n-WSe_2 after washing the surface with distilled water. The peculiar behaviour found after 2 hours of illumination (see Figure 9) has vanished simply after washing with distilled water.

When this voltammetric response in $KI+I_2$ + 0.5 MH_2SO_4 (Figure 9) is compared with that in $KI+I_2$ + Borate Buffer (pH 9.1) (Figure 11), some interesting results ensue. The response in terms of photopotential as well as photocurrent has been observed to improve in the borate buffer. However, the magnitude of dark currents are relatively large in borate buffer solution. Moreover, when the bias potential reverses its direction, the cathodic branch of the curve exhibits enhancement in the cathodic current. At first sight, such an enhancement in the cathodic currents under illumination may be related to the acquirement of p-type character by the surface. This might occur on the semiconductor surface due to absorption of ions from the solution, amounting to a rise in the concentration of minority carriers, which contributes to the cathodic photocurrents.

When the n-WSe_2 specimen is illuminated for various time periods, the photocurrents are found to improve as suggested by the voltammetric responses in Figure 12. The voltammetric curve at 1 hr did not exhibit any rapid fall of current at the positive extremum of bias potential. However, the responses obtained after prolonged illumination started showing a sudden decrease in the current. Moreover, the photocurrents are found to increase with time of illumination. Despite the fact that the photocurrents have increased with illumination times, the point that current falls suddenly imposes limitation on the upper limit of forward bias potential. The interfacial nature of the rapid increase in the current apparently requires further studies.

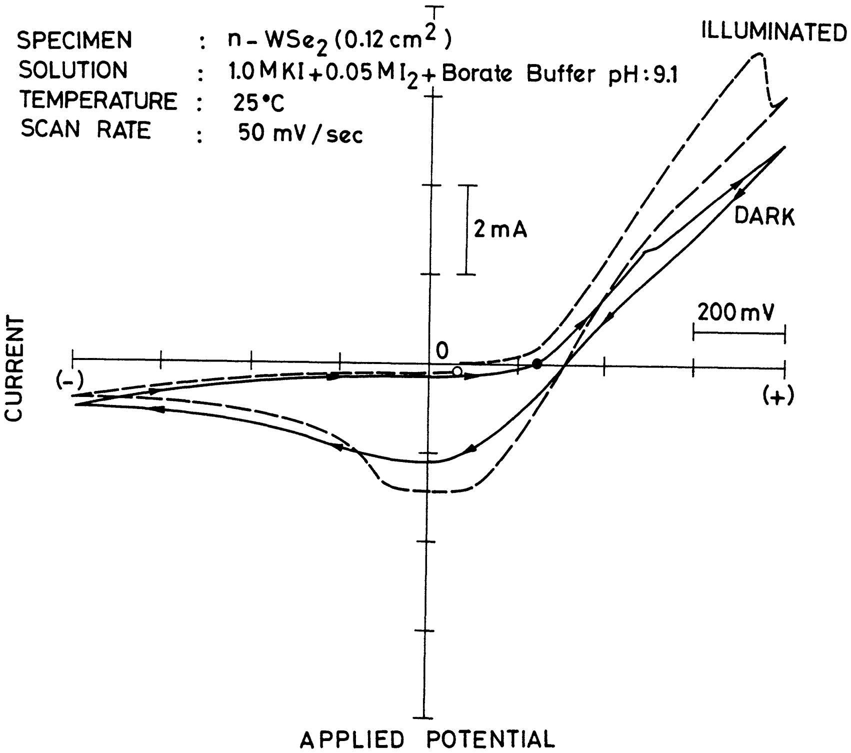

Figure 11. Voltammetric response of n-WSe_2 in Borate Buffer. Notice the improved photovoltage and photocurrent response (see Figure 9 for comparison).

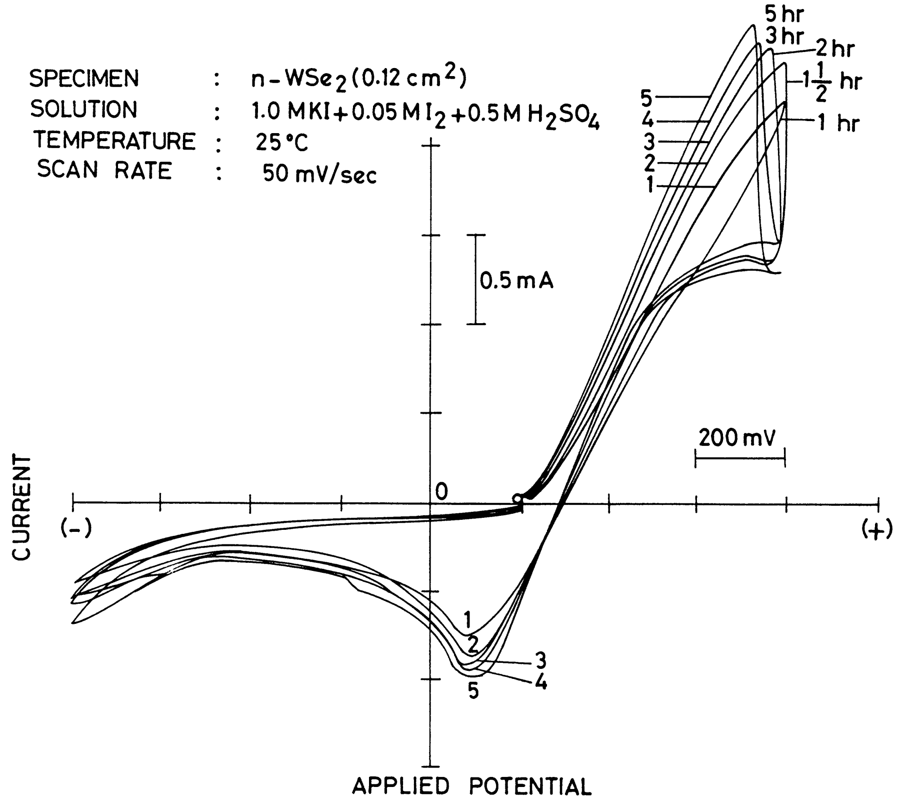

Figure 12. Voltammetric response of n-WSe$_2$ for extended periods of immersion under illumination. Notice that the illumination of the surface beyond 1 hour results in the sudden decrease of anodic current.

4.5. Relevance of n-WSe$_2$ PEC Solar Cells in Hydrogen Production

The PEC characteristics of n-WSe$_2$ discussed in the foregoing section clearly reveals that as a photoanode this material is quite attractive. In a PEC cell when used with iodine/iodide electrolyte in a borate buffer, it is capable of producing high conversion efficiencies. Another attractive point about WSe$_2$ is that it is capable of producing hydrogen from hydrogen-rich chemicals like HI (Bagalio et al., 1982). It is an anode material capable of sustaining the photoelectrolysis of HI represented by the equation $2HI \xrightarrow{h\nu} H_2 + I_2$. But for the solar light $h\nu$, no other energy input is required. The E^o (H /H_2), E^c (I_2/I^-) difference is about 0.5 V. A very interesting characteristic about WSe$_2$ as already suggested relates to the fact that it is not susceptible to corrosion under PEC conditions. This behaviour ensuing from the d-d transition on photoexcitation makes this material an outstanding one for PEC conversions. An interesting aspect concerning the MX_2 type layered materials concerns the fact that the flat band potentials of n-MOS_2 and n-$MOSe_2$ are slightly less negative and those of n-WS_2 slightly more negative than the standard hydrogen potential. This point is of particular interest in connection with the possibility of utilising these semiconductors in photoelectrochemical cells where hydrogen could be produced.

5. CONCLUSIONS

The results outlined in the above reveal that at present the material problem relating to photoelectrolysis is not satisfactorily solved. Both types of materials - the large band gap materials like TiO_2 and low band gap materials like WSe_2 should be explored. For photoelectrolysis of water employing solar energy, the photoelectronic properties of TiO_2 will have to be modified so as the solar spectral response improves and consequently high conversion efficiencies ($\sim$1%) could be achieved. For low band gap materials like WSe_2 which are suitable for photoelectrolysis of fluids like HI/HBr, it appears that the role of the surface defects both macroscopic and microscopic will have to be clearly monitored and analysed before these could become viable photoelectrodes for hydrogen production.

ACKNOWLEDGEMENTS

The authors are grateful to Prof. B. Venkatraman, Prof. A.P.B. Sinha and Prof. M.V.C. Sastri for helpful discussions. The present work was carried out under a project sponsored by the Department of Non-conventional Energy Sources, Ministry of Science and Technology, Government of India.

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HYDROGEN PRODUCTION BY MICROORGANISMS

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1. INTRODUCTION

A variety of microorganisms have the ability to evolve H_2 according to the equation

$$2H^+ + 2e \rightleftharpoons H_2$$

These organisms belong to diversified morphological and physiological groups as follows:

(a) Strict anaerobic bacteria (e.g. Chlostridium pasteurianum).
(b) Facultative anaerobic bacteria (e.g. Bacillus polymyxa).
(c) Aerobic nitrogen fixing bacteria (e.g. Azotobacter, Rhizobium legume root nodules).
(d) Photosynthetic bacteria (e.g. Chromatium, Rhodospirillum/ rubrum.
(e) Blue green algae (e.g. Oscillatoria limnetica).
(f) Green algae (e.g. Chlamydomonas, Scenedesmus, Chlorella).

2. CAPABILITIES OF ORGANISMS TO PRODUCE HYDROGEN

Many strict and facultative anaerobic bacteria ferment organic substrates to hydrogen but they do not have the ability to degrade organic matter completely to CO_2 and H_2. The highest yield ever measured was 4 moles of H_2 formed from 1 mole of glucose. This value decreases to about 2.6 moles of H_2 per mole of glucose when cultures are grown under a hydrogen pressure of about one atmosphere. Four moles of hydrogen contain only 33 per cent of the combustible energy of glucose and 2.6 moles contain approximately 20 per cent of energy of glucose. In contrast to this, during methane production from glucose 85 per cent of the energy is conserved. Therefore, energetically, it is much efficient to produce methane instead of hydrogen when organic matter is to be converted to energy by microorganisms.

The situation may, however, be different with photosynthetic organisms which use solar radiation to produce chemical energy.

R. P. Dahiya (ed.), Progress in Hydrogen Energy, 53–57.

Photosynthetic bacteria in marine environment and green and blue green algae appear to be more rewarding.

3. HYDROGEN PRODUCTION BY PHOTOSYNTHETIC BACTERIA

Photosynthetic bacteria utilise hydrogen as electron donor for autotrophic CO_2 assimilation. Hydrogen photoproduction in these organisms is largely or completely associated with the action of nitrogenase, i.e. nitrogen fixing system. The exact mechanism of electron transfer in hydrogen metabolism and nitrogen fixation is not resolved so far. A possible scheme of electron transport and hydrogen metabolism in the photosynthetic bacterium Rhodo-spirillum rubrum is given in Figure 1.

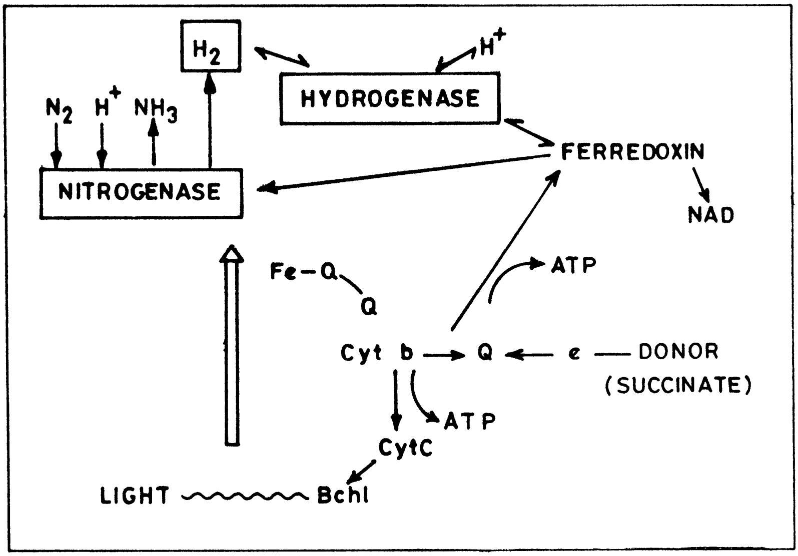

Figure 1. Hydrogenase-nitrogenase catalyzed hydrogen metabolism in Rhodorubrum.

(BChl - Bacterial chlorophyl; Cyt b - Cytochrome b; Cyt c - Cytochrome c; Q - Quinones)

In photosynthetic bacteria, carbohydrates can be completely degraded to H_2 and CO_2 through a light dependent anaerobic Krebs cycle. One mole of glucose yields 12 moles of hydrogen. Almost 100 per cent of the combustible energy of glucose would be conserved.

$$\text{Glucose} + 6H_2O \longrightarrow 6CO_2 + 12H_2$$

In practice about 70 per cent energy conservation efficiency from lactate has been reported.

Hydrogen photoproduction has been found in species of all families of photosynthetic bacteria (Rhodospirillaceae, Chromatiaceae and Chlorobiaceae). In general, photosynthetic bacteria utilise a wide spectrum of organic substances such as carbohydrates, lipids, fatty acids and some inorganic sulfur compounds. The substrate specificity for hydrogen production varies from species to species. Some of the common electron donors used for hydrogen production by photosynthetic bacteria are summarised in Table I. Prolonged hydrogen evolution from whey or other lactic acid containing wastes have been demonstrated. Hydrogen production is limited by the availability of appropriate waste materials.

TABLE I : Electron Donors used for Hydrogen Production by Photosynthetic Bacteria

Rhodospirillaceae	Chromatiaceae	Chlorobiaceae
Acetate	Acetate	Citrate
Butyrate	Fumarate	Formate
Formate	Malate	Glucose
Fructose	Oxalacetate	α-Ketoglutarate
Fumarate	Pyruvate	Lactate
Glucose	Succinate	Mannitol
α-Ketoglutarate	Sulfide	Pyruvate
Lactate	Thiosulfate	Xylose
Malate		
Oxalacetate		
Propionate		
Pyruvate		
Succinate		
Sucrose		
Thiosulfate		

4. HYDROGEN PRODUCTION BY BLUE GREEN ALGAE

Nitrogen fixing blue green algae need only light, water, carbondioxide and mineral salts for growth. They thrive without combined nitrogen and have, therefore, the simplest nutrient requirements among all organisms. The best known examples for N_2-fixing blue-green algae are Anabaena sp. and Nostoc muscorum. The filamentous forms contain two cell types; the vegetative cells and the heterocysts. The vegetative cells perform photosynthetic CO_2 fixation and O_2 evolution, and the heterocysts lack the photosynthetic water splitting reaction (Figure 2). Under anerobic condition nitrogenase is located in these specialised cells.

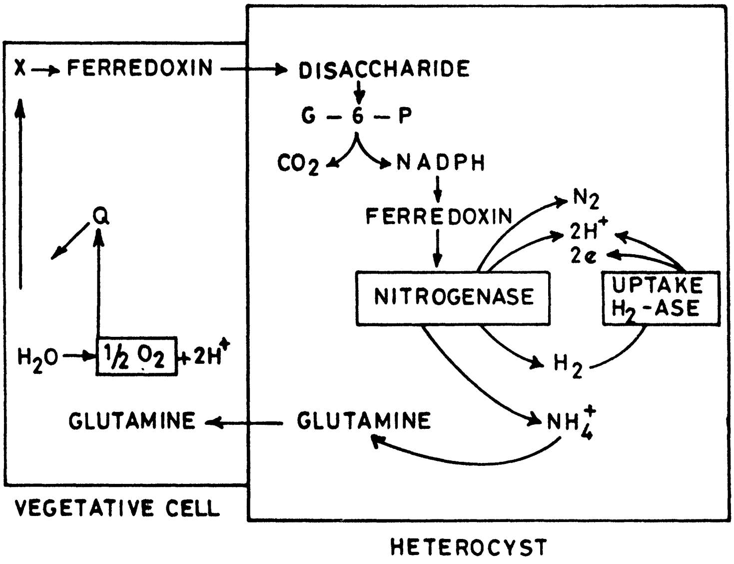

Figure 2. Metabolism of photosynthesis in vegetative cells and N_2-fixation and H_2-production in heterocysts of blue-green algae.

(X - Unknown compound; G-6-P - Glucose-6-phosphate; Q - Quinones)

Photoproduction of H_2 catalyzed by hydrogenase has unambiguously been shown for the marine algae Oscillatoria limnetice. Using severely nitrogen starved Anabaena, long lasting H_2 formations have been achieved where the ratio between H_2 formation and photosynthetic O_2 evolution approached one. The efficiency of converting solar energy to hydrogen was maximally 0.4 per cent and the cells produced H_2 up to 30 days.

It has become quite clear that H_2 formation rates depend not so much on the algae strains used but on the culture and assay conditions employed. A major factor influencing H_2 formation capability is the nitrogen content of the cells. Prolonged nitrogen starvation leads to the synthesis of additional nitrogenase and increases H_2 formation capabilities. During the growth of the organisms, hydrogen production is also influenced by other factors, such as temperature, the supply of the culture with iron and CO_2, the O_2 tensions, and the light intensities.

Aerobic nitrogen fixing unicellular blue green algae Synechococcus sp. Miami BG-043511 and non-heterocystous high and stable hydrogen producing marine blue green algae Oscillatoria sp. Miami BG-7 have been isolated at Division of Biology and Living Resources, School of Marine and Atmospheric Science, University of Miami, Florida, USA. These strains are considered promising for biological hydrogen photoproduction from water as yields up to 8 micromoles per mg protein per hour (malate as substrate) have been recorded (Ramachandran and Mitsui, 1984). Extensive work is in progress in many laboratories for prolonging the period of continuous hydrogen production in both cell free and immobilized cell system of these and many other promising strains.

5. CONCLUSION

Biophotolysis like artificial photobiological is likely to be found practicable in the long run for production of fuels and chemicals in particular hydrogen, fixed carbon and ammonia. Only biophotolysis type systems have the following three features: (a) a ubiquitous substrate (water), (b) an unlimited driving force (the sun) and (c) a stable and non-polluting product (hydrogen). At present, the biological system is the only one that is able to use wide range of visible light spectrum to catalytically split water to H_2 and O_2. The state-of-art is however still rudimentary, but the present indications are that it has enormous scope.

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OCEAN THERMAL POWER FOR HYDROGEN PRODUCTION

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1. OCEAN THERMAL RESOURCE

Roughly three-fourths of the earth's surface is covered by the oceans and thus receives the major share of the Sun's radiant energy falling on the planet. Allowing for the loss of part of this energy income by back-radiation, evaporation, convection and diffusion towards the colder polar regions, the net gain of solar energy by the ocean-surface in the tropical and sub-tropical regions (i.e., the ocean belt between the latitudes 25°N and 25°S) is estimated to be around 450 million joules per square metre per year (4.5×10^8 J/m^2.yr). This net income helps to keep the surface of water of tropical oceans (to a depth of 50 to 100 metres generally) at a temperature of 22 to 26°C. At the same time, at a depth of about 700 to 1000 m below the surface, the temperature is always around 4°C, due to the flow of cold water streams from the polar regions. This results in a difference in density between the top and bottom layers of water which, coupled with the absence of turbulence in the water below 100 metres, sustains a temperature difference of 22 to 25°C, 24 hours of a day and 365 days a year, between the surface-layers and deep below. Figure 1 is a simplified version of a typical temperature profile, or "thermocline" which exists in the oceans. Figure 2 shows the actual temperature profiles recorded for four different locations in the North Atlantic Ocean. Notice that at each location the surface temperature lies within a narrow range throughout the year. The oceans thus serve as a huge natural reservoir of solar thermal energy.

The temperature difference ΔT (between the surface and 1000 m below) varies from region to region. It is generally 20-24°C in the tropics, but lower in the temperate regions. Maps of the eastern and western hemispheres showing the average ΔT values in different regions are shown in Figures 3(a) and (b). The highest ΔT values are found in the equatorial belts of the Pacific Ocean and the Indian Ocean.

It follows from the Second Law of Thermodynamics that the existence of this temperature difference would, in principle, permit the operation of a heat engine which could continuously transform into work heat drawn from the warm surface water of the oceans. This, in short, is the basic

R. P. Dahiya (ed.), Progress in Hydrogen Energy, 59–80.

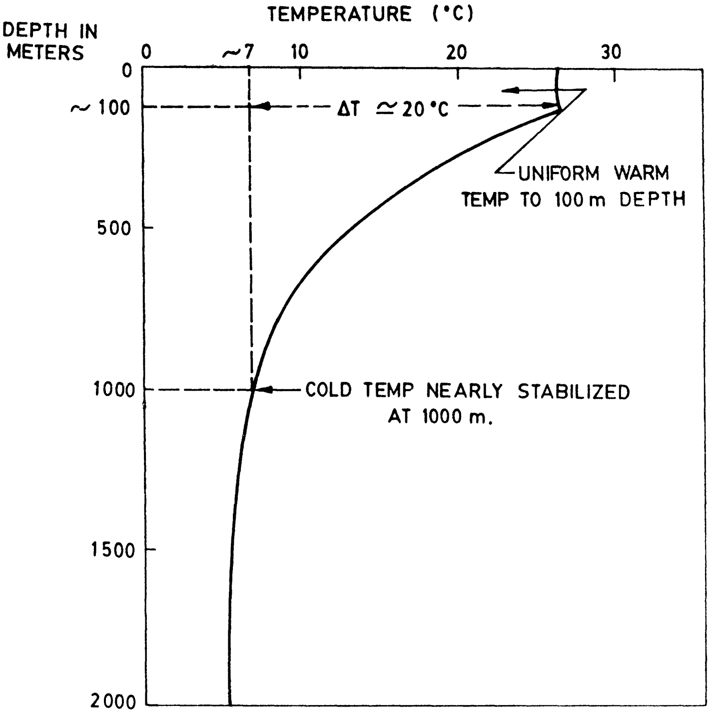


Figure 1. A typical temperature profile in the tropical seas

principle of Ocean Thermal Energy Conversion or OTEC, for short. In the wake of the global energy crisis, the practical realization and development of OTEC is currently receiving very active consideration, backed by massive fund support, in the U.S.A., Europe and Japan.

Basically, two types of heat engines are under design and development for OTEC. The essential difference between them consists in the working fluid that is employed and the consequent mechanical features.

In what is called the Closed Cycle Rankine engine, represented schematically in Figure 4, the working fluid is a refrigerant with a low boiling point (< 20°C), such as ammonia, which is rapidly vaporized at the temperature of the warm surface water. The vapour expands through a turbine and is later condensed by the cold water pumped up from deep below. The liquefied fluid is recirculated through the evaporator. (The Closed Cycle Rankine engine may be compared with a household refrigerator working in the reverse direction.)

In the alternative system, called the Open Cycle, shown in Figure 5, the warm sea water itself is used as the working fluid. It is first subjected to a "flash evaporation" at reduced pressure. The vapour, after expansion through the turbine-chamber, is condensed to yield desalinated clean water as a valuable by-product in addition to mechanical

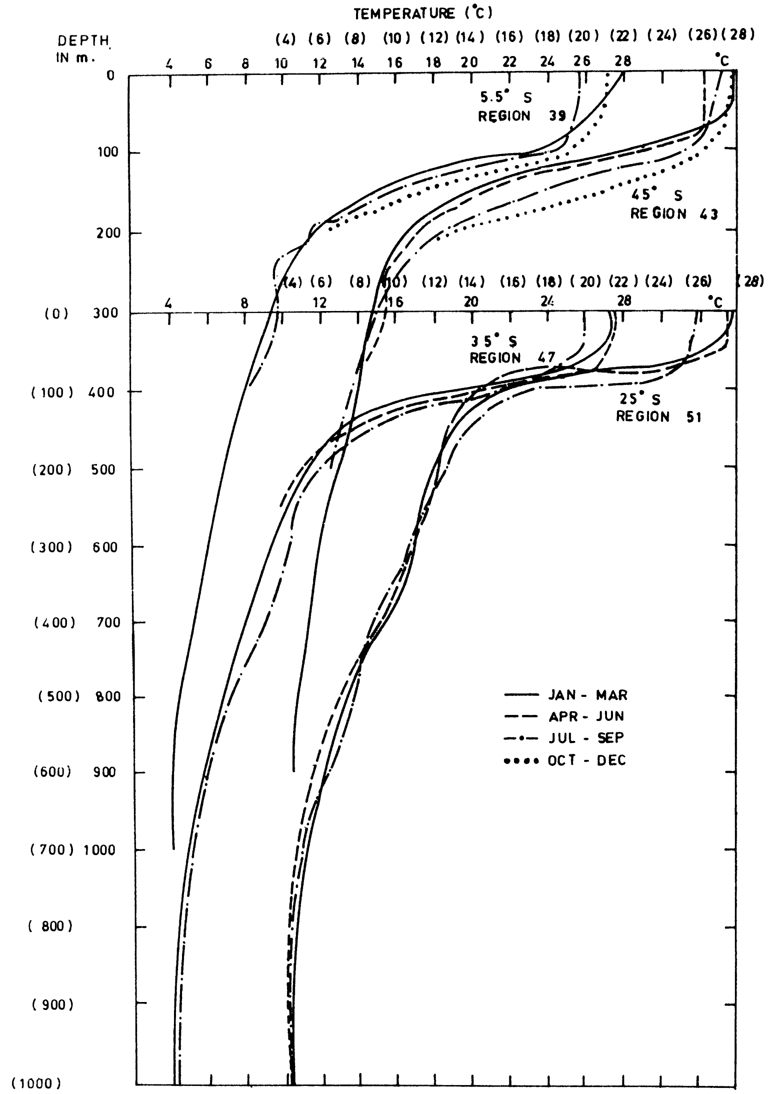
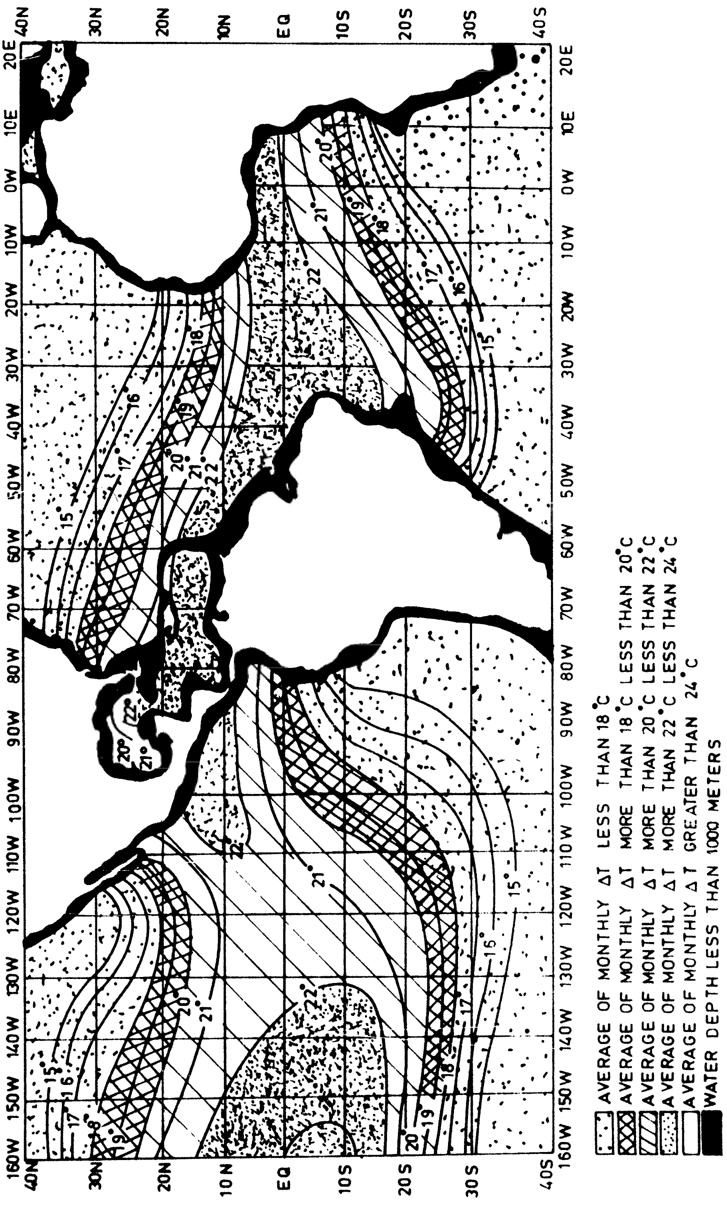
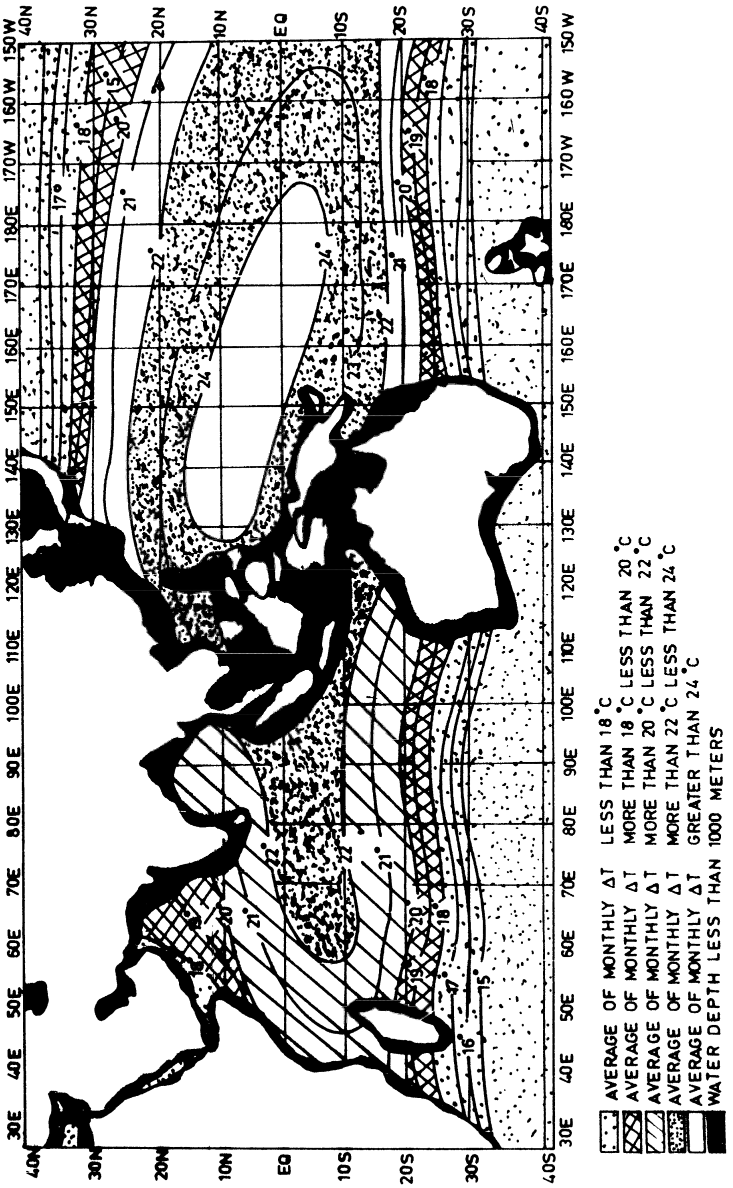


Figure 2. Average ocean temperature profiles by seasons at four locations between longitudes 25°W and 30°W



⬚ AVERAGE OF MONTHLY ΔT LESS THAN 18°C
▩ AVERAGE OF MONTHLY ΔT MORE THAN 18°C LESS THAN 20°C
▨ AVERAGE OF MONTHLY ΔT MORE THAN 20°C LESS THAN 22°C
⬚ AVERAGE OF MONTHLY ΔT MORE THAN 22°C LESS THAN 24°C
☐ AVERAGE OF MONTHLY ΔT GREATER THAN 24°C
■ WATER DEPTH LESS THAN 1000 METERS

3(a)



3(b)

Figure 3. Contours for stated annual average monthly temperature difference (in °C) between the ocean surface and depths of 1000 m for (a) the Western Hemisphere and (b) the Eastern Hemisphere. The most promising ocean thermal resources are contained within the areas having annual average temperature difference of 20°C or larger. Shading in coastal areas indicates water depths less than 1000 m.

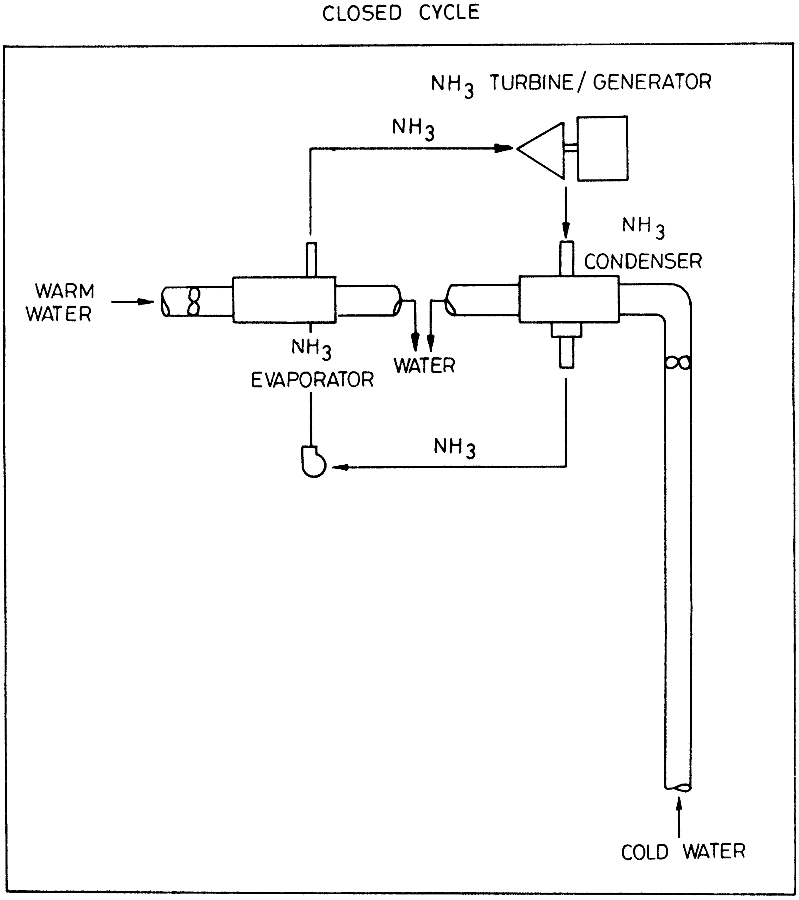


Figure 4. OTEC Closed Cycle

energy. In spite of this advantage of open cycles, the main thrust of OTEC development effort so far has been on Closed Cycle Rankine engines, mainly because of the engineering simplicity and technical prospects of the latter.

In both cases, the primary output of the OTEC plant is electrical power and the quantum of this output is limited primarily by the Carnot theorem, which restricts the maximum theoretical efficiency of conversion of heat to work to

$$n_c = \frac{\Delta T}{T^{o}K \text{ (surface)}} \qquad (1)$$

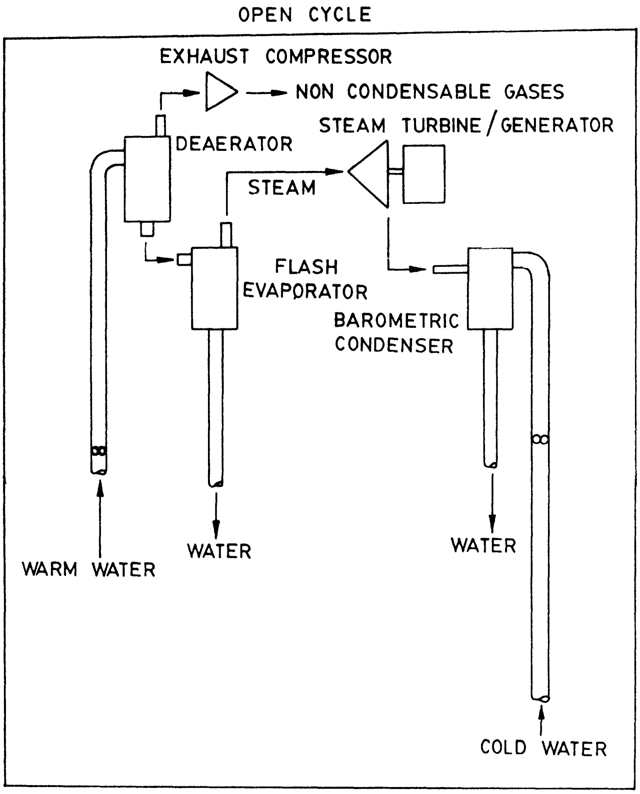


Figure 5. OTEC Open Cycle

This relation underscores the importance of the ΔT value. At the present state of heat engine technology, ΔT values less than $\sim 20^oC$ are uneconomical. Apart from $\Delta T > 20^oC$, there are other oceanographic criteria to be satisfied in the choice of ocean sites for OTEC plants, apart from geopolitical considerations and legal issues.

Some of the major engineering problems associated with OTEC development on a large scale have been reviewed recently by the present author (Sastri and Krishna Murthy, 1981).

2. POTENTIAL OF OTEC

Assuming $T_{cold} = 4^oC$, the limiting Carnot efficiency for $\Delta T = 20^o$ is

$$n_c = \frac{20}{273+20+4} = 0.067 \text{ or } 6.7\% \qquad (2)$$

In practice, this is further reduced by several loss factors in the plant such as the heat transfer efficiency (n_h) the turbogenerator or conversion efficiency (n_g) and internal energy consumption for running the pumps and other ancillary facilities (f_i). The maximum overall output efficiency (n_o) of the OTEC plant, given by

$$n_o = n_c \cdot n_h \cdot n_g \cdot (1-f_i) \qquad (3)$$

is generally (rather conservatively) put at 2.3%. However, even at this low conversion efficiency, OTEC is considered to be an attractive proposition because of the vastness and inexhaustible nature of the ocean energy resource. Let us see how this is so.

The total extent of potential OTEC sites worldwide ($\Delta T > 20^{o}C$, between latitudes $25^{o}N$ and S) $\sim 1.2 \times 10^{14} m^2$.

The aggregate annual gain of solar energy by this much ocean surface, at $4.5 \times 10^{8} J/m^2$ yr is, therefore,

$$1.2 \times 4.5 \times 10^{22} = 5.4 \times 10^{22} J/yr$$

At 2.3% net attainable conversion efficiency, the total OTEC potential of the tropical seas amounts to

$$5.4 \times 10^{22} \times 0.023 = 1.24 \times 10^{21} J/yr$$

$$\approx 40 \text{ terawatts } (40 \times 10^{12} W)$$

This is nearly equal to the estimated total global energy requirement of all kinds in the middle of the next century, when the world population is expected to level off at 8-12 billion. This means that the entire energy requirement of the world can be met everlastingly by just this one source alone, without having to pay for the fuel; but there are several practical constraints (such as availability of fabrication materials, limitations of engineering and technology, financial resource limitations, geopolitical barriers etc.) which will limit or delay the attainment of full potential of the OTEC prospects. Nevertheless, there is no doubt that in the decades to come the oceans will become a major source of energy ranking on par with coal, nuclear fission fuel and even nuclear fusion. Indeed, OTEC represents one of the most promising means of harnessing the sun's radiance for terrestrial energy production on a magnum scale. This assurance is sustained by several economic projections and technical feasibility studies of which some samples are shown in Figures 6 and 7.

Credit for the first practical demonstration of the OTEC concept goes to a group of U.S. firms, who, in August 1979, successfully operated a small Mini-OTEC plant off Hawai in the Pacific Ocean. The plant yielded 10 KW_e of net electrical power. This has given a filip to the U.S. Government's support for OTEC R, D & D efforts, marked by the following schedule of programme goals (Dugger et al., 1981):

(a) 100 MW_e by 1986, (b) 500 MW_e by 1989, (c) commercial competitives mid-1990's and (d) 10,000 MW_e by 1999.

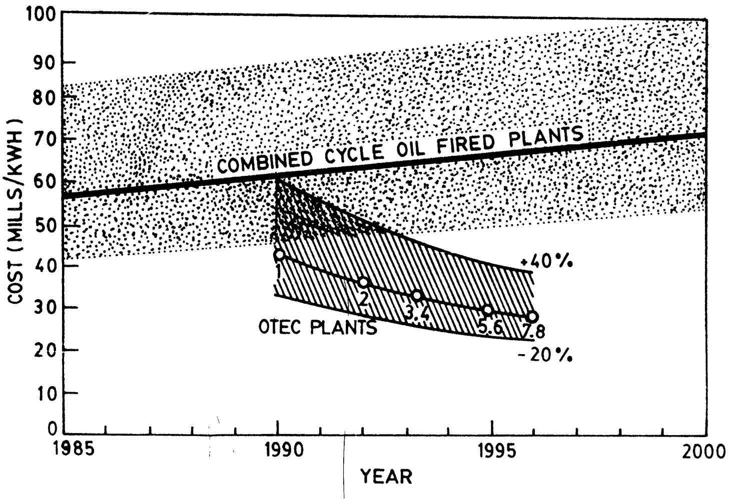


Figure 6. Comparison (in constant 1976 dollars) of baseload electrical costs projected for Puerto Rico for oil-derived electricity with energy costs for electricity derived from 250-MW_e OTEC plants a few kilometres offshore. Possible cost projections (solid lines) are shown within bands of estimated uncertainty. Numbers near points refer to cumulative number of OTEC plants.

3. TRANSMISSION AND DELIVERY OF OTEC POWER

One of the major problems arising in the development of OTEC concerns the transmission of the energy produced at sea to users on shore. Transmission of electricity via submarine cables is no doubt a possibility, but it is distance-limited. It would be applicable only to a few small and medium-sized offshore OTEC plants, i.e. those generating 100 MW_e or less and situated no more than 100 Km offshore. This would indeed be an economical source of power to many island locales which are situated far away from the mainland and could help to accelerate the economic development of these islands. Most of the big OTEC sites are, however, situated mid-ocean, 1000 Km or more from the mainland shores. In such cases, economic considerations warrant installed OTEC capacities of 500 MW_e or even more and, further, such big OTEC platforms should have the additional facility to "graze" over a certain area to avoid excessive cooling of the surface water. Cable-transmission of such large chunks of electricity from mid-ocean OTEC ships is, frankly, out of the question. It will be neither practical nor economical. The economics and logistics of transmission through rechargeable batteries have been examined and found to be unattractive commercially (though technically feasible) when all the relevant factors are considered.

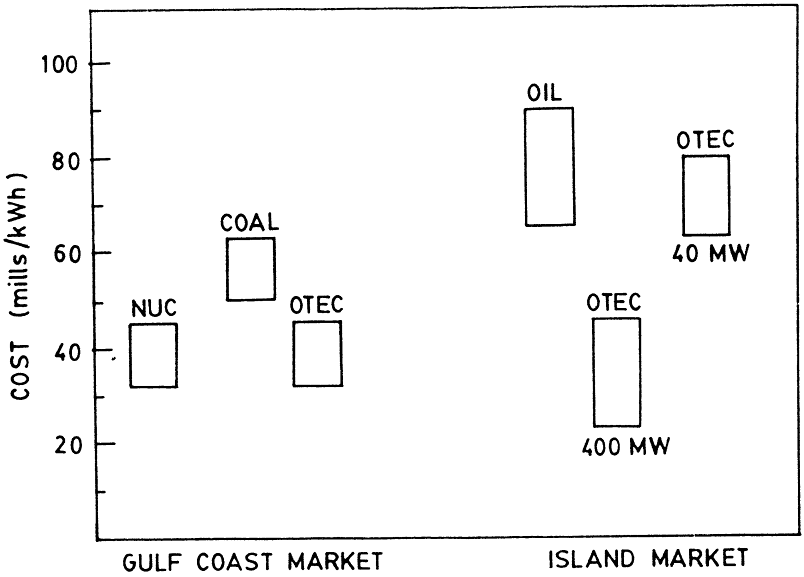


Figure 7. Qualitative estimates for ranges of projected OTEC energy costs estimated for year 2000 in constant 1978 dollars compared to ranges of projected energy costs for baseload electricity derived from coal, uranium, and oil for Gulf Coast and U.S. island markets. Note the variation in energy cost estimated at two different OTEC plant sizes for the island markets. OTEC plant sizes for the Gulf Coast market were assumed to be 400 MW_e.

Many studies have favoured the on-board utilization of OTEC power for the production of energy-intensive materials which could be shipped to any part of the world. Such schemes will be workable only if the raw materials are either available at sea (in the sea-water or on the sea-bed)or can be shipped economically to the OTEC sites.

4. PRODUCTION OF HYDROGEN WITH OTEC POWER

Hydrogen is the first choice for production with OTEC power, because it can be produced quite simply by the electrolysis of sea water. All the technological aspects (including plant design) and economics of this option have been worked out in detail, notably by G.L. Dugger and his associates at the Johns Hopkins University, Maryland, U.S.A. (Dugger and Francis, 1977). The versatile utility of hydrogen in many chemical and metallurgical industries and its emergence in recent years as a fuel substitute for petroleum are strong plus points for hydrogen.

The essential requirements for electrolytic hydrogen production are just two: D.C. electricity at the required voltage and water. The former can be produced straightaway by using D.C. generator, thus obviating the need for expensive power-conditioning equipment which would be needed if primary generation were A.C.

Turning to the other requirement, namely water, technology for electrolysis of virgin sea water itself for hydrogen production (with fresh water as a valuable byproduct) is under development, but it is yet to reach the stage of economic viability. Until then, sea water has to be desalinated for use in electrolysis. This may be achieved in a variety of ways such as distillation with solar heat, selective ion-exchange, reverse osmosis, electrodialysis and so on. Among these, there is a strong preference for reverse osmosis, because it takes up less deck-area and requires less attention and maintenance than the other alternatives just mentioned.

Having produced the hydrogen, the next question that arises is what to do with it. (The oxygen produced simultaneously is mostly vented into air.) There are two broad options for disposing of the hydrogen: (1) export it to shore markets, and (2) consume it on board the OTEC platform to produce other energy intensive chemical or metallurgical products. We shall now examine these options one by one.

5. TRANSMISSION OF HYDROGEN

Hydrogen can no doubt be transmitted as gas through flexible pipelines, but this will be practical only over short distances, i.e. for off-shore OTEC plants. This will not offer any notable advantage over cable-transmission of electrical power. For transmission over longer distances of the order of several hundred kilometres, the gas should be liquefied on board and shipped as liquid hydrogen (LH_2) in large, super-insulated, cyogenic containers. A schematic diagram for OTEC hydrogen production, liquefaction and shipment based on a 325 MW_e plantship sited in equatorical waters is shown in Figure 8. The plantship would produce 146 metric tons of liquid hydrogen per day. At 345 days operation per year it would deliver an annual average of 135 mt of liquid hydrogen per day (after allowing for 2% boil-off loss in transit) to mainland ports for storage and use.

The estimated plant investment, operating cost and delivered hydrogen costs for this system evaluated by Avery et al. (1984), are presented in Table I. The costs stated are in mid-1983 dollars.

With the rapid advances that are taking place in hydrogen liquefaction and cryogenic containment technology, there need be little doubt about the technical feasibility of this option, but its commercial prospects and profitability should also be considered because OTEC is highly capital intensive. The use of liquid hydrogen as an alternate fuel for commercial jet aircraft is receiving serious consideration because of the numerous technical and economic advantages that it offers over other fuel alternatives. While this has a big market potential for LH_2, it will take a lead time of 20 to 30 years for it to develop on a truly commercial scale. Until then, we have the other option of on-board utilisation of hydrogen.

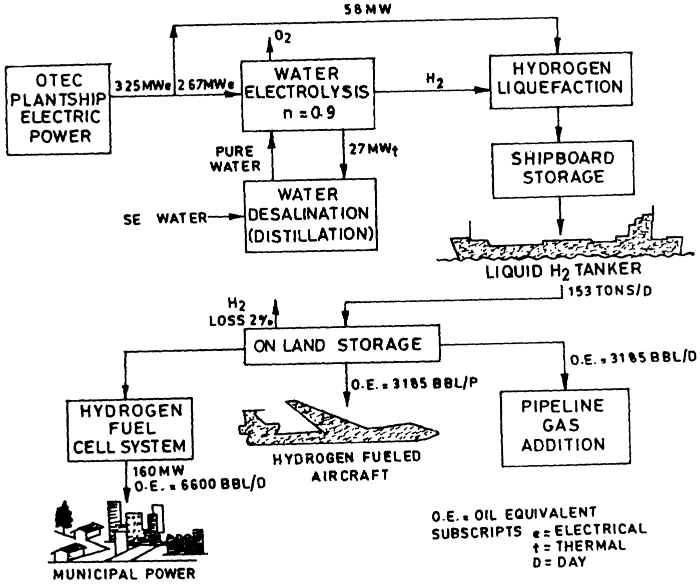


Figure 8. OTEC liquid hydrogen plantship

TABLE I : Estimated Costs of OTEC Liquid Hydrogen (1983 $)

Plant Investment	($M)
Basic plantship	473
LH_2 plant	114
Interest during construction (14.8%)	67
Total 0% contingency	654
50% contingency	981

Annual Cost ($M)	0% Contingency	50% Contingency
Real fixed cost	38.6	57.9
Annual O & M	9.1	13.7
Shipping	8.6	12.9
Total	56.3	84.5
Annual Production (1000 mt) (minus boil-off)	49.4	49.4
LH_2 cost ($/mt at U.S. port)	1140	1711
Sales price ($/mt at U.S. port) to yield net profit of 25% per year after taxes are deducted	1736	2605

Though an immense variety of commercially worthy chemical products can be made with hydrogen, the choice, in the present context, is limited by techno-economic constraints to just a few which can be produced on a big scale by relatively simple processes in plants that can be accommodated and operated on floating platforms and the delivered cost of which will be competitive with those produced indigenously on land.

U.S. based study groups have advocated the on-board utilization of hydrogen for the production of ammonia or methanol which can be transported economically over sea or land. Ammonia (NH_3) would be produced on board the OTEC ship by combining the hydrogen with nitrogen extracted from air. To produce methanol, carbon (not available at sea) is transported as coal to the OTEC site from land sources in huge coal bunkers. Conversion to $CO+H_2$ water gas using steam and oxygen (co-generated with H_2 by electrolysis of water) and enrichment with hydrogen yields the synthesis gas of the required composition for methanol synthesis. The technical features and economic aspects of these alternatives are discussed in the following sections.

6. CONVERSION OF OTEC HYDROGEN TO AMMONIA

Ammonia is formed by the combination of nitrogen and hydrogen. The synthesis reaction

$$N_2+3H_2 = 2NH_3$$

occurs favourably at high pressure and moderate temperature in the presence of a specially prepared iron catalyst (Haber-Bosch Process). The product is an equilibrium mixture from which ammonia is easily separated.

Ammonia is easily liquefied and the liquid can be stored at room temperature at moderate pressure and transported in existing ammonia tankers, trucks, tank-cars and pipelines. Liquid ammonia contains significantly more hydrogen per unit volume than either liquid hydrogen or metal hydride. (The weight of hydrogen in L-NH_3 is 136 g/li as against 71 g/li in LH_2 and 66 g/li in Mg_2Ni hydride.) Ammonia is easily and quantitatively dissociated into its constituents by the application of heat at moderate temperature. The combination of these properties makes ammonia an ideal carrier for hydrogen.

Ammonia is currently produced in large quantities for use as a base material for nitrogen fertilisers. The current industrial process,based mainly on natural gas as hydrogen source, requires about 1100 cu.m. of natural gas per metric ton of ammonia produced. Because of the large demand, the infra-structural facilities for the storage, transportation and distribution of ammonia already exist.

The basic design of an OTEC plant-ship for ammonia production has been drawn up by Professor Dugger of Johns Hopkins University (Dugger and Francis, 1977). A schematic representation of his design is shown in Figure 9. It shows all the constituents of the OTEC plant and its D.C. generator, the sea water desalination unit and the electrolyser for hydrogen production. An air-liquefier and fractionator supplies nitrogen

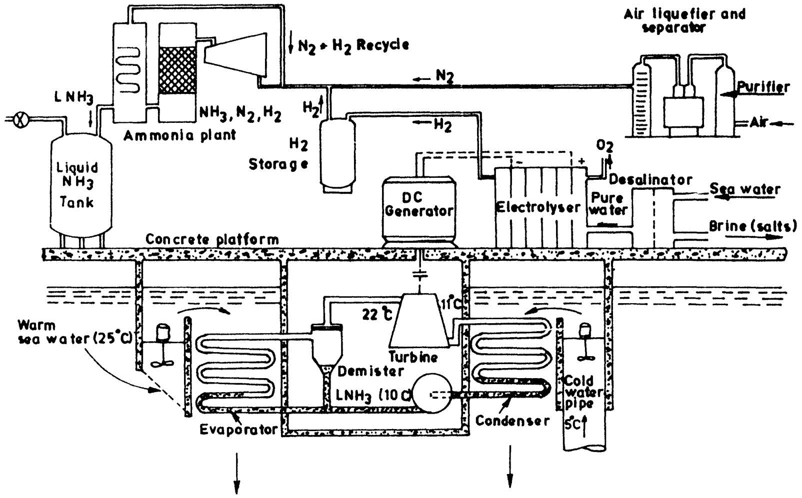


Figure 9. The OTEC power plant with integrated ammonia plant.

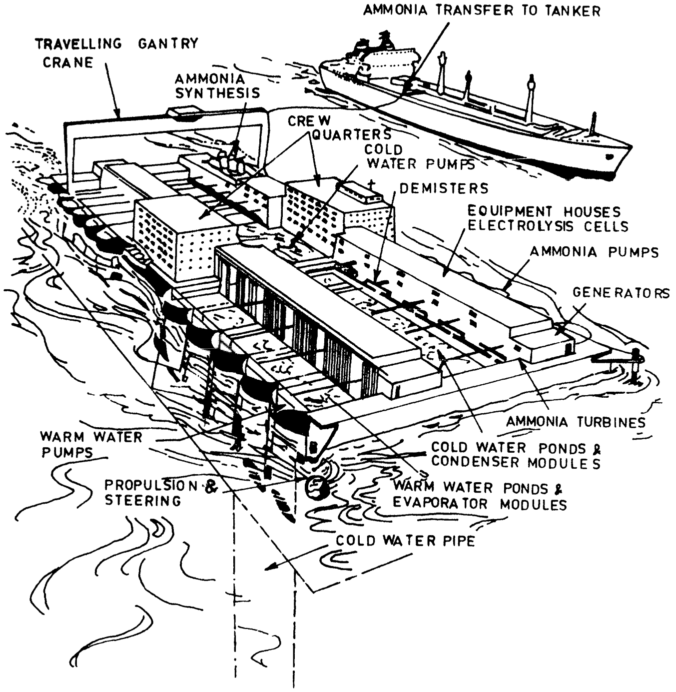


Figure 10. An APL conceptual design of a 100-MW$_e$ plant ship for producing ammonia, containing twenty 5-MW$_e$ modules and the ammonia fabrication equipment.

which is combined with hydrogen in the catalytic converter. The product ammonia is liquefied, stored and exported in special liquid ammonia tankers. An artist's view of the OTEC-ammonia plant-platform is shown in Figure 10. Notice that the OTEC platform is large enough to provide housing for the crew.

6.1. Cost Estimates

Tentative cost estimates for OTEC-ammonia have been made by the study groups of IGT, JHU-APL and others (Dugger and Francis, 1977; Avery et al., 1984; Talib et al., 1978). The JHU-APL's estimate (Avery et al., 1984) for 325 MWe eighth OTEC plant-ship (i.e. incorporating the experience gained and economies learnt in building and operating seven previous OTEC-plants of comparable size) is given in Table II in 1983 dollars.

TABLE II : Estimated Cost of OTEC Liquid Ammonia (1983 $)

	325.MW ($M) 8th Plantship	
Plant Investment		
Basic plantship	482.0	
Ammonia plant	99.0	
Interest during construction (14.8% of PI)	86.0	
Total 0% contingency	667.0	
30% contingency	868.0	
Annual Cost	0% Contingency	30% Contingency
Real fixed	39.3	51.2
Annual O & M	10.0	13.0
Shipping	6.9	9.0
Total	56.2	73.2
Annual Production (1000 mt)	345.0	
Ammonia Cost ($/mt at U.S. port)	163	212
Estimated Economical Ammonia Sales Price ($/mt)	250	325
Present Wholesale U.S. Price ($/mt)	209-220	

The estimated nett delivered cost at U.S. port is $163-212 per mt. Providing 50% over cost for handling costs, profit and taxes, the estimated sales price is $250 for 0% contingency and $325 for 30% contingency. These are higher than the present wholesale market price of $209-220/mt ammonia in U.S. produced from natural gas feedstock. However, as natural gas and other petroleum feedstock prices are bound to escalate in the future, there are bright prospects for OTEC ammonia cost to become competitive with, if not cheaper than, production from hydrocarbon feedbacks. This is illustrated in Figure 11.

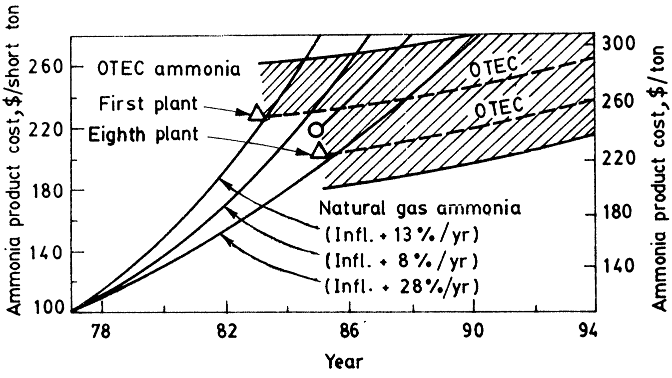


Figure 11. Projected ammonia production costs - OTEC ammonia costs rise more slowly than onshore natural gas ammonia.

6.2. Ammonia as Energy Carrier

Though the present market demand for ammonia is almost wholly for fertiliser production, the demand for which will continue to grow in the future, there is a potential alternative use for energy production. Its high volumetric content of hydrogen, which is easily liberated by passing the ammonia over a heated catalyst, opens up new markets for ammonia as a capacious, easily transportable, hydrogen carrier. Cracked ammonia (which is 3 parts of H_2 + 1 part of N_2) can be used as a hydrogen-feed for fuel cell power generators (Roney, 1980) and for charging the metal hydride tanks of hydrogen-fueled automobiles. These examples show how ammonia can serve as an energy link - a chemical energy link - between sea-based OTEC plants and on-shore energy markets. A schematic block diagram of the OTEC-ammonia energy distribution concept is shown in Figure 12.

Figure 13 illustrates the OTEC-ammonia-fuel cell - electricity concept and its advantages over the conventional oil fired thermal power generation and distribution. In the first place, the ammonia-fuel cell system operates at a much higher overall efficiency. Secondly, since ammonia can be distributed over large distances at lower cost than electricity, it offers greater potential for dispersed power generation. This is illustrated in the figure by a multiplicity of ammonia delivered points and fuel cell plants.

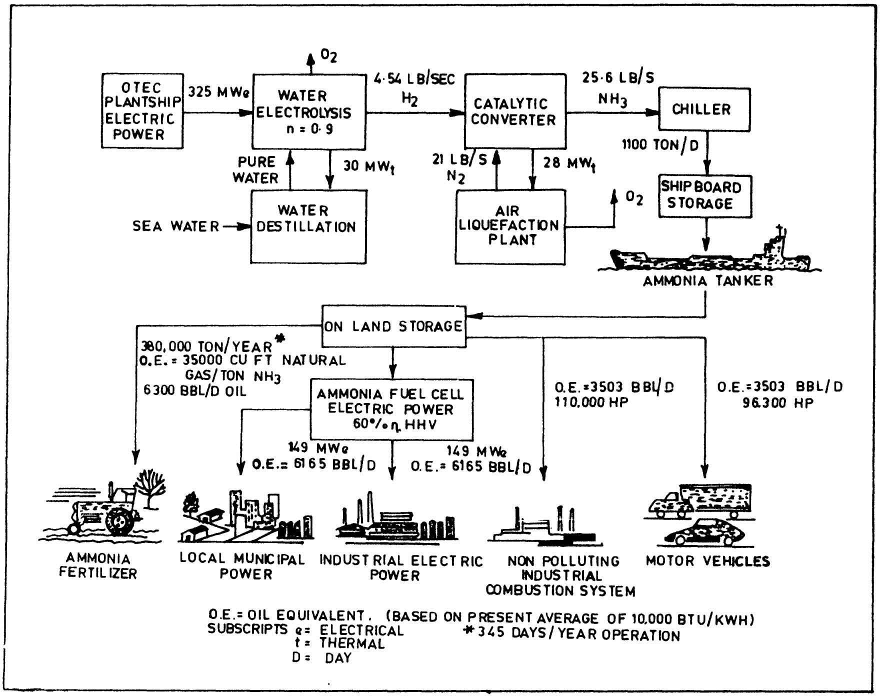


Figure 12. OTEC ammonia plantship fuel utilization

7. CONVERSION OF OTEC HYDROGEN TO METHANOL

Methanol (CH_3OH) is an important industrial chemical used in large quantities as a solvent and as a feedback for a variety of organic chemical products, especially plastics. In recent years, it has gained recognition as an automotive fuel in place of gasoline and as a feedstock for molten carbonate fuel cells which are coming up as strong competitors to hydrogen-fueled phosphoric acid fuel cells.

OTEC-hydrogen can be converted to methanol by combination with carbon monoxide in accordance with the reaction:

$$CO + 2H_2 = CH_3OH$$

which has to be conducted at high pressure in the presence of a zinc oxide catalyst. The synthesis gas mixture required for this process can be produced by first reacting coal with oxygen (co-produced with hydrogen by electrolysis of water) and steam to produce water gas ($CO+H_2$) and adding hydrogen to get the required synthesis gas composition.

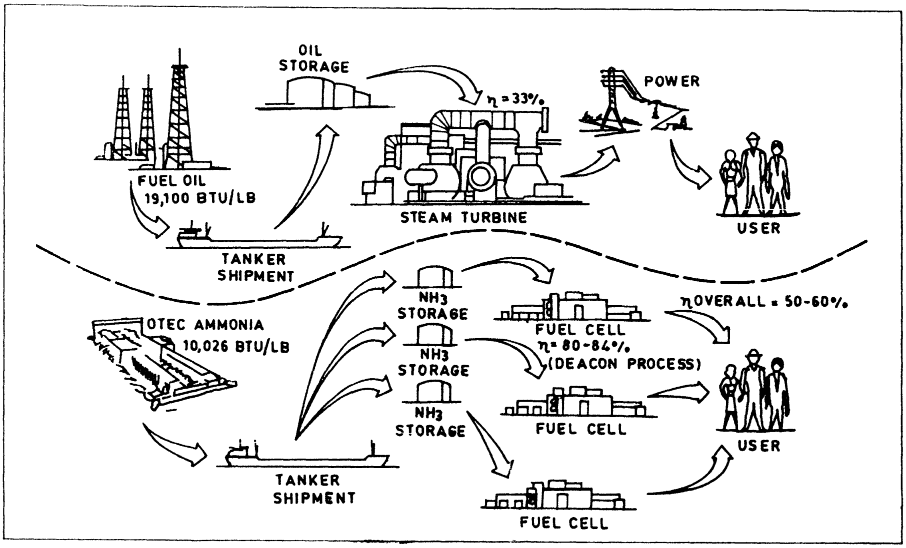


Figure 13. Comparison of OTEC ammonia/hydrogen fuel cell/ electricity power system with petroleum/steam turbine/electricity power system

The complete scheme of chemical reaction is as follows:

$2H_2O = 2H_2+O_2$ (electrolysis of water)

$$\underset{}{2C + O_2 + H_2O \text{ (steam)}} = \underset{\text{(reject)}}{CO_2} \quad + \underset{\text{(water gas)}}{CO + H_2}$$

$$\underset{\text{W.G.}}{(CO + H_2)} + H_2 = CO + 2H_2 \longrightarrow CH_3\,OH$$

$CO_2 + C = 2CO$

In the conventional land-based methanol plants the additional quantity of hydrogen would be produced by reacting part of the CO with steam in presence of a catalyst, when the following shift-conversion reaction occurs:

$CO + H_2O = CO_2 + H_2$

This step is avoided in the OTEC-methanol plant due to the availability of electrolytic hydrogen produced with OTEC power.

For the production of water gas, coal has to be transported to the OTEC plant site from mainland coal sources. Fortunately, coal shipment costs are low (ca. $12/mt) and the same ship could be used to transport the methanol product to the mainland markets.

The tasks of basic plant design and cost projection have been carried out by the JH/APL OTEC research group with the assistance of commercial sub-contractors. A major factor is the choice of the type of coal gasifier, best suited for use on OTEC plant ships. The type preferred is the molten carbonate, CO_2-acceptor gasifier, originally developed by M.W. Kellogg Corporation and later extended and improved by Rockwell International Corporation. In this process, pulverised dry coal is injected along with steam and oxygen into a cylindrical vessel containing molten sodium carbonate at 1000°C. The ash and sulphur in the coal react with the molten carbonate and are retained by it. The gasification reaction occurs very rapidly resulting in the formation of a concentrated mixture of CO and H_2, with minor amounts of CO_2 (6%), CH_4 (2.8%) and H_2O (7%) - by volume. The general layout of the OTEC-methanol plant is shown in Figure 14.

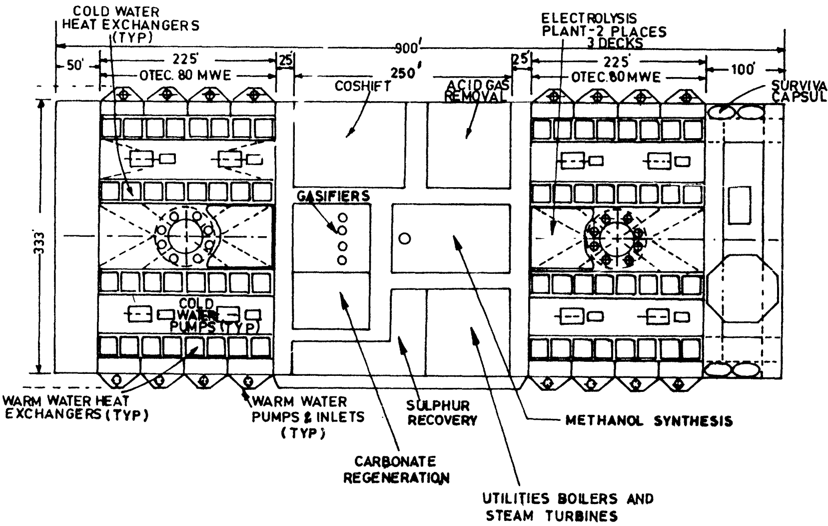


Figure 14. 160 MW (nominal) OTEC methanol plantship layout.
1750 mt/d - Rockwell/Ebasco Process design.

On a 160 MWe OTEC plant, 1750 mt/d of methanol can be produced with a gross coal input of about 1400 mt/d - representing a coal-to-methanol ratio of 0.8 compared 1.5 to 2.1 for land-based methanol-from-coal processes. The economy in coal in the OTEC methanol plant is due mainly to the availability of electrolytic hydrogen which would otherwise be produced by partial shift conversion of CO

$$CO + H_2O = CO_2 + H_2$$

The overall process flow for OTEC methanol production and disposal is shown in Figure 15.

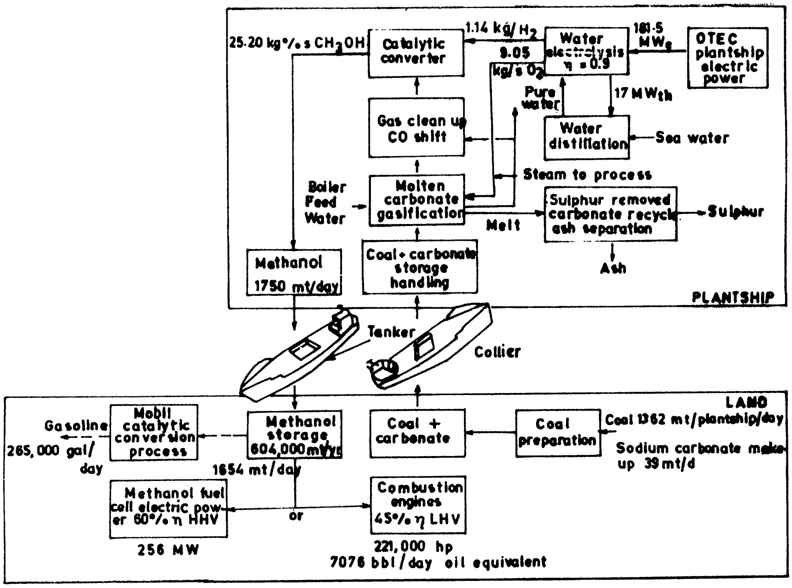


Figure 15. OTEC plantship process flow

The projected cost estimates for OTEC methanol are presented in Table III. The estimated production cost (49 to 63 cents/gal, delivered) is comparable with the current wholesale U.S. market price of methanol produced from natural gas, but this is bound to shift in favour of the OTEC product by the time large OTEC plantships become practical.

8. SUMMARY AND CONCLUSION

The oceans offer an immense resource of stored solar energy which, in principle, can be exploited to supply a substantial part of the world's energy requirement. The primary output of ocean thermal energy conversion (OTEC) is electricity. Vast areas of ocean with thermal and other features propitious for OTEC on a very large scale (i.e., several hundred megawatts) are located mostly in the middle of the Atlantic, Indian and Pacific oceans, separated from the continental mainlands or major island shores by several hundred kilometres. Transmission of large quantities of OTEC-produced electricity over such long distances either directly through submarine cables or through electrochemical storage batteries will pose serious technical problems and will not be feasible.

TABLE III : OTEC Methanol Cost Estimate (1983$)
Commercial 1st Plantship 160 MW 1750 mt/d

	($M)
Plant Investment	
Basic plantship	389
Methanol plant	305
Subtotal	694
Interest during construction (14.8% of P.I.)	86
Total 0% contingency	780
30% contingency	1014

Annual Cost ($M)	0% contingency	30% contingency
Real fixed cost	46.0	59.8
Operating cost		
Crew	8.8	11.4
Catalysts and materials	700	9.1
Coal $50/mt	23.3	30.3
Coal shipping $11/mt	5.2	6.8
Methanol shipping	6.6	8.6
General Managers	0.3	0.4
Total annual cost $	97.2	126.4
Annual production	2 x 10^8 gal	
Methanol cost ($/gal at U.S. port)	49c	63c
Methanol sales price ($/gal at U.S. port)	66c	86c
Equivalent unleaded (Gasoline price ($/gal))	88c	1.14

Hydrogen has been projected as secondary energy vector of great merit and versatility and its production on-board an OTEC plantship by electrolysis of water offers a capacious means of conversion of OTEC power into a transportable energy intensive product. This concept has found favour among all the major research groups working on OTEC-projects. This paper summarises the technical and economic issues connected with the production of hydrogen with OTEC and its transportation as liquid hydrogen, liquid ammonia and methanol - all of which can, in principle be produced on an OTEC plant deck.

To sum up, the OTEC-H_2 concept serves the following two-fold objective: On the one hand, it provides a highly efficient transportable carrier for transferring very large chunks of OTEC-power from mid-ocean sites to the mainland. At the same time, by providing the necessary material and energy inputs for the production of ammonia and methanol, it helps conservation of terrestrial fossil-energy resources.

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SOLID STATE MATERIALS FOR HYDROGEN STORAGE

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This paper seeks to review the hydride/hydrogen technology and to describe the work being done in our laboratory for the development of rare earth pentanickelide (RNi_5) type solid state materials for hydrogen storage. To start with a brief review of the basic theme for solid state storage mode of hydrogen has been given. The salient features of this storage mode have been outlined. For the RNi_5 type materials, more emphasis has been laid on the discussion of a new result obtained by us. It has been found that it is possible to synthesise amorphous phases of RNi_5 ($LaNi_5$, $MmNi_5$) materials and this phase has been found to have a higher hydrogen storage capacity. Another new result in regard to the RNi_5 type hydrides is relating to the variation of electrical resistivity (ρ) as a function of hydrogenation time (t). The curious nature of ρ-t curve has been explained in terms of the variation of electronic density of states as a result of the hydrogenation process.

1. INTRODUCTION

When the latest desirability attached to any nonconventional energy option namely the environmental invariability (the non-polluting aspect) is coupled with the well known factor - the depletive trend of the fossil fuels, it becomes evident that 'Hydrogen' is the most potential candidate on the renewable energy scenario. Produced from water and on utilisation burned back to water 'Hydrogen' represents on one hand the complete renewable cycle and on the other it corresponds to almost zero pollution energy vector. Hydrogen is a complete substitute for the important fossil fuel oil (petroleum) (Veziroglu, 1984). Hydrogen can also be used in a fuel cell to produce electricity. Thus for the mixed energy system (oil and electricity), in which we are presently living, 'Hydrogen' is a complete energy vector and can meet all the demands presently being met with fossil fuels. One of the most attractive features of 'Hydrogen' as a fuel is that its primary raw materials is water. Thus if it can be produced from water through solar energy (Prasad et al., 1986), it can be described as a primary energy source even though it does not occur as such in nature. The non-polluting

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aspect of hydrogen is of special significance for India. The pollution in the form of 'green house effect' and 'acid rains' which arises due to excessive burning of fossil fuels may turn the vast portions of land infertile and thus may affect the agricultural production which is the key factor in our national economy. Besides this important factor, an immediate aspect which should put the focus on 'Hydrogen' relates to the fact that a significant fraction of our total oil (petroleum) needs are fulfilled through imports which drains a large portion of our foreign exchange resources.

Hydrogen can be produced in a variety of ways. The most attractive method being splitting of water through electrolysis (on hand technology) or through photoelectrolysis (the most attractive futuristic technology). Regardless of the technique employed for hydrogen production, an inescapable aspect associated with the use of hydrogen as an energy vector is its 'storage'. Unlike fossil fuels like coal or petroleum, hydrogen will have to be effectively stored before its employment in energy systems. It is not difficult to perceive the reason for this. Hydrogen produced under ambient conditions is a gas, in fact the lightest gas and as such it would immediately escape upwards in the atmosphere. Its use at an appropriate site requires 'storage' which is a crucial aspect of the total 'Hydrogen Energy' concept (Andresen, 1978; Suda, 1983). This article is about a special storage mode; this is the solid state storage mode where hydrogen is stored by arresting it within the lattice of special solids (intermetallics) which are capable of absorbing large quantities of hydrogen reversibly. After giving a general review of the 'solid state' storage characteristics, we would describe the work done at the Physics Department (B.H.U.) on solid state materials for hydrogen storage which is sponsored by the Department of Non-conventional Energy Sources (DNES).

2. GENERAL CHARACTERISTICS OF METAL HYDRIDE MATERIALS

The fundamental aspect to the understanding and use of rechargeable metal hydrides (Buschow, 1982; Wallace, 1981) is the simple reversible reaction of a solid metal M with gaseous H_2 to form a solid metal hydride MH_x according to the following reaction:

$$\frac{2}{x} M + H_2 \underset{\text{(Endothermic)}}{\overset{\text{(Exothermic)}}{\rightleftharpoons}} \frac{2}{x} MH_x + \text{Heat}$$

All the metals or intermetallics do not react directly with gaseous H_2 and of those which do only some undergo reverse reaction liberating gaseous hydrogen. Nevertheless there are a number of metallic systems (intermetallic compounds) which react directly and reversibly with hydrogen to form hydride and do so at room temperature and nearly atmospheric pressure. These hydrides are called 'rechargeable' metal hydrides. In effect, the metallic system becomes a solid 'sponge' for hydrogen that can be repeatedly charged and discharged at will. One can draw a physical analogy with a water sponge and chemical analogy with a rechargeable electric battery.

It may be mentioned that rechargeable metal hydrides offer a number of advantages over its two counterpart modes namely the compressed gas and cryogenic liquid storage systems. Some salient features in regard to this are outlined in the following:

(a) Hydrides have an extremely high volume packing density for hydrogen. As shown in Table I, the volumetric density of H in typical hydrides is many times that of high pressure gas and even significantly greater than that of liquid hydrogen. This results from the fact that H-atoms are chemically bound compactly within the hydride crystal lattice.

(b) Storage of hydride mode requires low pressure. This aspect holds special importance in regard to the safety factor.

(c) Hydride storage is more energy efficient as compared to liquid hydrogen.

(d) The negative points related with hydride storage are the cost and the weight factors.

The hydriding characteristics generally become intelligiblein terms of absorption-desorption curves which embody pressure composition isotherms. If we start with the metal phase at point 1, maintain a constant temperature and slowly increase the H_2 pressure, relatively little happens (see Figure 1a) at first. As the H_2 pressure increases, some amount of hydrogen goes into solution into the metal phase. A little later, hydriding reaction begins at some point 2, and the sample starts absorbing large quantities of hydrogen at nearly constant pressure. The pressure P_p is called the 'Plateau Pressure'. The plateau region 2-3 corresponds to a two-phase mixture of metal M and metal hydride MH_x. At point 3, the sample has been completely converted to the hydride phase and a further increase in applied H_2 pressure to point 4 results only in a small additional pick-up of hydrogen in solution in the hydride phase. Ideally speaking, this curve should be completely reversible. As hydrogen (H_2) is extracted from the gas phase in contact with the sample, the hydride phase will dissociate i.e. dehydride to M + H_2 gas and attempt to maintain the equilibrium plateau pressure until it is completely dissociated - this corresponds back to point 2. The absorption-desorption isotherms at various temperatures are shown in Figure 1(b). In practice, generally we get p-c curves (Figure 2) which deviate from the ideal behaviour. Figures 1(b) and 2 show the strong dependence of temperature on the plateau pressure. The higher the temperature, the higher is the plateau pressure. This is a consequence of the heat of reaction ΔH of the process (Boureau, 1979; Flangan, 1980). The hydriding and dehydriding reactions are exothermic and endothermic respectively. The plateau pressure P_p can be shown to be related to the temperature T by the van't Hoff equation

$$\mathrm{Ln}\ P_p = \frac{\Delta H}{RT} + C$$

where T is the absolute temperature, ΔH is the enthalpy change (heat) of the hydriding reaction per mole of H_2, R is the Universal gas constant and C is a constant related to the entropy change of the hydriding reaction. Thus, from a series of experimental isotherms such as those shown in Figure 2, a van't Hoff plot of $\mathrm{Ln}P_p$ vs. 1/T can be made and the value of ΔH for a particular material can be readily determined from the slope of the plot.

TABLE I : Comparison of Hydrogen Storage Media

Medium	Hydrogen Content	H Storage Capacity	Energy Density Heat of Combustion (higher)**	
	Wt%	g/ml of Vol	Cal/g	Cal/ml of Vol
MgH_2*	7.0	0.101	2373	3423
Mg_2NiH_4	3.16	0.081	1071	2745
VH_2	2.07		701	
$FeTiH_{1.95}$	1.75	0.096	593	3245
$TiFe_{0.7}Mn_{0.2}H_{1.9}$	1.72	0.09	583	3050
$LaNi_5H_{7.0}$	1.37	0.089	464	3051
$R.E.Ni_5H_{6.5}$ $(MmNi_5H_6)$	1.35	0.09	458	3050
Liquid H_2	100	0.07	33900	2373
Gaseous H_2 (100 atm pressure)	100	01007	33900	244
N-Octane			11400	8020

* Starting alloy 94% Mg-6%Ni

** Refers to H only in metal hydrides

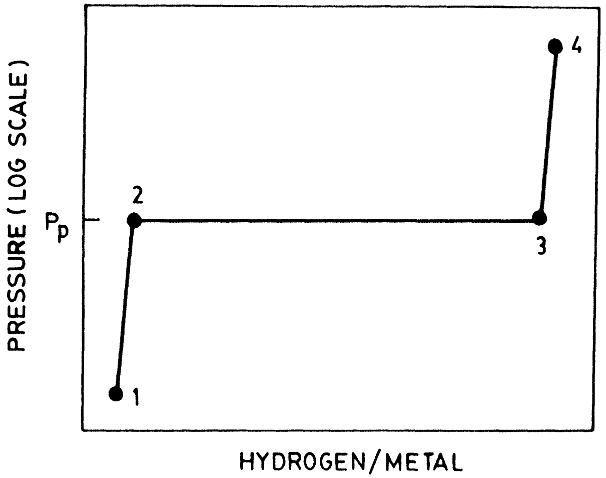


Figure 1(a). Ideal absorption-desorption isotherm for a metal-hydrogen system.

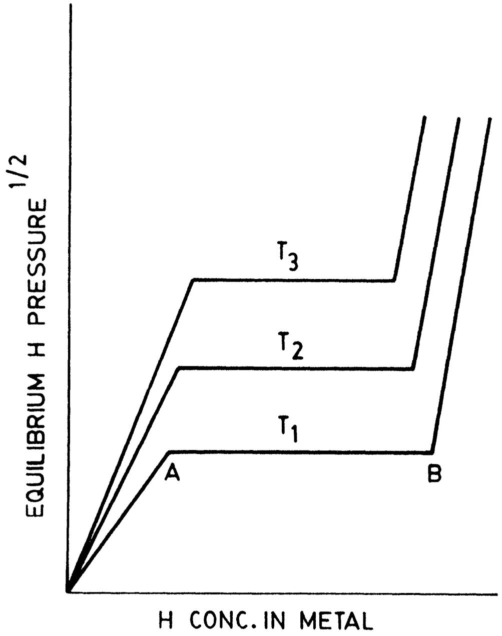


Figure 1(b). Various ideal isotherms at different temperatures. For practical applications the length of the isotherm (AB) is the measure of the effective hydrogen capacity.

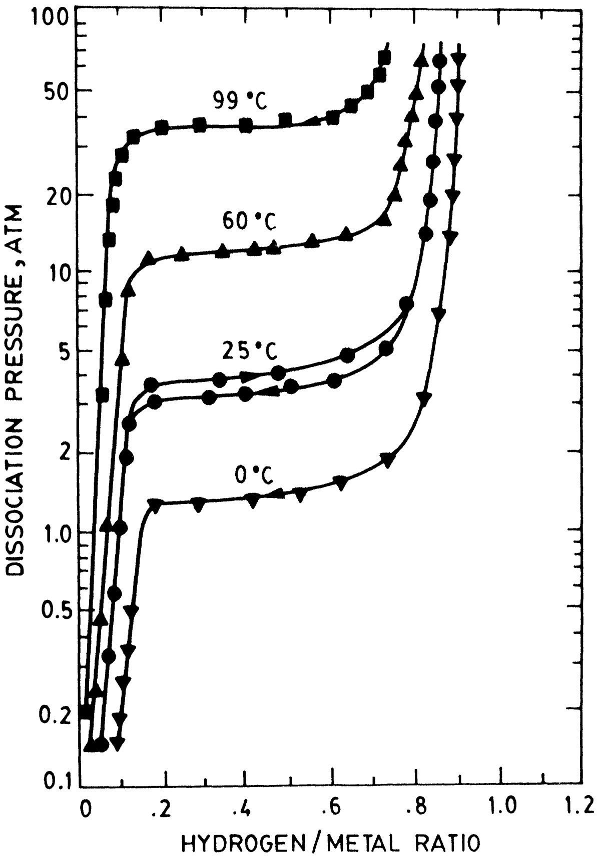


Figure 2. Various isotherms for $MmNi_{4.5}Al_{0.5}$ intermetallic storage system.

Metal hydride compounds may be divided into three general classes: ionic, metallic and covalent. This division is based on the predominant character of the hydrogen bond. For application purposes covalent hybrides can be left out since they cannot be formed by the direct reaction of hydrogen with the metal except under very special conditions. The ionic hydrides with the exception of magnesium hydride are too stable for use in practical hydrogen systems. It is the metallic hydrides which are most often employed in practical hydrogen storage systems. It has been shown that many alloys or intermetallics react directly and reversibly with hydrogen to form hydride phases which are often distinctly different than the binary alloy hydrides of the individual alloy constituents. Extensive explorations of the intermetallic phases which store hydrogen has led to the following general rules followed by these storage systems:

(a) An intermetallic compound which reacts directly and reversibly with hydrogen, has at least one of its metal components reacting directly and reversibly to form stable binary metal hydride.

(b) If the hydrogenation reaction takes place at a temperature where the metal atoms are mobile, the system will assume its most favoured thermodynamic configuration.

(c) In case the metal atoms are not mobile at the hydrogenation temperatures, only such hydride phases which are structurally similar to the starting intermetallic phases are formed.

Out of the three rules, the first one is empirical based on experimental observations. The other two rules are firmly based on known thermodynamic and structure principles. In passing it may be useful to mention two empirical hypotheses which have been found to be quite helpful in predicting the behaviour of alloy hydrides. The first hypothesis which was proposed by Miedema, is termed as 'rule of reversed stability'. According to this for a given series of intermetallic compounds, the thermodynamic stabilities of the corresponding hydrides will decrease with increasing stability of the intermetallic compound (for details refer Buschow et al., 1982). The second hypothesis relates to the correlation between the hydrogen storage capacity and the volume of the interstitial site. It has been found that as the volume of the interstitial site increases, the more readily it will accommodate the hydrogen atom.

3. SPECIFIC INTERMETALLIC HYDRIDE SYSTEMS

Extensive researches have led to the development of three different alloys (intermetallics) which have adequate hydrogen storage capacity for application in hydrogen based utility systems. These are magnesium nickel Mg_2Ni, iron titanium FeTi (Reilly, 1978) and rare earth metal nickel RNi_5 (the pentanickelides of lanthanum and mischmetal are two widely studied materials of this variety). The hydrogen storage capacities of these materials are outlined in Table I. Of these the FeTi and RNi_5 based systems can be hydrogenated and employed as storage systems at nearly room temperature; on the other hand Mg_2Ni can only be used at higher temperatures ($\gtrsim 250^{\circ}C$). Because of significant hydrogen storage capacity and their feasible application at nearly room temperature, the FeTi and RNi_5 alloys are categorised as moderate temperature - high pressure storage alloys. Contrary to this, Mg_2Ni is often labelled as 'low pressure high temperature' storage alloy. The Mg_2Ni is, therefore, not an often used storage system, it is employed for certain specific purposes e.g. it has been employed in special vehicular applications in conjunction with FeTi.

The phase diagram of the Mg-Ni system indicates the existence of two intermetallic compounds, Mg_2Ni and $MgNi_2$. The latter does not react with hydrogen at pressures up to 540 atmospheres in the temperature range -196° to $300^{\circ}C$. However, Mg_2Ni will react readily with hydrogen at around $200^{\circ}C$ and at about 14 atmospheric pressure. It has been found that on reaction with hydrogen initially a solid solution corresponding to $Mg_2NiH_{0.3}$ is formed which then reacts according to the following reaction to form hydride:

$$1.08Mg_2NiH_{0.3} + 2H_2 \rightleftharpoons 1.08Mg_2NiH_4$$

The hydride Mg_2NiH_4 evolves hydrogen at a temperature above 200°C.

The iron-titanium phase diagram exhibits two stable intermetallic compounds, FeTi and Fe_2Ti. The latter does not react with hydrogen at around room temperature even up to 540 atmospheres. On the other hand FeTi reacts readily with hydrogen directly and reversibly to form two ternary hydrides. The reactions which take place stepwise are outlined in the following:

$$2.13FeTiH_{0.1} + H_2 \rightleftharpoons 2.13FeTiH_{1.04}$$

$$2.20FeTiH_{1.04} + H_2 \rightleftharpoons 2.20FeTiH_{1.95}$$

The dissociation pressure of both these hydrides $FeTiH_{1.04}$ and $FeTiH_{1.95}$ is appreciably above 1 atmosphere at about 25°C. A particular tenary alloy namely $TiFe_xMn_{1-x}$ is of significant practical utility since it has been found that addition of even small quantities of Mn turns FeTi amenable for easy activation at room temperature.

Besides Mg_2Ni and FeTi, yet another hydrogen storage system corresponds to RNi_5 intermetallic where R stands for a rare earth metal. The prototype and most widely investigated of these intermetallics is lanthanum pentanickelide $LaNi_5$. The other extensively studied intermetallic system (Sandrock, 1978) in the rare earth metal nickel system corresponds to $MmNi_5$ (Mm = Misch-metal which is a mixture of several rare earth metals, a typical composition being Ce, 44.63%; La, 21.63%; Nd, 21.36%; Pr, 6.17%; Fe, 4.00% and others including organic/voltaic, 2.21%). A research and development project sponsored by DNES on the development of RNi_5 type hydrogen storage intermetallics has been in progress at the Physics Department, B.H.U., since 1982. In the following we proceed to discuss the results of this work with emphasis on the new results which have been obtained during the course of this investigation (Singh et al., 1985 a&b).

4. RELEVANCE OF CRYSTAL STRUCTURE AND ELECTRONIC BAND STRUCTURE IN RELATION TO HYDROGENATION CHARACTERISTICS OF METALLIC ALLOYS

In order to decide the capacity of a metallic alloy to absorb hydrogen, it is essential to consider the available voids which can accommodate the hydrogen. As it is an established fact that hydrogen in the metal hydrides is in the atomic form, we are required to consider the accommodation of atomic hydrogen in the metallic alloy.

Two obvious requirements are, the suitable size of the interstitial void and the favourable electronic structure to make the hydrogen bonded with the atoms of the metallic alloy. Whereas the voids' size and shape are determined by the crystal structure of the material, the electronic structure is determined by the details of the energy levels of the atoms in the alloy.

The following description intends to illustrate the hydrogen absorption phenomenon in RNi_5 (R = rare earth metal) alloys:

The crystallographic structure of RNi_5 alloys is $CaCu_5$ type hexagonal. The space group being $P_{6/mmm}$ (see Figure 3). Such a structure provides several voids of different details (tetragonal, octahedral) and varied sizes. Conventionally, the size of a void is measured as the radius of the biggest sphere which can be accommodated in it. Figure 4 shows the various types of voids which are present in the $LaNi_5$($CaCu_5$ type) structure.

They are of dodecahedral, octahedral and tetrahedral type. Hydrogen is known to occupy tetrahedral and/or octahedral voids. It thus merits to account for the total number of such voids. The various types of tetrahedral and octahedral voids are given below:

(a) A_2B_2 type or 6'm' type (in Wyckoff notation)
(b) AB_3 type or 12 'n' type
(c) Another AB_3 type or 12 'o' type
(d) A_2B_4 type or 3 'f' type.

The first three of the above are tetrahedral and the fourth one is octahedral type void. The total number of voids are 37 in each unit cell containing one lanthanum. However, in no case $LaNi_5$ absorbs so many hydrogen atoms per unit cell. Indeed it has been suggested that the few conditions regarding the size and separation of the voids must be satisfied for the hydrogen atom to be absorbed in the material. They are: (i) the minimum size of the void should be large enough to accomodate a sphere of radius 0.4 Å and (ii) two adjacent voids cannot be occupied simultaneously unless they are at least 2.1Å apart (Switendick length).

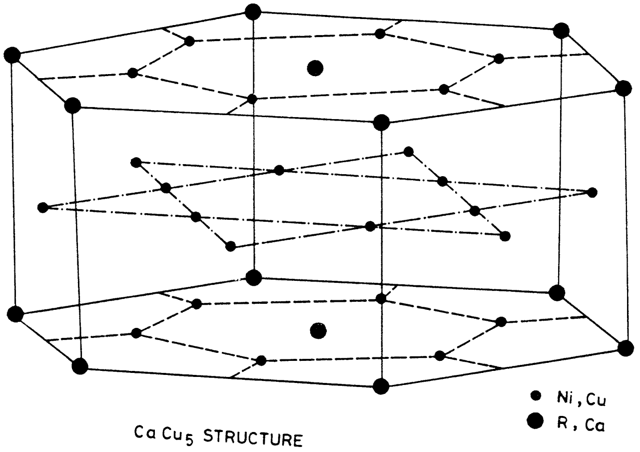


Figure 3. Structure of $LaNi_5$($CaCu_5$ type).

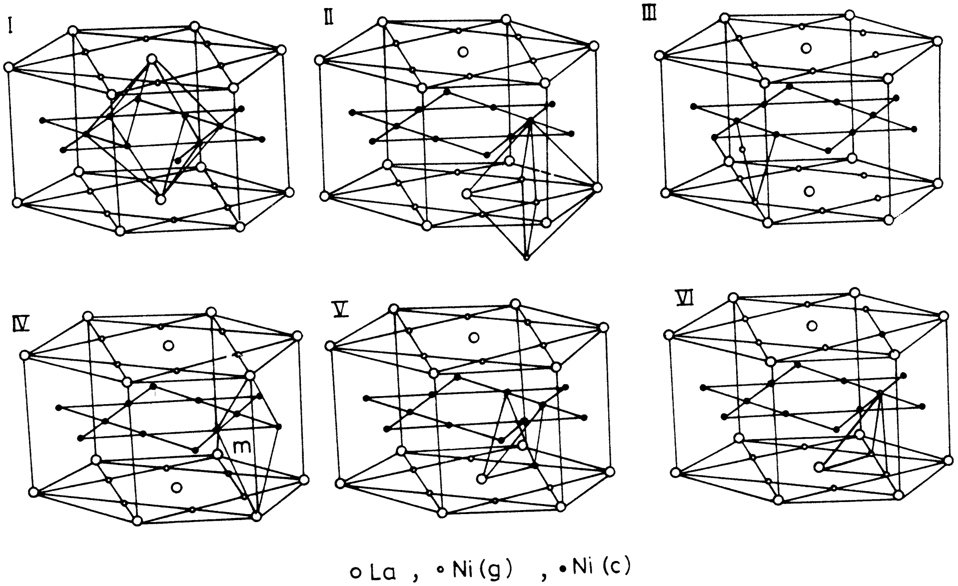


Figure 4. Various interstitial voids in $LaNi_5(CaCu_5$ type) structure.

(I) the doecahedral 'b' type site
(II) the octahedral 'f' type site
(III) the tetrahedral 'h' type site
(IV) the tetrahedral 'm' type site
(V) the tetrahedral 'o' type site
(VI) the tetrahedral 'n' type site

Keeping the above facts in view we find there are five voids, 2 in '6m' octahedral voids and 3 in '6m' tetrahedral voids which can accomodate hydrogen atoms. Actually one finds even larger number of hydrogen (deutarium) absorbed by the material e.g. $LaNi_5D_6$. This apparent discrepancy can be solved by considering the details of the model. It so happens that the 6m octahedral voids are very large with radius equal to 0.5548 Å. Now if we imagine the hydrogen (deutarium) atom to be placed slightly off centred one may conceive the occupancy of adjacent void (distant at least 2.1 Å) which otherwise is not possible. As a matter of fact using this concept one can explain still higher hydrogen (deutarium) concentration e.g. [H] or [D] / [La] = 7 (Westlake, 1983).

Indeed the same model can explain the hydrogen absorption in several other systems as well. It is appreciable that electronic band structure calculations also show that when H-H distance is made closer than 2.1 Å (Switendick, 1971, 1978) repulsive energy becomes too much and the situation is energetically unfavourable. Thus we find that the criterion derived from both ways are consistent.

In the following, some aspects of electronic structure (Wallace, 1978 and Westlake, 1978) and bonding in metal hydride (mono, di and trihydrides) shall be discussed.

In view of the observed facts there are three models which have been proposed for metal hydrides. They are (1) anionic model; (2) protonic model and (3) covalent model. In the anionic model it is assumed that the hydrogen accepts an electron from the host metal, becomes anion and causes the bonding e.g. LiH, CaH_2 etc. The protonic model assumes that the hydrogen in its dissociative absorption in the host metal loses its electron and consequently causes an ionic bonding. This model is mostly used for the transition metal hydrides. In fact this model has been superseded by its modified form 'Alloy model' which shall be described a little later. The examples of the third model - the covalent model - are H_2O etc. where hydrogen is bonded through covalent bond. As mentioned before, the protonic model has been superseded by the alloy model the latter will be described below: whereas the protonic model assumes that the hydrogen adds an electron to the host metal the photo-emission experiments reveal a different picture. The results of photo-emission experiments reveal that hydrogen adds not merely an electron to the host metal but also new states. Some aspects in this regard, viz., the variation of band structure with hydrogenation are mentioned below, for mono, di and trihydrides.

A comparison of band structure for Pd and PdH (or for YHo and YH) reveals that (a) the 'd' and 'f' states are only slightly perturbed and (b) the metal 's' and 'p' state hybridise with the hydrogen ls orbit and are strongly perturbed. These states are lowered substantially in energy and become very much hydrogen like (see Figure 5b). These results show that protonic model cannot be correct.

4.1 Dihydrides

These possess fluorite type structure with 8 hydrogen atoms per unit cell. They have Fermi energy which falls in a band derived from metal 'd' states. In the dihydrides the antibonding combination of the ls orbitals of the two hydrogen atoms in the unit cell gives rise to a new band which appears below the 'd' band. Such a band is not present for the case of monohydrides where the hydrogen concentration is only half that of dihydrides. The stability of dihydrides is attributed to this new band which can accommodate electrons at a rather low energy. The position of this band is determined by hydrogen-hydrogen separation. If the hydrogen-hydrogen separation is small, the band has high energy and is unlikely to be filled by electrons originally associated with hydrogen. For large H-H separation the band is low lying and will be filled (see Figure 5c). The dihydrides of Y and Pr are the examples where the band mentioned above lies below the metal 'd' band and also below the Fermi energy. These dihydrides are quite favourably formed.

4.2 Trihydrides

These correspond to the situation where both O and T sites are occupied. The calculations show that the interaction of antibonding states of

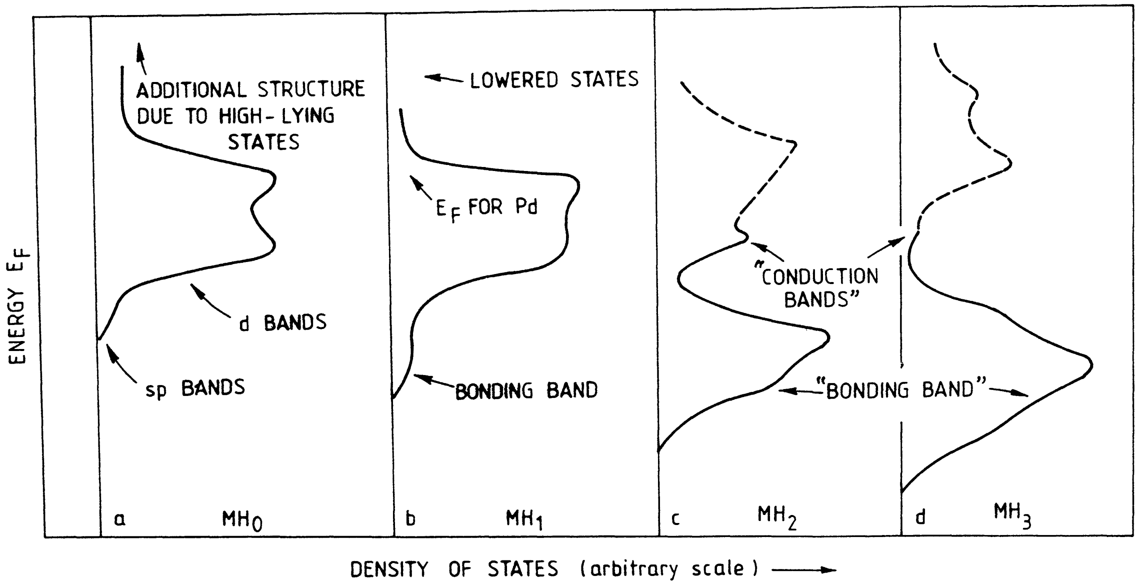


Figure 5. Variation (schematic) of density of states (DOS) with hydrogenation:
(a) the host metal MH_0, (b) the monohydride MH_1,
(c) the dihydride MH_2, (d) the trihydride MH_3 (after Westlake et al., 1978).

't' and 'o' site hydrogen gives rise to another band which also lies below the d-band (see Figure 5d). The H-H separation or the interstitial separation determines the energy of this band. The interstitial separation in turn is dependent upon the metal-metal distance. This fact governs an interesting transformation in the rare earth metal trihydrides - in going from cubic rare earth dihydrides to cubic trihydrides the metal-metal distance decreases while it increases or remains the same in going from cubic dihydride to hexagonal trihydride. This influences the position of the energy level and hence the stability of the structure. Thus the cubic structure is preferred for light rare earth trihydrides and hexagonal structure by heavy rare earth trihydrides.

5. GROWTH, SYNTHESIS, CHARACTERISATION OF RNi_5 ($LaNi_5$, $MmNi_5$) INTERMETALLIC PHASES

Rare earth pentanickelides i.e. RNi_5 intermetallics are the ones which form hydrides having high hydrogen capacity (RNi_5H_6) and having nearly completely reversible hydrogenation characteristics (Van Mal, 1974 and Buschow, 1975). The low association and dissociation pressure (1-2 atmospheres) at ambient conditions make these materials specially suitable for practical hydrogen storage systems. We have studied extensively the RNi_5 materials and studied their adoptability to practical systems. The work was first initiated by taking the case of lanthanum pentanickelide. Structural and hydrogenation characteristics of $LaNi_5$ was carried out both in bulk and thin film forms. These are synthesized by repeated melting of the mixtures rare earth and nickel in a vacuum sealed silica tube using R.F. induction furnace. These agglomerates were characterized by Guinier focussing camera. It revealed the hexagonal $CaCu_5$ type structure (Figure 6). Thin films of these intermetallics were prepared by thermal evaporation technique in vacuum of the order of 10^{-6} torr having the thickness 300-1200 Å. The structural characterization of these films were carried out by transmission electron microscopy in imaging and diffraction modes. Figures 7(a) and 7(b) show the electron micrographs of the as-deposited films and diffraction pattern, exhibited halos. After annealing the material to 600°C in situ by focussed electron beam for about 5-15 seconds, the films underwent amorphous to crystalline transformation. It revealed the transformation to $CaCu_5$ type crystalline structure (see Figures 8 and 9).

Analytical electron microscopy EDAX of these films revealed that the chemical composition in general corresponded to RNi_5. In some cases the film was found to be slightly nickel deficient. However, the current stoichiometric ratio was restored on annealing.

Scanning transmission electron microscopy mode was employed to investigate the surface analysis of these films. Figure 10 reveals a representative example of surface structure of the $LaNi_5$ film. It can be noted that surface is not planar but instead contains several protrusions. In passing, it may be mentioned that surface plays a very crucial role in the kinetics of hydrogenation in these alloys.

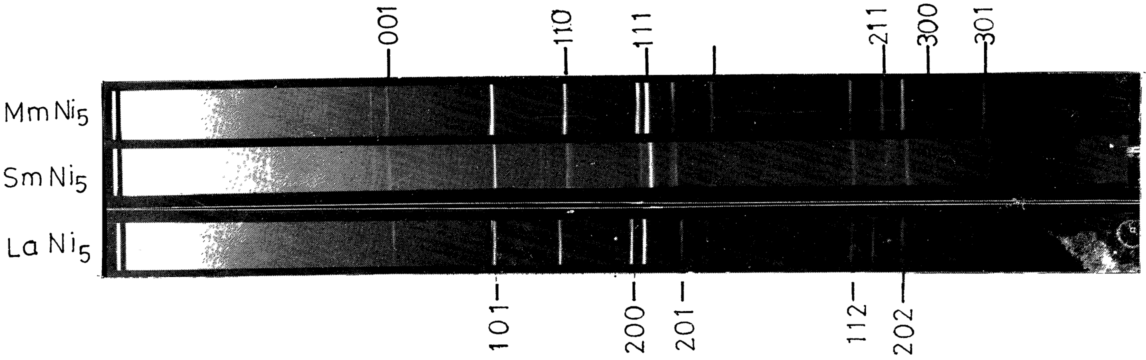


Figure 6. X-ray powder diffraction pattern of $LaNi_5$, $SmNi_5$ and $MmNi_5$. Several lines have been indexed.

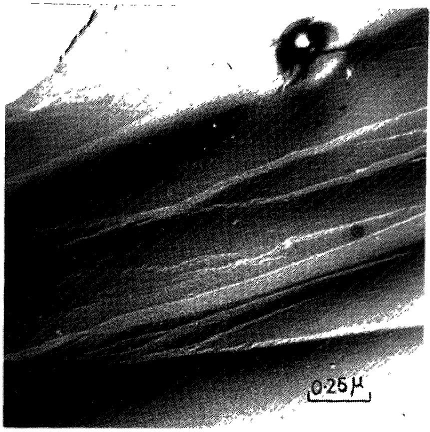


Figure 7(a). Electron micrograph of the as grown thin film of $CFMmNi_{4.5}Al_{0.5}$. Lack of diffraction contrast signifies the amorphosity of the thin films.

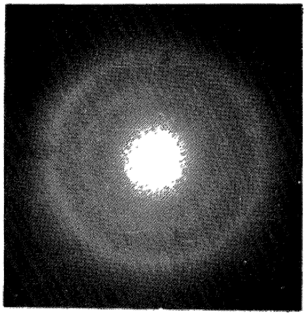


Figure 7(b). Electron diffraction pattern of the as grown thin film of $CFMmNi_{4.5}Al_{0.5}$. The diffuse halo evidences the amorphosity of the thin film.

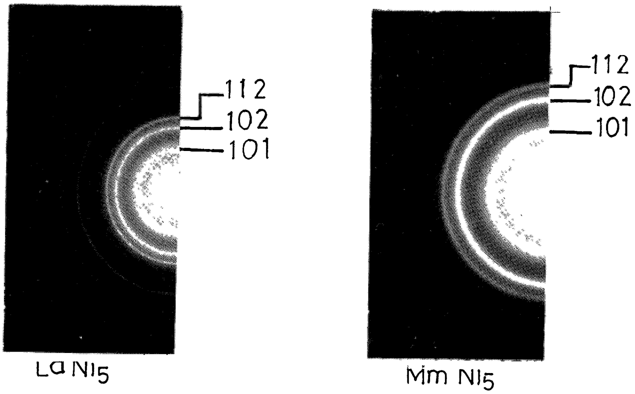


Figure 8. Electron diffraction patterns of the transformed crystalline phases of $LaNi_5$ and $MmNi_5$.

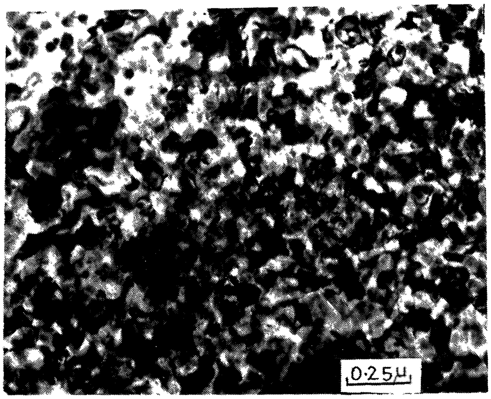


Figure 9. Electron micrograph of the transformed $LaNi_5$.

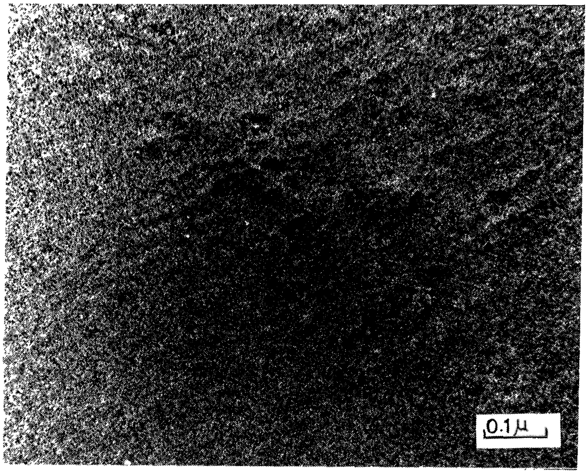
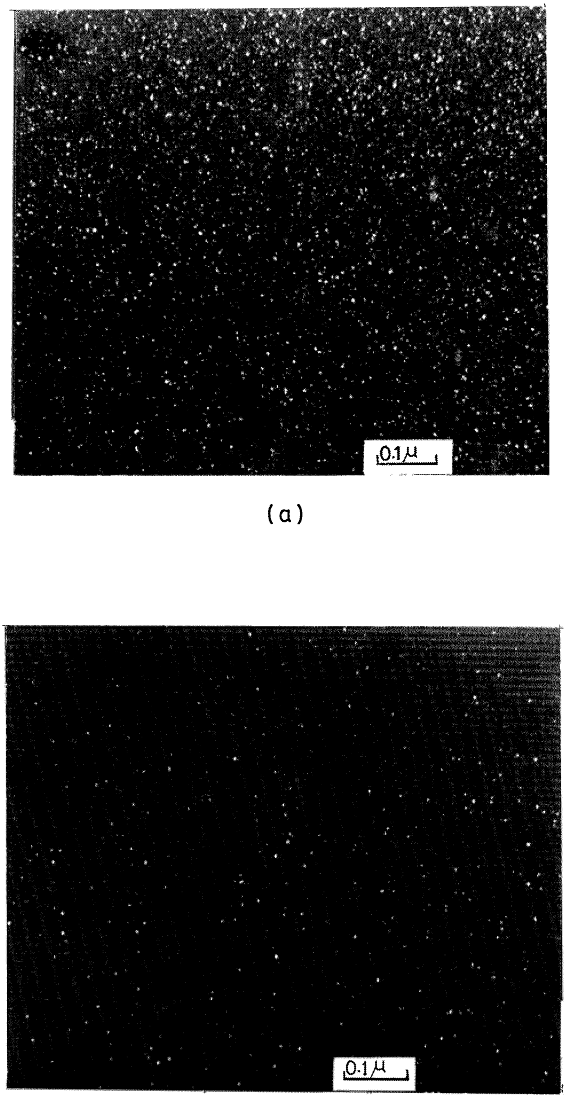


Figure 10. Scanning electron micrograph revealing the protrusions at the surface.

In spite of the obvious importance of the possible variation in microstructure resulting from the hydrogenation treatment of these alloy films, no such investigation seems to be available to date. In view of this an attempt was made to monitor the changes in the microstructural characteristics ensuing from the hydrogenation of RNi_5 thin film. It may be mentioned that in view of the decrepitation problem, variation in physical properties on hydrogenation cannot be assessed in bulk samples. Since contrary to bulk, thin films are much less sensitive to decrepitation and hence most of the physical property (structure, electrical resistivity) variations are monitored for thin films. The results of such study are outlined in Figures 11(a) and 11(b). These figures bring out the microstructural characteristics of $LaNi_5$ before and after hydrogenation. As can be noted, these figures reveal the interesting result that hydrogenation leads to enhancement of amorphosity which has been brought out by the decrease of the density of the tiny scattering regions. This is expected since the hydrogen absorption presumably distorts the local bondings.



(b)

Figure 11. Effect of hydrogenation - electron micrograph in dark field mode:

(a) before hydrogenation
(b) after hydrogenation (see text)

6. LOW PRESSURE HYDROGEN ABSORPTION

This was accomplished by employing the electrolytic (Rai et al., 1982) cell consisting of platinum electrodes. For making the water conducting small quantity of sulphuric acid and thiourea (0.02% Wt/vol) were added to the distilled water. The electrolysis (d.c. voltage ≈ 10 V , distance between electrodes 10 cms) of water produces hydrogen and oxygen, liberated at the cathode and anode, respectively in 2:1 ratio. For monitoring low pressure absorption, known quantity of RNi_5 were placed on the cathode. The amount of hydrogen absorbed was calculated using the following formula:

$$\text{Volume of hydrogen absorbed} = 2 \times \text{Vol. of } O_2 \text{ liberated at anode} - \text{Vol. of } H_2 \text{ liberated at cathode}$$

The results of absorption studies of RNi_5 in the thin films (as grown) and bulk (synthesized and quenched) is shown in Figure 12.

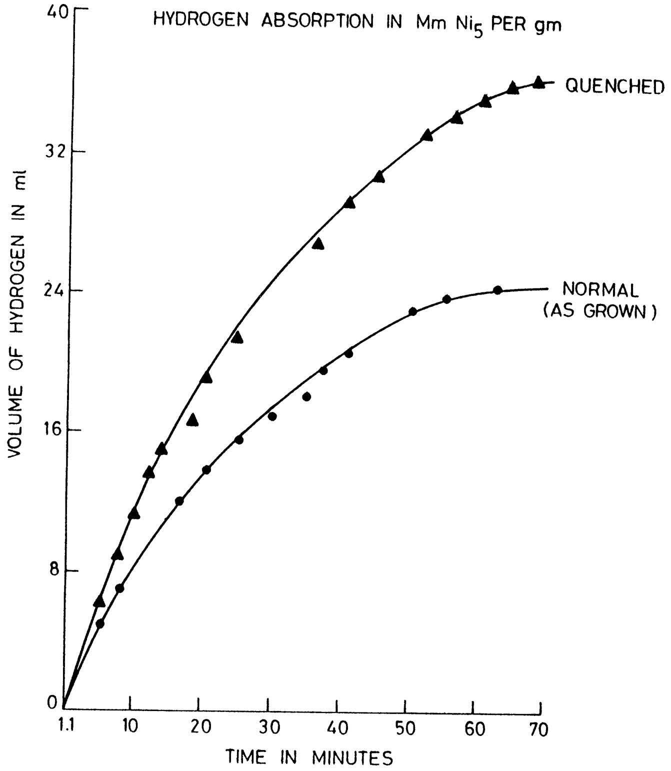


Figure 12. Low pressure hydrogen absorption of as synthesized (polycrystalline) and quenched (amorphous like) $MmNi_5$.

The salient features of these are as follows: The quenching was done in liquid nitrogen by dropping vacuum sealed quartz capsule containing the melted RNi_5 flux. X-ray diffraction characterization of the quenched materials revealed that they did not contain sharp Bragg reflection and had characteristics representing phases varying from microcrystalline to amorphous. In order to find out the difference between the crystalline and the amorphous like RNi_5 phases, hydrogenation of these two phases was carried out simultaneously under identical conditions embodying low pressure hydrogenation. It was found that the amorphous like phases possess higher hydrogen capacity than their crystalline counterparts. This is brought out by Figure 12. As is evident from this figure, the amorphous phase has a noticeable higher hydrogen capacity than their crystalline versions. This result was verified on a large number of samples. It represents a novel hydrogen storage characteristics - the first of its kind for the RNi_5 intermetallic phases. The larger capacity of amorphous phase is presumably due to the possibility of larger number of voids per unit volume for the occupation of hydrogen (Maeland, 1980). The behaviour shows that crystal structure is slightly relaxed and the atmos are less strictly defined in as-quenched (amorphous) material. These amorphous materials have the following advantages over their crystalline counterparts (Suzuki, 1983):

(a) Less subject to pulverization (decrepitation) on hydrogenation,
(b) High ductility with respect to crystalline form,
(c) High hydrogen storage capacity.

7. HIGH PRESSURE HYDROGEN ABSORPTION STUDIES

Generally, hydride formation in ambient conditions is not possible in these intermetallics. Several activation methods are employed by applying high temperatures and hydrogen pressures. In the case of $LaNi_5$, 30-40 atmospheres of hydrogen pressure is needed for initial hydride formation. This process requires 8-9 hours to form complete hydride. Surface plays an important role in the hydrogen absorption kinetics. A proposed model was given by Schlapback and coworkers (1980, 1981). According to this "self restoring mechanism" lanthanum converts into lanthanum oxide and lanthanum hydroxide leaving the nickel clusters at surface. This clean nickel loosens the H-H band and acts as a catalyst. It also restricts the contamination of $LaNi_5$.

Activation of granulated sample was carried out in the high pressure reactor (see Figure 13) using 30-40 atmospheres of hydrogen. Fine powder of alloy with grain size ranging 4 to 10 μ was observed. Pressure-composition isotherms were measured through a reservoir and with pressure gauges. The desorption isotherms were obtained by collecting the hydrogen into an inverted glass cylinder placed in a water bath. The displacement of water is the direct measure of total quantity of hydrogen released. One can calculate hydrogen concentration from PVT readings. Figures 14 and 15 show the desorption isotherms for $LaNi_5$ and $MmNi_{4.5}Al_{0.5}$ respectively at room temperature. It can be noticed from Figure 14 that plateau pressure of $LaNi_5$ is nearly 1.2 atmosphere and the maximum hydrogen per molecule of $LaNi_5$ is 6. From Figure 15 it is evident that plateau pressure of $MmNi_5Al_{0.5}$ is in between 2-3 atmospheres and H/mole of $MmNi_{4.5}Al_{0.5}$ is 6.5.

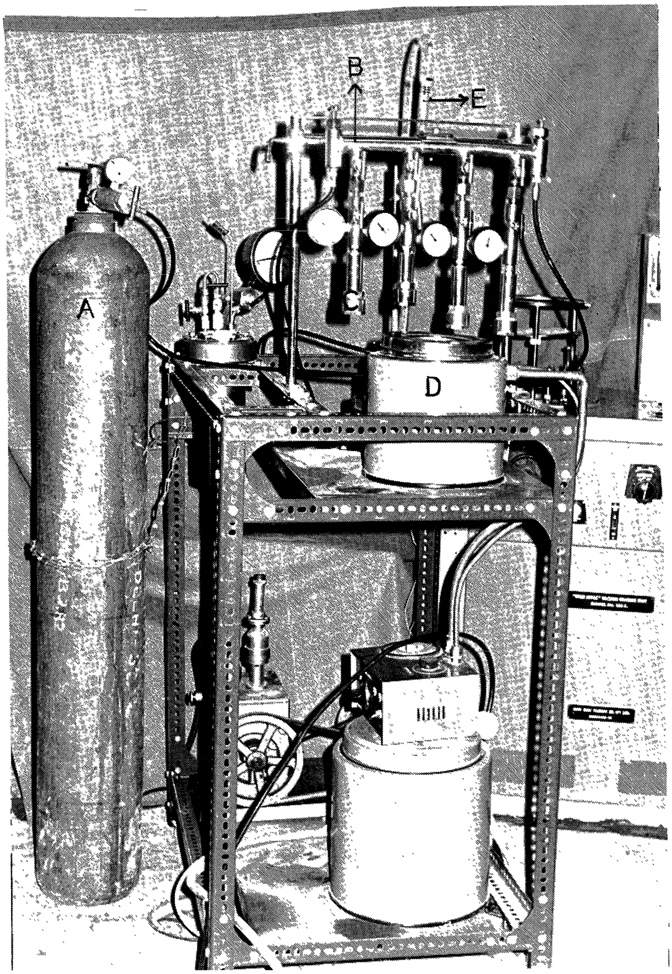


Figure 13. High pressure reactor:
(A) Hydrogen cylinder
(B) Reservoir
(C) Sample holder
(D) Controlled heating bath
(E) Hydrogen collector

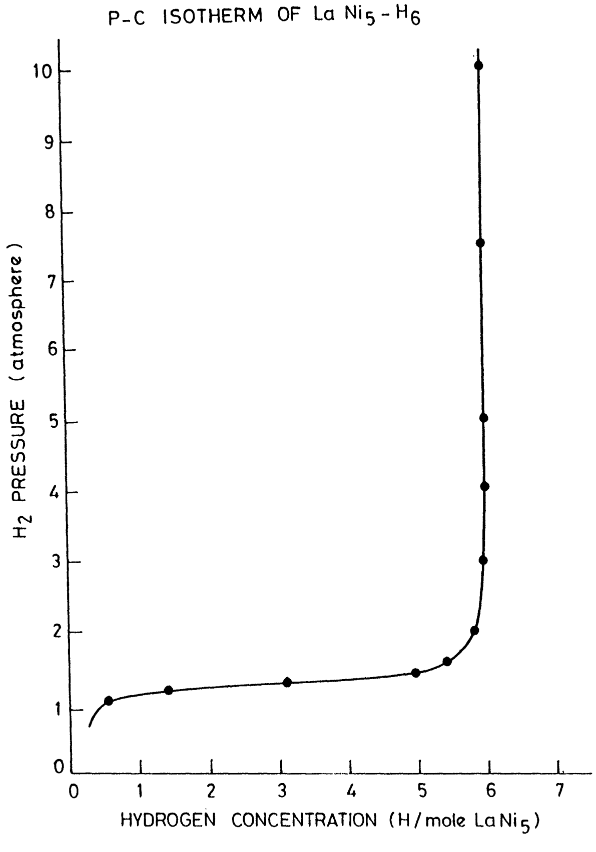


Figure 14. Desorption isotherm of $LaNi_5$.Max H/M = 6 .

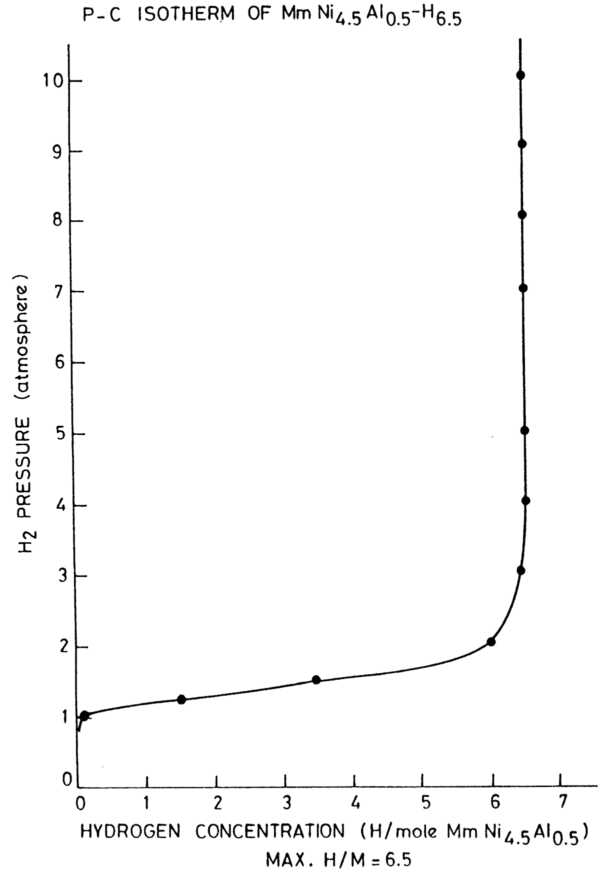


Figure 15. Desorption isotherm of $MmNi_5$.Max H/M = 6.5.

8. VARIATION OF ELECTRONIC BEHAVIOUR ON HYDROGENATION

In regard to hydrogenation characteristics, electronic properties are as important as the structural ones. It is well established that the various hydrogen absorption features are crucially influenced by electronic band structure characteristics. The embrittlement (decrepitation) of these intermetallics in hydrogenation process does not permit the experiments to be carried out in bulk forms. So efforts were made to bring out the variation in electronic properties due to hydrogenation by employing thin films where decrepitation unlike bulk is not a serious problem (Adachi, 1982). Hydrogenation effects in these films are monitored through resistivity variation. Films of thicknesses ranging from 1000 to 1500 Å are prepared by vacuum thermal evaporation technique. The films were deposited on glass slides using suitable masks. The change in the resistivity is measured in $CFMmNi_{4.5}Al_{0.5}$, $MmNi_5$ and $LaNi_5$. The nature of variation is same in all these films. Figure 16 shows the resistivity vs. time plot of $CFMmNi_{4.5}Al_{0.5}$ under the hydrogen pressure of 200 psi. It can be seen that the resistivity increases slightly when the thin films are exposed to hydrogen (region AB in Figure 16). The initial rise is followed by a curious resistivity region where it decreases (BC). It then rises again and attains a saturation value (EF of Figure 16).

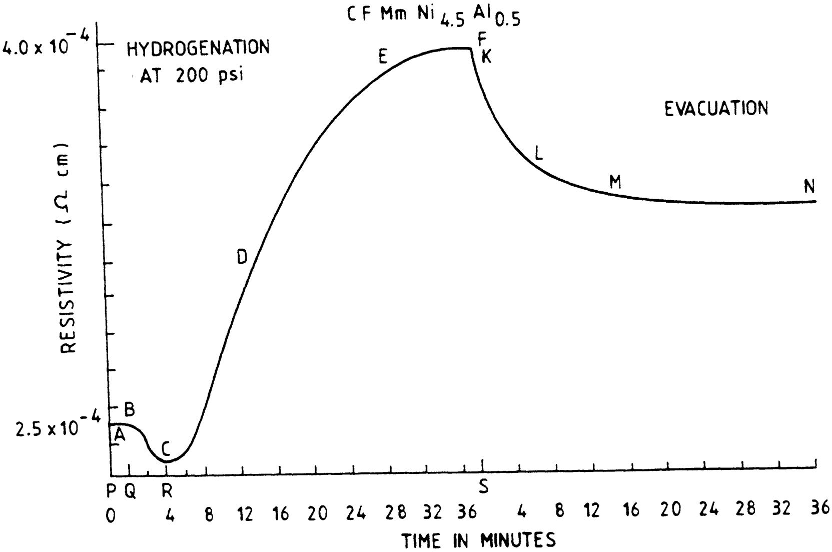
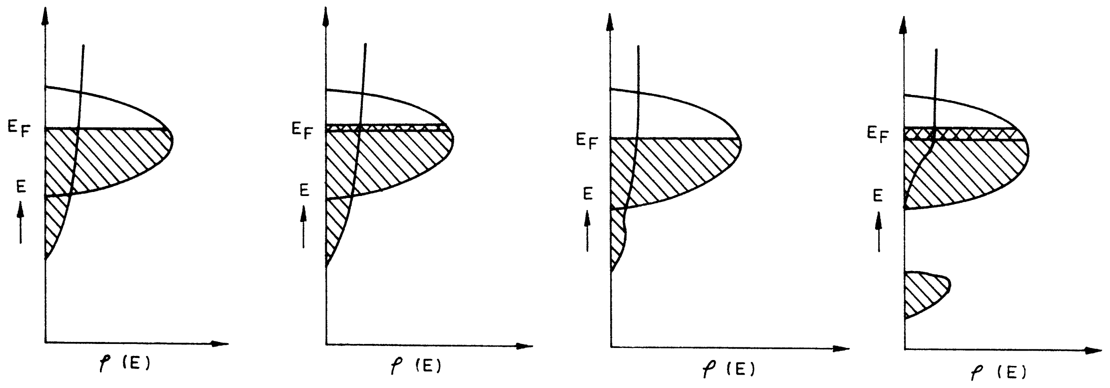


Figure 16. Resistivity variation of $CFMmNi_{4.5}Al_{0.5}$ thin film on hydrogenation (see text).

Electronic band structure of RNi_5 is mostly dominated by nickel-derived 3d bands (Malik et al., 1977). On hydrogenation the change in the 3d level effects the electronic properties crucially. 0.6 holes (Gschneidner, 1982) are present in the nickel and the Fermi level lies at the narrow band of 3 d level. As is well known, the variation in the electronic and optical properties of metals/intermetallics on hydrogen absorption becomes intelligble in terms of the changes in the density of states (DOS) consequent to hydrogenation. Gellett et al. (1978) proposed a model showing the effect of hydrogenation in terms of DOS, particularly the 3d states of nickel. In the present study we invoke the effect of variation in DOS due to hydrogenation to explain curious characteristics of the variation of resistivity with time. Schematic features showing changes in the DOS on hydrogenation are shown in Figure 17.



(a) NO HYDROGENATION

(b) VERY LITTLE CHANGE AS COMPARED TO (a) (LOW HYDROGENATION)

(c) OCCURRENCE OF NEW STATES DUE TO M-H INTERACTION (MEDIUM HYDROGENATION)

(d) METAL HYDRIDE (HIGH HYDROGENATION)

Figure 17. Schematic representation of density of states (DOS) on hydrogenation (After Gellett et al., 1978)

(a) No hydrogenation
(b) Very little change as compared to (a) (low hydrogenation)
(c) Occurrence of new states due to M-H interaction (medium hydrogenation)
(d) Metal hydride (high hydrogenation)

We can take the initial (PQ), middle (QR) and final (RS) time interval regions as the low, medium and high concentration regions of hydrogen in the starting intermetallic phase. DOS of initial intermetallic-phase is shown in Figure 17(a). The presence of low hydrogen concentration is known to let the initial DOS structures of the parent intermetallic phase remain nearly unchanged. Thus in this case the electrons from hydrogen will fill the unoccupied states near the Fermi level. The highest filled level will then correspond to smaller DOS. Consequently, the resistivity will increase. It is shown in Figure 17(b) by slight modification of the states of initial matrix at Fermi level EF. We believe that the initial rise in the resistivity is due to this reduction in DOS at the Fermi level. In the medium hydrogen concentration region corresponding to middle time interval region in the ρ -t curves, the band structure starts changing due to onset of M-H interactions. The 'd' state gets lowered down on energy scale and the new structure corresponds to a larger value of the DOS at the Fermi level (Figure 17c). In this region the conductivity (resistivity) is expected to increase (decrease). The drop in resistivity in the curve (see Figure 16 region BC)is due to the foregoing reasons. As the hydrogenation proceeds further we enter the high hydrogen concentration region. Here the H-H interaction onsets. Together with the M-H interaction it affects the DOS drastically. It is known that these changes incorporate considerable reduction in the DOS available (at the Fermi level) for conduction and the changes may be thought of leading to a situation where electronic conduction would require intra-band transition. Figure 17(d) shows the well separated parabolic sp band and most of the d-states are occupied at the Fermi level. The conductivity (resistivity) would therefore get reduced (increased) drastically. This is to be the reason for the significant rise in resistivity (Figure 16 region DE) corresponding to high hydrogen concentration region.

On evacuation the resistivity decreased first (Figure 16 region KL) and then saturated (MN) with time. Hydrogen desorbs from the film on evacuation. The desorption eventually stops when the hydrogen is taken out nearly completely. This is the reason for the fast decrease of resistivity and post-saturation (Figure 16 KLMN). The effect of film thickness on hydrogen absorption properties are also under investigation presently.

9. APPLICATION OF METAL HYDRIDES

For serving as effective hydrogen storage medium, a metal hydride must satisfy several criteria. The most important criterion of course is that it must be easily formed and dissociated. From this point of view the choice of useful metal hydrides automatically falls on the hydrides which will decompose at low temperatures ($\leq$ 300°C). Such hydrides get formed prominently from inter-metallic phases Mg_2Ni, FeTi and RNi_5. For the application of metal hydrides in utility devices, the consideration of heat of decomposition of the hydrides is an important factor. To make the use of metal hydrides self sustained energy wise, the heat of decomposition must be supplied from the waste heat of the converter with which it is coupled. From this point of view the operating temperature, the waste heat output of the energy converter and the pressure-temperature characteristics of the metal hydride must be properly matched. Some other characteristics of hydrides which are pertinent for their use in energy devices such as internal combustion engines, fuel cells etc., relate to their cost, safety, suitable reaction rate, reversibility, weight and physical and chemical stability. The relative importance of these factors will depend on the specific application to which the hydride is put to. As for example, weight is not a critical parameter for stationary applications but for mobile storage media, for example in automative uses, weight is very important.

Hydrides have been put to a variety of applications, perhaps the latest being their use in sophisticated aircrafts as fire detectors.

In the common usages hydrogen can serve all the energy needs of a household. Figure 18 brings out the variety of uses to which hydrogen can be employed for a closed cycle household usage.

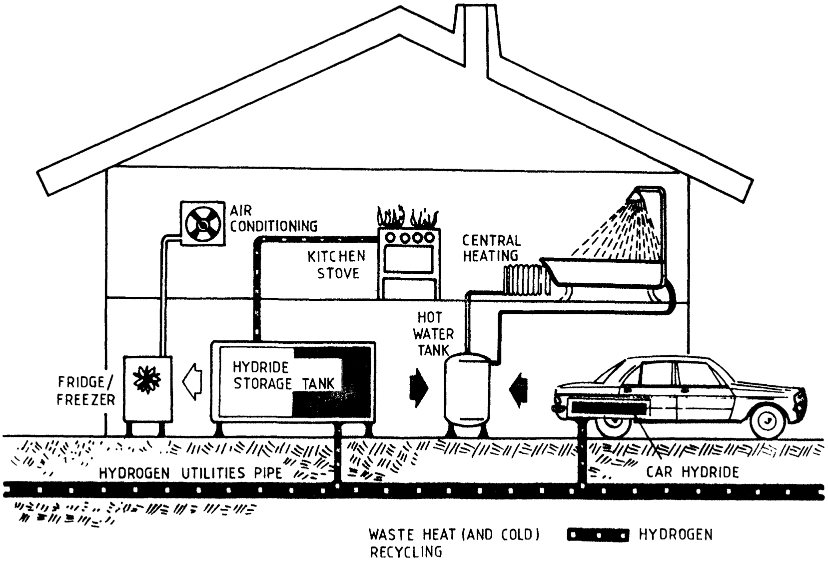


Figure 18. A closed cycle Hydrogen Home (Waste heat is recycled by charging hydride tanks).

The more general usage of hydrogen can be categorised as in the following:

(a) Automotive
(b) Electricity load levelling - Electricity storage
(c) Thermal storage - Heating or cooling
(d) Waste heat storage
(e) Electricity generation
(f) Hydride compressors
(g) Pumping (e.g. water lift pump)
(h) Hydrogen purification
(i) Deuterium separation.

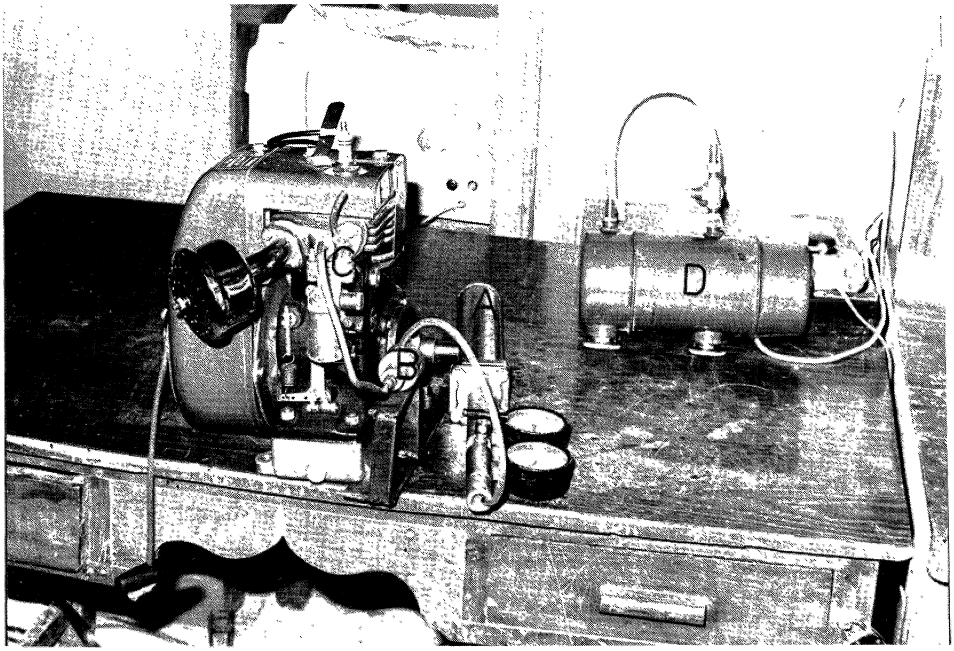


Figure 19. A hydride/hydrogen fuelled I.C. engine. The hydride corresponded to RNi_5H_6 and was synthesized under a DNES sponsored project on the development of hydrogen storage material. The I.C. engine was a standard Villier's 1.75 H.P. (3000RPM) cane crushing machine which usually runs on gasoline (the gasoline tank (D) is abandoned in the present work). Carburettor (C) of the engine was modified and a cam induced injector system (B) was fabricated for running the engine on hydride/hydrogen (contained in tank A).

Out of the above listed uses, the one which is of immediate importance in the Indian context is that in automative area. Road transportation starting from small vehicles, e.g. mobike, scooters through medium ones, e.g. cars to heavy vehicles, e.g. trucks etc. corresponds to the sector which should find first priority in the application of hydride/hydrogen technology. The primary step in the automative applications apparently would be to run a hydride/hydrogen powered internal combustion engine. To meet this goal we have utilised RNi_5H_6 type hydride for running a Villiers' internal combustion engine (1.75 H.P.; 3000 RPM; Figure 19). This is the four stroke I.C. engine generally used for cane crushing, but can also be used for running a mobike/scooter. The carburettor of this engine was modified on lines similar to those suggested by Bindon et al. (1985). The hydrogen injection into the main chamber was carried out by cam induced fuel injection pump (see Figure 19). The hydrogen gas was supplied by a $LaNi_5H_6$ hydride which partly dissociated to yield hydrogen at ambient condition. At later stages the dissociation was obtained by the engine exhaust gases which raised the temperature up to ~ 50°C. It was possible to control the back-firing of the engine through controlled injection of hydrogen. The above hydride/hydrogen driven engine which is the first effort of its kind in the country gave satisfactory performance and it is hoped that in the near future it would be possible to power the mobike/scooter I.C. engines with the hydride/hydrogen fuel.

ACKNOWLEDGEMENTS

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THIN FILM HYDROGEN STORAGE SYSTEM

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1. INTRODUCTION

In the last one decade the use of hydrogen as an energy carrier has attracted world wide interest. As a result of this studies are being made on the technology involved for the production, storage and use of hydrogen. In this paper we discuss storage aspect of hydrogen.

When hydrogen is stored as a gas it needs large and heavy vessels. At a typical pressure of 136 atmospheres hydrogen gas in a steel container weighs about 30 times more than an equivalent amount of gasoline, and the container size is 24 times more than that of gasoline container (Reilly and Sandrock, 1980). Metal hydrides in contrast store hydrogen in a compact form and are rather safe. Properties of a few metal hydrides are compared with liquid and gaseous hydrogen in Table I.

In discussing the physical properties and the applications of metal hydrides, the following questions need to be examined carefully:

(a) Why do certain structures easily absorb hydrogen?
(b) How do the constituent elements and properties of the intermetallic compounds govern this?
(c) What determines the location of hydrogen in the various phases?
(d) How is the electronic structure of a material altered by hydrogen absorption?
(e) What mechanisms determine the hydrogen absorption-desorption processes?
(f) What are the kinetics of such processes?

For the present discussion we will not consider the bulk hydrides and confine our attention to the hydrogen storage in thin film. The incorporation of hydrogen into thin film form is relatively a new field of research and provides opportunity to examine a number of unusual properties which are not easily visible in bulk hydrides.

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TABLE I : Hydrogen Concentration in Different Systems

System	Density gm/cm^3	Atoms of H per unit volume ($x10^{22}/cm^3$)	Weight per cent H
Liquid H_2	0.07	4.2	100.0
H_2 gas (100 bar, 300 K)	0.008	0.5	100.0
H_2O (Liquid)	1.0	6.7	11.2
NH_3 (Liquid)	0.6	6.7	18.0
LiH (Solid)	0.8	5.3	12.7
MgH_2	1.4	6.7	7.6
CaH_2	1.8	5.1	4.8
MgH_2NiH_4	2.6	5.8	3.6
TiH_2	3.8	9.1	4.0
$FeTiH_2$	5.6	6.2	1.9
VH_2	5.0	11.2	2.1
ZrH_2	5.6	7.3	2.2
UH_3	11.0	8.5	1.3
$LaNi_5H_6$	6.5	7.0	1.4
$CaNi_5H_6$	5.0	7.0	1.8
CH_4 (Liquid)	0.46	7.4	25.0
C_2H_5OH	0.78	7.5	15.0
C_6H_6	0.78	4.0	7.7
C_6H_{12}	0.84	7.1	14.3

2. HYDROGEN ABSORPTION MECHANISM

The absorption process involves two distinct stages: (i) the dissociation of hydrogen molecule at the surface of the material into atomic hydrogen, and (ii) the atomic hydrogen then penetrates the surface and dissolves in the lattice. Hydrogen reacts reversibly with the metal by means of the following reaction:

$$M + \frac{x}{2} H_2 \rightleftharpoons M H_x + \Delta Q$$

In the desorption process, the atomic hydrogen first comes to surface from the lattice and then combines at the surface to form molecular hydrogen.

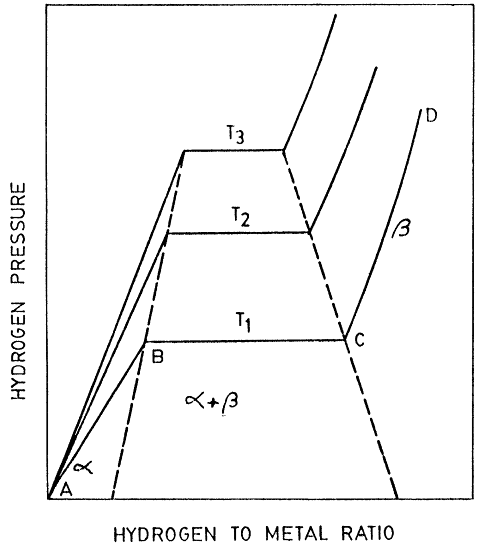

Figure 1. Pressure - composition isotherms showing the relationship between the equilibrium hydrogen pressure and the hydrogen concentration (Reilly,1977)

The behaviour of a metal hydride system can be best represented by a pressure composition temperature (PCT) diagram. It is a plot of pressure or composition at various temperatures as shown in Figure 1 (Reilly, 1977). The initial steep slope corresponds to hydrogen going into solid solution and this single phase region is usually denoted as the α-phase. When the solid solution becomes saturated with hydrogen, the non-stoichiometric hydride phase begins to form. With the formation of second phase (α+ β) the hydrogen pressure remains constant and a plateau results, as more hydrogen is added. The position where the curve begins to change slope denotes the appearance of a metal hydride or β-phase. The curves represented by T_1, T_2 and T_3 show the effect of temperature, as the temperature is increased there is a decrease in the plateau length resulting in α-phase approaching β. At some critical temperature the plateau disappears and the α-phase converts continuously into the β-phase.

The materials to be developed for hydrogen storage should fulfil the requirements of larger storage capacity; ease of charging and discharging; longer life; low cost; insensitive to poisioning;and low weight.

Bulk hydrides in the form of intermetallic compounds or alloys are kept in a stainless steel container in the form of powder with average particle size of the order of 5 to 100 mesh, with provision of suitable heat transfer mechanism. The cold water is circulated in such systems during charging of hydrogen. The hydrogen is recovered by circulating hot water in it and discharge pressure is controlled by the temperature of the container.

Based on the above mechanism, prototype hydrogen storage systems have been built in USA by Billing Energy Corporation, Brookhaven National Lab and Argonne National Lab; in Germany by Daimler Benz Co. and K.F.A. Julich and in France by CEN Grenoble. Apart from the bulk hydride storage systems, three research groups, i.e. Wenzl (1982, 1983) group in Germany, Eatons (1981) group in USA and Ron (1978) group in Italy, are working in the field of thin film hydrogen storage systems.

The main advantages of thin film hydrides over bulk hydrides are:

(a) The hydrides in thin film form provide large surface area and hence fast charging discharging rate is possible (Wenzl et al., 1983).

(b) Pulverization is slower (Adachi et al., 1982).

(c) Both the critical pressure Pc and critical temperature Tc of thin hydride films are significantly lower than those of bulk (Bakker and de Bruin-Hordijk, 1985).

(d) Heat transfer arrangements are better in thin films than bulk because of metallic substrate (Vijay and Jain, 1985).

(e) It is in general difficult to design an experimental arrangement where the clamping of a bulk specimen can be reached without hampering hydrogen absorption. For thin films, however, an effective clamping is obtained by evaporating them on a massive substrate (Bakker and de Bruin-Hordijk, 1985; Ron and Elemelach, 1978)

(f) Protective surface coating could be done on a thin film to stop poisioning by oxygen and other gases (Papathanassopoulos and Wenzl, 1982).

(g) Activation of thin film hydrides is possible by coating a layer of catalytic material (Shenoy et al., 1981).

3. POISIONING

The hydriding and dehydriding rates drop to zero (Wenzl et al., 1983) in case of vanadium films within seconds if samples are exposed to oxygen partial pressure of more than 10^{-7} mbar. Thin palladium overlayers, however, provide a very effective protection against this 'poisioning' effect. The hydriding behaviour of the palladium overlayer is known (Frazier and Glosser, 1979) to contribute only a few per cent to the total amount of hydrogen stored in the sandwich film used and is neglected.

Similarly hydrogen absorption rate from the gas phase by tantalum (Fromm and Uchida, 1979) is strongly impeded by oxygen sorption layers for temperatures below 700 K. The removal of these layers increases the absorption rate by several orders of magnitude. The hydrogen absorption rates of Ti, Ta, W, Fe and Pd film, 15 - 20 nm were measured by Uchida and Fromm (1983) at room temperature between 10^{-9} and 10^{-4} mbar. The reaction rates are strongly reduced if the film surface is coated with oxygen at thickness equivalent to several monolayers. Therefore, it is important to prepare thin film under ultra high vacuum conditions followed by a protective coating as overlayer on it.

Bakker and de Bruin-Hordijk (1982) studied the critical temperature and critical pressure of thin PdH_x and bulk PdH_x. Figure 2(a) shows typical absorption pressure - composition isotherms of a 122 nm thick

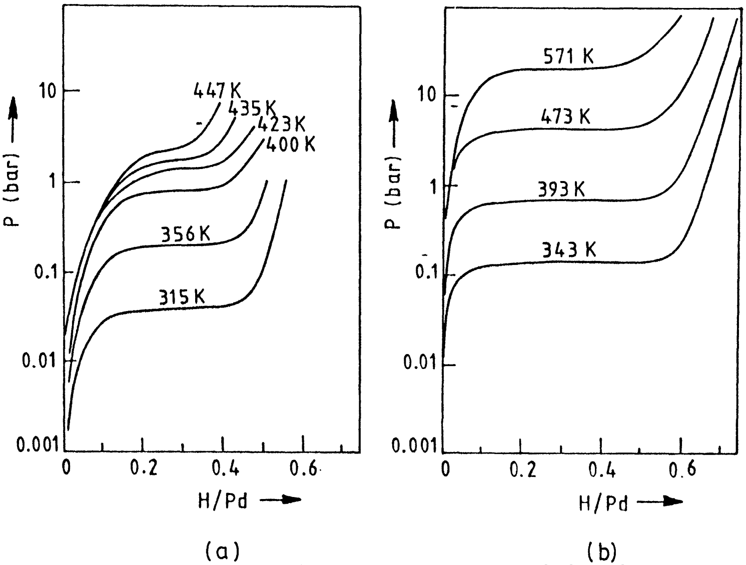

Figure 2. Hydrogen absorption pressure-composition isotherms of: (a) a 122 nm PdH_x film, and (b) bulk PdH_x (Bakker and de Bruin-Hordijk, 1982).

palladium film. From a comparison of the isotherms in Figure 2(a) with those of bulk palladium in Figure 2(b) it is clear that both the critical temperature and the critical pressure of the films are considerably lower than the values for bulk samples.

The main disadvantage of thin film approach is the weight consideration due to massive base material as a substrate, without increase in hydrogen storage capacity. But seeing the other advantages weight becomes of secondary importance. While working on thin film hydrogen storage devices the points of interest are:

(a) How much thick layer is good enough for hydrogen storage purpose?

(b) What kind of surface over layer helps in catalytic action and for protective purpose, e.g. Pd, Ni and V?

(c) What would be the thickness of the surface layer and base material in order to hold the hydride mechanically stable.

These types of investigations will help us to understand the hydride formation in thin film form and for better design of hydrogen storage system.

4. EXPERIMENTAL METHOD

4.1. Sample Preparation

A material which we want to use for hydrogen storage may have a surface layer of oxide on it. The formation of hydride will then require that hydrogen somehow should penetrate this oxide layer. The removal of these layers increases the absorption rate of hydrogen by several orders of magnitude. It was found that vanadium films (Papathanassopoulos and Wenzl, 1982) which are vapour deposited in situ in an ultra high vacuum system show rather large absorption and desorption rates. These rates can also be enhanced by depositing a thin palladium film on top of the vanadium film sample immediately after preparations. Even exposure to air is then possible without poisoning the surface against hydrogen transfer between the sample and the gas phase.

4.2. Hydrogen Content

The hydrogen content in thin film hydrides can be determined with the help of a vibrating quartz micro balance which is basically a very sensitive quartz crystal thickness monitor. This kind of arrangement has been demonstrated and used by Bucur and Franagan (1974) and Wenzl et al. (1982, 1983). In this type of thickness monitor the sample in the form of thin film is simultaneously deposited on to the quartz crystal whose frequency change Δ_f during film deposition and hydrogen absorption is determined and is linearly related to the deposited mass Δ_m by the relation (Sauerbrey, 1959)

$$\Delta_f = \frac{-\rho_o tF}{f_o} \Delta_m$$

where ρ_o is density, t is thickness, F is area and f_o is initial frequency of the crystal vibration. This is an important technique to determine hydrogen content of a thin film hydride.

4.3. Thin Film Hydrides

The effect of hydrogen absorption on the electrical resistivity of $LaNi_5$ and $MmNi_{4.5}Mn_{0.5}$ films (Mm Mish Metal) were extensively studied by Adadhi et al. (1982). They used the flash evaporation technique for film deposition in hydrogen atmosphere. One of the most serious problems in the use of $LaNi_5$ as a hydrogen storage material is that the intermetallic compound pulverises during the hydrogen absorption desorption cycle. The thin films of thickness equal to 2000 Å obtained by Adachi et al., however, do not form powders even after 150 cycles of the absorption desorption of hydrogen. Resistance of such films initially increases and then decreases during the absorption process of hydrogen. The reverse is true for the desorption process. Uchida and Fromm (1983) had studied the hydrogen absorption rate of 15 - 20 nm thick films of titanium, tantalum, tungsten, iron and palladium at room temperature and hydrogen pressure between 10^{-9} to 10^{-4} mbar. Recently investigations have been carried out by Wenzl et al. (1983) on vanadium films and also using Al (20 μm/Pd (100 nm)/V (10 μm)/Pd (100 nm) films for prototype hydrogen storage containers. They found that the vanadium films can be hydrided almost reversibly from the gas phase within seconds to $VH_{0.5}$ at 300 K and a hydrogen pressure of 1 bar and within 1 minute to $VH_{1.8}$ and a hydrogen pressure of 30 bar. In such films 2 per cent mass fraction of hydrogen was stored and a much higher heat exchange rate was attained than in the bulk.

The sample preparation and part of the measurements were performed in a standard all metal ultra high vacuum (UHV) chamber with a base pressure of 10^{-10} mbar and a maximum pressure of about 2 bar. A separate chamber was used to create pressures up to 40 bar. Thin palladium over layers were used to protect the oxygen sensitive material in case of exposure of the samples to air. Palladium also acts as a catalyst as it increases the rate of absorption of hydrogen by vanadium films. Samples covered with Pd did not change their hydriding dehydriding behaviour during exposure to the atmosphere at room temperature over several weeks. Longer exposure times have not been analysed.

5. THIN FILM HYDROGEN STORAGE SYSTEM

In this part the discussions will be confined to two systems - one by Wenzl et al. (1983) and the other by Vijay and Jain (1985).

Wenzl has suggested a prototype stainless steel storage cylinder 15 cm long with an inside diameter of 3.3 cm and a volume of 120 cm^3. This system was filled with Al/Pd/V/Pd. In such a system a mass of about 30 g of vanadium was available with a storage capacity of 0.7 g of H in $VH_{1.8}$. Depending on the pressure and temperature the film can be hydrided to $VH_{0.9}$ and $VH_{1.8}$. Desorption from $VH_{1.8}$ to $VH_{0.9}$ is possible within minutes by reducing pressure to about 1 bar at 20°C or by heating to 80°C at 30 bar.

The films were subjected to 20 absorption-desorption cycles. Changes in the hydriding capacity or the film peeling were not observed. The macroscopic structure of powder storage and film storage materials after several hydriding-dehydriding cycles are compared in Figure 3 (Wenzl et al., 1983). Table II gives the data for vanadium thin film storage systems.

Recently, Vijay and Jain (1985) have suggested a new design for hydrogen storage. In this system hydrides are in the form of thin layers supported on a suitable base material with a protective catalytic surface layer. The hydrogen storage device can be represented by a three layer structure as shown in Figure 4(a). The surface material acts as a catalyst for the dissociation and association of hydrogen molecules and also prevents poisioning. The base material supporting the metal hydride acts as a heat exchanger and also provides mechanical stability to the structure.

The base material can be used in the form of a foil, a wire or a tube. Foil provides a larger surface area than that of the tube and wire for the same mass and mechanical strength. However, the mechanical stability of the thin surface layers will be greater for a curved

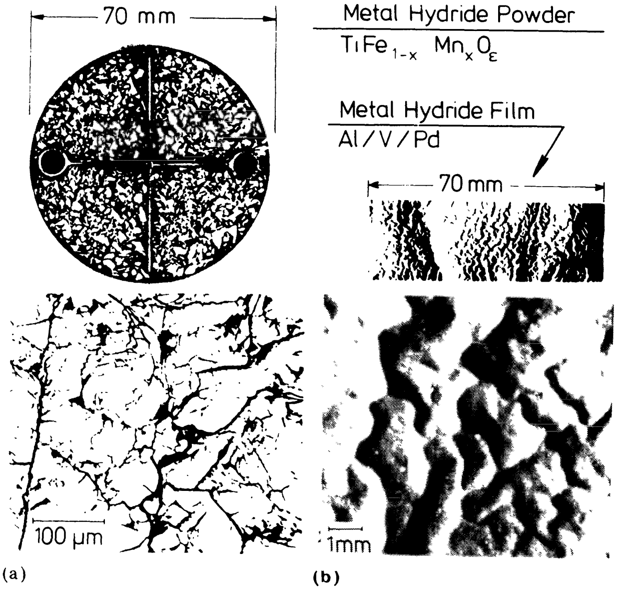

Figure 3(a) Powder storage material $TiFe_{1-x}Mn_xO$ ($x = 0.02$; $\epsilon = 0.1$ at.%) (top, cross section through the storage container showing the powder and the heat exchanger tubes; bottom, scanning electron micrograph of the material showing the crack pattern (dark regions)).

(b) Film storage material after 10 hydriding - dehydriding cycles (top, optical micrograph; bottom, scanning electron micrograph). The undulating patterns on the initially flat surface were generated by buckling of the film on a scale of about 0.1-1 mm due to expansion and contraction of the vanadium deposit during hydriding and dehydriding (Wenzl et al., 1983).

surface. The concentration gradient of the hydrogen atoms at the surface will create mechanical stress which will be less for tube and wire than for foil. In addition, the cooling arrangements can easily be incorporated into the tubing. Therefore, it is suggested that the tubular geometry be adopted for the base material.

The base material for supporting the metal hydride can be in the form of tubes. As shown in Figure 4 either an internal Figure 4(b) or an external Figure 4(c) type of geometry can be adopted. In order to have a large surface area several tubes can be used. The design of such a complete hydrogen storage system is shown in Figure 5. The details of the conventional design are shown in Figures 6 and 7.

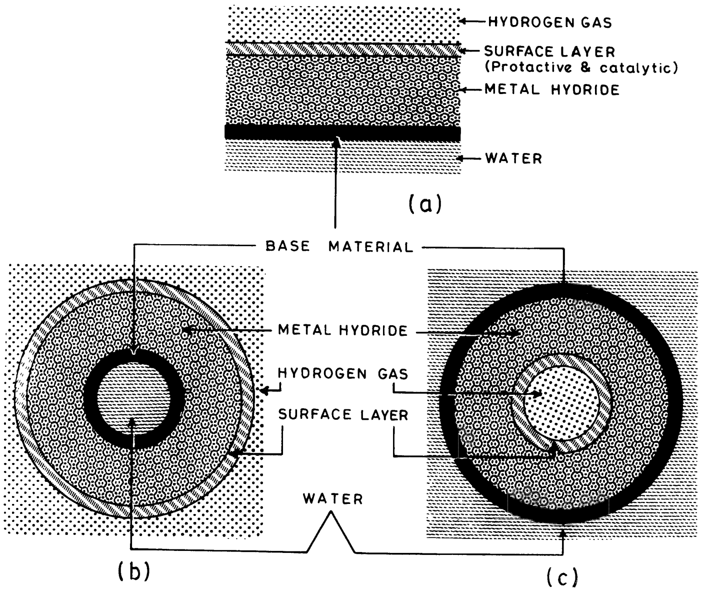

Figure 4(a) Schematic diagram of a hydrogen storage device
(b) tubular arrangement with internal geometry
(c) tubular arrangement with external geometry
(Vijay and Jain, 1985)

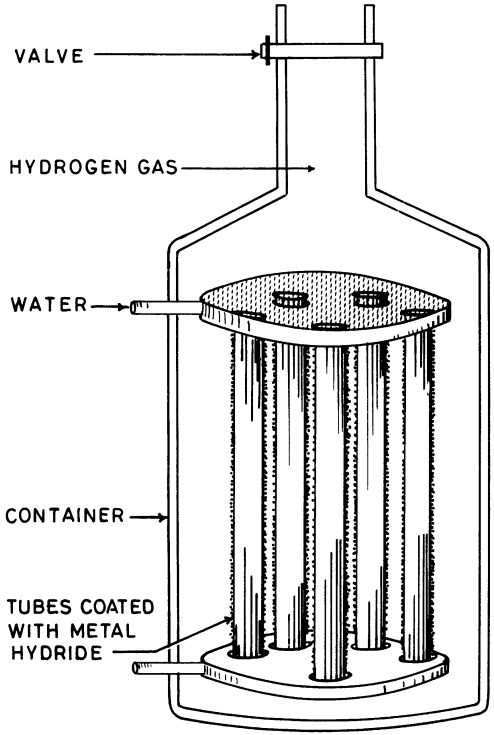

Figure 5. Design for a noval hydrogen storage system
(Vijay and Jain, 1985)

TABLE II : Data for Vanadium Thin Film Hydrogen Storage System

Specific mass	
5 μm Al	14 gm^{-2}
10 μm V	61 gm^{-2}
0.1 μm Pd	1.2 gm^{-2}
H	
$0 \leq x \leq 0.6$	0.72 gm^{-2}
$0.9 \leq x \leq 1.9$	1.2 gm^{-2}
Mass ratio	
$m_H/m_{substrate}$	
$0 \leq x \leq 0.6$	0.9%
$0.9 \leq x \leq 1.9$	1.6%
m_H/m_{FeTi}	
$Fe_{0.5}\ Ti_{0.5}\ H_{0.1-0.9}$	1.5%
Specific volume	
Film storage with void space equal to film space	101(kg H)$^{-1}$
Powder bed FeTi	101(kg H)$^{-1}$
Elective thermal conductivity	
FeTi powder	1 W mK^{-1}
Film stack	230 W mK^{-1}

The advantages of our design are as follows:

(a) The thermal conductivity of this arrangement is much higher than that of the powder bed and hence the charging-discharging rates can be fairly high.

(b) Peeling of the layers can be avoided by careful preparation of thin films, which also results in an increase in the life of storage system.

(c) The design is quite simple. A large number of tubes can be easily coated with suitable material by vacuum evaporation.

(d) The volume expansion of the metal hydride during charging results in a change in the effective diameter of the tube which will attain its normal value during discharge.

The wall thickness, diameter, length and cross-section of the tubes can be chosen to suit the requirements of the system. Therefore, this design with thin film hydrogen storage media has a potential in the application of metal hydrides for hydrogen energy storage.

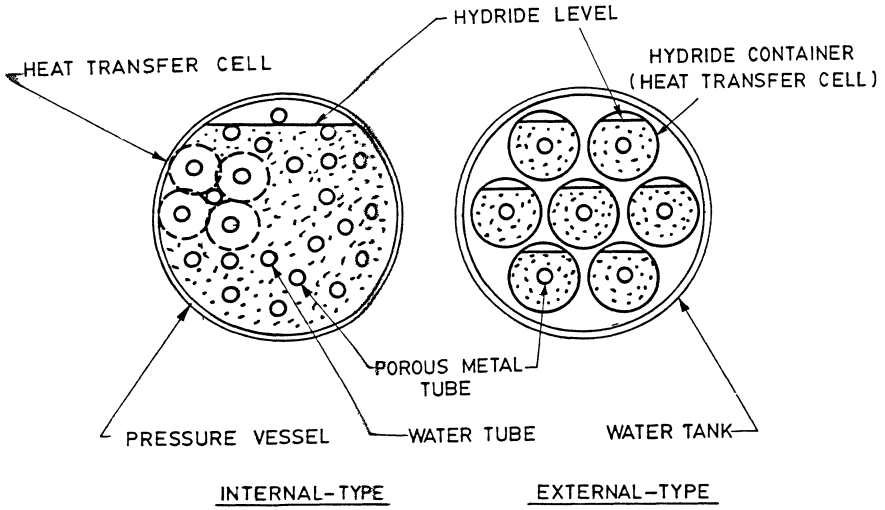

Figure 6. Cross-sectional view of heat transfer arrangement.

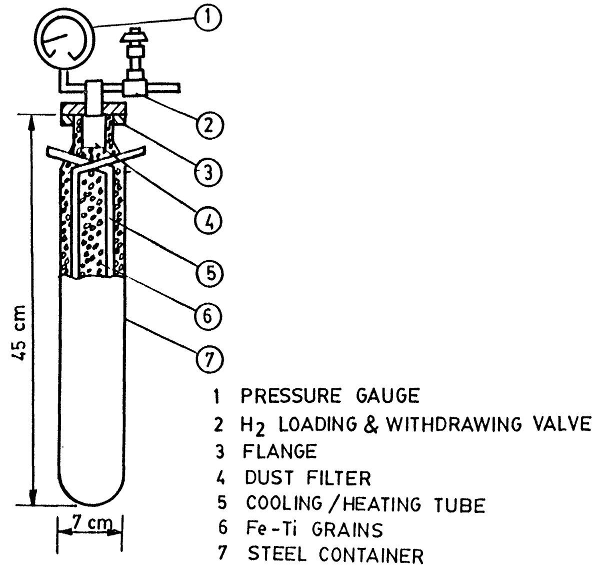

Figure 7. Schematic of KFA Laboratory hydrogen storage container.

ACKNOWLEDGEMENT

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CRYOGENIC STORAGE OF HYDROGEN

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1. INTRODUCTION

Hundred years ago a fog of liquid hydrogen droplets was created by two dedicated scientists at the Cracow University in Poland. The scientists, Wroblewski and Olszewski least suspected that a century later their effort will help place man on the moon and fill automobile fuel tanks of the common man. In 1898, James Dewar in England obtained liquid hydrogen as a visible liquid body in test tube (instead of a mist) by using the vacuum insulated container invented by him. The technology of liquefying hydrogen has matured over the years and today it is used in thousands of tonnes in many parts of the world.

Hydrogen exists in the liquid form in the temperature range 14-33K. It is the most volatile of all substances except helium. However, in many ways its behaviour as a liquid is quite normal. Unlike helium, liquid hydrogen does not show the phenomenon of superfluidity. Its properties in the liquid state can be estimated using available theories of liquids about as accurately as can the properties of other simple substances (Corruccini, 1965). Liquid state theories, however, are normally not adequate for most technological purposes, which must depend on experimental data and semiempirical correlations. Some important thermophysical and transport properties are given in Table I (Arkharov et al., 1981). The corresponding values for liquid nitrogen and liquid helium are given for comparison. An extensive compilation of thermophysical properties of liquid and gaseous hydrogen is given by Mc Carty (1975).

The low boiling point and low density of liquid hydrogen stand on its way to large scale commercial use. Low liquefaction temperature means a larger refrigeration cost and low density means a larger volume and hence a greater investment in containers and structural members.

2. WHY LIQUID HYDROGEN?

Today liquid hydrogen is almost exclusively used for rocket propulsion and for the production of heavy water by distillation of its two major

R. P. Dahiya (ed.), Progress in Hydrogen Energy, 123–132.

TABLE I : Thermodynamic and Transport Properties of Saturated Liquid Hydrogen

	LH_2	LN_2	LHe
Freezing point (K)	13.96	63.2	*
Boiling point (K)	20.4	77.36	4.22
Specific gravity	0.071	0.808	0.125
Latent of vaporisation (kJ/kg)	447	199	20.8
Specific heat (C_p) (kJ/kgK)	9.7	2.05	5.0
Viscosity (Pa.s)	0.13×10^{-4}	1.52×10^{-4}	3.6×10^{-6}
Thermal conductivity (W/mK)	0.099	0.14	0.0197
Triple point pressure (kPa)	7.20	12.54	**
Triple point temperature (K)	13.95	63.15	**
Critical temperature (K)	33.24	126.26	5.20
Critical pressure (MPa)	1.297	3.398	0.2275

* The properties of LN_2 and LHe are given for comparison.

** Liquid helium does not solidify at atmospheric pressure and does not show a triple point.

isotopes. As the conventional fossil fuel reserves are depleting fast throughout the world, mankind is looking for alternative sources of energy in sunlight, wind, tides, oceans and nuclear fusion. It is expected that during the next century these sources will provide a colossal amount of energy in the form of heat and electricity in remote locations. For example, an ocean thermal energy conversion system(OTEC) will provide power in 10^{12-13}watts range, thousands of kilometres away from continents and major islands. An 'Energy Vector' is needed to carry this massive amount of energy to our factories, our offices, homes, planes, trains and automobiles. Hydrogen has been recognised as the sole candidate for this purpose mainly due to its clean combustion characteristics and large energy density. The applications that have been envisaged can be summarised as:

(a) Large scale storage and transportation of primary energy
(b) Space propulsion
(c) Automobile fuel
(d) Aircraft fuel
(e) Electrical cryomachines
    (i) Non-superconducting, (ii) superconducting (?)
(f) Nuclear engineering
    (i) Bubble chambers, (ii) Heavy hydrogen

There are several forms in which hydrogen can be conveniently stored and transported, such as:

- High pressure gas,
- Hydrogen rich chemicals,
- Metallic hydrides and
- Cryogenic liquid.

Later in this section we shall discuss in detail the suitability of the above options for specific applications. Some general characeristics of the above four forms of hydrogen are given here.

Engineers have very long experience with high pressure gas which can be adapted for use in new applications with the least development effort. But the weight and cost of the heavy high pressure cylinders is usually prohibitive for most applications. The use of stronger materials such as cryoformed stainless or maraging steels, titanium or composite materials containing glass, boron or carbon filaments may result in reduction in weight by as much as a factor of five. The required weight and cost of material will still be prohibitive. Even if the weight of these tanks could be reduced further, high pressure cylinders will still be unsuitable for many mobile applications because of the hazard associated with a sudden collision of sufficient magnitude to rupture the high pressure tanks.

Hydrogen rich chemicals such as ammonia (NH_3), hydrazine (N_2H_4), methanol (CH_3OH), gasolene (C_8H_{18}) offer promise of low pressure, room temperature storage and transportation of hydrogen. The chemical can either be consumed in its original form or be cracked to give hydrogen at the user site. The former technique can be used for methanol and gasolene, whereas the latter is more relevant to ammonia. Williams (1973) has given a comparative performance for six different fuels for the same heat load. Most of these synthetic fuels are advantageous from a volume standpoint whereas liquid hydrogen is by far the best on a weight basis. In future, in the absence of natural sources of fossil fuels these chemicals will have to be synthesized from hydrogen and will be more expensive than hydrogen itself. In addition, Ammonia and Hydrazine have serious problems of toxicity and the carbon containing fuels will present environmental problems which we are fighting today.

The technology of metallic hydrides for hydrogen storage has made significant progress in recent years. In particular, Ferrotitanium and $LaNi_5$ have been found quite suitable for storage and subsequent withdrawal of hydrogen at near ambient temperatures. Cheaper alternatives with high performance are under investigation in our country(Ramakrishna et al., 1987). Metallic hydrides, apart from the advantages cited above, offer large storage density, even higher than the liquid itself resulting in compact containers. They, however, suffer from a major drawback: the large deadweight of the metal that must be carried with hydrogen. The lowest ratio of metal to hydrogen capable of operations at ambient temperature and pressure, reported so far, is nearly 60.

Now let us take a close look at the merits and drawbacks of using a particular form of hydrogen in the applications envisaged earlier in this section.

(a) Large scale storage and transportation of primary energy from remote locations needs an energy vector that is light and easy to handle.

Because of the large deadweight of metal that must be carried, compressed gas and metallic hydrides are unsuitable for this purpose. Carbon containing chemicals such as methanol can largely be discounted, because a fossil fuel must be transported to the production site to provide the carbon atoms. Ammonia (NH_3) and liquid hydrogen are two serious contenders for this task. Because of high toxicity ammonia is probably a little less desirable form than liquid hydrogen.

(b) The cryogenic fuel combination, liquid hydrogen and liquid oxygen, has largely been responsible for success of the advanced space missions to the moon and beyond. It has been shown by Bass (1965), that for a fixed launch weight the total payload capacity of a rocket with LH_2-LOX upper stage is nearly twice as much as that with upper stage propelled by petroleum-LOX combination. This ratio increases to 3 for escape from earth's gravity and to higher values for more advanced missions. This advantage is due largely to the large specific impulses of the cryogenic propellant. The specific impulse for LH_2-LOX combination is 4335 Newton-sec/kg whereas that for petroleum-LOX is only 3335 Newton sec/kg. The low bulk specific gravity (0.35) of the LH_2-LOX system is a definite disadvantage that leads to higher tank volume and greater structural weight. This problem has been successfully tackled by using special high strength alloys. Fuel combinations using liquid fluorine have greater specific impulse combined with higher specific gravity. But fluorine, in addition to being expensive, is too corrosive to handle and undesirable to the environment and hence is unsuitable as a fuel.

(c) Even before the fossil fuel resources are over hydrogen is being considered as an alternative fuel for cars, trucks and buses to reduce the air pollution caused by the combustion of hydrocarbons. There is a rather extensive literature on the subject of hydrogen powered automobiles, particularly those employing liquid hydrogen (Cryogenics Research News, 1975; Furuhama et al., 1984; Peschka, 1984; Stewart, 1984; Williams, 1973). Several conventional automobiles have been successfully run on liquid hydrogen (Cryogenics Research News, 1975; Furuhama et al., 1984; Peschka, 1984; Stewart, 1984) with minor modification of fuel tank and carburettor. A comparative study of different fuel tank options (metallic hydrides, high pressure gas, hydrogen rich chemicals and cryogenic liquid) was made by Williams (1973) a decade ago. He examined the existing technology based on several criteria: (i) reasonable volume and weight, (ii) reasonable refuel time and (iii) safety, and concluded that "While much of the hydrogen will be handled in the gaseous form, the mobile sector of the economy and bulk storage will require the use of cryogenic liquid hydrogen."

The technology of metallic hydrides has progressed a lot since the days of Williams, particularly that of Ferrotitanium and $LaNi_5$. Still, because of a large deadweight of the metal to be carried, hydrides can compete with the cryogenic liquid only for those vehicles which are limited to intracity transport.

The biggest hurdle for the liquid hydrogen powered automobile, however, are (i) public acceptance of a new fuel that has a reputation of being explosive, and (ii)the creation of a massive network for production and handling of liquid hydrogen.

(d) The utilisation of liquid hydrogen as an aircraft fuel has been discussed in a recent paper by Brewer (1983) vis-a-vis conventional petroleum based fuels, Jet - A and JP-4. Contrary to popular belief, liquid hydrogen has been found to be a much safer fuel than other alternatives. This is primarily because the high volatility and rapid diffusion of hydrogen creates a fire that is very shortlived unlike that due to other fuels. The fireball extinguishes itself before the fuselage melts. In addition, hydrogen as a fuel has the advantages of global availability, clean combustion and reduced noise. The other forms of hydrogen such as compressed gas and metal hydride can easily be discounted because of the large weight penalty associated with their use. The present higher cost of hydrogen fuel and the lack of a global network for production and distribution of liquid hydrogen are expected to be overcome by the turn of the century.

(e) A nonfuel application of liquid hydrogen has been described by Burnier and de la Harpe (1965). The authors observe that (i) high purity aluminium (about 10 ppm impurity) has very low resistivity at about 20K with low magnetoresistance, (ii) it is easy to be manufactured and to use, (iii) the performance of hydrogen refrigerating cycles is high using relatively simple systems, and (iv) liquid hydrogen is an excellent dielectric and a reasonable heat conductor. A composite loss parameter incorporating the energy lost by Ohmic heating and the energy needed for refrigeration has a minimum value at 20K, the temperature of liquid hydrogen. Electrical generators and transformers made of high purity aluminium conductors promise better utilisation of available energy.

(f) Liquid hydrogen has long been used in nuclear research for (i) bubble chambers and (ii) production of heavy hydrogen (deuterium) by distillation. In our country deuterium is produced by this technique at Nangal Fertilisers. There are only few plants in the world that use this technique for production of deuterium.

3. HOW HYDROGEN IS LIQUEFIED?

The techniques of attaining very low temperatures are well established and are treated in many standard texts (Arkharov et al., 1981; Barron, 1966). These techniques can broadly be divided into four classes:

- Isenthalpic expansion,
- Isentropic expansion,
- Regenerative cycles and
- Magnetic cooling.

It will be naive to attempt even rudimentary descriptions of all these processes within the limited scope of this paper. Only in order to explain the basis of a cryogenic refrigeration/liquefaction process the following example is given.

Figure 1 gives the flow chart and temperature entropy diagram for a hydrogen liquefier based on the Linde cycle. Hydrogen gas at ambient conditions (state 1) is compressed isothermally to pressure p_2. After passing through a heat exchanger to recover the cold content of the low pressure return stream and that of the nitrogen vapour it is cooled to the temperature of liquid nitrogen in a nitrogen bath. The high pressure

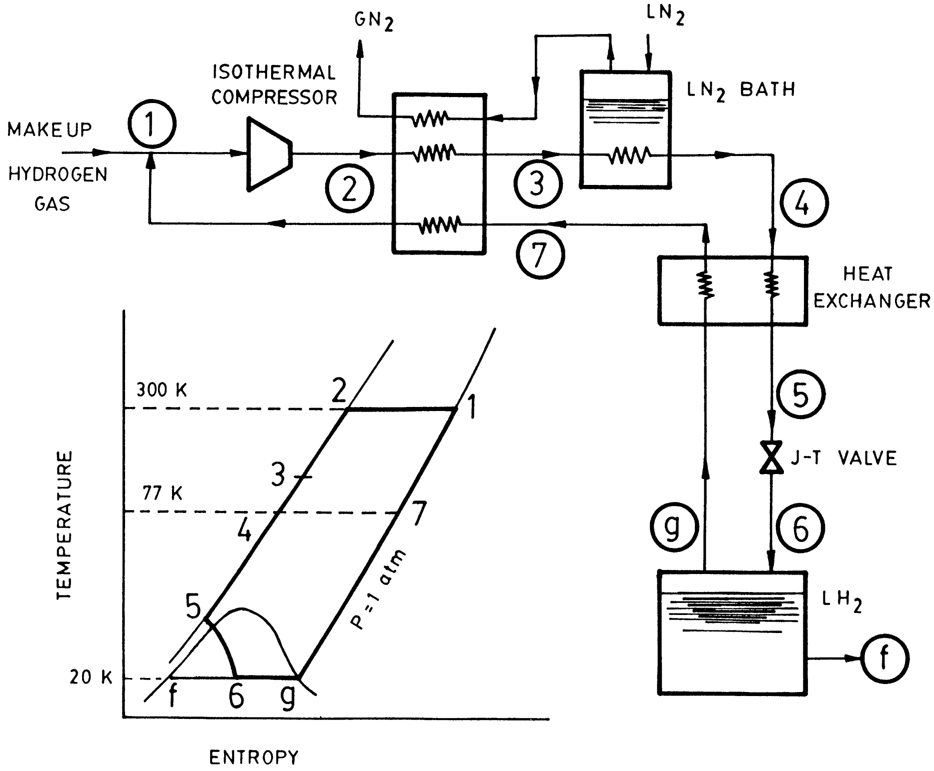

Figure 1. Liquid nitrogen precooled Linde Hampson system for liquid hydrogen.

stream, now at temperature of liquid nitrogen and pressure p_2 (state 4) is cooled further by the low pressure return stream (state 5) and expanded isenthalpically through a narrow constriction (state 6). State 6 is a combination of liquid and vapour. The liquid is collected as product and the vapour constitutes the low pressure return stream. Makeup hydrogen gas equal in mass to the liquid withdrawn is added in state 1. This system is simple and has no low temperature moving parts, but it does need a rather high operating pressure and liquid nitrogen precooling. Both these constraints can be dispensed with by using an expander in conjunction with J-T valve and heat exchangers.

Several regenerative cycles such as Stirling and Gifford-McMahaon have been used for attaining low temperatures. These are suitable for production of liquid hydrogen in small quantities. Detailed description of these devices is given by Walker (1983).

Adiabatic demagnetisation of paramagnetic salts has shown remarkable success in achieving temperature below 1 Kelvin. On the other hand its applications to higher temperatures was hampered by the predominance of lattice entropy over magnetic entropy. However, recently new high field superconducting magnets and Gadolinium based ferromagnetic materials offer the promise of high efficiency magnetic refrigeration in the 77-20 K temperature range (Barclay, 1981).

3.1. Ortho-Para Conversion in Hydrogen

Hydrogen can exist in two distinct molecular states: the Ortho state in which the nuclear spins of the two atoms are parallel ($S = 1$) and the para state in which the nuclear spins of the two atoms are opposed ($S = 0$). When wave-mechanical symmetry requirement is applied to the total wave function of the molecule (ground electronic and vibrational states assumed) it is found that only the even rotational states $j = 0, 2, 4, ...$ are accessible to the para molecules and only the odd rotational states $j = 1, 3, 5, ...$ are accessible to the ortho molecules. The transition ortho-para and vice versa has a very low probability except in the presence of certain paramagnetic catalysts. At ordinary temperatures all the rotational states are populated according to Maxwell-Boltzmann statistics and the ortho to para ratio is equal to the ratio of their degeneracies ($2S+1$) i.e. 3:1. As the temperature is lowered the ortho molecules (75%) condense to the $j = 1$ state whereas the para molecules (25%) condense to the $j = 0$ state. On the other hand, the equilibrium concentration at 20 K for ortho states (odd j) should be 0.21% and that of para states (even j) 99.79%. This transition normally takes a few days to complete but can be accelerated by catalysts such as hydrous Ferric Oxide, which is normally incorporated in liquefaction systems.

3.2. Energy Requirement for Liquefaction of Hydrogen

Work must be expended in cooling the hydrogen from ambient (gaseous, normal) state to a state of liquid parahydrogen at 20 K. The following enthalpy values (at $p = 1$ atm) have been taken from McCarty (1975). It may be noted that being read from figures the accuracy of these numbers is not very high.

h (20K, para, liquid) = -255 kJ/kg
h (77K, normal) = 1310 kJ/kg
h (300K, normal) = 4220 kJ/kg

By assuming that the refrigeration load in the temperature range T = 300-77K is provided at 77K and that for T = 77 to 20K with the latent heat of evaporation and ortho-para conversion is provided at 20K, we compute the energy input to a Carnot refrigerator to produce one kg of liquid hydrogen.

$$W = (1310 + 255) \times 280/20 + (4220-1310) \times 223/77 = 30{,}400 \text{ kJ/kg}.$$

If a real refrigerator operates at (say) 20 percent of Carnot efficiency the energy needed is 152,000 kJ/kg = 42.25 kWh/kg, which may also be written as 3 kWh/litre of liquid hydrogen. This expenditure of high level energy, though not trivial, is acceptable as necessary cost of storage and transport of energy.

4. HOW HYDROGEN IS STORED?

Thermophysical properties which have to be considered in designing of cryogenic storage vessels are the density, latent heat of vaporisation and specific heat of the liquid. Considering the comparative data on these properties (Table I) for several cryogenic liquids some interesting points emerge.

The normal boiling point of liquid hydrogen is very low - lower than any other liquid except liquid helium.

Although the latent heat of vaporisation in kJ/kg is high, because of its low density (even lower than that of liquid helium), the latent heat in kJ/m^3 is very small.

If the total heat, i.e. the latent and sensible heats taken together required to boil the liquid and bring it up to normal atmospheric temperature is considered, liquid hydrogen shows more favourable values. Thus if a way can be found to utilise the sensible heat in the insulation of the vessel its performance may be greatly improved. If the vessel is not connected to a reliquefaction system, it will also be worthwhile to attach a para-ortho converter at the warm end to utilise the refrigeration associated with this process.

Because of the peculiarities in physical properties of hydrogen conventional double walled containers insulated by (i) powder insulation or (ii) hard vacuum are inadequate for the storage of liquid hydrogen, excepting in very large scale applications. For liquid hydrogen and helium high efficiency insulation and special techniques must be employed. Broadly speaking, LH_2 containers are of three main types:

(a) Double jacketted vessels containing liquid nitrogen in the outer jacket,
(b) 'Superinsulated' vessels containing either a reflecting powder or the multi layer type insulation together with a hard vacuum in the interspace, and
(c) Vessels using 'gas-cooled' shields in addition to superinsulation.

In addition, extreme care must be taken to minimise the heat leak by conduction down the neck and through structural support.

The salient features of liquid hydrogen containers are discussed below:

(a) A typical double jacketted vessel consists of an inner vessel containing liquid nitrogen and surrounded by a vacuum jacket. This, in turn, is surrounded by a jacket of liquid nitrogen and finally an outer vacuum space. The inner vessels are suspended by thin walled stainless steel tubes (stainless steel is chosen for its low thermal conductivity) from the top flange, which in turn is welded to the outermost vessel. Snubbers are provided to limit the lateral movement of inner vessel during transit. Heat inleak in these vessels by conduction and convection is quite low due to the use of thin walled stainless stell necks and insulating supports. It is only to reduce radiative heat transfer that a liquid nitrogen jacket is provided. Considering that radiative heat transfer is proportional to $(T_{hot}{}^4 - T_{cold}{}^4)$ liquid nitrogen intercepts more than 99.5% of the radiation coming from the outermost vessel. Liquid nitrogen, which is considerably cheaper than LH_2 in energy terms substitutes the latter in absorbing the heat inleak.

(b) The double jacketted vessel requires a continual supply of liquid nitrogen in addition to being heavy and bulky. Its use has largely been discontinued after high performance insulations came to the market.

Opacified powder insulation in conjunction with vacuum serves well in vessels of moderately large size. Exfoliated perlite (a mineral) powder with a few percent of aluminium flakes and vacuum of the order of 10^{-3} torr has a conductivity below 10^{-3} W/mK. Usual care must be taken in filling the evacuation of the vessels.

Multilayer insulation, which has become the most common method for smaller vessels, consists of a few layers of aluminium coated (400Å thick) mylar films interposed between the inner and outer vessels. Its theory is based on the principle that radiative heat transfer between two surfaces is reduced by a factor of $1/(n+1)$ if n reflecting surfaces are interposed between them. By maintaining vacuum better than 10^{-4} torr an average thermal conductivity less than 10^{-4} W/mK has been achieved.

(c) Simple multilayer insulation shows excellent performance in medium sized vessels. However, this is not true for smaller vessels with an adverse surface/volume ratio. It is here that the sensible heat of the boiloff gas is used to cool two or three radiation shields interposed between the inner and outer vessels. The boiloff gas cools the radiation shields before leaving the vessel.

All three types of vessels have been discussed in detail by Barron (1966) and Kugler (1965). Several manufacturers all over the world supply containers ranging in size between a few litres and close to million litres. Although the largest containers are fabricated in situ for storage application, a large number of mobile vessels suitable for rail and road transport are made by mass production techniques. A few decades from now, when we do switch over to a hydrogen economy, the cryogenic industry will certainly be able to meet the challenge of providing production, storage and transportation equipment for liquid hydrogen.

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LIQUID HYDROGEN AS A FUEL FOR GROUND, AIR AND NAVAL VEHICLES

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1. INTRODUCTION

Today, with the advancement of technology, man consumes enormous amount of fossil fuels to meet his growing energy needs. Petro-chemical industries have become the economic base of our society and the limited fossil fuel resources are fast depleting. It is estimated that at a nominal growth rate of 4% per year, the oil and gas reserves will be depleted within 30 years. Also, the steep rise in the prices of petroleum based fuels, is a pointer towards the possible energy crisis in the near future. This triggered many countries to think seriously about an alternative fuel which is abundantly available, safe, pollution-free and cost effective. For some time, the quick solution seemed to be coal, natural gas and nuclear fuel. But one has to think in terms of sources which will not lead to environmental pollution and face eventual depletion. This has led to the developments in the field of 'Hydrogen Energy' which is renewable, non-polluting and has all the characteristics of a good fuel.

This paper reviews the recent developments in some of the advanced countries in the use of hydrogen as an effective fuel for road and rail transportation, as well as the studies pertaining to its use in aircrafts and ocean vessels. Also, the technology goals for Hydrogen storage systems as well as the unconventional methods for its production are briefly highlighted.

2. DEVELOPMENT HISTORY OF LIQUID HYDROGEN

Liquid hydrogen (LH_2) technology was first developed in other countries for their space programmes. Liquid oxygen (LOX) and liquid hydrogen combination in rocket engines yields about 50% higher specific impulse when compared with that of conventional rocket fuels of storable liquids or solid types. This could reduce the lift-off weight of the launch vehicle considerably, thus achieving simplicity and economy. Some of the space exploration programmes such as space shuttle or lunar missions could not have been possible without the use of LH_2 as the fuel.

R. P. Dahiya (ed.), Progress in Hydrogen Energy, 133–157.

In 1950s, only USA was concentrating on this technology, whereas today there are many countries actively working in this area.

In USA, after the successful development of RL-10 engine to power the Centaur stage, they developed J-2 engine, for the Apollo programme, both of which used liquid Oxygen-liquid Hydrogen (LOX-LH_2) propellant combination. The large scale production of liquid hydrogen was initiated for these projects. With the introduction of space shuttle, LH_2 is needed in larger quantities. Similar is the case in Europe. ESA, based on their success with the comparatively small cryogenic engine and stage (HM7/H8) used on Ariane-1 is planning to develop a large LOX-LH_2 engine (HM-60) for their new Ariane-5 satellite launch vehicle. The production of LH_2 in Europe will have to be increased manifold for this programme. In Japan, the development of their first cryogenic engine (10.5 Tonnes thrust) is in the final phase and plans are being finalised to go ahead with a 100-Tonne class LOX-LH_2 engine for their future high capacity satellite launch vehicle. This will, obviously, call for substantial augmentation of their LH_2 production. Thus it can be seen that the space programmes in these advanced countries have triggered the large scale production, handling, transportation and utilization of LH_2, leading to the establishment of the infrastructure and augmentation of the production of related materials, components and equipments. It is certain that India will not be an exception to this.

Encouraged by the performance of liquid hydrogen as a high energy rocket fuel, utilization of this as an alternative fuel for aircrafts, automobiles and other applications were conceived. In addition, importance of liquid hydrogen as an energy carrier in power transmission has been well understood in the context of harnessing energy from unconventional sources. The spectrum of LH_2 technology utilization, is given in Figure 1, which is based on the 'Report submitted by a subcommittee in 1982'. Although lot of work in this direction has been carried out in many countries, to make it cost effective or at least comparable with that of petroleum based fuels, extensive developmental efforts are needed.

The problems of liquid hydrogen are related to comparatively higher production cost, low boiling point, low bulk density, and the lack of incentives to switch over to a new system in view of the huge investments already made in the existing petroleum based plants. It is foreseen that with the development of new techniques for the production of hydrogen by unconventional methods as well as with the rising cost and dwindling stock of fossil fuels, hydrogen technology utilization will come into prominence by the turn of this century and that the new areas for using hydrogen as an alternative fuel will be well established.

3. WHY HYDROGEN?

The potentiality of Hydrogen as the fuel for future is well recognised today. The reasons that led to this finding and its advantages are summarised in Figure 2 (see Report submitted by a Sub-Committee in 1982). The limitations of hydrogen are with respect to its low density, critical insulation requirements, necessity to restrict the choice of materials to a few types in order to avoid the problem of ductile to brittle transition

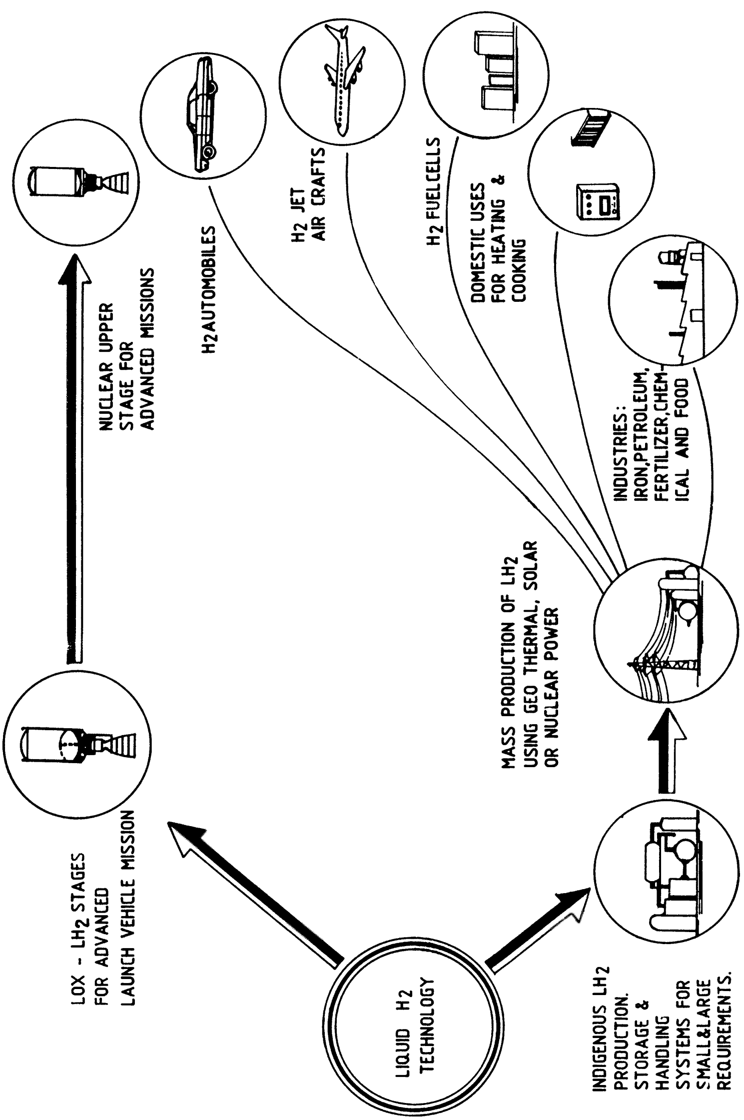

Figure 1. Liquid hydrogen technology utilization.

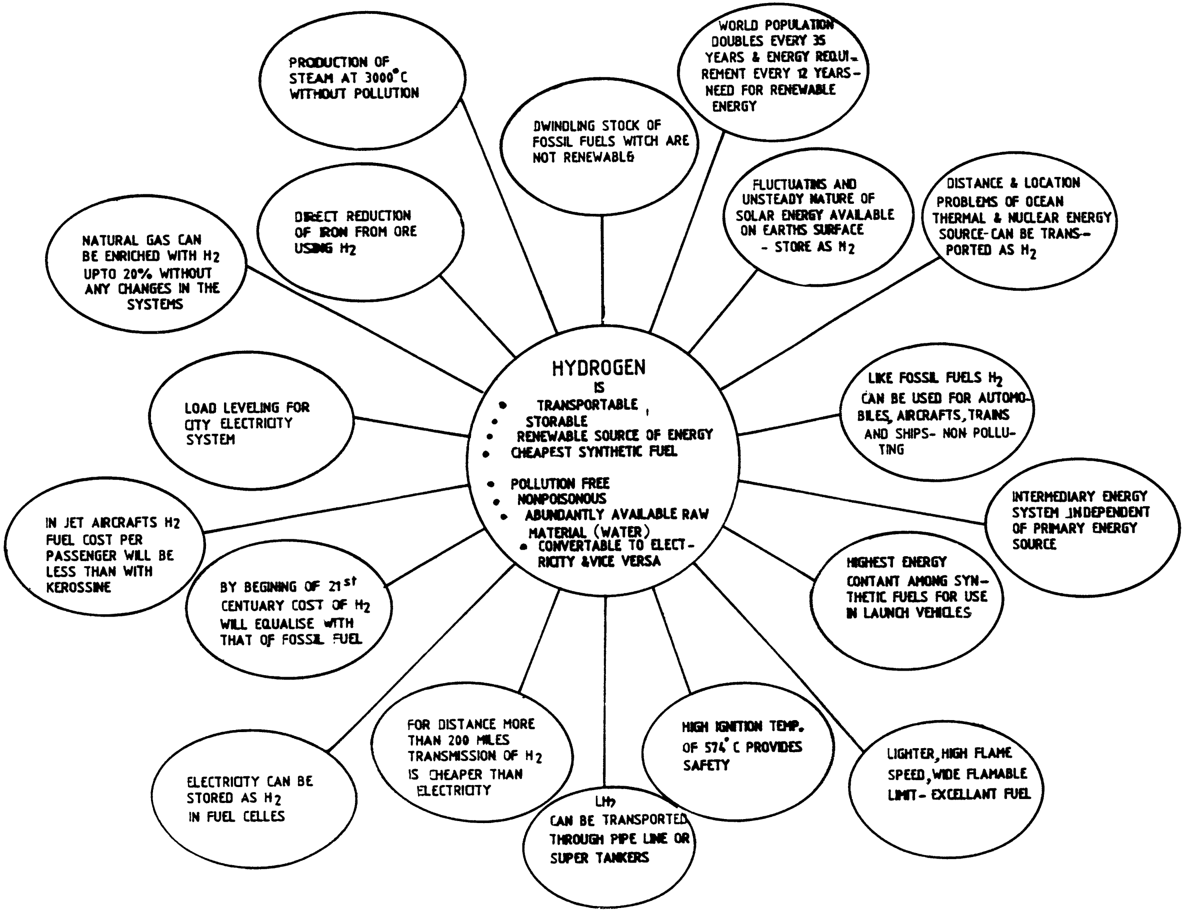

Figure 2. Why hydrogen?

and the precautions to be taken with regard to safety in handling and transportation of liquid hydrogen. The above drawbacks are easily shadowed because of its abundant availability, the renewable nature, non-polluting combustion products, etc. Hydrogen exists in two forms, viz. ortho hydrogen and para hydrogen; the equilibrium composition of these elements change with temperature. Results of the research carried out during the last 30 years or so have confidently established the means to convert hydrogen from its ortho to para form with the use of catalysts and, hence, it is no more considered as a problem. Number of agencies independently have taken up the studies relating to the safety of LH_2. It is conclusively proved that it is safer than liquefied-petroleum-gas and similar petroleum based fuels.

4. LIQUID HYDROGEN AS AN EXCELLENT FUEL - REVIEW OF RECENT STUDIES

The use of hydrogen as a fuel, stored in liquid, gaseous or metal hydride forms for the following systems, is being tried:

- as a vehicular fuel for passenger cars, buses, trucks and trains
- as a fuel for aircrafts (subsonic and supersonic)
- as a fuel for ships
- as a fuel for instant steam generation for running steam — turbines for power generation.

Details of these studies for the above applications are discussed below:

4.1. As a Vehicular Fuel

Efficient hydrogen fueled internal combustion engines need (i) achieving good internal fuel mixing using cryo fuel injection pump, (ii) selection of simple and cost effective insulation system for LH_2 storage and fuel pumping system, (iii) simple and cost effective on-board fuel storage system which can be in liquid, hydride or dual mode.

Hydrogen, because of its excellent characteristics, could become the fuel for future automobiles, if (i) an incentive is given to change over to the new system, (ii) a source is established that can produce cheap hydrogen from water, (iii) an efficient engine is developed that can run on hydrogen. Realising the potentiality, countries like USA, West Germany, Japan, etc. have conducted extensive studies in this regard. Some of the specific studies conducted elsewhere (see Report submitted by a Sub-Committee in 1982) are:

- In USA, a 1960 model Ford-F250 pick-up truck having 6 cylinders was converted to run on hydrogen. On trial runs, 70 Kms/Kg of hydrogen was achieved.

- Billing Energy Corporation, USA, operated a 1973 model Cheverlot engine with hydride storage system, 8 Kg of hydrogen was stored in a horizontal tank. The boil-off loss was 4.9% per day with a lock-up pressure for 44 hours. Fuel consumption reported is 35 Kms/Kg for city driving which was 86% increase when compared with gasoline fuelled engine.

- Musashi Institute of Technology, Japan has conducted studies using DATSUN B210 car. The LH_2 tank of 240 litres capacity had a boil off loss of 2.5% per day. The vehicle successfully completed 2800 Kms drive without maintenance.

The performance studies on the modified two stroke direct injection engines using LH_2 pumps has established the practical feasibility. The important results of the tests carried out were (1) the engine output increased with the increase in compression ratio from 6.9 to 8.0 by injecting cold hydrogen from LH_2 tank, (2) under the above conditions, the combustion oscillations were minimum and NO_x emission was found to be reduced (Foruhama and Kobayashi, 1982).

Also, Suzuki Motor Company developed a liquid hydrogen fuelled mini car as a test vehicle. The original engine had 61 mm bore, 61.5 mm stroke, 3 cylinders with a total volume of 539 cm^3 and a hemispherical combustion chamber having a maximum power output of 20.6 KW at 4500 rpm. This was modified as shown in Figure 3 (Foruhama and Kobayashi, 1982).

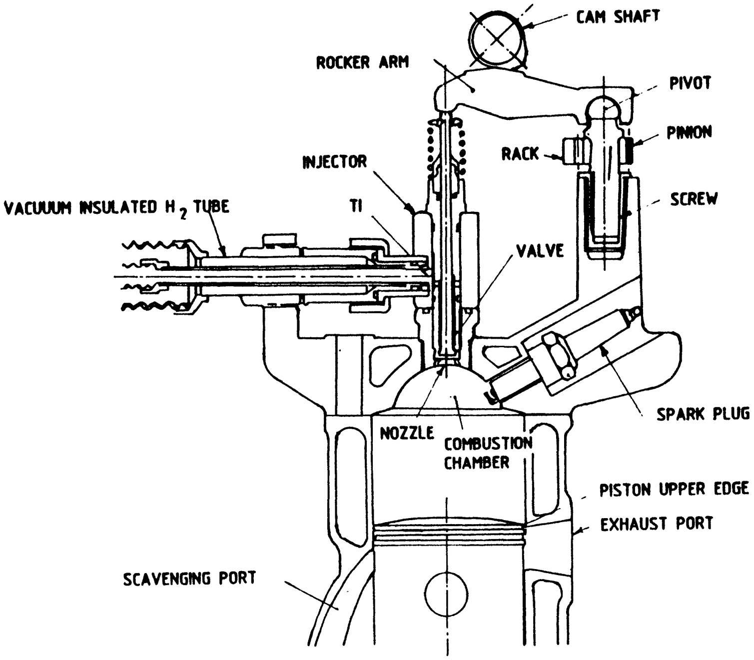

Figure 3. Structure of test engine
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The test layout is as shown in Figure 4. The injector is installed at the centre of the cylinder head. The injection started immediately after the closure of exhaust port with the upper edge of the upgoing piston. The pressure was kept at 1 MPa. During the test, the effect of air throttling on brake thermal efficiency for constant speed and load were studied. The results showed that the thermal efficiency reduced for rich mixture ratios. Also on the lean mixture side due to cycle to cycle

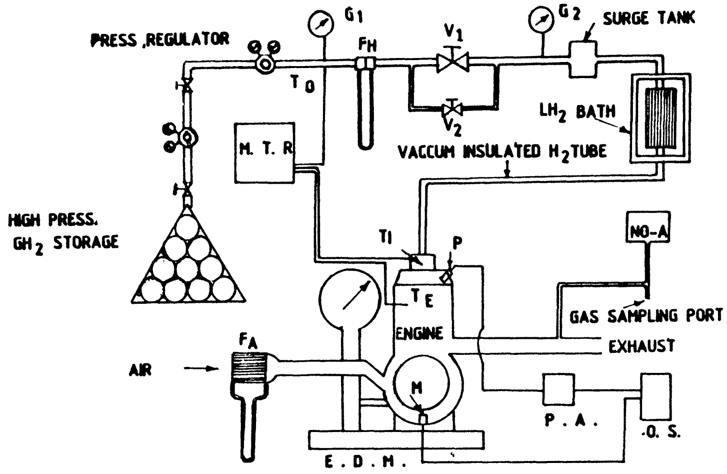

Figure 4. Experimental set up.
G_1, Pressure Gauge before orifice; G_2, H_2, Injection Pressure Gauge; T_o, H_2, Temperature before orifice; T_i, H_2, Temperature before injector; T_e, Engine Wall Temperatures, M.T.R., Multi Temperature Recorder; F_h, H_2, Orifice Flow Meter; F_a, Air Laminar Flow Meter; P, Piezo Pressure Indicator; P.A., Piezo Amplifier; O.S., Oscilloscope; M, Time Mark; E.D.M., Engine Dynamometer; V_1, Stop Valve; V_2, H_2, Flow Minute Control Valve; NO-A, NO_x Analyser.
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variation the effect of air throttling on thermal efficiency was comparatively more pronounced than that for rich mixture ratio. Figure 5 shows the results. It was also found that with use of cold H_2, NO_x emission was reduced substantially for $\lambda a = 1.5$ or less, as the air was throttled at low loads. It controlled the pre-ignition also. Figure 6 shows the comparison of NO_x emission of LH_2 engine with other engines. It was found unexpectedly that the best way to inject fuel was in a conical shape between the valve and the seat by cutting off the areas of the holes as indicated in Figure 7. The effect of the jet pattern on the performance was greater at higher loads and about 23% increase of power was achieved. Figure 8 shows the engine performance map of a cold hydrogen injection engine and original gasoline engine.

The liquid hydrogen pump is inserted in a separate heat insulated chamber connected to the tank. The pump is designed with 2500 rpm and specially manufactured with low clearance to minimize leakage. Figure 9 shows the construction of LH_2 pump. With the aid of heat exchanger, the GH_2 stored in the reservoir is injected at an optimum value of $-30^{\circ}C$. The above mentioned engine and fuel systems were installed in a mini car as shown in Figures 10 and 10(a).

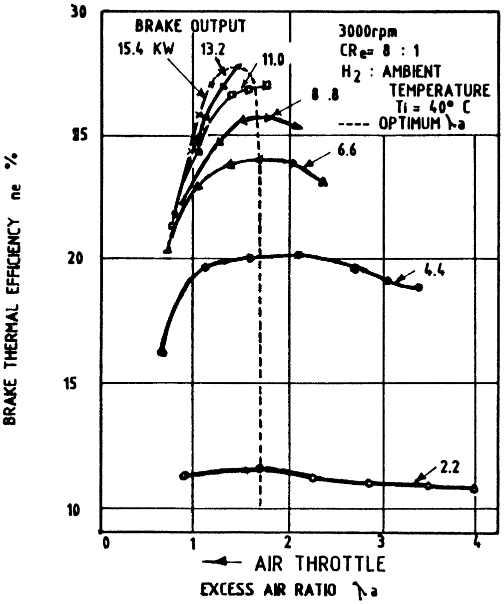

Fig.5. Effect of air throttle at constant brake output on Ne vs λ_a curves.

CR_e, Effective compression ratio $= \dfrac{\text{Cylinder volume above exhaust port}}{\text{Clearance volume}}$

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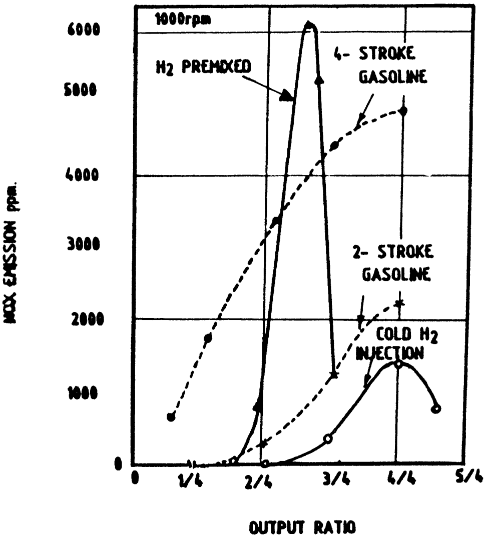

Fig.6. Comparison of NO_x emission with other type engines.
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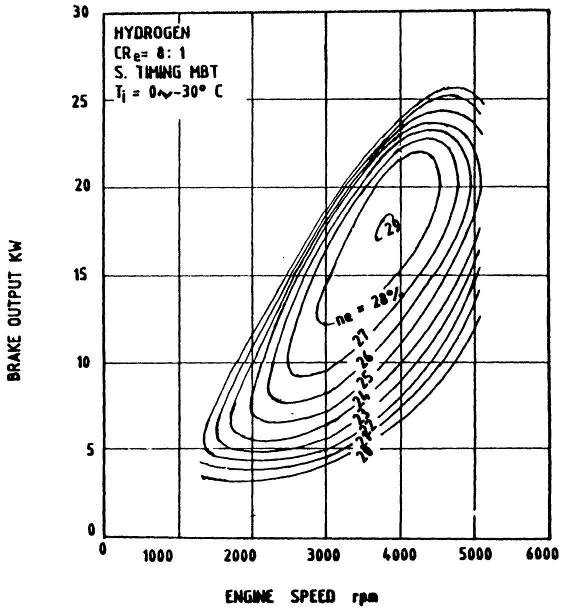

Figure 7. Engine performance map under the high CR_e, cold GH_2 injection two-stroke engine.
(Reprinted with permission, Int. J. Hydrogen Energy, 7, 815, 1982)

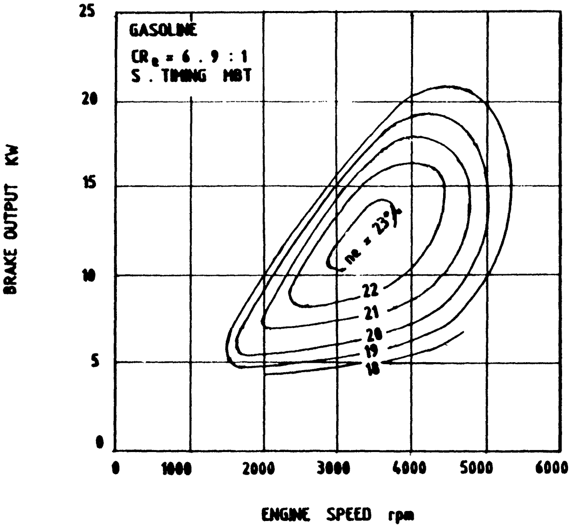

Figure 8. Engine performance map of original two-stroke gasoline engine.
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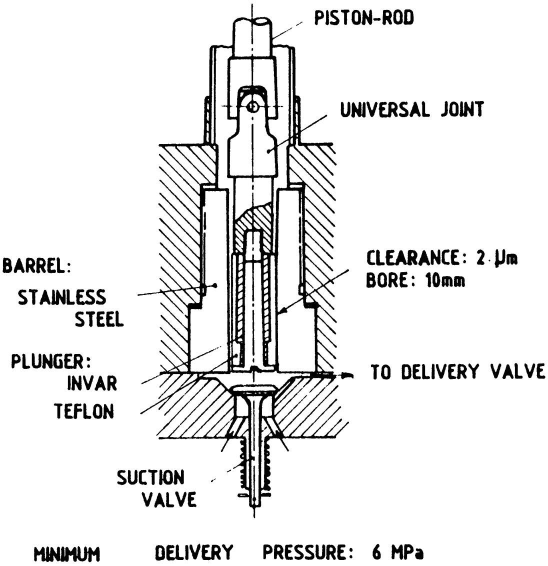

Figure 9. Construction of high pressure LH_2-pump
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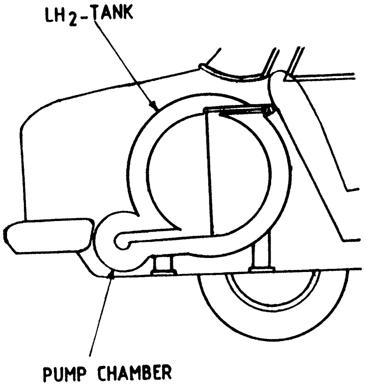

Figure 10. 80 l, cylindrical LH_2-tank installed in car

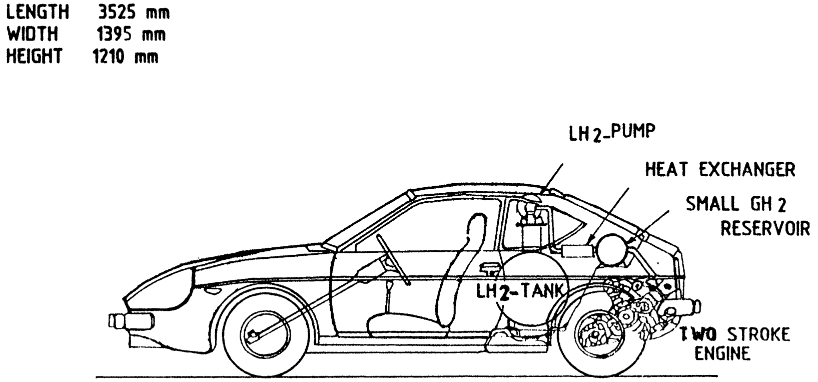

Figure 10(a). The LH$_2$-car Musashi III converted from Suzuki-Cervo. (Reprinted with permission, Int. J. Hydrogen Energy, 7, 818, 1982)

4.1.1. Rail Transportation: In recent years, high speed surface transit systems have been developed in many countries. In Japan, superconducting magnetically levitated high speed train is under development. For this, two different electric propulsion systems are under investigation. One of them is the linear synchronous motor (LSM) and the other one is the linear induction motor (LIM). The former has to be provided with a huge electric power system on ground. On the other hand the latter requires a light weight electric power source on board. And as a light-weight prime mover, a gas turbine engine fuelled by LH$_2$ can be used. Hydrogen has a very high energy density and it produces no harmful exhaust products. Moreover, latent heat of LH$_2$ can be utilized for liquid helium refrigerator. Japan National Highways made a conceptual design of hydrogen fuelled magnetically levitated superconducting train (HMST).

The fundamental configuration of the HMST is given in Figure 11 (Ishigohka). As can be seen from the figure, the propulsion system is composed of four main parts, viz. the cryogenic liquid hydrogen tank, the gas turbine, the super-conducting AC generator, and the linear induction motor.

The use of on-board power source is preferred due to its efficiency when compared with the huge ground-based power supply system. The light weight on-board power source with a gas turbine engine and superconducting AC generator ensured high reliability. High power, light weight gas turbine engines are widely used in the aeronautical field as turboprop engines. On the other hand, for high power, light weight generator, a superconducting generator would be the only possible selection. The refrigeration power necessary for the HMST is determined by the evaporation rate of liquid helium in the superconducting generators. The latent heat of LH$_2$ is utilised for the refrigeration of liquid helium.

To supply the required power of 130 MW, four gas turbine engines were used, with each gas turbines producing 32.5 MW and the gas turbines

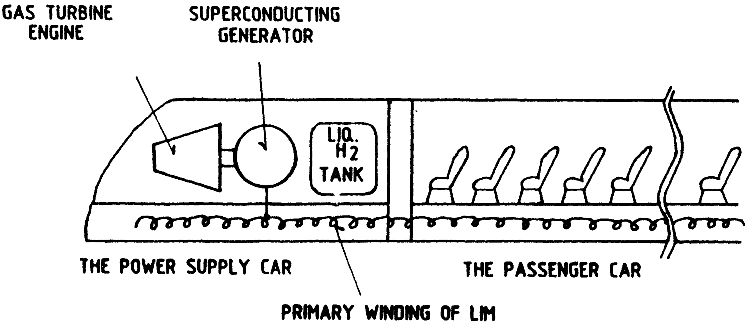

Figure 11. Fundamental configuration of the HMST.

placed in parallel with each other. The size of the LH_2 tank is considerably large because of its low specific weight. For 10 Tonnes of LH_2 the tank volume was 140 m^3. The configuration of the power supply car is shown in Figure 12. The overall efficiency of the HMST came nearly 25.4% (Ishigohka). To sum up, as a future efficient high speed surface transit system, the hydrogen fuelled magnetically levitated superconducting train (HMST) would be the most attractive and the economical choice, provided further developmental work improves the overall efficiency of the system to bring it at par with the existing systems and also provided the cost of liquid hydrogen is brought down.

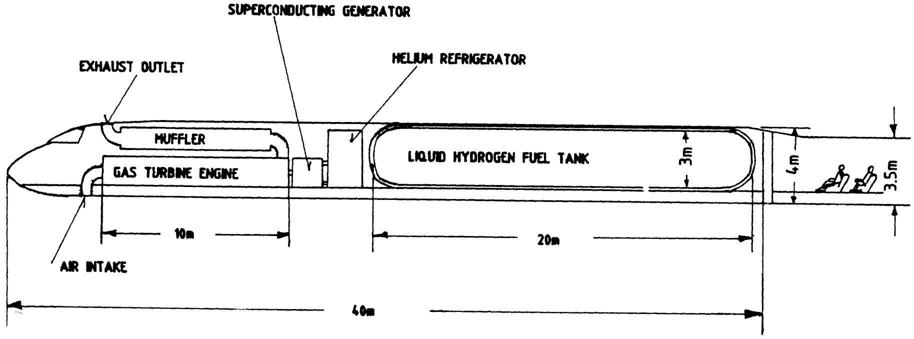

Figure 12. Configuration of the power supply car.

4.2. Liquid Hydrogen as a Fuel for Aircrafts

Choice of fuel for air transportation is an important matter, because it is an energy intensive form of transport. Price and energy density of the selected fuel are therefore equally important. Advanced versions of commercial transport aircrafts, which may begin service in the 1990s, may well be fuelled with LH_2. Conventional petroleum-based jet fuel is predicted to become economically unattractive by the turn of the century due to its higher price as the world's crude oil is being consumed continuously. Airlines are completely dependent upon the availability of ample quantities of a high quality fuel at an economically acceptable price wherever they fly. International operations demand worldwide availability of the fuel. Even at today's prices, fuel for U.S. domestic air carriers accounts for 40% of the direct operating cost.

For any major industry switching over to a new fuel will be traumatic and costly experience. It will be particularly so with commercial avaiation because the requirements for fuel for airlines throughout the world must be coordinated. The choice of a new fuel should be made in full recognition of all the economic, sociological and technological ramifications which will be involved in a change over. Selection of the alternative fuel must be done carefully taking into account the following factors:

- The preferred fuel for avaiation should be selected on the basis of overall system cost, energy, performance, emissions, noise, long term availability.
- The transition to a new fuel should be capable of being implemented without serious disruption of existing commercial airline service or undue financial burden on the airlines.
- The cost of providing handling facilities may be large and good planning is a must for its realisation.
- International coordination (technical, financial and political) will be essential to ensure a smooth transition.

There are three candidate fuels which can be seriously considered as an alternative for the future transport aircrafts, viz. liquid hydrogen, synthetic jet fuel and liquid methane.

Jet-A is the currently used fuel in aircrafts which has heat of combustion of 42.76 KJ/g and specific heat of 1.97 J/g K. In contrast, LH_2 has the highest heat of combustion of 120 KJ/g and specific heat of 9.66 J/g K making it the best fuel with high energy content apart from its capability for use as a coolant (Brewer, 1978). Moreover, it is environmentally acceptable since the combustion products are free from carbon.

Figures 13 and 13(a) show the plan forms and profiles of the airplanes using syn jet fuel and liquid hydrogen (Brewer, 1978).

Although the fuselege of LH_2 airplanes is larger, compared to planes using syn jet fuels, the reduction in the wing area with these planes reduces the gross weight.

4.2.1. Subsonic Aircraft: Figure 14 shows the general arrangement drawing of an LH_2 fuelled aircraft with 400-passenger capacity, designed to cruise at Mach 0.85 with a range capability of 10,190 km. The performance estimation of the LH_2 fuelled subsonic aircraft with Jet-A fuelled one is given in Table I. It will be observed that there is little to distinguish this configuration from current, conventionally fuelled subsonic transport aircraft.

Internally the fuselage of a hydrogen fuelled aircraft may be arranged differently. Insulated tanks to contain liquid hydrogen fuel are placed at both forward and aft portions of the passenger compartment,

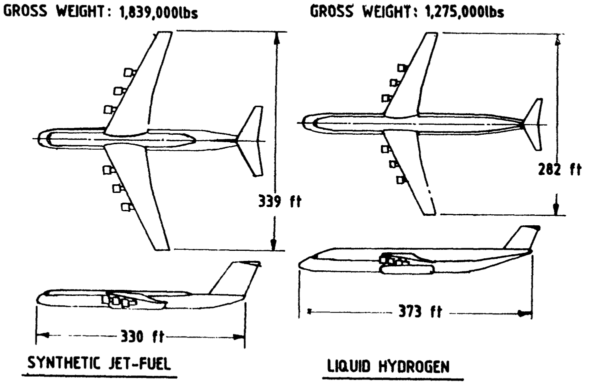

Figure 13. General arrangement of the alternative airplanes (Reprinted with permission, Int. J. Hydrogen Energy, 3, 451, 1978)

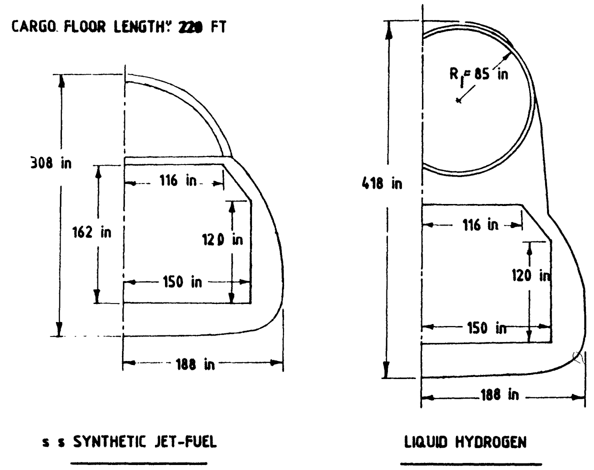

Figure 13(a). Fuselage cross-section of the alternative airplanes (Reprinted with permission, Int. J. Hydrogen Energy, 3, 451, 1978)

where they occupy the full circular cross section of the fuselage. The advantages with this arrangement are the minimization of surface to volume ratio of the container and reducing the potential heat leak into the fuel tanks. In addition, it provides for minimal shift of the aircraft centre of gravity as the load varies. In the case of LH_2 fuelled aircraft design discussed above, the weight, performance and cost advantages, far outweigh the operational inconvenience of non-access between passenger and flight crew cabins.

It is seen that LH_2 fuelled aircraft has advantage in many respects. It is lighter, uses smaller engines, has a smaller wing (but a longer fuselage) and can operate using short runways. It appears that cost of

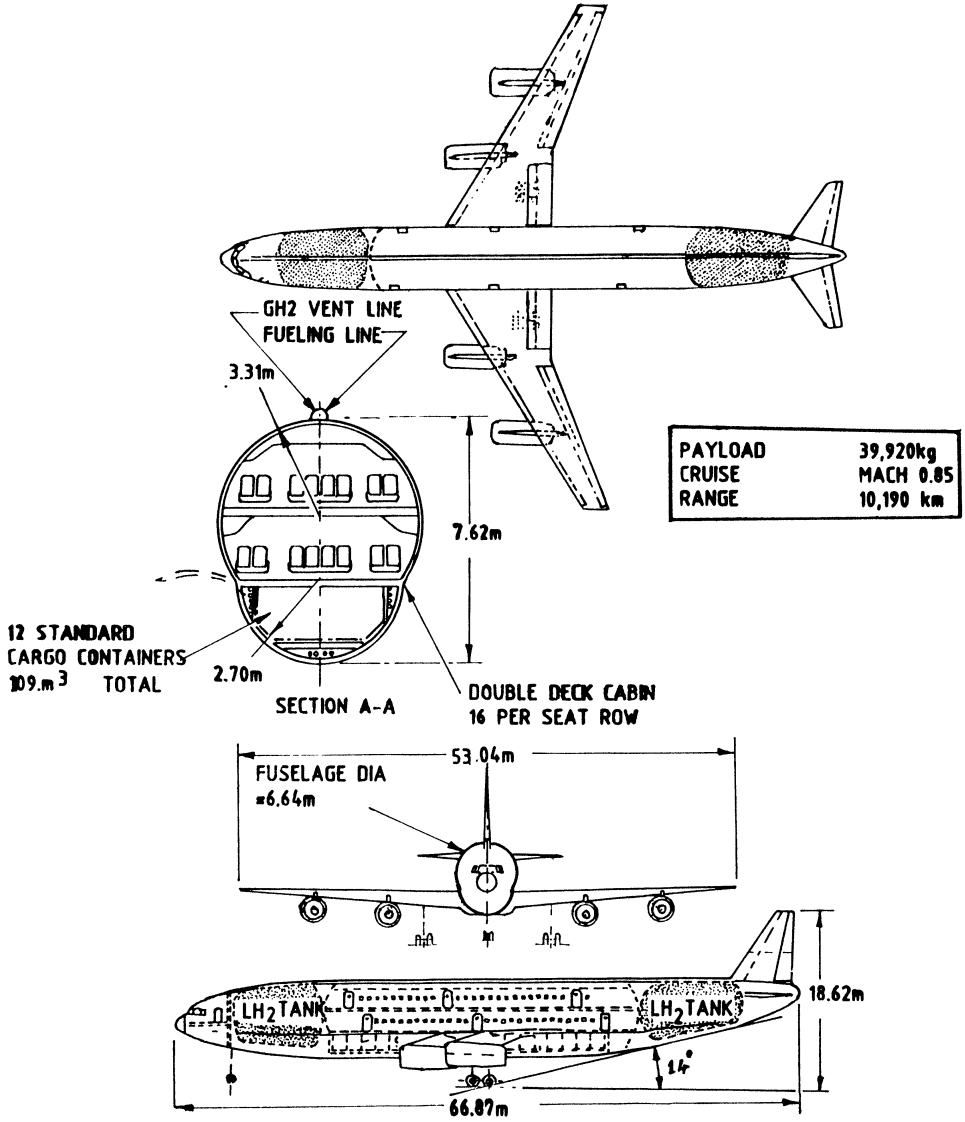

Figure 14. General arrangement - 400 passenger LH_2 fuelled subsonic transport.

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TABLE I* : Comparison of LH_2 and Jet A Transport Aircrafts
(Mach 0.85; 10,190 km; 400 passengers)

	LH_2	Jet A	Ratio (Jet A/LH_2)
Gross weight (kg)	177,800	237,200	1.34
Operating empty weight (kg)	110,000	110,800	1.01
Block fuel weight (kg)	24,000	75,000	3.13
Thrust per engine (N)	127,700	145,400	1.14
Wing area (m^2)	313	389	1.24
Span (m)	53	59.2	1.12
Fuselage length (m)	66.7	60	0.90
Field length required (m)	1,900	2,435	1.28
Lift/Drag (cruise)	16.07	17.91	1.12
Specific fuel consumption (cruise) (kg/hr/daN)	0.203	0.590	2.92
Aircraft price ($ 10^6)	26.9	26.5	0.99
Energy utilization (Kj/seat km)	1,550	1,735	1.12
Noise,sideline (EPNdB)	87.2	87.8	-
Flyover (EPNdB)	89.2	94.2	-

* Reprinted with permission, Int. J. Hydrogen Energy, 3, 222, 1978.

two LH_2 fuelled aircrafts could be almost same as that of a single Jet-A fuelled aircraft for the same capability. Moreover, LH_2 fuelled aircraft is quieter during take off by about 5dB.

The basic reason for the superiority of LH_2 fuelled aircraft design stems from the combination of two characteristics, viz, lift-to-drag ratio and specific fuel consumption (SFC) realised during cruise. The LH_2 airplane has a lower L/D because of the very low density of the fuel and also because of the volume of the insulation required for the fuel tanks to minimize loss of fuel through boil off. The fuselage must be made longer to contain the fuel and this results in higher drag. However, the disadvantage in L/D is more than overcome by the overwhelming advantage in SFC. The value of 2.92 in the 'ratio' column of Table I indicates that the engines in Jet-A fuelled aircrafts must consume nearly three times more fuel/hour to deliver a given level of thrust.

4.2.2. Supersonic Aircraft: Figure 15 gives a three view general arrangement drawing of an LH_2 fuelled Mach 2.7 SST capable of carrying 234 passengers with a range of 4200 nautical miles. Table II gives the comparison of LH_2 and Jet-A fuelled supersonic aircraft parameters (Brewer, 1978).

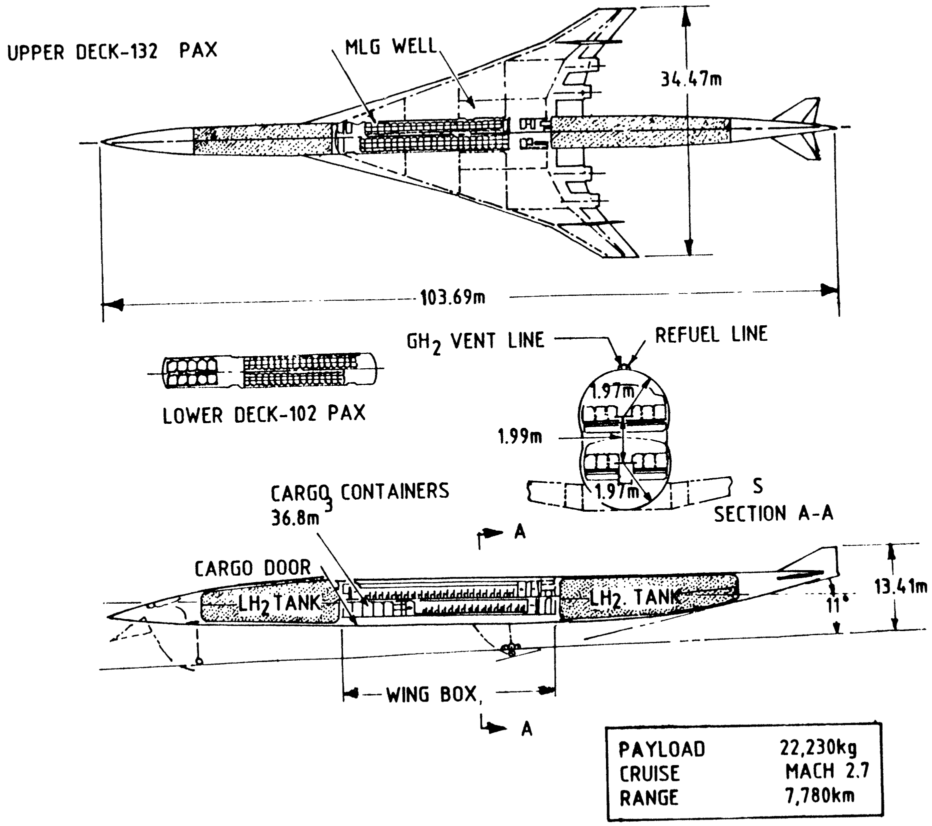

Figure 15. General arrangement, 'Mach 2.7 LH_2 fuelled' supersonic transport.
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It will be observed that the advantages shown for liquid hydrogen SST in Table II are greater, in nearly every instance than those for LH_2 subsonic aircrafts. This is attributable to the fact that supersonic mission involves use of more fuel than that of the subsonic designs.

Feasibility studies on the use of liquid hydrogen as an effective aircraft fuel were carried out mainly in USA by Boeing Company and the Lewis Research Centre. Conclusions of the finding of the former agency which has used a modified 747 aircraft was that the use of hydrogen can reduce the total gross weight by 25% for standard payload and range. This demonstrated the economic viability of LH_2 fuelled air transportation system in comparison with fossil or synthetic fuels. Lewis Research Centre, on the other hand, has successfully flight tested a modified B-57 aircraft in which only engines were converted to accept hydrogen as fuel. The LH_2 was pressurised by the helium and fed to engine through a heat

TABLE II* : Comparison of LH_2 and Jet A Supersonic Transport Aircraft (Mach 2.7, 7780 km, 234 passengers)

	LH_2	Jet A	Ratio (Jet A/LH_2)
Gross weight (kg)	179,130	345,720	1.93
Operating empty weight (kg)	111,240	143,980	1.29
Block fuel weight (kg)	38,735	149,960	3.88
Thrust per engine (N)	234,940	386,470	1.64
Wing area (m^2)	739	1,031	1.39
Span (m)	34.4	40.7	1.18
Fuselage length (m)	103.7	90.5	0.87
Field length required (m)	2,377	2,893	1.22
Lift/Drag (cruise)	7.42	8.65	1.17
Specific fuel consumption (cruise) (kg/ha/daN)	0.585	1.528	2.61
Aircraft price (\$ 10^6)	45.5	61.5	1.35
Energy utilization (kj/seat km)	2,551	3,522	1.38
Noise, sideline (EPNdB)	104.0	108.0	-
Flyover (EPNdB)	102.2	108.0	-
Sonic boom overpressure (N/m^2)	63.2	89.1	1.41

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exchanger. The specific fuel consumption achieved was about 1/3rd as compared to JP fuel. Also, the engine had very low emissions and no smoke which will result in significant savings on aircraft as well as airport maintenance cost. The NO_x pollution can be further reduced by injecting water at the exhaust.

From the studies and experiments conducted by other countries, it has been established beyond doubt that LH_2 can be the "fuel of tomorrow" for passenger and transport aircrafts. Design and production of such aircrafts in India may take many years. But in the international scene, LH_2 fuelled aircrafts will be in operation during the next decade. Therefore, the ground facilities for LH_2 fuelling, servicing, etc., will have to be developed in our country so that the international aircrafts can land and take off. This aspect needs immediate attention.

4.3. Liquid Hydrogen as a Fuel for Ships and Submersibles

At present ship propulsion depends mainly on oil and is shipped in large supertankers in increasing quantity. However, oil in sea environment has special problems caused by oil spills and offshore oil well leakage, resulting in pollution. It has an adverse effect on marine and coastal life forms and degrade the scenic areas in the coast. But liquid hydrogen will vaporize more or less instantaneously when it contacts the water. Thus it has no lasting impact.

In the case of submersible power applications the combustion of hydrogen-oxygen offers the following unique advantages:

- It provides a highly concentrated energy source.
- It is adaptable for powering a number of types of prime-movers.
- It produces only water exhaust thus obviating gaseous effluents.
- The water exhaust is compatible with the life-support and environmental control system.
- The ballast control for effecting depth settings is simplified by the retainment of water exhaust in the case of liquid hydrogen.

In addition to oil for ship propulsion, nuclear power plants have had widespread application. In the case of nuclear powered ships, hydrogen power system can be used to augment the basic propulsion capability for special high power mode operation while nuclear power source providing ordinary cruising speed capability. Hydrogen-oxygen prime movers as a supplement to nuclear power system would be relatively light weight and compact. Moreover, specialised applications such as those for vessels smaller than tanker class, capable of higher speeds, may profitably select hydrogen based gas turbines. By harnessing the unconventional energy sources such as solar power and ocean currents, the new methods of splitting abundantly available sea water for the production of hydrogen can be conventionally adopted. If the above concept is proved for shipping transportation the load carrying capacity will considerably increase, achieving substantial cost savings on the fuel.

5. STORAGE SYSTEM FOR AUTOMATIVE TRANSPORTATION

5.1. Vehicle Fuel Storage

Hydrogen can be stored on-board a vehicle as a compressed gas, as a cryogenic liquid or as a metal hydride. Though cryogenic liquid storage requires tanks of less weight and volume as compared to storage of hydrogen as a compressed gas, it involves handling the cryogenic fluid with the associated losses from boil off, chill down, flashing, etc. However, storage of hydrogen as a cryogenic liquid on-board was studied and it has been found that it is a practical alternative.

According to the test data given by Perris Smogless Automobile Association, a vehicle with a 20 gallon gasoline tank would require a 50 gallon capacity LH_2 Dewar for an equivalent driving range (Mathis, 1976). A 175 litres LH_2 Dewar with a 1.5% per day boil off rate and capable of withstanding high acceleration loads is available. It was found feasible that a rugged 189 litres capacity LH_2 Dewar could be built to withstand collisions. This would be approximately 61 cm outside diameter and 99 cm long and weighs about 181 kg. A 1.3 cm dia fill line and 5.1 cm dia vent line are adequate to fill the car dewar at a rate of 15 gallons of LH_2 per minute, with the refilling time of 3 minutes. The number of connections for refilling the dewar should be minimum and it should have a reliable QCDC type of fitting. During periods when the vehicle is not being operated, the boil off hydrogen could be utilized in numerous ways such as to power a fuel cell for battery recharging; to store energy in battery and to react in a catalytic burner to keep the engine and vehicle warm during cold weather. Extensive studies in DFVLR, Germany, on cryogenic hydrogen storage and refuelling system for automobiles were carried out. A number of configurations and flow diagrams for refuelling have been tried with a view to evolve a standard procedure for operations. The unit underwent extensive trials with liquid nitrogen using two tankers: one of stainless steel (120 Lit, 88 kgs), the other of aluminium (150 Lit, 43 kgs). The tanks had normal operating pressures of 1 to 3.5 bars. The pressure increase due to lack of high vacuum insulation was low (0.4 bars for LN_2 and 2.5 to 3.5 bars for LH_2). Therefore, in case of an accident, the pressure build-up due to loss of vacuum will not be alarming. Refuelling time was about 5 minutes for 120 to 150 Lit. capacity tanks. This is much less when compared with the hydride system and is very close to that for gasoline powered cars. The most important aspect of this exercise was to demonstrate a safe and simple refuelling procedure for LH_2 vehicles, even by untrained persons. A comparison of the weight and volume for the fuel and the tankage for different methods of hydrogen storage, is given in Table III (Mathis, 1976). Figure 16 shows the layout of the automobile dewar system.

TABLE III : Comparison of Fuel Storage System for a Vehicle Range of 420 km

		Gasoline	Cryogenic LH_2	Compressed CH_2	Metallic Hydride
Fuel	Weight (kg)	53.5	13.4	13.4	181
	Volume (m^3)	0.07	0.19	1.0	0.23
Tankage	Weight (kg)	13.6	181	1361	45.4
	Volume (m^3)	0.08	0.28	1.53	0.25
Total weight (kg)		67	195	1374	227

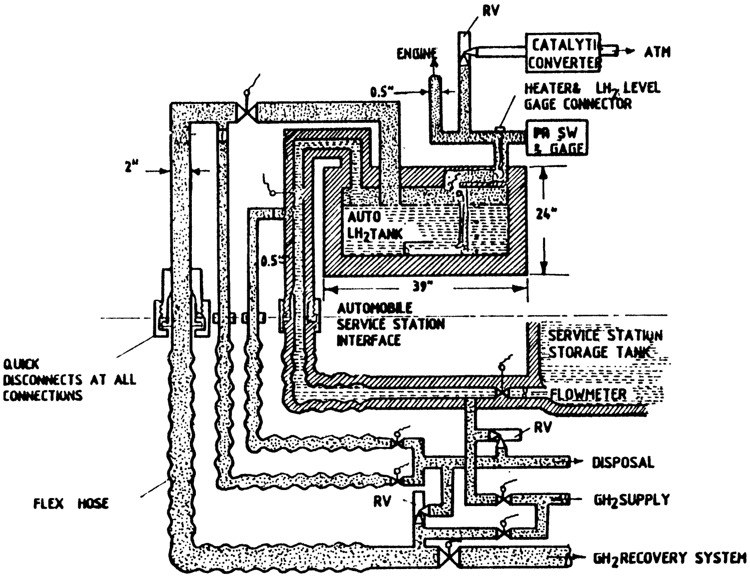

Figure 16. Automobile dewar system.

6. HYDROGEN GAS PRODUCTION AND UNCONVENTIONAL ENERGY SOURCES

Economic production of gaseous hydrogen in bulk quantity for making liquid hydrogen is another important area which needs attention. At present, bulk of world's hydrogen production is from steam reforming of naptha, natural gas and conventional water electrolysis process. For countries like India, coal gasification is an attractive option since it is dependent upon the locally available feed stock. Unconventional methods of hydrogen production concepts are in various stages of development in other countries. These techniques need concentrated development efforts to make hydrogen production inexpensive. These methods should not be too much dependent upon electrical power or petroleum based feed stock. With the perfection of such methods, the hydrogen technology utilisation can be speeded up.

In other countries, developmental efforts are concentrated mainly towards splitting of water to get gaseous hydrogen. The various approaches being adopted abroad are:

(a) Solid polymer electrolyte (SPE) process.
(b) Thermochemical and hybrid hydrogen production:
  - Metal oxide decomposition cycle,
  - Sulfuric acid metal sulphate cycle,
  - Metal halide - Hydrogen cycle.
(c) Photochemical method to split water.

A brief description of these processes is given below:

(a) Solid Polymer Electrolyte (SPE) process is derived from the conventional water electrolysis process. SPE is a solid plastic material which has ion exchange characteristics making it highly conductive to hydrogen ions. The catalyst is pressed on each face of the sheet to form anode and cathode. Efforts to develop more reliable polymer based electrolyte, are made by various agencies. For example, in France, Polyethelene based polymer electrolytic membranes for hydrogen production is being evaluated. By reinforcing with organic fibres, physical degradation is stopped and tested at 2 kA/m^2 current density for 3000 hrs. Studies conducted in Japan, on electro-catalyst and their plating to SPE, has resulted in reducing the resistance to catalyst/SPE interface. Thermal efficiency of the cell, thus achieved was 93-95%. Many institutions are working on the selection of various types of electrolytes for improving the performance and the major objectives are to reduce the electrical power inputs and to increase the operational life.

(b) Thermochemical and hybrid hydrogen production processes are based on three basic principles. All these processes assume the heat recovery for reaction systems from nuclear reactors through closed loop helium cycle. In general, all these reactions do not involve energy intake and liberation of oxygen from water via metal oxide is a highly endothermic process. Efforts are underway in search of metals which decompose water, liberating hydrogen and oxides. Oxides thus formed should be easily decomposible. For example, Cd and Cd-CO_3 cycle is being tried to split water and the reaction is carried out in vapour phase. Heat evolved during condensation of Cd from vapour to solid is utilised in decomposing Cd CO_3. This cycle operating at about 600°C has many advantages but the toxicity of Cd and CdO is the major disadvantage.

Sulfuric acid-metal sulfate cycle attempts the decomposition of H_2SO_4 to water and SO_2. The reaction at about 1500 K is highly endothermic. Reaction with calcium molybdate is tried. H_2 is evolved in the primary reaction of SO_2 and water vapour at 350 K. The cycle operates in 350 K and 1200 K temperature range (see Report submitted by a sub-committee in 1982). Lanthanum sulfate used as catalyst is found to improve the yield. In this cycle the major energy consuming step is the decomposition of H_2SO_4 and metal sulfate. Metal halides - halogen containing cycles are the other options being tried out. Use of halogens especially Br_2 and I_2 brings down the energy requirements for producing H_2 from water.

In USA, decomposition of HI thermally in the presence of Pt and Ru catalyst over TiO_2 are studied. The decomposition energy is reported to be around 12 kCal/mole. Major reactions being studied are MgO-I_2 system, Vicorglass membrane-HI, Metallic Ni as catalyst and H_2SO_4, and organic halide CH_3I systems. These schemes are at various stages of development in other countries.

(c) Efforts to split water to get H_2 and O_2 through photochemical methods are being made in Japan. In electrochemical photo cell, O_2 is liberated at the semiconductor both 'n' type (TiO_2, Sr TiO_3 etc.) and p-type and H_2 is liberated at the Pt electrode. Theoretical efficiency that can be achieved is 5%. It is reported that this efficiency itself is the break even point. Major efforts are being made in finding out the efficient semiconductors which can readily separate the photo-generated electron to cathode where H^+ ion gets converted into H_2. Fe_2O_3 coated silicon electrodes as anode and Pt as cathode were found to be efficient in absorbing solar energy.

In conclusion, it may be stated that the above methods can be perfected by various institutions, R&D laboratories and industries. Only if such low cost techniques are developed for the production of gaseous hydrogen, the liquid hydrogen technology utilisation can be speeded up. Perfecting SPEC process, recovery of H_2 from H_2S, and biological reactions are of prime importance because of their obvious advantages.

By the end of this decade, the availability of cheaper electrical power by harnessing solar, OTEC, tidal and geothermal power, is anticipated. This will help to make the electrolysis of water more attractive irrespective of the techniques used. Concentrated efforts in this direction are essential to produce gaseous hydrogen at acceptably low cost so that hydrogen energy concept and the related developments will gain momentum.

7. SAFETY ASPECTS OF LIQUID HYDROGEN

Very elaborate and indepth studies have been conducted by different agencies with regard to the safety aspects of liquid hydrogen. Usual objections for the use of hydrogen as a fuel are related to its wide flammability limits as well as its colourless and non-luminous flame. It is pointed out that hydrogen with 4% to 75% flammability limits, form a combustible mixture with air which can lead to explosive/fire hazards. Also the low ignition energy requirements (0.02 milli joules/mole) for hydrogen is quoted as a negative point from safety point of view. But studies have conclusively proved that hydrogen as a fuel is as safe as LPG or gasoline and in some respects, hydrogen is better. Federal regulations already exist for its bulk transportation and storage.

In case of LH_2 spillage or an accident (causing LH_2 to flow out into the atmosphere), sustained burning concentrated in one location will not take place because of the high diffusivity and low density of hydrogen gas. Liquid hydrogen, when released to atmosphere, rapidly evaporates, expanding in volume to about 850 times and rises fast and disappears from the spot of spillage or accident. From this point of view, LH_2 is much safer as compared to gasoline or Jet-A fuel. Thus from the safety point of view, liquid hydrogen in comparison with the conventional petroleum based fuels, has got certain merits, while its disadvantages are well understood today, so that by proper planning and by adopting proven procedures, absolute safety can be ensured. There is no doubt that the confidence level will improve further with more and more familiarisation with LH_2 fuelled transportation systems.

8. THE TECHNOLOGY STATUS IN INDIA

Gaseous hydrogen, of various purity levels, is produced in India mostly by steam reforming of Naptha and used in fertilizer and alkali plants. Today only National Fertilisers Limited, Nangal, produces LH_2 in India using an imported electrolysis plant for the production of heavy water. But experience for handling or transportation of liquid hydrogen does not exist, since LH_2 has never been taken out of the Heavy Water Plant at Nangal. However, many institutions and industries do have expertise to handle cryogenic fluids such as liquid helium, liquid oxygen, liquid nitrogen, etc. For the next few years, probably only Indian Space Research Organisation will need bulk quantities of liquid hydrogen for application in high performance Satellite Launch Vehicles.

9. ROLE OF INSTITUTIONS AND RESEARCH AND DEVELOPMENT LABORATORIES

Realisation of an integrated liquid hydrogen technology needs concentrated developmental efforts with respect to design and fabrication of equipments, development of compatible materials, low cost insulation and simple and safe storage systems. A collaborative scheme between educational institutions, R&D laboratories as well as public and private sector industries can yield good results in harnessing the available expertise for developing hydrogen technology indigenously.

Further, in the development of systems using hydrogen as a fuel for ground and air transportation as well as in realising domestic and industrial appliances using hydrogen in place of petroleum based fuels, these institutions and laboratories can contribute significantly.

10. CONCLUSIONS

The potentiality of hydrogen as a renewable high energy fuel is well recognised. In order to exploit this energy system in India and to make it fully operational by 2000 A.D., it is essential that by 1990 the development of related technologies should be completed and in the following decade infrastructure for the utilization of LH_2 technology should be available throughout the country.

In order to achieve the above objectives, many action points have been identified. Some of the very important aspects which are to be considered on priority are given below:

- Quantity assessment of available hydrogen gas from sources such as natural gas, refinery off-gas, industrial byproduct gases, etc. should be carried out and the comparative cost figures should be generated.
- New techniques for efficient production of hydrogen by splitting water using unconventional energy sources should be tried.
- Hydrogen liquefier technology and low cost insulation systems for LH_2 are to be developed.
- Critical assessment of technology elements involved in utilization areas should be carried out and prioritised so as to synchronise this with overall LH_2 technology growth.

- For establishing the infrastructure for the LH_2 technology utilization in India during 1990's, a coordinated effort involving institutions, R&D laboratories as well as public and private sector industries, is essential. In each area number of work packages should be identified which should be taken up by competent agencies for development. This will ensure indigenisation of almost all elements by 2000 A.D.

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HYDROGEN FUELLED INTERNAL COMBUSTION ENGINES

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1. INTRODUCTION

The economic and industrial growth of a nation is greatly dependent upon modern means of surface transport. This is all the more so for developing countries like India where the demand for automobiles and other light and heavy vehicles is growing rapidly with the pace of economic development and industrialization. These vehicles are powered by internal combustion engines which are quite reliable and efficient. In fact presently there is no other power-plant in sight for surface transport vehicles which can compete with internal combustion (I.C.) engine in cost, size, flexibility and reliability. It appears that at least for next few decades I.C. engines will continue to have monopoly in the field of automobiles and other surface transport vehicles.

I.C. engines use petroleum fuels which were both plentiful and reasonably cheap in the world market up to 1973. The situation has since drastically changed and petroleum fuel prices have increased manifold causing great scarcities and an unbearable strain on the economy of those developing countries which have been depending on imports to meet their motor fuel requirements. Moreover, the resources of petroleum fuels are fast depleting, making the availability of their supplies in future a matter of serious concern.

Apart from their irreplaceable nature, and growing scarcity, another problem associated with the use of the petroleum based fuels is the nature of their combustion products which cause environmental pollution. Petroleum fuels powered vehicles are the main contributors to atmospheric carbon monoxide, hydrocarbons, particulate matter and lead pollution in metropolitan cities. The hazardous effects of vehicular exhaust pollution on human health, plant and animal life are well known.

These problems of fast dwindling resources of petroleum fuels and the hazards of environmental pollution caused by their combustion have focused the attention on the task of finding alternate "clean" burning renewable fuels for use in vehicular engines. Broadly two types of alternative fuels have been under investigation. These are the two types of alcohols (ethanol and methanol) and hydrogen.

R. P. Dahiya (ed.), Progress in Hydrogen Energy, 159–177.

2. HYDROGEN AS AUTOMOBILE ENGINE FUEL

From many technical and economic considerations, hydrogen seems to be the most suitable candidate fuel to substitute gasoline. Hydrogen can be manufactured from nuclear energy through electrolysis or thermal decomposition of water and it has been suggested as the most feasible future fuel (Mathur and Bansal, 1979).

Tasteless, odourless and non-toxic by itself, hydrogen produces just clean energy and water vapours upon combustion with air, thus restoring quantitatively to the environment, the water from which it is produced. Hence, there would never be a 'resource depletion' when hydrogen is burned as fuel.

Hydrogen would be a particularly good fuel for spark ignition engines, because its wide flammability limit would permit high efficiency and unthrottled engine operation. Engine emissions of hydrocarbons, carbonmonoxide and carbondioxide would be completely eliminated (Mathur and Bansal, 1978).

Hydrogen mixes easily with air and the mixture is quite stable at room temperature. However, the ignition energy of hydrogen is low compared to other gaseous and liquid fuels. It is ignitable at very low equivalence ratios. The flammability limits of hydrogen vary between 4 and 74 per cent by volume in air at room temperature and pressure. One of the consequences of this is the wide range of flame speeds and temperatures obtainable from hydrogen air mixtures.

S.I. engines using gasoline as fuel must be run very close to stoichiometric or richer mixtures, thereby producing conditions, favourable to the formation of nitrogen oxides, unburned hydrocarbons and carbonmonoxide in the exhaust. Hydrogen, on the other hand, may be burned so lean as to reduce peak temperatures to values at which dramatically less NO_x is produced, and of course it is no source of hydrocarbons or carbonmonoxide.

However, a number of practical difficulties are likely to be encountered in the use of hydrogen as spark ignition engine fuel. Hydrogen's higher flame velocity could result in higher rates of pressure rise and rough running of the engine. Hydrogen-air mixtures are more susceptible to surface ignition by engine hot spots than are hydrocarbon-air mixtures, since the minimum energy required for ignition is lower for hydrogen than for hydrocarbons. Surface ignition can precipitate flash back past the intake valve and preignition during compression stroke, with consequent loss of power, rough running and over-heating of the engine (Billings et al., 1974). With hydrogen the gas temperatures at the end of combustion are likely to be higher than with hydrocarbons and one would expect greater NO_x emission from hydrogen fuelled engine.

These and other matters pertaining to adaptation of conventional I.C. engine to operate on hydrogen need detailed experimental and analytical investigation. The present work has been undertaken with this object in mind, and the following pages describe briefly the nature and scope of work being carried out at IIT Delhi on hydrogen fuelled I.C. engines.

3. HYDROGEN FUELLED ENGINE SET UP

A single cylinder 95.25 cm x 114.3 cm 4-stroke variable compression engine with a speed range of 1000-3000 rpm has been selected for this study. The engine has been provided with arrangements which permit wide and independent variation of various controlling parameters. Ignition is by means of a megneto and spark timing which is fully adjustable. The dynamometer which can be used for motoring the engine also, has been provided with a spring balance fitted with an oil filled dash-pot to maintain steady spring balance reading. A temperature indicator and a selector switch has been provided which enables checking of cooling water, temperature, lubricating oil temperature and air intake temperature.

A pressure pick up has been fitted on top of the cylinder to measure the gas pressure inside the cylinder. A charge amplifier has been connected to this pressure pick up and its output could be used for recording.

An EC- 4-channel storage oscilloscope has been employed to measure the cylinder pressure. One channel of the oscilloscope has been connected to the signal from charge amplifier, and the other channel to the timing pulses.

A magnetic pick up has been placed adjacent to a timing disc driven by the engine crankshaft via toothed belt. The disc and pick up have been mounted such that the pulses correspond to every 20 degree arc of crank rotation with two additional pulses 10 degree before and after TDC.

Since the major pollutant appearing in the exhaust of a hydrogen fuelled engine is NO_x, a chemilluminescent gas analyser has been employed for accurate measurement of exhaust NO_x concentrations.

A special gas carburettor has been fitted in the engine intake system to obtain a premixed hydrogen-air mixture. The hydrogen flow rate has been regulated by a needle valve incorporated in the system. A gas pressure regulator has been fitted beyond the needle valve to regulate the line pressure to about 0.14 kg/cm^2 above atmospheric pressure.

A conventional dry type gas flow meter has been incorporated in the intake system. The meter has been directly calibrated to indicate hydrogen flow rate of twenty litres per revolution of the counter. It has been provided with a manometer and a thermometer to measure the supply pressure and temperature respectively.

A suitably designed flame trap has been fabricated, tested and fitted in the intake system as shown in Figure 1 which is the flow diagram of the experimental set up. This flame trap has been found to be very effective in arresting the flame during flash back in the intake system, thereby protecting the carburettor and other engine components.

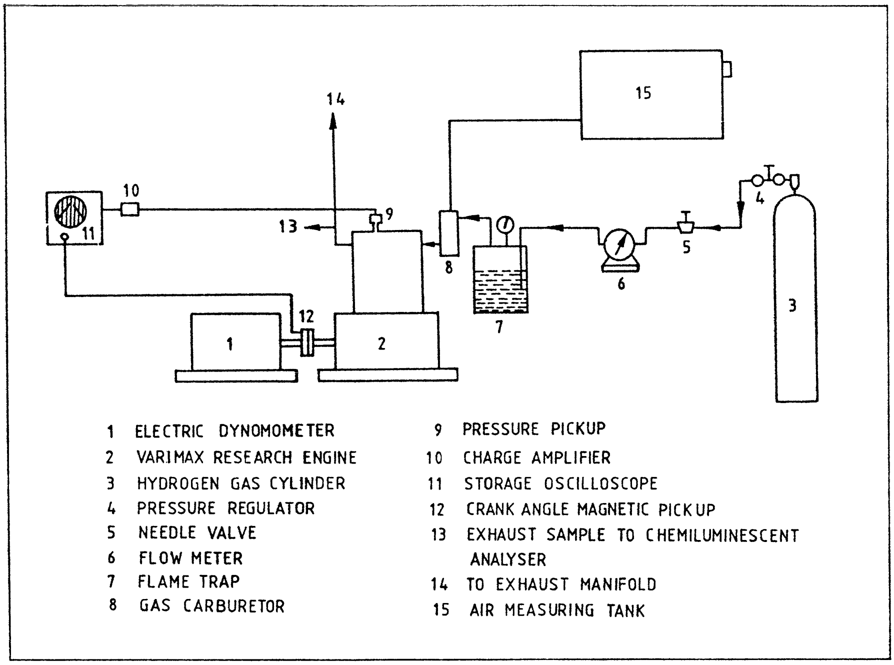

Figure 1. Flow diagram of experimental set up

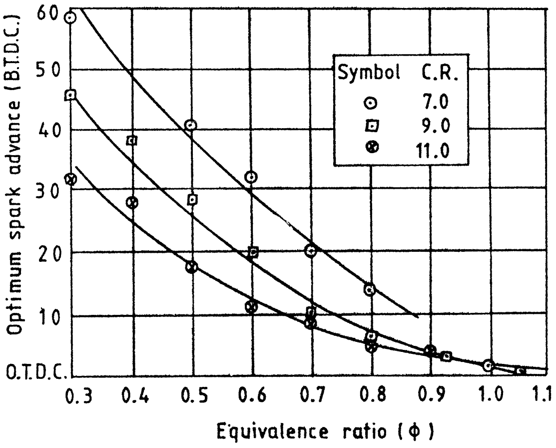

Figure 2. Optimum spark advance as a function of equivalence ratio for various compression ratios

4. HYDROGEN FUELLED ENGINE - PERFORMANCE AND EMISSION TEST TECHNIQUES

In order to assess the performance of a hydrogen fuelled engine, it has been found necessary to find minimum spark advance for best engine torque. Therefore, initially a series of experiments have been conducted to obtain best torque ignition timings.

In each set of these experiments the engine has been operated at a given speed and at a fixed compression ratio. Mixture strength has been varied and at each equivalence ratio the spark has been adjusted to give best torque. From the experimental data the ignition timing has been plotted as a function of equivalence ratio as shown in Figure 2. Such plots have been obtained at various speeds and compression ratios.

In the next series of experiments engine performance tests have been carried out. These tests have been conducted at five different compression ratios (7, 8, 9, 10 and 11). At each compression ratio constant speed test runs have been made for four different speeds (1000, 1200, 1400 and 1600 rpm). During these performance tests the throttle has been kept wide open and the load has been varied from no load to full load. At each load setting the speed has been kept constant by controlling the hydrogen flow rate and the spark timing has been adjusted to minimum for best torque as determined earlier.

Rates of air and fuel consumption have been measured with the help of instruments already described. The brake mean effective pressure values have been obtained from the electric dynamometer readings and they have been converted to indicated values using the motoring test data. This procedure has been repeated for different engine speeds by keeping compression ratio constant. After completing one set of observations the compression ratio has been changed to another new value and a new set of observations has been recorded as described above. A typical set of results obtained is shown in Figure 3.

To determine friction losses at different speeds, the engine has been motored at wide-open throttle with ignition switched off at desired speed. The power required has been measured and it gives the friction horse power. This procedure has been repeated and motoring tests have been conducted at various speeds. From this data, mechanical efficiency has been computed at various engine operating conditions.

To obtain pressure crank angle traces, the signals from pressure pick up have been fed to the charge amplifier. The cooling water supply to pressure pick up has been maintained throughout the experiment. The output from the amplifier has been fed to oscilloscope. The signals from crank angle timing marker have also been fed to the oscilloscope. The pressure crank angle diagrams at various engine operating conditions have thus been obtained and photographed.

Hydrogen fuelled engine exhaust is free from carbonmonoxide and unburned hydrocarbons which are the principal pollutants in gasoline fuelled engine exhaust effluent. However, nitrogen oxide exhaust emission continues to be a source of pollution.

Extensive experiments have been carried out to assess exhaust nitrogen oxide emissions from hydrogen fuelled engine under various conditions of engine operation. Exhaust NO_x concentrations have been measured at various equivalence ratios at different engine speeds of operations and at five different compression ratios (7, 8, 9, 10 and 11) and appropriate graphs showing the variation of exhaust NO_x concentrations with fuel air equivalence ratio at various compression ratios and speeds, have been plotted.

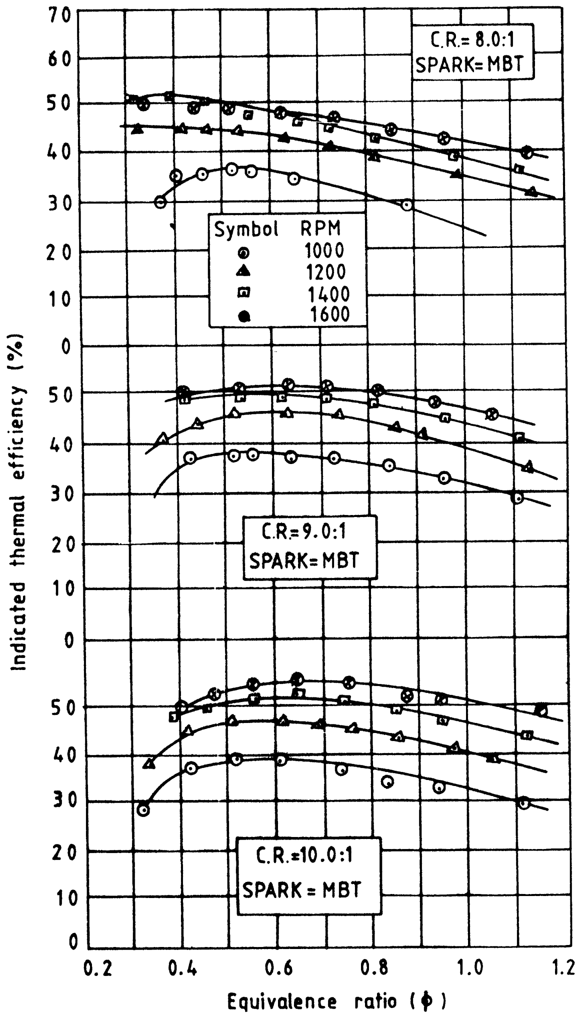

Figure 3. Indicated thermal efficiency as a function of equivalence ratio (Ø) at constant compression ratio for various speeds at WOT and MBT.

5. HYDROGEN FUELLED ENGINE PERFORMANCE

On the basis of extensive experiments carried out with hydrogen as fuel on a single cylinder S.I. engine under different engine operating conditions, a series of graphs have been plotted showing the inter effect of various parameters on the engine performance and emission characteristics. A set of typical graphs are shown in Figures 3 through 13.

Figure 3 shows variation of indicated thermal efficiency with fuel-air equivalence ratio at various speeds and three different compression ratios of practical utility. These graphs indicate that indicated thermal efficiency is higher at low equivalence ratio and use of hydrogen permits efficient engine operation even at equivalence ratio as low as 0.3. There is an improvement in efficiency with increase of speed. With hydrogen operation maximum indicated thermal efficiency of the order of 50% is obtained, which is much higher than that obtainable with hydrocarbon fuel.

There can be two major possible reasons for higher efficiencies. Use of hydrogen permits higher compression operation of the engine; the only limiting factor being the onset of pre-ignition which can be avoided by a number of means including fuel injection, water injection, use of appropriate spark plug and keeping the combustion chamber free of deposits (Levi and Kettleson, 1978; King et al., 1958).

If pre-ignition is avoided, it is possible to use compression ratios which are much higher than those acceptable for gasoline engines. Apart from this ability of higher compression operation, the wide flammability limit of hydrogen permits engine operation with a large amount of excess air. This lean operation increases the value of adiabatic index of compression significantly. Both these factors contribute towards improvement in the indicated thermal efficiency of hydrogen-fuelled engine.

At higher equivalence ratios the indicated thermal efficiency is reduced. This may be due to the fact that the availability of oxygen is depleted and there is fall in volumetric efficiency at higher equivalence ratios. For instance, at a given pressure and temperature of the inducted stoichiometric mixture of hydrogen and air, hydrogen is estimated to take up about 30 per cent of the volume while the figure of gasoline vapour in the corresponding gasoline air mixture is only about 2 per cent. This shows that less oxygen is introduced per engine cycle into the cylinder of a carburetted hydrogen-fuelled engine than of a gasoline engine (Khajuria, 1981; Mathur and Khajuria, 1980).

Figures 4 and 5 show the variation of indicated thermal efficiency as a function of compression ratio for various equivalence ratios at different constant speeds. The increase in efficiency is quite obvious and the reduction in indicated thermal efficiency with increase in equivalence ratio is also glaringly brought out in these figures which confirms the observation made in the previous paragraph. These trends are in conformity with those reported by other investigators (De Boer et al., 1975).

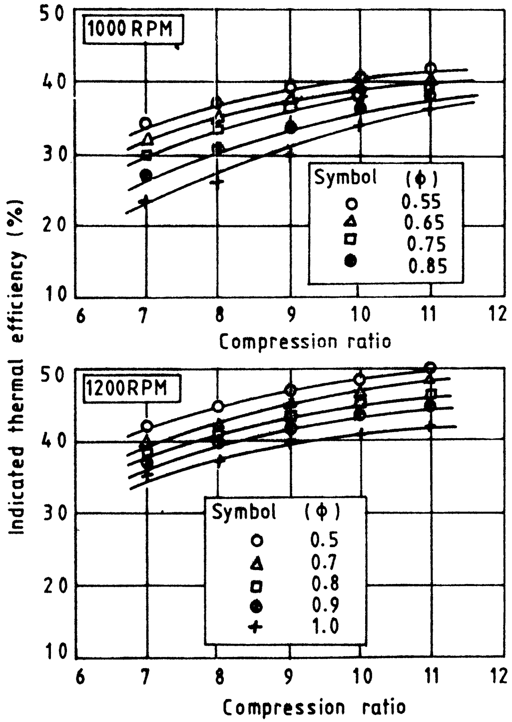

Figure 4. Indicated thermal efficiency as a function of compression ratio at constant speed for various equivalence ratios (Ø) at MBT and WOT.

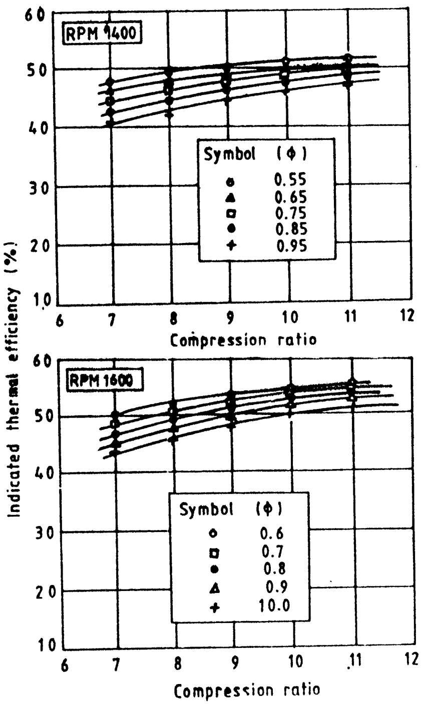

Figure 5. Indicated thermal efficiency as a function of compression ratio at constant speed for various equivalence ratios (Ø) at MBT and WOT.

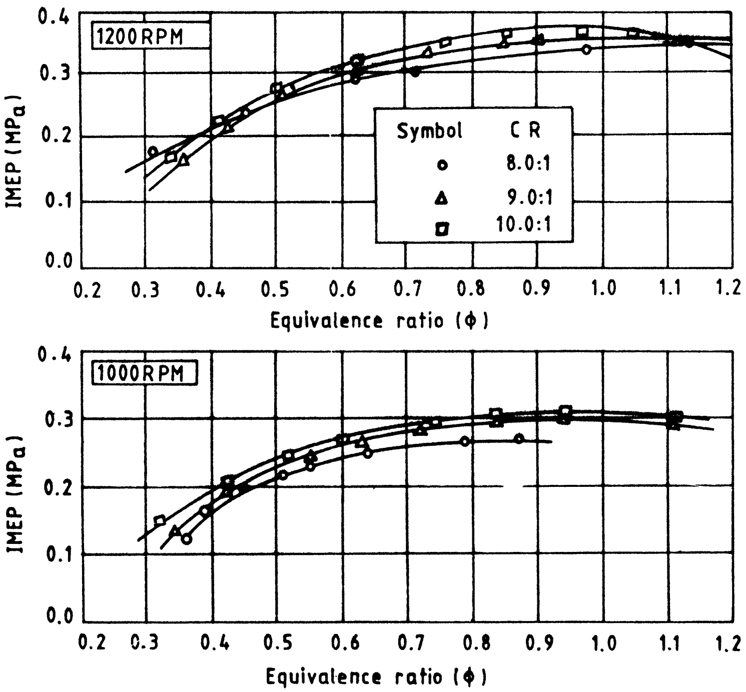

Figure 6. Indicated mean effective pressure (IMEP) as a function of equivalence ratiosat constant speed for various compression ratio at MBT and WOT.

Figures 6 and 7 show the variation of indicated mean effective pressure (IMEP) with fuel-air equivalence ratio (Ø) at various compression ratios of practical utility and four different engine speeds of operation. These graphs show that IMEP increases with equivalence ratio as also with compression ratio. IMEP values are maximum at equivalence ratio around 0.9. Another note-worthy trend indicated by these figures is that in low equivalence range the effect of compression ratio is not significant, particularly at higher speeds.

Hydrogen has wide flammability limits which make it possible to use very lean mixtures. Present results indicate that a more practical lean limit for combustion in engine is around 0.3. The use of lean mixtures in a hydrogen fueled engine not only results in fuel economy but also opens up the possibility of controlling the power output of the engine by changing the fuel flow rate while keeping the air flow unthrottled. Thus "quality governing", as opposed to "quantity regulation" provided by throttling, has the very important advantage of eliminating air pumping losses which account for a significant fraction of engine power output under light load and idle conditions where many engines operate most of the time.

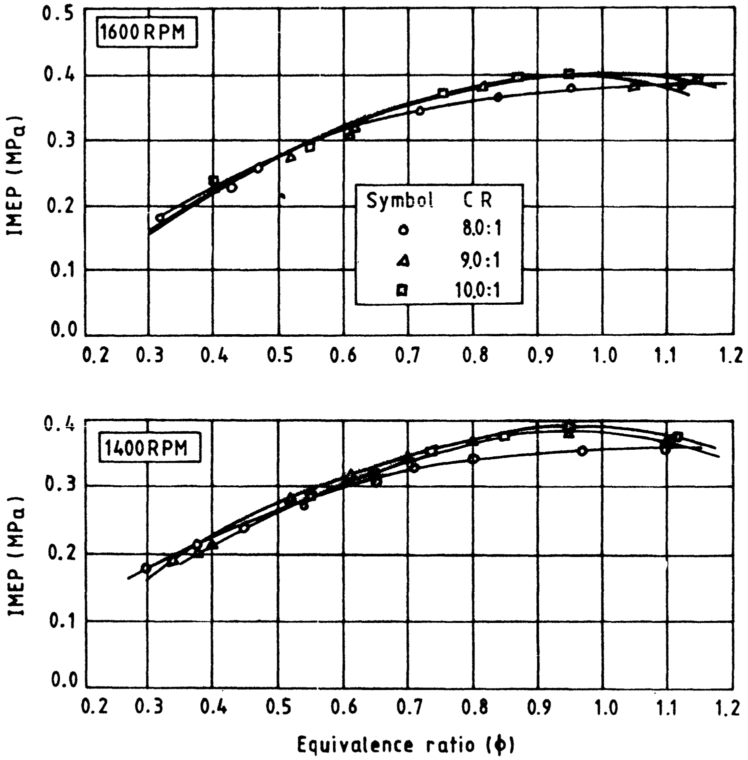

Figure 7. Indicated mean effective pressure (IMEP) as a function of equivalence ratio at constant speed for various compression ratios at MBT and WOT.

Figures 8 and 9 show the variation of IMEP with compression ratio at various fuel-air equivalence ratios and at four different engine speeds. As expected IMEP increases with compression ratio as well as with equivalence ratio. Although it has been possible to have higher compression operation of the engine, compression ratios have been restricted in the range 7 to 11 as higher compression ratios aggravate the problem of undesirable combustion such as pre-ignition and backfiring. Backfiring could be prevented by keeping the engine scrupulously clean and by using a cold spark plug with an appropriate narrow gap. Any other modification resulting in reducing flame speed, increasing ignition energy and quench distance should eliminate backfiring. This can be achieved by using lean mixture, exhaust gas recirculation or by water injection.

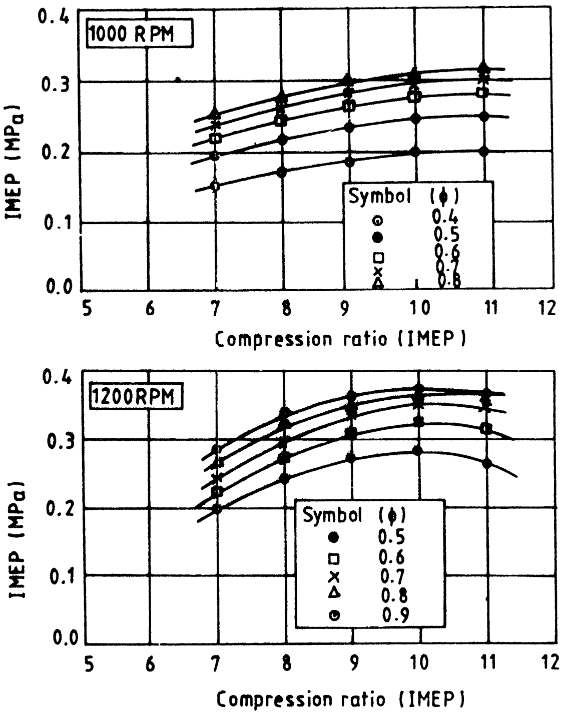

Figure 8. Indicated mean effective pressure as a function of compression ratio for various values of equivalence ratios (Ø) at constant speed and WOT and MBT.

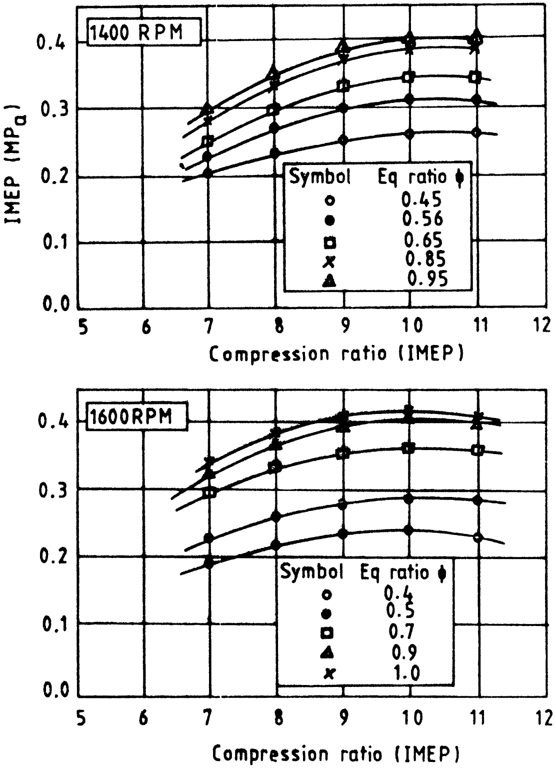

Figure 9. Indicated mean effective pressure as a function of compression ratio for various values of equivalence ratios (Ø) at constant speed and WOT and MBT.

The brake thermal efficiency as a function of power output (brake mean effective pressure) at various compression ratios are plotted in Figures 10 and 11. The highest efficiencies are obtained by a hydrogen engine operating unthrottled with quality governing and these values are much higher than those obtainable with gasoline operation. These curves show the standard trend of brake thermal efficiency increasing with compression ratio.

6. HYDROGEN FUELLED ENGINE EMISSIONS

The experimental results pertaining to nitrogen oxide emissions with hydrogen operation of the engine are shown in Figures 12 and 13. These diagrams show the variation of exhaust NO_x concentrations with fuel-air equivalence ratio at various compression ratios and speeds. As seen in these figures NO_x emission reaches maximum value at an equivalence ratio of around 0.8. In the lower equivalence ratio range NO_x concentrations are negligibly small.

These trends can be explained by the fact that NO_x formation reactions depend upon temperature and available oxygen, and they occur primarily in the post flame gases (De Boer, 1976). The type of the fuel used affects the flame temperatures and, through the stoichiometry, the available oxygen. For equivalence ratios below 0.8, NO_x formation is restricted due to thermal quenching during the formation process. For mixtures richer than 0.8, thermal dissociation of NO_x is the limiting factor.

7. HYDROGEN OPERATED GENERATING SET

On the basis of the work done so far it can be safely concluded that a hydrogen-fuelled S.I. engine is a feasible proposition.

Such an engine having quality governing can operate with very lean mixtures giving 25-100% higher values of the maximum thermal efficiency as compared to that obtainable from the conventional gasoline engine.

It has the additional advantage of giving a clear exhaust, free from hazardous carbon-containing pollutants and as much as 90% lower NO_x emission level as compared to that given by the gasoline engine.

A narrower spark plug gap has to be used to account for hydrogen's "low quench" distance and low ignition energy, which can also be taken care of by the use of water injection.

These coupled with a deposit-free combustion chamber can ensure smoother operation without the problems of flashback during induction or pre-ignition during compression.

These factors have been incorporated in an engine-generating set developed for performance monitoring-cum-demonstration. Figure 14 shows a photograph of this hydrogen fuelled engine-generator set of 4 KW rating developed at IIT Delhi. The engine-generator set has been operating on hydrogen net as fuel without any problems.

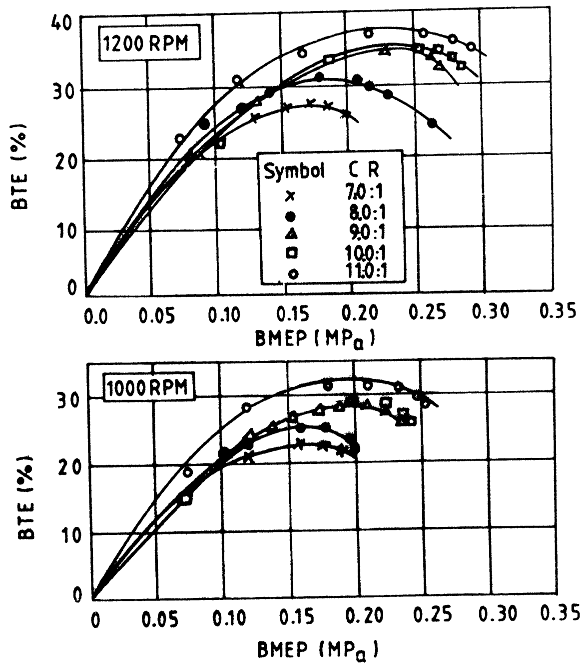

Figure 10. Brake thermal efficiency (BTE) as a function of brake mean effective pressure (BMEP) at constant speeds for various compression ratios at MBT & WOT.

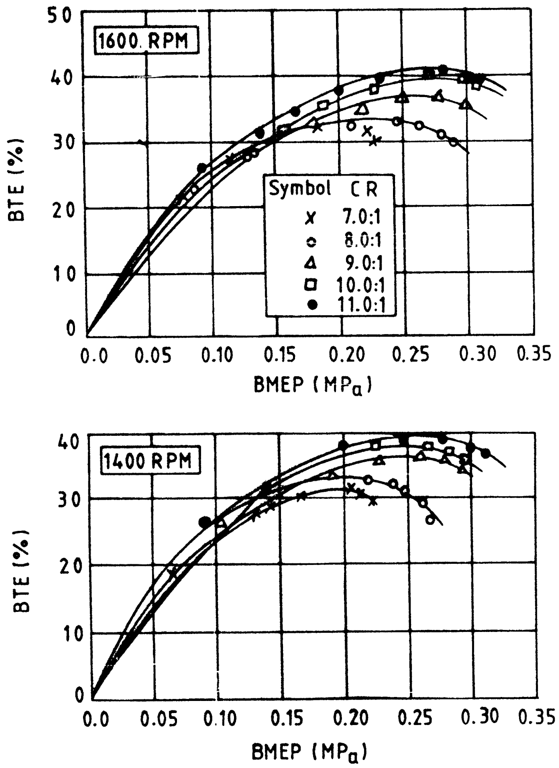

Figure 11. Brake thermal efficiency (BTE) as a function of brake mean effective pressure (BMEP) at constant speeds for various compression ratios at MBT & WOT.

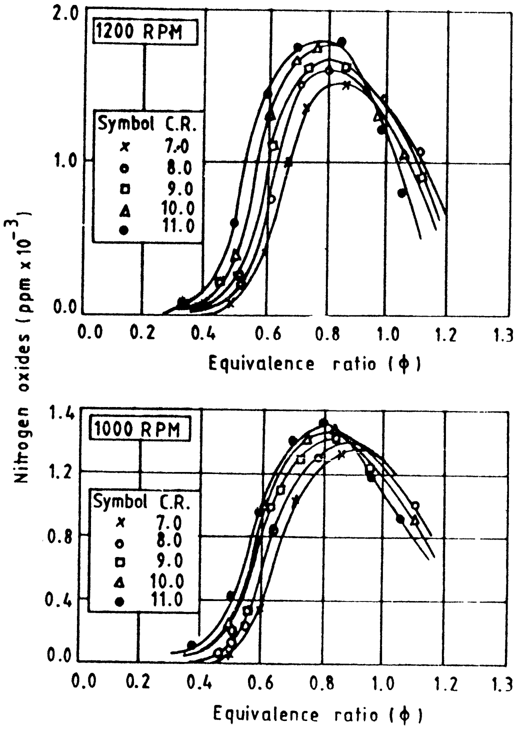

Figure 12. Nitrogen oxide emissions as a function of equivalence ratio at constant speeds for various compression ratios.

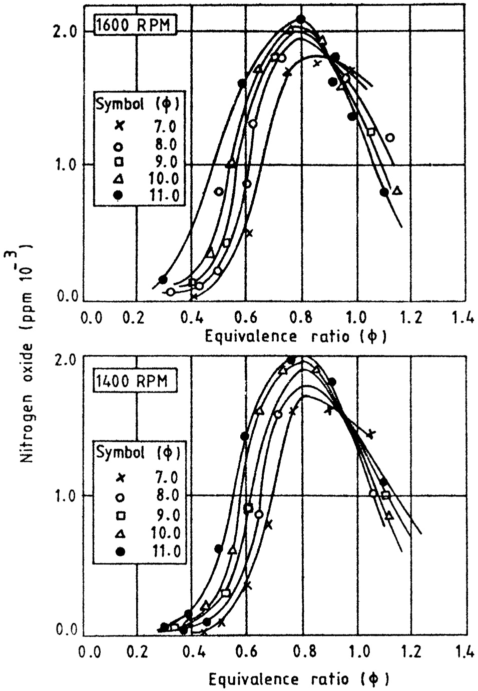

Figure 13. Nitrogen oxide emissions as a function of equivalence ratio at constant speeds for various compression ratios.

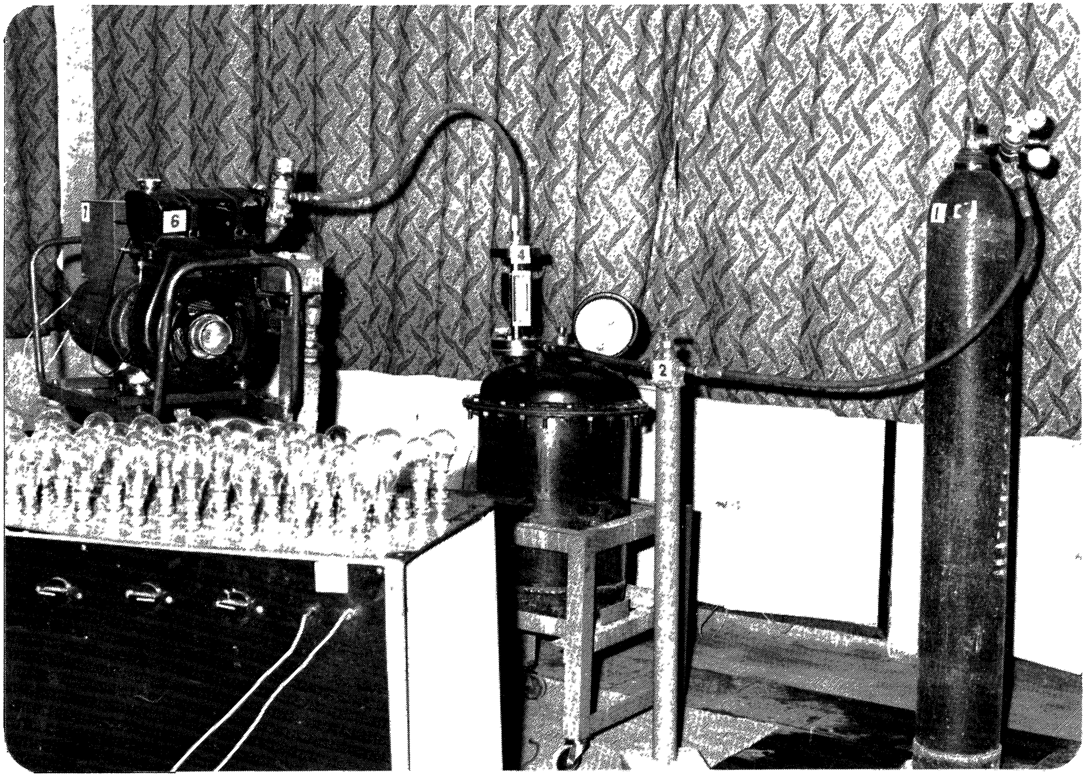

Figure 14. Hydrogen operated engine-generating set

8. HYDROGEN INJECTION IN ENGINE

Fuel-air mixture formation technique seems to have a very great impact on engine performance. Backfiring during suction of the hydrogen-air mixture happens to be one of the greatest problems associated with hydrogen engine. To overcome this problem different fuel induction techniques have been tried to find the best possible induction method suitable for wide range of hydrogen operation without backfire.

The methods that have been tried at IIT Delhi include Timed Manifold Injection (TMI) and Low Pressure Direct Cylinder Injection (LPDI). With LPDI it was found difficult to cover the entire engine range of load, speed and equivalence ratio. Even though the injector worked satisfactorily and the nagging problem of leakage was virtually solved it was difficult to have sufficient hydrogen flowrate to provide a rich mixture at relatively low pressures.

Timed Manifold Injection (TMI) has been finally adopted as the fuel induction technique for extensive engine trials. It involves timed injection of fuel delivered under a pressure of 1.4 to 5.5 Kgf/cm^2 at appropriate positions in the intake manifold, but upstream the intake valve. The timed injection is scheduled such that the fuel is being injected after allowing a sufficient quantity of fresh air to enter the combustion chamber, and to reduce the temperature levels of potential hot spots.

The most difficult practical problem encountered in using TMI technique was the development of a suitable injector without any leakage. Several injection designs were developed and tested to satisfy the combined requirement of ensuring appropriate injection duration with flow controllability. Cam-actuated and hydraulically operated injectors were specifically designed, fabricated and tested with Timed Manifold Injection (TMI) and low pressure direct cylinder injection.

Since the leakage of hydrogen at an unscheduled point in the cycle could lead to serious combustion as well as safety-related problems, the development of a leak-proof injector over an extended period of operation seemed to be one of the most stringent requirements in the implementation of the system hardware. Different materials after various heat treatment methods were tested in the severe thermal environment of the engine combustion chamber to eliminate long range reliability problems connected with leakage, wear, corrosion and material compatibility. It was only after a series of severe endurance tests that the injector was put fully to use on the hydrogen fuelled engines to prolonged performance evaluation testing programme.

Two different designs of hydrogen injectors were developed. One of these was hydraulically actuated while the other one was cam-operated. The finally accepted version was evolved through a series of modifications keeping in view the injection pressure, injection duration and hydrogen fuel controllability. With these injections, quality governing of the fuel delivery could be easily achieved as it was not strictly dictated by intake air-flow. Figures 15 and 16 show the photographs of these two types of injection systems fitted on the hydrogen engine.

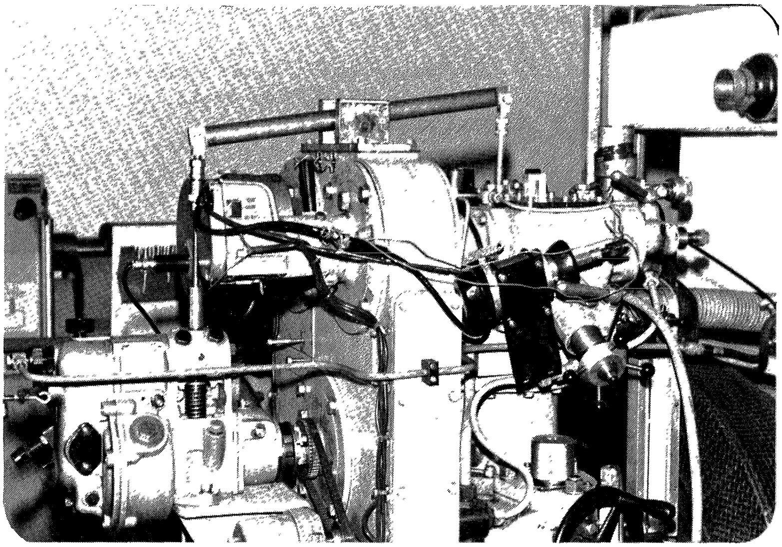

Figure 15. Hydrogen fuel injection system drive mounted on the hydrogen engine.

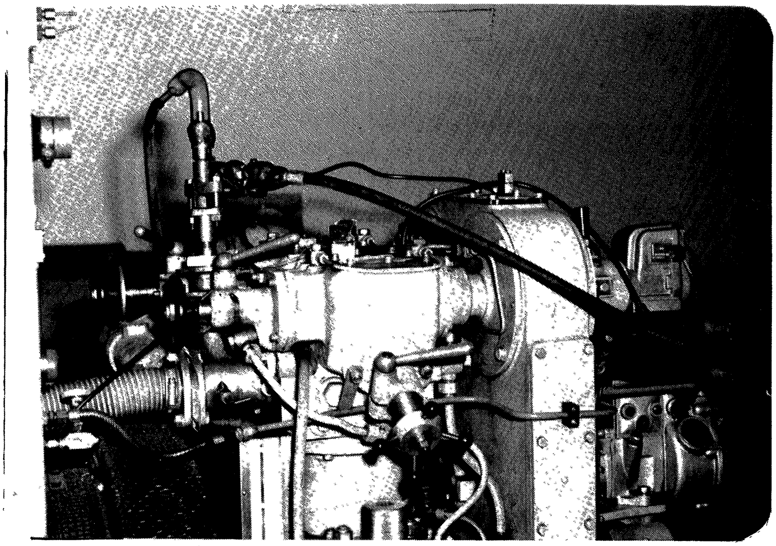

Figure 16. Timed manifold injection of hydrogen in the hydrogen engine.

Detailed experiments were carried out with hydrogen injection over entire range of engine speed and load. A series of tests were also conducted at consecutively increasing equivalence ratios from lean combustion limit to the rich mixture, a little above the stoichiometric. Compression ratios were changed from 6 to 11.

Based on the test results various graphs have been plotted to correlate mean effective pressure and thermal efficiency with equivalence ratio and compression ratios at different engine speeds. Other important engine parameters such as fuel consumption, power output and mechanical efficiency have been calculated to obtain hydrogen engine characteristics at various operating ranges.

Optimum injection timing was found to be a function of both engine speed and equivalence ratio. It was also observed that injection timing influenced the power output of the engine at a particular equivalence ratio. As the equivalence ratio was decreased, the maximum power output occurred at further advanced timings. This is thought to be due to decrease in flame speed of hydrogen with decreasing equivalence ratio, thereby necessitating earlier ignition of the fuel charge to ensure full combustion and peak power output during the combustion part of the cycle.

Although the engine was able to run at a very low equivalence ratio (0.218), it was observed that for an equivalence ratio below 0.28, the ignition could not be sustained for long. Peak power output calculations showed it to be quite high if the unique advantageous features of hydrogen as a fuel are appropriately explored and capitalized whenever possible.

9. HYDROGEN FUELLED C.I. ENGINE

Conventional C.I. engines can be made to operate on hydrogen fuel by any one of the following methods: (i) Conversion to Otto cycle operation by the incorporation of a spark plug. Such a modification can enable engine operation entirely on gaseous hydrogen fuel. However, it involves relatively complex and expensive changes on the engine, hence is not an attractive proposition particularly for C.I. engines below 50 horse power range. (ii) Duel fuel operation by intake system modification enabling induction of hydrogen gas-air mixture during suction stroke, and injection of appropriate diesel charge near the end of compression stroke, in the usual manner. There is a minimum diesel pilot charge which is essential to initiate and sustain combustion with hydrogen gas as the main fuel. This charge may vary from as low as 10-12% to as high as 60-70% of its original quantity at rated load. Dual fuel operation requires incorporation of a retrofit in the intake system of the conventional C.I. engine to achieve induction of hydrogen - air mixture of proper quality and in desired quantity.

Experimental results show that as the diesel pilot charge decreases from around 40% to 25%, the percentage energy derived from hydrogen fuel increases from around 50 to 60 per cent and the maximum knock free power-output increases by around 20 per cent.

Lowering of the compression ratio of the conventional C.I. engine in dual fuel mode is found to improve hydrogen energy substitution. Thus in an experiment lowering of the compression ratio from 16.5 to 14.5 was found to increase percentage hydrogen energy substitution from 60% to 65% at 25 per cent diesel pilot charge and from 50% to 55% at 40 per cent diesel pilot charge. The corresponding increase in the maximum knock free power-output values were of the order of 12.8% and 7% respectively.

The power-output of hydrogen fuelled C.I. engine in dual fuel mode of operation is limited by the onset of knock as hydrogen derived energy increases beyond a limit. The dual fuel mode of operation has, however, the advantage that it needs minimal engine modifications and permits switching back to conventional diesel operation whenever desired.

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UTILISATION OF HYDROGEN FOR DOMESTIC, COMMERCIAL AND INDUSTRIAL APPLICATIONS

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1. INTRODUCTION

At present the world energy demand is mostly met by fossil fuels except for a small contribution made by nuclear and hydroelectric power. However, the reserves of fossil fuels are limited and their combustion adds to the pollution problem of the environment. Serious attempts are, therefore, being made to increase the use of non-fossil energy resources such as solar, wind, nuclear, geothermal etc. But these resources are usually site specific which makes it essential to search for an energy carrier. Moreover, with the present level of technology the energy requirements of the transportation sector (based on petroleum fuels) cannot be fulfilled by these resources. It may be possible to generate electricity from the renewable sources of energy for transmission to the consumer places. In this process low efficiency of energy conversion, high percentage of losses and very high costs of putting up transmission lines over long distances make it an unfavourable proposition. The use of electricity from the present about 20 per cent in industrial countries and about 10 per cent in developing countries cannot possibly be expanded more than 35 per cent. Therefore, there is a need to get a fuel which should not only replace the fossil fuels but also be derivable from non-fossil energy resources, energy efficient, easily storable and transportable over long distances, safe to use in the residential, commercial, industrial and transportation sectors, and environmentally acceptable. The physical and chemical properties of hydrogen combine to make it nearly an optimum fuel to meet these requirements when both its uses and environmental aspects are considered.

Basically there are three aspects of hydrogen economy: production, delivery (transmission, transportation and storage), and utilisation. The hydrogen energy system concept is represented schematically in Figure 1. Conventionally hydrogen is being produced using coal and steam and by electrolysis of water. Solar energy can be used either in the form of heat in a thermochemical process or in a photocatalysis process for hydrogen production. At high pressures, hydrogen as a gas can be stored in metallic cylinders, depleted oil/gas wells and aquifers. Metal hydrides have been developed for the storage of hydrogen to use it

R. P. Dahiya (ed.), Progress in Hydrogen Energy, 179–194.

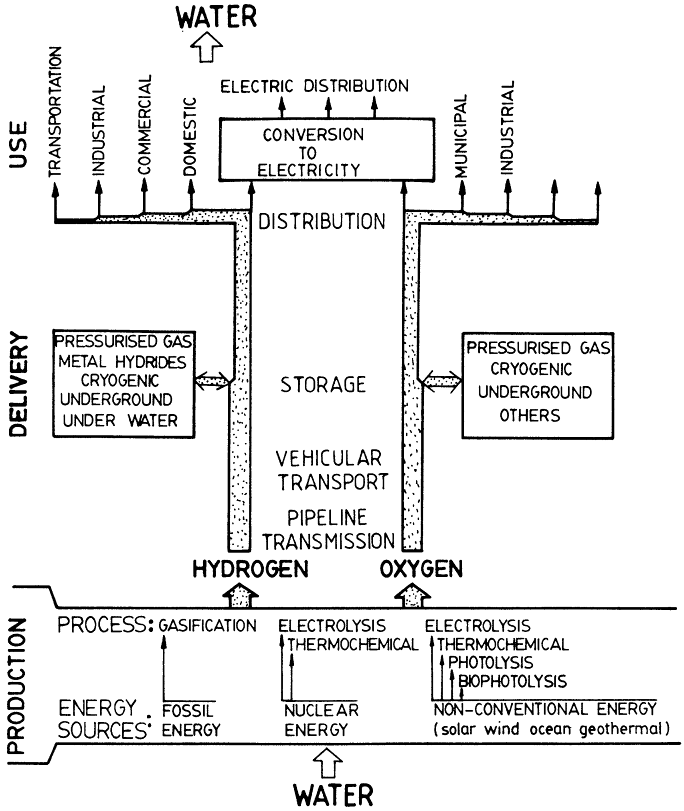

Figure 1. Hydrogen energy system concept

for automobiles. Hydrogen converted into liquid at low temperature is a very good light weight fuel for rockets, aircrafts etc. for space applications. Existing natural gas pipelines can be used for the transmission of hydrogen gas. It would be a cheaper means of transmission of energy for distances beyond 500-800 kilometres by transporting hydrogen through pipelines (Marchetti, 1985) compared to the transmission of electrical energy through overhead lines (Gregory et al., 1973).

Hydrogen may be utilised to meet the energy requirements when used as domestic and commercial fuel, industrial fuel, automobile fuel, and for electrical power generation. Combustion of hydrogen with oxygen and/ air poses minimal pollution problem since it produces its parent substance, water. Hydrogen has the potential to replace completely solid, liquid and gaseous fossil fuels presently being used (Sastri, M.V.C.) with some modifications in their combustion systems. In the initial stages, however, a suitable energy mix involving fossil fuels (with decreasing trend in their use), non-fossil fuels and hydrogen is necessary to keep pace with the growing energy demands world over.

2. HYDROGEN AS A FUEL

Hydrogen provides energy in chemical form which needs to be converted into other usable forms such as thermal, mechanical, electrical, etc. Like fossil fuels, the first step for converting the chemical form of hydrogen energy is to use it as a fuel and burn with an oxidant to obtain energy in the form of heat. It is, therefore, desirable to have a detailed knowledge of the combustion characteristics of hydrogen with oxygen and/or air for its applications. Some physical properties of hydrogen along with a few other fluid fuels are given in Table I.

TABLE I : Properties of Hydrogen and Other Fuels

	Hydrogen	Methane	Propane	Methanol	Gasoline
Density at NTP $kg\ m^{-3}$	0.084	0.717	1.870	791	735
Molecular weight	2.016	16.040	44.090	32.04	-
Normal boiling point K	20.35	111.45	231.0	338.15	398.15
Heat of combustion $kJ\ g^{-1}$	119.53	55.54	50.37	22.69	44.80
Viscosity at NTP Nsm^{-2}	$8.35x10^{-6}$	$10.3x10^{-6}$ at STP	$7.47x10^{-6}$	$0.59x10^{-3}$	-
Stoichiometric air-fuel ratio by weight	34.50	17.13	15.58	6.40	-

2.1 Flame Type Combustion

A clean, colourless flame is obtained on burning hydrogen. This can be used in internal combustion engines and for industrial, domestic and commercial applications. The hydrogen flame characteristics have been studied by several workers. Warnatz (1981) and Behrendt and Warnatz (1985) have investigated the effect of temperature, pressure and initial composition on the flame propagation in H_2-O_2-N_2 mixtures. They have simulated hydrogen combustion of pre-mixed flames by taking into account 25 chemical equilibrium reactions. While designing the combustion system, the physical properties of hydrogen like easy ignitability, wider flammability limits and explosive nature merit careful considerations from safety point of view. The flammability limits for the rich and lean mixtures, however, provide flexibility in the combustor design to optimise other factors such as pollution (while hydrogen is burnt with air NO_x is formed) or performance. For downward propagation of the hydrogen flame in air, the flammability limits become wider as the temperature is raised (Drell and Belles, 1958). At 373 K the limits are 9.0 to 73.5 volume per cent in air-fuel mixture which are broadened to 7.0 to 79.0

at 573 K. The downward propagating flames are very nearly planar (Levy, 1965) and the influence of the perturbing parameters thereby is reduced. Quenching of such flames with nitrogen in open tubes is most difficult near fuel-lean side. Cellular patterns are observed (Bregeon et al., 1978) near the flammability limiting zones and the conductive losses from the cellular flames are considered to be responsible for the quenching. The limiting mole per cent of nitrogen reduces from a maximum of about 84 per cent in the fuel lean mixture to about 70 per cent at a hydrogen to oxygen ratio of 5.0. The maximum does not correspond to stoichiometric ratio for hydrogen fuel but appears at a ratio of 1.6 (Bregeonet al., 1978) and 1.4 (von Heiningen, 1936) for downward propagation in closed and open tubes respectively and 0.8 (Jones and Perrott, 1927) for upward propagation. The lean flammability limits of gaseous fuel systems involving hydrogen and its mixture with inert gases at atmospheric pressure for the upward propagating flames get enhanced (Karim et al., 1985). The various gaseous fuel systems considered by Karim et al. are the combination of hydrogen with methane, carbon monoxide, propane and ethylene. Nitrogen, carbon dioxide and helium have been used as inerts. These investigations are useful for the smooth transition to hydrogen economy. In the initial stages a part of the conventional fossil fuel can be replaced with hydrogen which essentially will require minimum modifications to the existing gaseous fuel burners and combustors. The addition of inert diluents tends to increase the lean flammability limit almost linearly. As much as 15 times (by volume) of nitrogen is tolerable without the loss of combustion.

The flame propagation in a combustible gas mixture is characterised by the burning velocity or flame speed. The burning velocity of hydrogen-air mixture is substantially higher than that of methane-air mixture. The maximum burning velocity of hydrogen in air is about 300 cm/sec for gases initially at 573 K and atmospheric pressure (Gregory et al., 1973). The volume per cent of hydrogen in air corresponding to the maximum is nearly 41 per cent. One very important advantage of the high burning velocity is the reduced thermal loss due to the smaller chamber required for complete combustion. However, precautions to be taken against flash back become more stringent for hydrogen combustion. For H_2-O_2-N_2 mixtures the flame velocity peaks as the fuel concentration is increased (Behrendt and Warnatz, 1985). The flame velocity also varies with the nitrogen concentrations. The maximum flame velocity, however, lies far in the rich domain of initial mixture composition and thus does not coincide with the maximum adiabatic flame temperature, which is adjacent to the stoichiometric composition.

The adiabatic flame temperature of hydrogen-air system under stoichiometric combustion is about 2400 K and that of hydrogen-oxygen system is about 3100 K. In comparison to the temperatures attained with methane-air/oxygen and gasoline-air/oxygen, these are on the higher side. This would necessitate, for operation using the combustor infrastructure of the presently used fossil fuels, either cooling of the combustion products by spraying water or operation at off-stoichiometric conditions.

Since fossil fuel fired furnaces/combustors need chimney stacks for exhaust, this normally accounts for over 40 per cent of the heat loss. Such energy loss can be saved in the case of hydrogen fired furnaces/

combustors where no chimneys are necessary. The exhaust gases may be allowed to cool to form water.

2.2 Catalytic Combustion

Hydrogen can be made to react with oxygen at ambient temperature in the presence of a catalyst. This process of burning hydrogen at low temperatures is known as catalytic combustion. The heat released in the exothermic reaction can be transferred to the object or fluid to be heated by conduction and convection. The catalytic combustion of hydrogen is possible at room temperature because of its low ignition energy(0.02mJ), which is an order of magnitude lower than that of natural gas (0.3 mJ). Experiments have been conducted at the Institute of Gas Technology (IGT), Chicago (Sharer and Pangborn, 1974 and Pangborn, 1980) for burning hydrogen as well as methane at catalytic surfaces. The surface temperature in case of methane is kept between 350° to 450°C whereas hydrogen-air reaction can be initiated even below 5°C. During the catalytic combustion, the flame mode of combustion should not be allowed to occur to prevent flashback to the fuel injection line. The auto ignition temperature of hydrogen flame in air is 858 K. The flashback occurs when the ignition temperature is exceeded. In the normal burner design the laminar velocity of the fuel-air mixture is kept more than the burning velocity of the flame. But under these conditions it is difficult to achieve complete combustion over the entire catalytic surface. The flammability limit requirements, however, are not that stringent for catalytic combustion. Complete combustion may not occur under the fuel rich condition (75% fuel mixture) but in the properly designed system the catalytic combustion can be sustained even below the lean flammability limit (4% fuel mixture). This would also ensure 100 per cent fuel consumption.

The catalytic burner has a substrate on which a thin layer of catalysts is deposited. The substrate should have good thermal conductivity for efficient heat transfer, should be amenable to surface treatment and should have good adhering properties for the catalyst even after many cycles of operation. The materials normally considered for the household appliances to be used as substrate are: stainless steel, copper and aluminium. The Institute of Gas Technology, Chicago, has made heating devices using anodised aluminium substrates with aluminium oxide surface layer of 12 to 25 micron thickness. The catalysts can be made from platinum, palladium, raney nickel, lanthanum cobalt oxide ($LaCoO_3$) based materials and similar compounds. These are expensive materials. Therefore, the catalyst should not get easily poisoned. Platinum catalyst was applied in the IGT burners. The anodised sheets of aluminium were sprayed with 10 per cent solution of chloroplatinic acid (aqueous $PtCl_2.2HCl$) available commercially. There is 4 per cent platinum in the 10 per cent solution. The platinum coating on the surface was about 0.1 to 0.2 mg/cm^2. Activity can be guessed from the appearance of the coated surface. Black to chocolate brown surface has high catalytic activity, brown has moderate activity and light brown to grey has low activity.

3. DOMESTIC AND COMMERCIAL APPLICATIONS

In principle every existing fuel-consuming device can be converted to make use of hydrogen gas. The home and commercial uses account for approximately 20-30 per cent of the primary energy consumption. Hydrogen can take most of this load, electricity of course should supplement some specific requirements. Historically speaking the first large consumer for hydrogen has been the home. In the last century "town gas" was supplied to many cities through pipelines. The chemical composition of the town gas was 50 to 80 per cent of hydrogen and the rest of it primarily was carbon monoxide. Hydrogen can again replace the natural gas or liquefied petroleum gas presently being used for domestic and commercial applications. It can be transported via the existing pipelines, wherever available.

The lighting, heating, cooking, cooling and even electricity requirements for domestic and commercial sectors can be met with hydrogen. Candoluminescence can be exploited for lighting (Reid, 1971). A phosphor spread on the inner side of an open tube can emit radiations on coming in contact with small amounts of hydrogen in the presence of oxygen from air. This operation is cold. The catalytic combustion of hydrogen, described earlier can be used to meet the heating and cooking requirements. Catalyst impregnated heating panels can be made of porous plastics or wood. Cooking ranges can be made with metallic substates and a catalyst to provide flameless and intrinsically safe cooking device. Absorption refrigeration can give cooling, where catalytic burner can be used as the heat source. The electricity needed for running fans, vacuum cleaners, etc. can be generated by fuel cells.

It is not always necessary to use the catalytic burners. The existing gaseous fuel burners can burn hydrogen with some adjustments to accommodate the fuel/air mixture required for efficient hydrogen burning. A mixed fuel economy involving a mixture of the presently used gaseous fuel and hydrogen can be adopted until efficient methods of producing hydrogen are available. As much as 15 per cent of hydrogen, and possibly more, may be added to natural gas without a need to modify the existing burners. However, precautions are to be taken against flashback because of higher hydrogen-air flame velocity.

The combustion of hydrogen with oxygen gives water. Therefore, there does not arise the need of exhaust or a chimney for the home using hydrogen fuel. This not only reduces the cost of construction but also enhances the overall thermal efficiency. The oxygen in air is used up during the combustion. Proper arrangement is to be made to compensate for the oxygen loss and over-humidification by making a provision of air changes in the building in which hydrogen energy is used.

4. INDUSTRIAL APPLICATIONS

Large volumes of hydrogen are being used throughout the world in the chemical and petrochemical process industries, in ferrous and non-ferrous metallurgy, in agricultural fertiliser industries, in processing edible oils, and so on. Table II gives the hydrogen energy consumed in the USA during 1974 and also projections made for the year 2000(Kelley, 1975).

TABLE II : Consumption of Hydrogen in the USA

Consumption pattern of the year 1974

	SCF $x10^{12}$	Btu $x10^{15}$
Petroleum refining	1.41	0.47
Ammonia synthesis	1.08	0.36
Methanol synthesis	0.30	0.10
Miscellaneous uses	0.21	0.07
Total	3.00	1.00

In 1974, 1.3 per cent of the total energy consumption in the USA was used for hydrogen production.

Projected to the year 2000

	Low Btu/yr $x10^{15}$	High Btu/yr $x10^{15}$
Petroleum refining	0.7	1.0
Chemicals (methanol, ammonia, etc.)	2.5	8.0
Synthetic fuels	2.0	8.5
Direct reduction, transportation, etc.	0.5	4.5
Total	5.7	22.0

4.1 Petrochemical and Chemical Industry

The petroleum refining process requires hydrogen for catalytic cracking the crude oil to obtain gasoline. The ratio of hydrogen to carbon ranges from 2.0 to 2.2 in gasoline which has a chain of 5 to 10 carbon atoms (Williams, 1980). The higher boiling fractions of crude oil break into smaller chains on heating. The hydrogen deficiency in the unstable smaller chains can be made up by reacting the crude oil with hydrogen at high pressures in the presence of a catalyst. The properties of the product obtained are completely identical to those of gasoline. The sulphur content of the petroleum products is also reduced by the hydrogen reaction. The hydrogen sulphide (H_2S) gas escapes from the petroleum products. Since H_2S is acidic in nature it is made to react with a base such as lime or lime stone to obtain a stable compound (calcium sulphide). It is obvious from the above discussion that the hydrogen requirement will increase as the supply of the light crude oil dwindles, and we are forced to turn progressively to more viscous, heavier oils and to non-conventional sands and shales, all with the lower hydrogen to carbon ratios than lighter crudes. The hydrogen requirement for upgrading the crude can vary between 1000 to 2500 SCF per barrel depending on the composition of the feed (Crawford and Stuart, 1984). The sulphur removal from the upgraded product will need 500 SCF or more of hydrogen per barrel of crude. The daily hydrogen requirement for a plant treating 10,000 barrel per day would be 20 million SCF calculated at the ratio of 2000 SCF hydrogen per barrel.

The solid coal can be converted to fluid fuels by increasing the content of hydrogen in it. Liquefaction of coal is accomplished by reacting fine powder of coal and hydrogen in the presence of a catalyst. The amount of hydrogen required depends on the type and quality of coal. For the coal having hydrogen ratio of 0.1, nearly 2 kilogram of hydrogen is needed for every 15 kilogram of coal; this is almost twice the amount required for upgrading the crude oil having hydrogen to carbon ratio between 1 and 2.

At present, production of ammonia consumes more hydrogen than any other single industrial application. In the process of producing hydrogen for ammonia synthesis, water gas ($CO+H_2$) is first obtained by reacting natural gas with appropriate quantities of air and steam. This is called steam methane reforming operation. The carbon atoms and water are removed from the water gas. The nitrogen (from air) to hydrogen ratio is then adjusted and fed to an ammonia synthesis loop to produce ammonia in the presence of a catalyst. More than 30,000 SCF of natural gas per tonne of ammonia is required (Crawford and Stuart, 1984). Hydrogen produced electrolytically is also used where the electricity is available for this purpose. The significance of ammonia production stems from the fact that ammonia based fertilisers are largely responsible for increasing the agricultural production to feed the growing world population.

The production of methanol from coal, natural gas or wood is another important application of hydrogen. Steam at high pressure is made to combine with natural gas to produce a gas mixture of $CO+2H_2$ for synthesis into methanol. The gasification reactions of coal and wood with steam are relatively difficult. The methanol production is considerably enhanced from a given amount of feedstock if the hydrogen derived from the feedstock itself is supplemented by electrolytic hydrogen. For the case of pure carbon, twice the amount of methanol can be produced with electrolytic hydrogen per carbon atom. The pressurised oxygen, fluid bed, wood gasifier coupled to methanol system can produce 37 per cent more of methanol by using electrolytic hydrogen.

Hydrogen is used in a number of other industries - in food processing, in metallurgical and plastic industries - and also as an important chemical in scientific research. The melting point of the hydrogenated edible oils gets raised such that it is a solid at room temperature. The hydrogenation is possible in the presence of rainey nickel as catalyst. Since the hydrogenated oil is a food product, the purity of hydrogen used is very important. In the metallurgical industry the metal oxides are reduced with the help of hydrogen to produce metals. It is a very important reducing agent for the processes where carbon is not desirable. In the manufacture of tungsten, for example, carbon cannot be used because its presence makes the metal extremely brittle.

4.2 Process Heat

Hydrogen as a clean fuel has the capability of replacing the dwindling fossil fuels for meeting the thermal energy requirements of various industries. It can easily take the place of natural gas and other gaseous fuels in the furnaces and combustors. The fuel properties and methods of using hydrogen for thermal applications are discussed in section 2.

One very important application of hydrogen can be in the combustors of thermal power plants. Though adequate hydrogen supply is not available to meet the entire fuel requirement of the power plants, the oil support burners used in the coal fired plants can be replaced with hydrogen burners. Part of the electrical power generated during peak hours can be used for producing hydrogen in electrolytic plants installed at the site. The electrolytic hydrogen can be stored and used as and when required. This is an interesting mechanism for storing the electrical power. Hydrogen produced electrolytically can be stored in one of the several ways, which include metal hydride, liquid hydrogen and compressed hydrogen gas storage.

4.3 Electrical Power Generation

It is difficult to think of the industrial revolution without electrical power. Almost all the industries use electricity in some form or the other. Thermal (fossil fuel operated), nuclear and hydroelectric power plants meet most of our electrical energy requirements. In the first two types of plants steam is raised at high pressure and temperature to drive a turbine which in turn supplies motive power to the electrical generator. Hydrogen has the potential to replace completely the fuel used for the steam boilers. The corrosion and erosion problems encountered because of impurities in coal would be eliminated in the hydrogen fired boilers. Moreover, the hydrogen operated plants can be installed even in thickly populated areas since there are no pollutants (except NO_x which can be readily controlled by changes in air fuel ratio) in the combustion products of hydrogen. The problems encountered in the transportation of coal to the power plant sites would be eliminated when hydrogen fuel is chosen, because hydrogen gas can be transported through underground pipelines.

The chemical energy of hydrogen can be directly converted to electrical energy by fuel cell, without going through the intermediary of heat and so escaping a step which is always associated with marked increase in entropy. A hydrogen-oxygen fuel cell consists of two catalytic electrodes, anode and cathode separated by an ion exchange membrane. The electrons driven through the external load connected between the cathode and the anode supply electrical power. These electrons are liberated at the anode in the dissociation reaction of hydrogen atom to hydrogen ion and electron The ions migrate through the membrane and the electrons reach via the load to the cathode where reaction with oxygen (supplied from outside) takes place to produce water. The kinetics of the fuel cell are critically dependent on electrocatlysts, besides the pressure and temperature. Fuel cells offer greatly improved thermodynamic efficiency. The hydrogen-air fuel cells have the potential of converting the hydrogen energy to electrical energy at about 80 per cent efficiency. Further discussion on fuel cells and enzyme electrodes are given by Sonawat et al. (1987) and Sonawat (1987) respectively.

Gas turbine and magnetohydrodynamic (MHD) generator technologies compete with fuel cells in converting hydrogen energy to electrical energy. The gas turbine technology is in use for hydrocarbon fuels. The advanced gas turbine and steam generator operated in combined cycle mode offer thermal efficiencies to beyond 50 per cent. The other alternative, MHD generator topping a steam turbine, also has the potential for quite high overall efficiency. The MHD generator has no moving part and hence can be operated at much higher temperatures than those of turbines. The Carnot cycle efficiency is, therefore, increased with the increased temperature of the source. For MHD power generators, the higher operating temperature is also desirable from the electrical conductivity point of view. Thermal ionization of the seeded (by K_2CO_3) combustion products of the hydrogen air/oxygen governed by Saha equation gives rise to electrically conducting plasma. This is the working fluid in the MHD generator channel where the electrical power is generated by electromagnetic interaction. H_2-O_2 combustion powered MHD-steam turbine power plants can be constructed with negligible efflux of pollutants. It may also be pointed out that hydrogen as a fuel tends to minimise the difficulties associated with oxygen use since hydrogen requires a minimum of oxygen per unit of heat release. The overall efficiency of a steam-bottomed MHD power generator can be around 50 per cent. The detailed design specifications of a portable and a steam-bottomed MHD power plant are given by Ami Chand et al. (1987). The first commercial power plant of 500 MW (electric) capacity is being set up in the USSR at Ryazan near Moscow. In this plant MHD generator will produce 250 MW power and the rest will be produced by the steam turbine. The fuel for this plant is not hydrogen but natural gas. Its success, however, will give a significant boost to the MHD generator programmes throughout the world.

5. ENVIRONMENTAL CONSIDERATIONS

The use of hydrogen fuel would reduce pollution, to a great extent, caused by combustion of fossil fuels. The principal pollutants resulting from the combustion of fossil fuels are CO, CO_2, SO_2, NO_x, particulates and waste heat. These produce air pollution, acid rains, acid snow and acid smog. While discussing the fuel merits of hydrogen, Awad et al. (1984) have considered the environmental effects and damages of the pollutants on humans, fauna and flora, historical monuments, modern buildings and structures, drinking water sources and beaches. In case of hydrogen-air combustion NO_x, waste heat and possibly excessive amounts of water vapours are of concern. The carbon and sulphur based toxic wastes are completely eliminated by using hydrogen. However, most environmental problems would arise in the production of hydrogen and not in the consumption. The process utilising coal or petroleum for production of hydrogen would lead to usual environmental pollution. The non-fossil energy resources such as solar, wind, geothermal, ocean thermal etc., when available on commercial scale for hydrogen production, would eliminate this problem. The hydrogen combustion is cyclic $(2H_2+O_2 \rightleftharpoons 2H_2O)$ on a short time scale compared with the fossil fuels. The amount of water released in the atmosphere by the use of hydrogen fuel would be more or less similar to the amount of water obtained from the combustion of fossil fuels. In the case of hydrogen fuel, the amount of water vapours released from a combustion engine would be only twice the amount released when hydrogen fuel is replaced by a light hydrocarbon fuel to generate the same amount of energy. Since water is a source for hydrogen production, it is recycled on a short time scale. If the energy consumption of 6×10^{18} Btu per year is to be met by the use of hydrogen energy, the incremental amount of water cycled through the atmosphere is estimated by Penner and Icerman (1984) to be 4.74×10^{11} mt per year whereas the usual global evaporation of water normally adds 4.48×10^{14} mt of water per year.

The equilibrium concentration of NO and NO_2 have been calculated by Williams (1980) at various air-fuel equivalence ratios for hydrogen and gasoline. Since the hydrogen flame temperature is higher than that of the gasoline flame, the nitric oxide concentration in the hydrogen flame is somewhat higher under fuel-lean conditions. It is possible to reduce significantly (by a factor of 10^{10} or more) the nitric oxide concentration by burning air-fuel mixture under fuel-rich condition. In case of gasoline the amount of CO and unburnt hydrocarbons becomes greater as air-fuel equivalence ratio is increased. The fuel-rich combustion of hydrogen results into the increase of the concentration of unburnt hydrogen and ammonia. Their concentration, however, is about the same as that produced by the combustion of gasoline. Murray et al. (1972) have compared the NO_x emission from an engine operated with petroleum fuels and hydrogen. They have also observed a substantial decrease in the concentration of NO_x in the fuel-rich zone of operation. Namboodirv and Krishnamurthy (1987) have given a comparison of NO_x emission between various types of engines.

The increase of CO_2 concentration is making qualitative changes in the global environment. The earth's atmosphere contains about 325 parts per million (by volume) of CO_2. The total mass of earth's atmosphere is approximately 5.14×10^{15} tonnes. There has been a 12 per cent increase in the concentration of carbon dioxide over a period of last 100 years as a result of burning the coal and petroleum fuels. The mass of carbon increased from 6.52×10^{11} tonnes in 1950 to 6.82×10^{11} tonnes in 1970 (Jones, 1975). This amounts to approximately 5 per cent increase in the atmospheric carbon dioxide. If we continue our present dependence on fossil fuels, and 50 per cent of the CO_2 released is retained in the atmosphere (present rate of retention), there would be six-fold increase in the atmospheric carbon dioxide by burning the recoverable coal in the earth's crust, 8×10^{12} tonnes.

The reason for the concern about the increasing concentration of atmospheric CO_2 is its predominant effects on the ecological balance. The carbondioxide is not transparent to the thermal radiations emitted by the earth's surface in infrared region, which leads to a "greenhouse effect". That means the earth's average temperature increases. A few degrees' increase in the average temperature has been observed over the last 20 years. This change in heat balance can cause shifts in weather patterns. The other effect is on the life structure of the ocean. The top 30 metres of the ocean contain dissolved carbon dioxide making the water acidic. The carbondioxide concentration in the ocean is in balance with the atmospheric carbon diode. It is predicted that with the present rate of increase in carbondioxide by 2010 the top 30 metres of the ocean will become acidic to the extent that it would not be able to support shellfish and thus jeopardise the balance of the living ocean (Fairhall, 1973).

6. SAFETY ASPECTS

Adequate safety measures have to be adopted for the potential hazards throughout all stages involved in the use of hydrogen, i.e. in hydrogen production, storage, transmission and transportation and end product use such as a source of heat for domestic and industrial purposes or vehicle propulsion. Los Alamos Scientific Laboratories have produced three very useful reports on hydrogen safety during 1976-1979 (LASL, 1976-1977, 1977-1978, 1976-1979). The physical, chemical and combustion properties of hydrogen should be understood while developing the devices and techniques for the prevention of explosion hazards and the prevention of material degradation problems. The safety relevant properties of hydrogen fuel are compared with non-solid fossil fuels of common use in Table III. For hydrogen, not only the limits of flammability in air are wider than those of the other fuels but also the limits of detonability in air range from 18 to 59 per cent (by volume). Studies conducted by Lee(1983) in large scale experiments have shown that deflagration-to-detonation transition (DDT) is induced by rapid turbulent mixing of hot product gases and the cold unburnt mixture. Eichert and Fischer (1986) have developed one dimensional model to simulate the DDT transition. According to them, the DDT consideration in a confinement under realistic conditions shows that hydrogen has better safety characteristics compared with methane and propane.

Hydrogen leaked into an unconfined space rises upwards quicker because its density is about 7 per cent of that of air, whereas that of methane is 56 per cent. The hazards associated with hydrogen leakage are, therefore, of less serious concern in open spaces but at the same time the buoyancy and diffusive properties of hydrogen make the leak detection difficult. The flame velocity for hydrogen under normal conditions is more than ten times that of methane. The burner design has to take this into account so as to avoid the flashback problem. However, the quenching distance for hydrogen flame in air is about 0.06 cm whereas for methane it is 0.25 cm.

The hydrogen ignition near stoichiometric ratio needs only 0.02 milli-joule at an ignition temperature of 858 K. In comparison to methane the ignition energy is lower but the ignition temperature is higher than for methane. To spark ignition of hydrogen is, however, relatively easier. The pure hydrogen flames are invisible and smokeless. Moreover, hydrogen itself is colourless, odourless and tasteless.

TABLE III : Comparison of Safety Relevant Properties of Hydrogen and Other Fuels.

	Hydrogen	Methane	Propane	Methanol	Gasoline
Autoignition Temperature K	858	813	783	847	501-744
Minimum Energy for ignition in air, mJ	0.02	0.3	0.26	-	0.24
Flame Temperature in air, K	2318	2148	2198	2467	2475
Limits of Flammability in air, vol.%	4.0-74.2	5-15	2.1-9.5	6.7-36.5	1.0-7.6
Limits of Detonability in air, vol.%	18.3-59.0	6.3-13.5	-	-	1.1-3.3
Burning Velocity in air at NTP, cm s^{-1}	265-325	37-45	-	44	37-43
Detonation Velocity in air at NTP, km s^{-1}	2.0	1.8	1.85	-	1.4-1.7
Diffusivity of Vapour in air at NTP, cm^{2}s^{-1}	2.0	0.5	-	-	0.17
Buoyant Velocity of Vapour in air at NTP, m s^{-1}	1.2-9.0	0.8-6.0	-	←Non-buoyant→	
Heat of Radiation to surroundings, %	17-25	23-33	-	27-38	30-42

It is, therefore, desirable to add suitable chemicals to hydrogen for smell to facilitate the leak detection. The chemical should not change much the combustion properties of hydrogen and also its combustion products should be non-toxic.

Skin exposure to liquid hydrogen can lead to tissue damage. It is because of the extremely low temperature (-252°C) of liquid hydrogen that the tissue damage is similar to that resulting from severe burns. When small quantities of liquid hydrogen fall on the warm skin, the liquid hydrogen sputters immediately and bounces away (Leidenfrost effect). The tissue damage is thus avoided as the contact time is not long enough. However, if large quantities of liquid hydrogen are trapped inside the clothes of a person it may prove to be hazardous. The safety aspects in the use of liquid hydrogen for ground transportation vehicles have been studied by a group of Chemetics International Company (Knowlton, 1984; Jones, 1984) with a technique known as Hazard and Operability Studies (HAZOP).

All gases, except helium, liquefy at the liquid hydrogen temperature. Since the boiling points of oxygen (-265°C) and nitrogen (-289°C) are different, air coming in contact with liquid hydrogen will get frozen and oxygen enriched, producing a momentarily explosive mixture.

The liquid hydrogen spill may occur as a result of the rupture of a large storage facility. Experiments have been conducted at NASA's White Sands Test Facility in New Mexico for investigating the potential hazards resulting from rapid spills of liquid hydrogen (Witcofski and Chirivella, 1984). The flammable clouds formed as a result of ground spills of up to 5.7 m^3 are observed to disperse to safe concentration levels due to thermal and momentum-induced turbulences and become positively buoyant.

The material degradation on account of hydrogen occlusion from both liquid and gaseous environments is of significance for the design of the hydrogen based systems. The hydrogen degradation problems have been classified by Hirth and Johnson (1976) and Dutton (1984) in the following categories: hydrogen stress cracking, hydrogen environment embrittlement, loss in tensile ductility, hydride formation, blistering and hydrogen attack. Stable austenitic stainless steel, aluminium alloys and copper are found to have negligible susceptibility to hydrogen embrittlement. The hydrogen energy embrittlement must be considered in the design of large scale pipeline distribution system operating at high pressures.

Hydrogen as a fuel is not dangerous as such and its use requires the learning of just a few new habits for safe handling. The major precautions to be adopted are: venting areas, prevention of leakage, inert gas purging of the working system, use of additives to impart smell and suppress explosion, safety devices such as flame arrestors incorporation in the pipelines, elimination of all possible ignition sources and frequent inspection of sealants.

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FUEL CELLS: PAST, PRESENT AND FUTURE

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1. INTRODUCTION

A Fuel Cell is an electrochemical device which comprises of two electrodes - anode and cathode separated by an electrolyte. The reactants are stored outside the cell and are introduced in the cell when required. The free energy of the reactants is converted directly into electrical energy without the intermediate steps of thermal and mechanical energies in contrast to the conventional power generators. A Fuel Cell works on the same principles as a primary battery. However, it differs from a battery in two respects. Whereas a battery consumes its chemicals irreversibly and dies out with time, a fuel cell continues to function with constant efficiency as long as fuel material is continuously supplied and end-products are removed. Moreover, the electrodes of a fuel cell are non-consumable. In principle, any oxidation-reduction reaction can be used in a fuel cell. The suitability for practical use is governed by the thermodynamics (availability of free energy) and kinetics (rate at which the electrical charges are transferred through the load). In addition to the thermodynamic and kinetic acceptability, the system must be economically viable.

2. PAST

Historically, Sir Humphrey Davy in 1802 built a carbon cell operating at room temperature using nitric acid as the electrolyte. This attempt was a failure due to bad kinetics. Sir William Grove was the first to generate electricity by supplying hydrogen and oxygen to two separate electrodes immersed in sulphuric acid. The basic principles of such a cell, which is reverse of electrolysis, are shown in Figure 1. The anode when bathed in hydrogen, absorbs some of it which splits into protons and electrons on coming in contact with the electrolyte. Electrons are released into external circuit. Hydrogen ions travel through the electrolyte. At the cathode the hydrogen ions combine with absorbed oxygen to produce water. The electrons essential to complete the reaction, are drawn from the external circuit while a proton current flows in the

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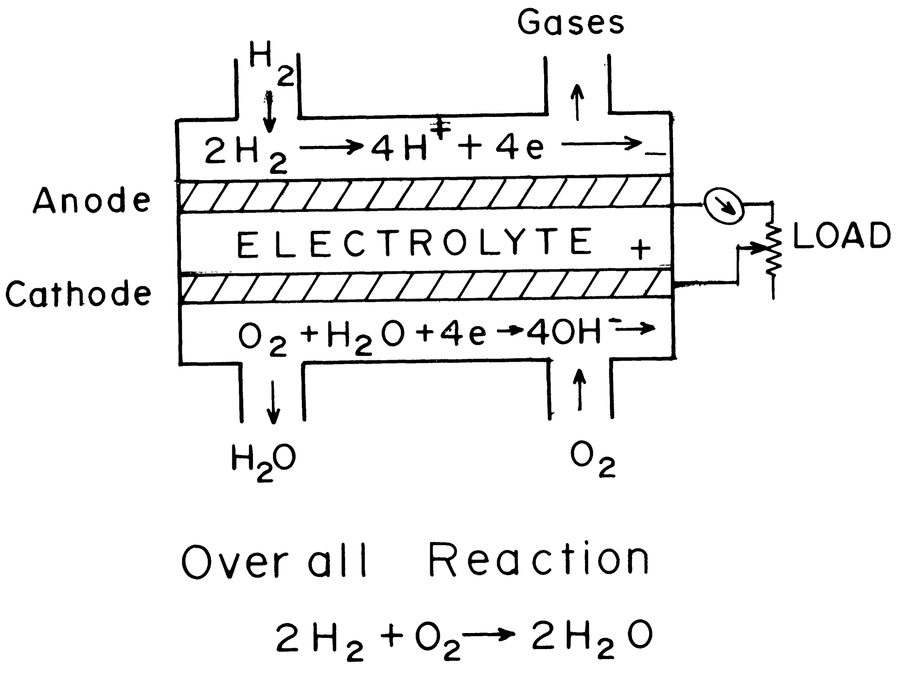

Figure 1. Hydrogen-oxygen fuel cell

internal circuit. The order of the current generated is about 200-300 milliamperes per cm^2 and the emf across the cell is of the ordder of one volt. Hence, it is essential to combine a number of cells in series in order to derive sizable amount of power from a fuel cell system.

Attempts have been made from time to time to improve and extend the fuel cell discussed above. Mond and Langer (1889) emphasised the necessity of maintaining the activity of the catalyst (Pt) absorbed on the electrode. Baur, in 1921, recognized the importance of kinetics of the redox reactions and designed a cell operating at high temperatures (1000°C) consisting of carbon as anode, iron oxide as cathode and molten alkaline carbonate as electrolyte. British scientists and engineers did a great deal of pioneering work in basic and applied fuell cell research. Bacon and Frost in 1959 built a 6-kilowatt power unit that could drive a welding machine. In the same year Ihring demonstrated that a 20-horse power tractor can be powered by a fuel cell. These events promoted fuel cell device from a mere laboratory curiosities to power sources of practical importance. The real impetus for fuel cell technology was provided when NASA decided to use fuel cells in space crafts. The technology attained prime importance during 1960's and 1970's when the prices of fossil fuels were continuously rising.

3. PRESENT

Present day fuel cells are essentially improved versions of William Grove's hydrogen-oxygen fuel cell. The development is centered around the theme that hydrogen is going to be the ultimate fuel. This demands conversion of available fuel into hydrogen. Thus a fuel processor (Figure 2) becomes a primary requirement of the fuel cell power plant. A present day fuel cell consists of three main parts: the fuel processor, the fuel cell stack and power convertor.

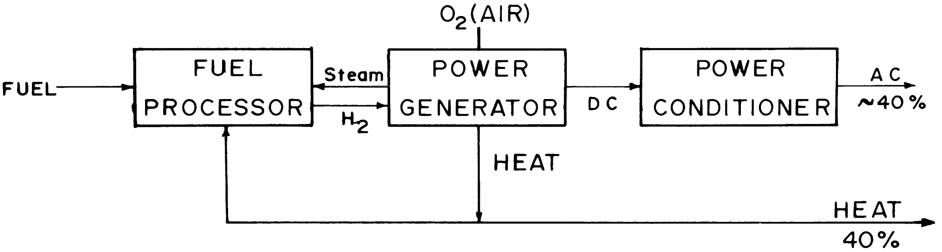

Figure 2. Fuel cell power plant (block diagram)

3.1. The Fuel Processor

It may consist of a number of components depending on the fuel used. Impurities like sulphur and nitrogen should be removed prior to its processing. Fuels like methane are converted into hydrogen by partial oxidation with steam at 750°C in the presence of nickel. Higher alkanes require cracking and partial oxidation. Methanol can be, however, reformed at relatively lower temperatures (250-300°C). The critical features of fuel processor are supply of large quantities of water and removal of undesirable components like carbon monoxide.

3.2. The Fuel Cell Stack

The stack consists of repeating cell units. Cell units are composed of an anode, a porous matrix saturated with electrolyte and cathode. Anode and cathode are made up of porous graphite having a thin layer of finely dispersed catalyst like platinum. The conversion of chemical energy residing in fuel molecule into electricity takes place in these stacks. It is very important to maintain the temperature of the stacks at desired levels in order to achieve power generation.

3.3. Power Conditioner

The fuel cell stack generates DC voltage. However, in most applications, it is essential to convert this DC voltage into a regulated AC output.

Generally, the fuel cells are classified according to the electrolyte used. Associated with the type of electrolyte is a critical temperature range, over which it is active. Maintaining characteristic temperature poses a challenging engineering problem. The 40 MW power plant situated in New York could not become operational for a long time just because the fuel cell stack could not attain optimum temperature. The fuel cells currently in vogue are as follows:

(a) Alkaline Fuel Cell (50^o-100^oC)

This has been successfully used in space crafts - Apollo and Gemini.

(b) Phosphoric Acid Fuel Cell (PAFC) (150^o-200^oC)

A number of experimental plants (40 KW-40 MW) are being installed for commercial utilization all over the world.

(c) Molten Carbonate Fuel Cell (MCFC) (600^o-700^oC)

(d) Solid Oxide Fuel Cell (SOFC) (above 1000^oC).

Major research and development efforts are being made towards the development of the above four types of fuel cells to develop them as potential power sources of tomorrow. The alkaline fuel cell is being developed with a view to power buses and motor cars in addition to space crafts. The major problem lies in the limited life on account of fast corrosion of the electrodes. Moreover, the costs are not economically viable today.

PAFC is being tested for commercial production of power. It is the only system which has withstood long continuous hours of operation (6000 hours). The stacks are in fairly developed stage. It is expected that SOFC in a short time will give a real breakthrough in fuel cell technology. The efficiency of a single unit is high but the coupling between different units poses a serious problem.

Recent developments in fuel cell technology has brought into focus some of its advantages and problems which can be summarised as follows.

3.4. Advantages

(a) Efficiency: In a fuel cell the chemical energy gets converted directly into electricity without intervening conversion into heat. The process is thus free of Carnot cycle limitations. Hence high efficiencies are possible. As there are no moving parts as in turbo-generators, losses due to mechanical conversion are absent and noise levels are low. Power per unit weight and volume are high.

(b) Cogeneration Potential: The fuel cell's end products contain 40% thermal energy in form of steam and hot water. These can be profitably used in an industry requiring hot water and steam for its operation.

(c) Flexibility in Design: To obtain a desired voltage, a number of cells are connected in series. These individual cells need not be localized in a particular area but can be distributed. This gives

considerable flexibility in weight distribution and space utilization. Cells can be added as and when required and it is not necessary to build a large plant with spare capacity to keep future needs in mind.
(d) Easy Maintenance: Since there are no moving parts, sealing problems are minimal and there are no bearing problems. The wear and tear and aging are less. Except in cells operated at high temperatures, corrosion is not a problem. Thus, a fuel can provide long and trouble-free operation.
(e) Low Pollution: The noise levels are 30 db. as compared to 300 db. of conventional generators. There are no noxious fumes or harmful combustion products. These properties are of utmost importance for military and communication applications.
(f) Low Expenses When Idle: The overload capacity for brief periods is much more than that of conventional generators. Fuel cells consume fuel and oxidant only when they are in operation. There is no fuel consumption during the periods when there is no demand of power.

3.5. Limitations

(a) Socio-economic Factors: As the technology for utilization of hydrocarbons as fuels is well developed and has stood the test of time and since presently ample sources of cheap hydrocarbon fuels are available, the socio-economic considerations are not yet in favour of generalised use of fuel cells.
(b) Technical Factors: The physio-chemical properties of the catalysts are not yet fully understood. The actual construction and continuous operation are still in early stages of development. The catalyst used are expensive and intolerant to certain impurities.
(c) Only the hydrogen based fuel cells are currently available. There are no natural sources for hydrogen and therefore all the currently developed fuel cells depend on a fuel processor.

To summarise, though fuel cells offer a great promise as a potential future power source, there is a lot to be learnt before they can be used routinely.

4. FUTURE

The technology of the fuel cells utilizing hydrogen as basic fuel is marching fast towards perfection and these cells are likely to be readily available in market in near future. However, one major problem of these cells lies in the availability and storage of hydrogen. One has to manufacture it by oxidizing natural gas (CH_4) or higher alkanes. It is well known that the natural reservesof these materials are getting depleted at an alarmingly fast rate.

These limitations can be removed if we have a fuel cell which utilizes organic fuels like methanol, ethanol directly and have improved efficiencies of electron transfers under normal pH and ambient temperature conditions. This can be achieved by developing appropriate surface catalysts, which may be able to catalyse oxidation of hydrogen rich fuels. The area of heterogeneous catalysis may therefore contribute a great deal towards the development of future fuel cell technology.

Biotechnology offers an alternative to the conventional inorganic fuel cells. It is known that the living cells carry out their functions through energy derived from oxidation reactions. The biological oxidation reactions are catalysed by enzymes and coenzymes and the chemical energy and the proton and electron fluxes in these reactions are used to generate ATP. It may be possible to mimic these reactions in future and utilise them in a way that one can generate electricity.

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ENZYME ELECTRODES - A PRELUDE TO UTILIZING HYDROGEN OR HYDROGEN RICH FUELS IN BIOCHEMICAL FUEL CELLS

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Hydrogen and hydrogen rich compounds such as methane, methanol, ethanol, etc. are used as fuels in fuel cells for generation of electricity. The generally high temperatures of operation of fuel cells limit the half-lives of the electrodes and as a result, the magnitude and stability of the power output. The problem becomes more severe with the realization that attainment of higher fuel cell efficiency may require the use of even higher cell temperatures. With enzymes, it is possible to bring down the operating temperatures and pressures to ambient conditions. Hydrogenase, the enzyme that catalyzes the oxidation of hydrogen, seems to be an ideal candidate for most of hydrogen-oxygen type of fuel cells. However, since the study of hydrogenase is still a subject of basic research, it is essential that a well studied system may be used as a model. Glucose oxidase (GOD) is one such system which has been well characterized otherwise. In our laboratory, the enzyme has been immobilized on carbon electrodes, a conjugated double bond chain serving as a spacer between FAD - its coenzyme, and the electrode. This GOD immobilized electrode serves as a bioanode. At the cathode, where oxygen is reduced, the cytochrome C oxidase (COD) system has been chosen as the catalyst. This enzyme was copolymerized on carbon electrodes along with bovine serum albumin. The half-cell potentials of the GOD and COD are found to be -0.75 V and +0.1 V respectively. We are, at present, attempting to use these enzyme electrodes in biochemical fuel cells.

1. INTRODUCTION

A Fuel Cell (FC) is an electrochemical device which converts the energy of oxidation of a fuel (e.g. H_2, CH_4, CH_3OH,C_2H_6, C_2H_5OH, etc.) directly into low voltage direct current electricity. Essentially a FC consists of an anode, a cathode and a suitable electrolyte. The fuel is continuously fed to the anode whereas the oxidant i.e. oxygen or air is flushed through the cathode and current is drawn from the external circuit through a load. Recently, it has been realized that higher FC efficiency, in futre, may require higher operating temperatures and pressures (Appleby, 1983). These were also the conditions for obtaining better system heat-rates, i.e. low heat production per kWh.

R. P. Dahiya (ed.), Progress in Hydrogen Energy, 201–207.

2. CATALYSIS OF ELECTRODE PROCESSES BY MICROBES

The concept of using microorganisms to assist electrode processes was first reported by Potter (1911) when he showed that bacteria and yeasts produced electric currents by fermenting organic matter. Cohen (1931) showed growing cultures of bacteria, when connected in series and parallel, were capable of performing electrical work. Subsequent to these reports a couple of patents were taken out in the 60's in which fermentation of sugar to alcohol by yeast (Hunger and Perry, 1966), and oxidation of hydrocarbons by bacteria (Young, 1965) or actinomycetes (Davis and Yarborough, 1967) were some of ways of generating electric current. Over this period of half a century several definitions of BFC emerged the most elaborate and yet concise one being 'BFC is an electrochemical device in which energy derived from chemical reactions maintained by a continuous supply of chemical reactants is converted to electrical energy by means of the catalytic activity of living cells and/or their enzymes (Sisler, 1961). The main advantage of BFCs over conventional FCs is the wide range of compounds and organic matter which can serve as fuel. Also poisoning and corrosion of the electrodes does not pose a major problem because firstly the microorganisms are self-replicating i.e. they grow and reproduce,hence a continuously new crop of cells replaces the old one, and secondly extremely mild conditions of temperature, pressure, pH and concentration of reactants are required. Two types of BFCs have been described, the direct BFCs in which the organisms converting the substrate into useful fuel are located at the electrode and the indirect type where the microorganisms produce fuel in a separate chamber which is then fed to a fuel cell. However, the chief limitations of BFCs utilizing microbes has been that the conditions for optimum growth of the microorganisms were not necessarily those for optimum electrochemical activity. Another serious obstacle in using living systems was the need to transport the electrons across the cell and cell organelle membranes to the electrode.

3. CONCEPT OF ENZYME ELECTRODE SYSTEMS

Microorganisms carry out oxidations at ambient conditions because of the enzyme systems involved. Hence, if the oxidized enzyme is reduced chemically by its reaction with a substrate and the enzyme thus reduced is reoxidized electrochemically on the electrode, a continuous supply of electrons to the electrode is maintained if the enzyme shuttles between the oxidized and reduced form.

Berezin et al. (1975) suggested that use of enzymes as heterogenous catalysts accelerated the transfer of electrons from fuel to electrode which might result in high power densities, per unit volume or weight. Thus for a system where the enzymatic rate constant is 5×10^2 per sec, an enzyme concentration of 2 mM would result in a reaction rate of 1 mol/litre.sec corresponding to a current of 10^5 A/litre and a maximum power of 100 kW/litre. It is with this realization that work in BFCs has centred around the search and development of efficient enzyme electrodes. A number of enzyme systems were studied earlier by Yahiro et al. (1962) and glucose oxidase, D-amino acid oxidase and peroxidase were known to exhibit electroactivity. In another experiment Yahiro and coworkers (1964) reported the glucose oxidase, in conjunction with an oxygen electrode, to generate a potential of 175-350 mV. It was concluded that flavoenzymes are capable of generating electrical energy probably due to electron transfer via oxidation of the substrates unlike the pyridine linked enzymes e.g. alcohol dehydrogenase, which did not produce electricity at all. However, with enhanced reaction rates, problems associated with macrokinetics of the process become primary and must be tackled. With enzyme electrodes the major stumbling block is the effective transport of electrons from enzyme active site to the electrode which might account for the very low currents obtained with enzyme systems (Berezin et al., 1975). Two approaches have been tried.

(a) Electron transfer mediated by low-mol-weight highly electroactive compounds e.g. methyl viologen, benzyl viologen, methylene blue, phenazine methosulfate. Mizuguchi et al. (1966) and Berezin et al.(1975) studied the enzymatic oxidation of hydrogen by hydrogenase. The transfer of electrons to the pyrographite electrode occurs with the aid of methyl viologen. The system established a potential, close to the equilibrium potential of hydrogen electrode, and oxidation of hydrogen proceeded under nearly reversible conditions. The current density was reported to be dependent on the rate of the enzymatic reaction. Methylene blue was used as electron mediator and gave a current density of 0.2 mA/cm^2 (Mizuguchi et al., 1964).

(b) Immobilization of the enzyme on the electrode so as to carry out the enzymatic oxidation of the fuel on the electrode surface. This has been the favoured approach and reports of several studies with various systems exist. We will limit ourselves to the work on glucose oxidase system only because the enzyme has been otherwise well studied in its native state. Among the various methods used for immobilizing GOD, entrapment in polyacrylamide gel on platinum mesh (Wingard et al., 1971), glutaraldehyde crosslinking around a platinum-iridium wire (Wingard et al., 1979), covalent coupling on platinum screen which has been silanized and activated with glutaraldehyde (Wingard et al., 1979), localization of enzyme on glass electrodes by semipermeable membranes (Havas et al., 1980 and Koyama et al., 1981), covalent linking through a carbodiimide spacer arm (Bourdillon et al., 1980) and cyanuric chloride (Ianniello and Yacynych, 1981 and Ianniello et al., 1982). The entrapment and localization techniques suffer from the fact that they pose a barrier for the diffusion of substrate to the enzyme and diffusion of reaction products away from enzyme. This results not only in low current densities but long response times. The reaction schemes used, for direct covalent linking of enzymes to the electrode, are non-specific, meaning, thereby, that ϵ-NH$_2$ group of any lysine residue, of the large enzyme molecule, may be involved in binding and although direct electron swapping between GOD active site and electrode has been reported by Ianniello and Yacynych (1981) and Ianniello et al. (1982), the exact manner of such electron transfer is not addressed to. We believe that for any direct electron transfer from active site of the enzyme to electrode, the active site itself must be properly oriented with respect to the electrode. Furthermore the linkage must be conducting. To achieve this, knowledge of the nature of residues involved at the active site is a prerequisite.

GOD is a flavin linked enzyme, each molecule containing two molecules of flavin adenine dinucleotide covalently attached to its active site (Bright and Porter, 1975). The nitrogens at position 1 and 10 in the flaving ring system are the sites of redox reactions. A covalent hook up of the FAD on the electrode followed by protein part of GOD would immobilize the enzyme in such a way that the active site of the enzyme is oriented towards the electrode. Thus the problem of properly juxtaposed immobilized enzymes has now boiled down to immobilizing its coenzyme, FAD, on electrodes. A number of sites are available for binding FAD to the electrode. Wingard and Gurecka (1980) covalently immobilized the flavin moiety on carbon electrode through a conjugated double bond system to the methyl group on C-6. Cyclic voltammetric experiments showed successful immobilization but the coenzyme, once reduced, could not be reoxidized. We used the C-2, position instead, and covalently attached the coenzyme though this group. The cyclic voltammograms not only indicated positive hooking but also established that the reversibility of the redox reactions was still retained (Sonawat et al., 1984). In addition, the coenzyme immobilized electrode, when incubated with protein part of GOD, resulted in an active glucose oxidase electrode. The activity of the enzyme was though very low. Our subsequent experiments have shown that increasing the length of concucdting bridge (Figure 1) between FAD and electrode enhanced the immobilized enzyme activity. This improved GOD electrode had an electrode potential of -0.75 V with reference to calomel electrode (Figure 2), and could serve as a bioanode.

4. DEVELOPMENT OF BIOCATHODES

Complexes of iron with ethylenediamine tetracetate (EDTA) or nitrillotriacetate (NAT) have been employed to promote the cathode reaction - uptake of electrons with simultaneous reduction of oxygen to water (Takahashi et al., 1969). The use of enzymes to achieve this purpose has been limited though. A quinone-hydroquinone dependent enzyme, laccase, has been demonstrated to reversibly reduce oxygen (Mizuguchi et al., 1962) and current density of 1.3 mA/cm^2 was observed at a potential of about 1 V (Mizuguchi et al., 1966). In another experiment Berezin et al. (1977) observed a potential of 1.2 V in a system where laccase was adsorbed on carbon black electrodes. Cytochrome aa$_3$ or cytochrome oxidase (COD) - the last protein in the electron transport chain - has gone largely unnoticed as an enzyme system to catalyze the cathode process, barring a few isolated reports. We have, therefore, directed our efforts towards immobilizing COD on carbon electrodes. The enzyme was copolymerized on carbon electrodes along with bovine serum albumin by glutaraldehyde crosslinking (Table I). The electrode with COD immobilized on it has an electrode potential of +0.1 V with reference to the calomel electrode (Figure 3).

Current density that is available by the combination of GOD and COD electrodes is now under investigation. Preliminary experiments indicate the internal resistance of the BFC formed by these two electrodes, to be very high.

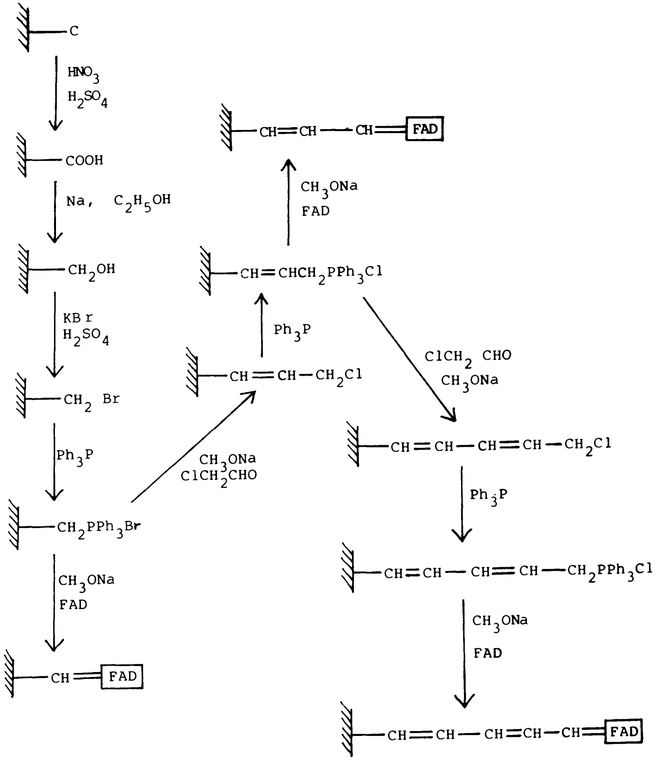

Figure 1. Reaction scheme for FAD immobilization and elongation of spacer arm length.

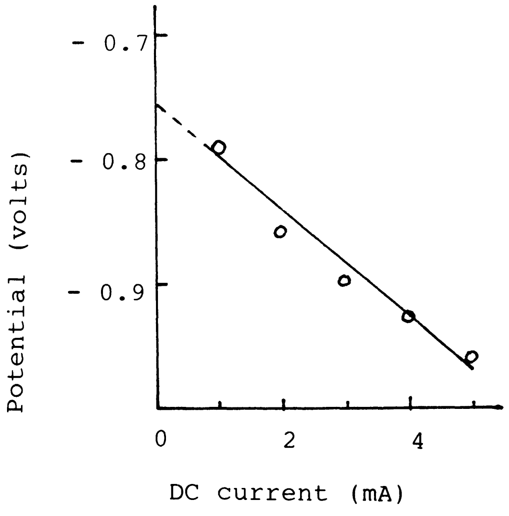

Figure 2. Determination of electrode potential of GOD electrode. 0.02 M glucose in 1.0 M phosphate buffer pH 7.0.

TABLE I : Copolymerization of Cytochrome C Oxidase (COD)

Washed carbon electrodes were incubated overnight with the following solution in 0.1 M phosphate buffer pH 7.4.

0.50 ml	Bovine serum albumin (33 mg/ml)
0.05 ml	Cytochrome C (10 mg/ml)
0.05 ml	COD (5 mg/ml)
0.06 ml	Glutaraldehyde (2.5 per cent)
0.40 ml	Buffer

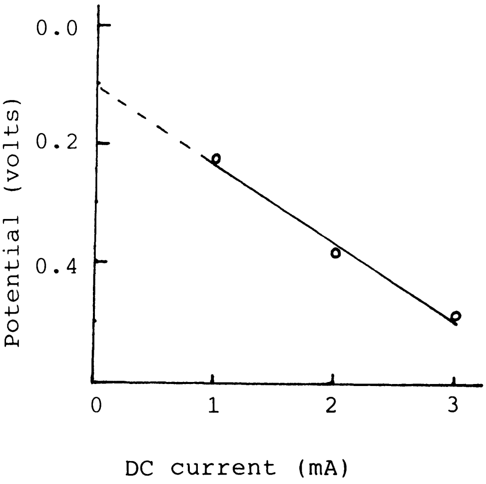

Figure 3. Electrode potential of COD electrode. 6×10^{-5}M Cytochrome C in 1.0 M phosphate buffer pH 7.0.

5. CONCLUSIONS

Lewis (1966) in his review on BFCs concluded, on the basis of information available till then, that no successful biochemical fuel cell has been demonstrated. The picture has not changed drastically as far as demonstration goes. However, we have come a long way in understanding the bioelectrochemical or electroenzymological aspect of the electrode processes. Utilization of hydrogen as fuel in BFC may become a possibility when more information accumulates on the mechanism of action of hydrogenase. Use of enzyme electrodes, in general, for producing large amounts of electrical energy is yet to be assessed. In analytical work, however, such electrodes find wide applications, for example in alcohol, glucose, urea and even protein estimations.

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ANALYSIS OF H_2-O_2 POWERED MAGNETO-HYDRO-DYNAMIC GENERATORS

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In this paper analytical model for evaluating the overall plant efficiency of H_2-O_2 powered portable and steam-bottomed MHD generators has been discussed. Composition, temperature and electrical conductivity of the seeded combustion products of H_2-O_2 system have been evaluated at various pressures. The dependence of electrical conductivity on the pressure and temperature has been expressed in the form of a power law for designing the MHD duct. In order to obtain maximum overall plant efficiency, the effect of duct inlet velocity, duct length and combustor pressure on the plant performance has been studied.

1. INTRODUCTION

The advantages of hydrogen economy and its importance as a fuel for energy systems has been well recognised. Conversion of hydrogen energy to electrical power has a variety of options such as fuel cells, gas turbines, magneto-hydro-dynamic (MHD) power generators, etc. The combustion of hydrogen with oxygen is not only pollution free due to the absence of oxides of sulphur, nitrogen and carbon in its combustion products, but it also gives rise to high temperatures suitable for operating MHD generators. The most important advantage of an MHD power generator stems from the fact that it can be operated at the highest achievable combustion temperature. As a consequence, the power plants incorporating MHD generators are thermodynamically more efficient than the conventional plants.

2. MHD POWER GENERATOR

In an MHD power generator a conducting working fluid (generally weakly ionised gases) at sufficiently high temperature (> 2500 K) is passed through a duct, which is subjected to a transverse magnetic field as shown in Figure 1. The working fluid is made conducting by the addition of some low ionisation potential material known as seed. The commonly used seeding materials are the compounds of potassium (ionisation potential 4.34 eV) or those of caesium (ionisation potential 3.89 eV).

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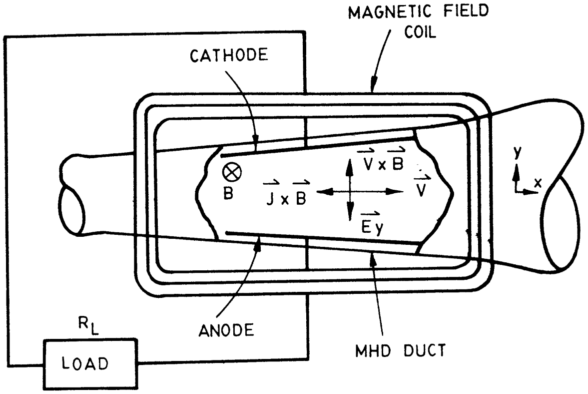

Figure 1. Schematic diagram showing the principle of MHD power generator.

When the gaseous conductor (plasma) interacts with the magnetic field, Faraday e.m.f. is induced normal to both the fluid velocity and the magnetic field directions. This induced electric field is used to drive a current by means of suitable electrodes connected with an external load (shown R_L in the figure). Thus a part of the thermal and/or kinetic energy of the working fluid is directly converted into electrical energy. The temperature of the outcoming gases from the MHD generator duct still remains appreciably high (1500-2000 K) and therefore a conventional steam turbine generator, which makes use of the part of the remaining thermal energy, can be coupled as a bottoming plant to the MHD generator.

There are two modes of operating MHD power plants: (i) open cycle and (ii) closed cycle. In open cycle mode of operation, mainly seeded combustion products are used as the working fluid and after extraction of power the flue gases are fianally rejected to the atmosphere. In closed cycle operation of the MHD generator, the working fluid, normally a heated noble gas seeded with pure ceasium or potassium metal vapours, is recycled after extraction of power. In the present investigations, potassium carbonate seeded combustion products of hydrogen burnt with oxygen have been used to realise an open cycle MHD power generator.

Considerable progress has been made in the technology of steam-bottomed open cycle MHD generators in the last few years. Now this technology is at an advanced stage of engineering and nearing commercialisation. The experience gained in the development and testing of MHD generators in different laboratories of the world has been summarised in Figure 2. The figure shows the bar chart of the energy produced which has been calculated based on the data given by Rohatgi and Venkatramani (1981) and Zong-xum et al.(1980). It may be mentioned that the figure lists only some of the major experiments. The dashed bars show projected range of energy to be achieved at the time of operation of the respective systems. A range for base load power plants has also been indicated in the figure.

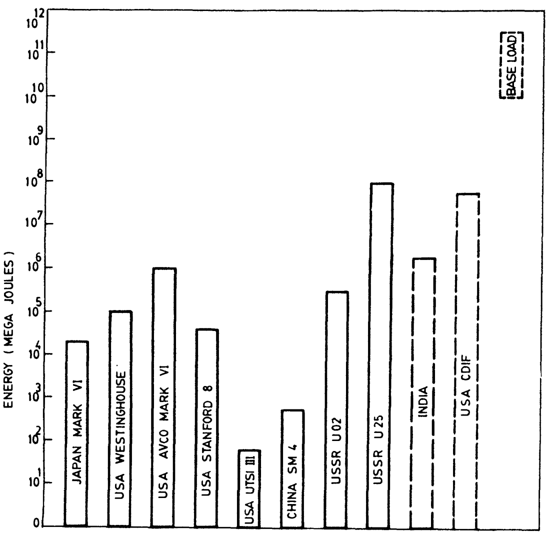

Figure 2. Status of MHD power generation.

The 500 MW_e steam-bottomed MHD power plant (U-500) being set up by the Soviet Union is expected to be commissioned in late eighties. Out of the rated capacity 250 MW_e will be generated by the open cycle MHD plant. The Indian pilot plant set up at Tiruchirapalli in Tamil Nadu has input thermal rating of 5 MW for which the fuel is blue water gas obtained from coal gasification. Recently trial runs have been made on this plant.

3. DESIGN AND ANALYSIS OF MHD GENERATORS

A complete steam-bottomed MHD cycle, shown in Figure 3, is envisaged to consist of a combustor, a nozzle, an MHD channel, an inverter, a diffuser, heat exchanger(s), a steam turbine, compressors and a magnet. Hydrogen (H_2) fuel is burnt with oxygen (O_2) under stoichiometric conditions at a desired pressure inside the combustion chamber. The combustion products are seeded with atomised solution of aqueous potassium carbonate.

The following chemical equilibrium reactions are considered while evaluating the temperature and composition of the combustion products:

$$H_2 + \frac{1}{2} O_2 \rightleftharpoons H_2O \; ; \quad K_1 = \frac{P_{H_2O}}{P_{H_2}\sqrt{P_{O_2}}} \qquad (1)$$

$$H_2O \rightleftharpoons OH + H \quad ; \quad K_2 = \frac{P_{OH}\,P_H}{P_{H_2O}} \qquad (2)$$

$$OH \rightleftharpoons O + H \quad ; \quad K_3 = \frac{P_O\,P_H}{P_{OH}} \qquad (3)$$

$$\frac{1}{2}H_2 \rightleftharpoons H \quad ; \quad K_4 = \frac{P_H}{\sqrt{P_{H_2}}} \qquad (4)$$

$$\frac{1}{2}O_2 \rightleftharpoons O \quad ; \quad K_5 = \frac{P_O}{\sqrt{P_{O_2}}} \qquad (5)$$

where P's denote partial pressure of corresponding species, and K's denote equilibrium constants of the respective reactions.

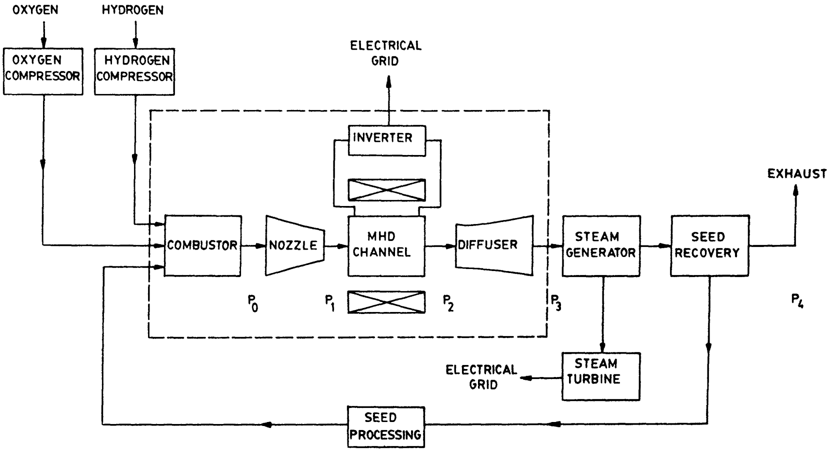

Figure 3. Typical layout of portable (enclosed in dashed line) and steam-bottomed open cycle MHD power generators.

For solving the above equations other additional equations used are:

$$R_H = \frac{n_H}{n_O} \qquad (6)$$

and

$$P = \sum P_i \qquad (7)$$

where n_H and n_O are the gram atoms of hydrogen and oxygen respectively, P_i is the partial pressure of the ith species, and P is the total pressure. The total pressure also includes the partial pressure of the potassium (seed) atom which is kept constant (0.01 atm) throughout the computation.

The partial pressures of the constituents are evaluated using an iteration technique described by Myers et al. (1958). Initially certain values of P_H and P_O are assumed in order to calculate partial pressures of O_2 and H_2O which in turn are used to determine new values of P_H and P_O using equations (4) and (5). In case the absolute value of the difference between the initial and final values is not close to the predecided tolerance (10^{-6} atm), new values are assumed and the process is repeated again. This iteration technique is, however, limited for the upper limits of R_H. The upper limit of R_H in their investigations was taken to be 1.2 while in the case of hydrogen burnt with oxygen the value of R_H is 2.0 according to the combustion reaction $H_2 + \frac{1}{2} O_2 \rightleftharpoons H_2O - 57.8$ kCal/mole. In such a case the initial values of P_H and P_O cannot be chosen at random because if the assumed value is smaller than what should have been for obtaining convergence, the final value of P_O turns out to be imaginary. On the other hand, if the assumed values are higher P_H becomes imaginary. A modification in the computation technique has, therefore, been made such that appropriate values of P_H and P_O are selected for which the iteration is convergent.

Having known the composition of the various species of the combustion products the adiabatic temperature is obtained by comparing the total heat released during the combustion of the fuel to the heat required to raise the temperature of the constituents from room temperature to a given temperature T, and the heat absorbed in the dissociation process.

The thermal input,and hence the mass flow rate to the combustor, is calculated from the total heat content of the constituent gases. The heat contents are evaluated at various temperatures and pressures. However, the effect of pressure is seen to be negligible. For the purpose of incorporating the variation of the heat contents with the temperature in the present analysis, a curve (shown in Figure 4) in the range of $2500 \leq T \leq 3400$ K has been obtained which satisfies the following equation:

$$\text{Heat content} = A + BT + CT^2 \text{ kCal/mole} \qquad (8)$$

where the numerical values of the constants A, B and C are 0.345, -7.502×10^{-5} and 1.25×10^{-7} respectively.

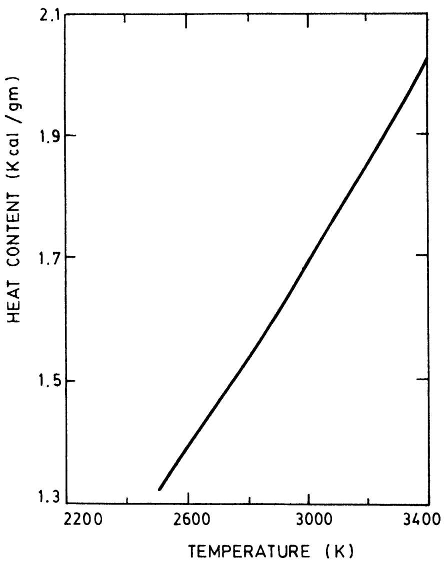

Figure 4. Variation of heat content with temperature.

The composition and temperature of the seeded combustion products calculated above are used to compute electrical conductivity (σ) of the seeded combustion products from the relation $\sigma = n_e e \mu$, where n_e, e, and μ are the electronic density, charge and mobility respectively. The methods for evaluating n_e and μ have been described by Frost (1961), Freck (1964) and Sodha et al. (1984). Since the electrical conductivity is a function of temperature and pressure for a given seeding ratio, it has been expressed in the form of a power law given by Swift-Hook and Wright (1963)

$$\sigma = C_s T^{\epsilon} P^{-\delta} \qquad (9)$$

where the values of C_s, ϵ and δ for a seeding ratio of 1 mole per cent of potassium are 1.8228×10^{-4}, 11.486 and 1.1826 respectively. The conductivity relation given by equation (9) is used for evaluating the dimensions of the MHD channel.

In the present investigations we have considered a subsonic flow of the gases for designing a constant Mach number MHD duct. To achieve the required velocity of the fluid, a convergent nozzle has been considered. The nozzle dynamics is analysed considering one dimensional steady state flow of the gases under adiabatic conditions. While evaluating the values of pressure, density, velocity and temperature at exit of the nozzle (or inlet of the duct) average values of the molecular weight and ratio of specific heats have been used.

The values of various physical parameters at the duct exit have been derived by solving the following fluid dynamic and MHD equations:

$$\rho u \frac{du}{dx} + \frac{dp}{dx} + JB = 0 \qquad (10)$$

$$\rho u \frac{d}{dx} (C_p T + \frac{1}{2} u^2) + JE = 0 \qquad (11)$$

$$J = \sigma (uB-E) \qquad (12)$$

as has been done by Swift-Hook and Wright (1963). In the above equations, B is the transverse magnetic field, assumed to be constant, E is the induced electric field, J is the current density, u is the fluid velocity, ρ is the density and C_p is the specific heat.

The enthalpy extracted by an MHD generator depends on the inlet and exit stagnation pressures along the duct. The enthalpy extracted is maximum when the stagnation pressure at the duct exit is minimum for constant combustor pressure. A diffuser at the exit of the duct is, therefore, employed to achieve a minimum duct exit pressure. The minimum pressure that can be kept at the duct exit should be such that the diffuser can recover it to a value sufficient enough for the exhaust to be possible to atmosphere. The pressure recovery factor, in the present investigations, has been taken to be 0.8 (Garrison et al., 1975) considering negligible viscous and boundary effects. The final recovered pressure from the diffuser to exhaust (1.04 atm) takes into account the pressure drop across the heat exchangers also.

The fuel (H_2) and oxidant (O_2) are assumed to be compressed from atmospheric pressure to the combustor pressure. The power consumed by the compressors in the process is calculated from the relation (Wark,1977)

$$W_c = \frac{\dot{m} C_p T_R}{\eta_c \eta_{ci}} \left[(P_o)^{\frac{\gamma-1}{\gamma}} - 1 \right] \qquad (13)$$

where η_{ci} is the stage (polytropic) efficiency, T_R is the room temperature, η_c is the compressor efficiency, m and C_p respectively are the mass flow rate and specific heat of the fluid to be compressed.

In case of the steam-bottomed generator, a superconducting magnet of strength 5 T has been considered. Since flow of heat would take place from the channel to the magnet, a refrigeration engine has been considered to remove the heat flux to maintain the superconductivity of the magnetic coils. The power consumed by the refrigeration engine has been calculated following Sodha and Bendor (1964).

If Q_3 is the heat content of the combustion products at T_{O3}, stagnation temperature at the diffuser exit, Q_s is the heat content at the stack, and η_T is the efficiency of the steam turbine generator, the work done by the steam turbine can be written as :

$$W_T = \eta_T (Q_3 - Q_s) \qquad (14)$$

The overall plant efficiency (E_b) is the net electrical power output per unit thermal input, Q_o, and is written as follows after taking into account the power produced and consumed by various components in the

MHD cycle:

$$E_b = \frac{W_M + W_T - W_C - W_R}{Q_o} \qquad (15)$$

where $W_M = \eta_M \cdot (Q_1 - Q_2)$ is the power produced by the MHD generator for heat contents Q_1 and Q_2 at the input and exit of the duct respectively, η_M is the a.c.-d.c. inverter efficiency and W_R is the power consumed by the refrigeration engine. In case of the portable generator the efficiency has been taken to be that of the MHD generator, i.e.

$$E_p = \eta_M \frac{Q_1 - Q_2}{Q_0} \qquad (16)$$

The numerical values of various parameters used for the analysis have been given in Table I.

TABLE I : Values of Various Parameters Used for Evaluating Overall Plant Efficiency (E_b)

Magnetic field strength	
Portable	2 T
Steam-bottomed	5 T
Compressor pressure recovery factor	0.8
Compressor efficiency	98%
Stage polytropic efficiency	90%
Steam turbine efficiency	40%
a.c.-d.c. inverter efficiency	95%
Thermal input	
Portable	1 MW
Steam-bottomed	1000 MW
Pressure at the exhaust	1.04 atm
Temperature at the exhaust	400°K
Pressure drop across heat exchanger	0.95

4. RESULTS AND DISCUSSION

The electrical conductivity of the potassium seeded combustion products of the H_2-O_2 system is evaluated under stoichiometric conditions and its variation with temperature at various pressures is shown in Figure 5. The conductivity obviously increases exponentially with temperature but decreases with pressure. The decrease in the conductivity with pressure can be attributed to the reduced mobility of the electrons at elevated pressures. The effect is, however, pronounced at lower pressures. The dependence of the electrical conductivity on the seeding ratio of potassium at various pressures and the corresponding temperatures has been shown in Figure 6. The figure indicates that the conductivity initially increases to a maximum value with the increase in seeding ratio; thereafter it starts decreasing with further increase in the seeding ratio because of larger electron collision cross-section with potassium particles resulting in smaller electron mobility. The conductivity maxima remain almost unaffected by the pressure. It can be seen from the figure that the conductivity achieved at one per cent seeding ratio by weight of potassium is above 10 mhos-m^{-1} which makes H_2-O_2 combination a suitable fuel for MHD generators.

The values of the constants appearing in the equations given in Section 3 have been evaluated using Figures 5 and 6 to facilitate the system analysis of the portable and steam-bottomed MHD power generators. The analysis has been carried out to obtain the values of the duct length, velocity and combustor pressure for the highest achievable efficiency. The efficiency of the steam-bottoming plant has been taken to be 40 per cent. The pressure at the exhaust of the systems has been assumed to be 1.04 atm.

In case of the portable generator, the effect of magnetic field on duct length for various values of the combustor pressure has been shown in Figure 7. The values have been computed for a thermal input of 1 MW and duct inlet velocity of 900 ms^{-1}. It may be mentioned that the enthalpy extraction remains almost constant for the given values of the pressures at the combustor and exhaust. The figure shows that the duct length decreases with the increase in the magnetic field as well as the combustor pressure.

The effect of the duct inlet velocity on the enthalpy extraction of the portable generator has been given in Table II and on the power output per unit length (P_L) of the steam-bottomed plant has been shown in Figure 8. Since the duct inlet velocity is gained at the expense of the fluid temperature, the power output shows an increase in the lower range of the velocity while it starts falling off at higher velocities. It is obvious from Table II and Figure 8 that the maximum power is obtained when the duct inlet velocity is in between 1100-1200 ms^{-1} and 1200-1400 ms^{-1} for the portable and the steam-bottomed generators respectively. In the foregoing analysis the duct inlet velocity for steam-bottomed generator has been chosen to be 900 ms^{-1} because the value of P_L for this velocity is marginally smaller than its maximum value.

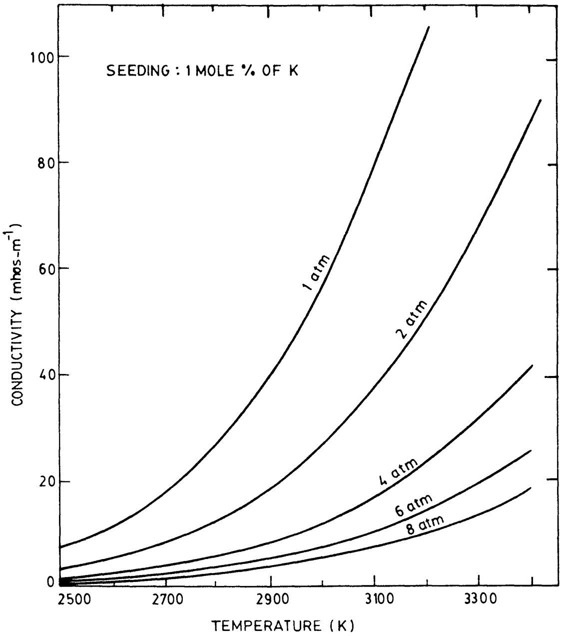

Figure 5. Variation of electrical conductivity with temperature.

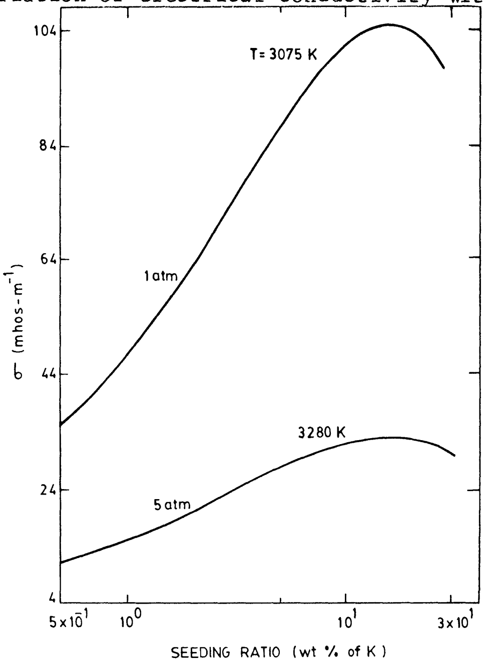

Figure 6. Variation of electrical conductivity with seeding ratio.

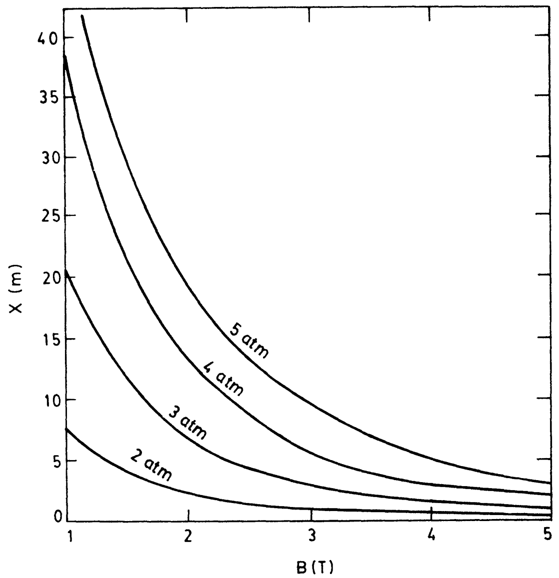

Figure 7. Effect of magnetic field on duct length in portable generator.

TABLE II : Enthalpy Extraction in Portable Generator for Combustor Pressure = 2 atm.

Velocity ms^{-1}	Enthalpy per cent	
	Duct length 2m	Duct length 3m
800	4.1	13.8
900	4.3	14.8
1000	4.5	15.5
1100	4.6	16.0
1200	4.5	15.7

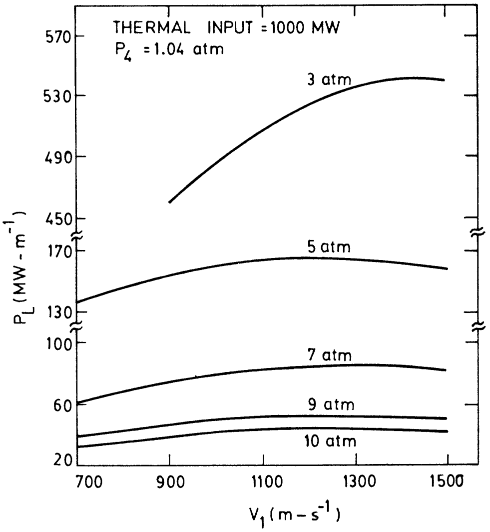

Figure 8. Variation of power output per unit length with duct inlet velocity in steam-bottomed plant.

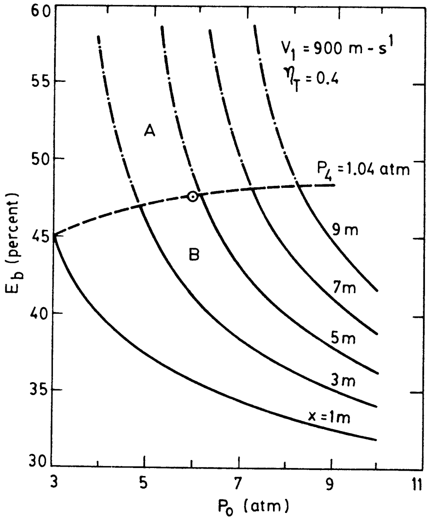

Figure 9. Variation of overall plant efficiency with combustor pressure in steam-bottomed plant.

If the exhaust pressure is held constant, the efficiency of the generator is an increasing function of the combustor pressure. But the increase in the power consumed by the compressor, to attain higher working pressure, has the reverse effect and consequently an optimum value of the operating pressure can be obtained for which the efficiency is maximum. The value of the combustor pressure corresponding to the highest achievable efficiency for steam-bottomed generator can be obtained from Figure 9, which shows the effect of the combustor pressure on the overall plant efficiency.The dashed curve corresponds to the exhaust pressure of 1.04 atm which indicates that the efficiency remains more or less unaltered at higher combustor pressures. At the duct inlet velocity of 900 ms^{-1}, 4.75 m duct length is adequate for a combustor pressure of 6 atm. The fuel and oxidant should be made available at the desired pressures when the portable generator is considered. So the compressor power is not taken into account. The duct length is chosen keeping in view the portability of the system; the efficiency of the generator alone is not so important. After deciding the duct length, the combustor pressure is worked out so that the flue gases coming out of the MHD generator are at a pressure not less than 1.04 atm. The values of the duct length, combustor pressure and enthalpy extraction are given in Table III for a portable generator. It can be noted from the table that the enthalpy extraction varies linearly with the combustor pressure.

In a steam-bottomed MHD generator, the effect of combustor pressure on various physical parameters has been shown in Figure 10. The values have been determined for a duct inlet velocity of 900 ms^{-1}. As expected the fractional power produced by the steam turbine (W_T/Q_0) decreases with the increase in the pressure while the fractional power produced by the MHD generator (W_M/Q_o)scales up with the pressure. The net effect turns out to be just a negligible increase in the overall efficiency. For a given exhaust pressure, the duct length would obviously increase with the combustor pressure and the same is evident from the figure.

5. CONCLUSION

In conclusion, the hydrogen fuel burnt with oxygen and seeded with potassium is seen to meet the technological requirements of MHD power generators. A portable generator operated with H_2-O_2 system can provide an efficiency of 11.4 per cent when the duct length and the combustor pressure are kept 3 m and 2.4 atm respectively. For the steam-bottomed plant maximum efficiency of 47.6 per cent can be achieved when the operating parameters, viz. the combustor pressure, duct inlet velocity and duct length, are kept 6 atm, 900 ms^{-1} and 4.75 m respectively.

TABLE III : Parameters of Portable Generator for Duct Inlet Velocity = 1100 ms^{-1} and Exhaust Pressure = 1.04 atm.

Duct length m	Combustor pressure atm	Enthalpy extraction per cent
2	2.1	9.4
3	2.4	11.4
4	2.6	13.0
5	2.9	14.5
6	3.1	15.5

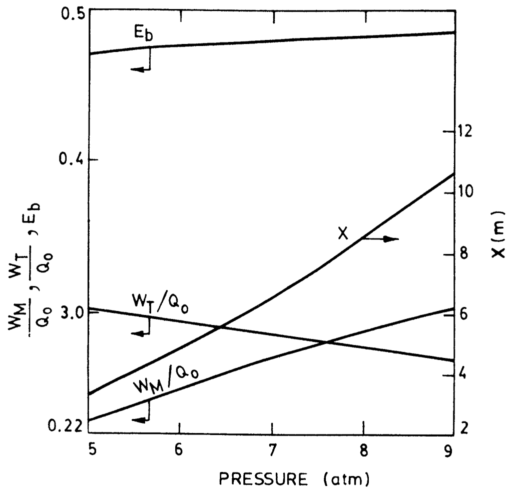

Figure 10. Effect of combustor pressure on the performance of various components in steam-bottomed plant.

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ENERGY TECHNOLOGY CHARACTERISATION AND ASSESSMENT USING INPUT-OUTPUT STRUCTURE: A CASE FOR HYDROGEN

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1. INTRODUCTION

Limited supply of conventional fossil fuels, increasing prices of crude oil due to monopolistic trends in the world market and exponentially increasing demand for energy, characteristic to most developing countries, has spurred attempts to develop alternate energy sources in India. Among the new energy options being debated and researched for development on commercial scale are: solar, geothermal and wind power, biogas, nuclear options such as for fusion, and hydrogen. All of these being emerging technologies are at various stages of maturity and compete for rather meagre research and development funds in case of India. Under the circumstances, it is needless to emphasize the necessity for a pre-investment technology assessment in case of these emerging options.

2. ASSESSMENT TECHNIQUES

An emerging technology can be assessed at three different levels, using diverse techniques.

The first one in the hierarchy is the engineering or process analysis technique which would give the most efficient process option. It meets a given demand for that energy form/fuel at the minimum production cost, and compares the current technology in that light. This is an assessment in absolute terms, as the technology in question is assessed in isolation, without considering other technologies, energy forms or fuels. The next in hierarchy is the assessment of the new technology in competition with other technologies or fuel options and takes into account possible substitutions among various energy forms and changes in their relative prices. For this, energy system models are used, and linear or non-linear programming techniques are in vogue. Even this assessment technique considers energy sector alone, without considering the inevitable inter-linkages of energy to other sectors of economy. This lack of consideration of intersectorial linkages often surfaces as 'bottlenecks' due to sectors other than energy sector and often results in a failure in the transfer of a technology tried and proven elsewhere.

R. P. Dahiya (ed.), Progress in Hydrogen Energy, 225–229.

An assessment technique which highlights this intersectoral dependence, and offers sectoral consistency is described below in its simplest form, along with modifications required for a long-term assessment. The application of this methodology for assessment of Hydrogen as an emerging energy option is demonstrated but without empirical detail due to the lack of a relevant database.

2. LEONTIEF'S INTERINDUSTRY FRAMEWORK

National economy is divided into various sectors, some energy producing and some others which are energy consuming. Part of the gross output of any sector goes as inputs to the production processes of other goods, and is termed 'interindustry inputs'. The rest is consumed by population in its final form which is termed 'final consumption'. The amount of inputs from various sectors to a particular sector depends on the current production process or technology (or combination of such) used for producing good/service in that sector. To give a common denominator or comparability to all these inputs with different units, all of the inputs and outputs are measured in money value. A simple, 6 sector model with coal, crude oil and petroleum products and electricity as energy producing sectors and agriculture, transport and industry as energy consuming sectors is explained below with the help of vector and matrix notations.

$$\sum_{j=1}^{6} X_{ij} + Y_{Fi} = X_{oi} \tag{1}$$

where X_{ij} is the part of the output of ith sector going as input to jth sector,

X_{Fi} is final consumption of ith sector goods/services,

X_{oi} is the gross output of the ith sector.

The above equation can be written also as

$$\sum_{j=1}^{6} a_{ij} X_{oi} + Y_{Fi} = X_{oi} \tag{2}$$

where $a_{ij} = \frac{X_{ij}}{X_{oj}}$ is the ijth technological coefficient or input-output coefficient,

$a_{ij} =$ input of ith sector goods in money value, required to produce 1 Rupee worth of jth sector output.

The matrix of these coefficients is denoted by A and represents the current technological or production structure of an economy. In the matrix form the above equation is

$$\begin{aligned} A X_o + Y_F &= X_o \\ Y_F &= [I-A] X_o \\ X &= [I-A]^{-1} \times Y_F \end{aligned} \tag{3}$$

Given the requirements of final consumption of goods and services needed by population, represented by vector Y_F, and the current technological structure given by matrix A, this framework gives the vector of gross outputs required to be produced to satisfy these demands.

3. APPLICATION OF I-O METHODOLOGY FOR ASSESSMENT OF HYDROGEN

Hydrogen (or any other emerging energy option/options) can be added to the six sector structure explained earlier, as an additional energy producing sector increasing the dimension of the structure by one. To augment the existing technology matrix for addition of hydrogen, it is necessary to know what resources constitute 'inputs' to the production technology (or a combination of technologies) for hydrogen, and consequently the methods and scale of production most likely to be used.

Similarly, the 'output' of the hydrogen energy sector would find applications in other sectors of the economy, for which possible areas of applications of hydrogen should be studied. Several studies have been carried out on both of these aspects, of which particularly useful are NASA hydrogen system technology study by Laumann(1976) and ERDA's hydrogen programme by Langrebe (1976). Four production methods proposed at present are:

(a) Steam reforming or partial oxidation of hydrocarbons such as natural gas, oil or coal.

(b) Electrolysis of water (using electricity produced using nuclear, geothermal, wind or solar options).

(c) Thermochemical water splitting using high temperature heat sources.

(d) Photochemical method.

Of these, the first two methods are widely used at present and likely to be used due to their relative economy, till the turn of this century.

The inputs to hydrogen as an energy sector in near future would be coal, oil, natural gas, electricity and water. In the distant future inputs may come from electricity produced from solar, geothermal, wind and nuclear means and heat as the byproduct of nuclear electricity.

Little data regarding the relative costs of inputs using alternative production methods is available, as none except the first method of production has been tested commercially and standardized.

Applications of hydrogen in the near future seem to be in the following areas:

(a) Chemical industry,
(b) Steel industry,
(c) Petroleum refining
(d) Experimental aircraft fuel,
(e) Synthetic fuel in liquid and gaseous form.

Again data regarding hydrogen as interindustry inputs or final consumption in money value are far from being available.

The detailed analysis of the advent of hydrogen technology using the input-output method is possible only if the data regarding hydrogen as input <u>to</u> various sectors of economy and inputs <u>from</u> various sectors of economy to hydrogen are available in monetary terms. For this technology characterisation for various production methods for hydrogen, will have to be carried out, in the form suitable for use in input-output framework. Some efforts towards this end have been made in Indian context. The DELPHI study of IIT Madras (Ramani, 1980) confirms two trends for India regarding likely production methods for hydrogen till the turn of the century and regarding applications of hydrogen. A document on energy technology characterization (Subhash et al., 1985) has been published at IIT Delhi which gives details regarding five production processes for hydrogen in terms of efficiency, operating and production costs. However, neither of these is adequate for assessment using input-output framework. For a particular year, a vector of final demands taking into consideration interfuel substitutions on advent of hydrogen can be projected, using the augmented technology matrix (if available) the levels of gross outputs of all sectors can then be computed. Knowing the target capacities and resource limitations, probable bottlenecks can thus be identified.

In absence of a detailed data in monetory units, only the structure of modified input-output for near future is given in Table I. (The entries of inputs to hydrogen sector and inputs from hydrogen to other sectors are indicated in appropriate rows/columns). For longer time frame when inputs from sources such as solar, geothermal, wind are likely, the matrix can be extended to a larger dimension including these options.

TABLE I : Structure of the Modified I-O Matrix with Hydrogen

	Agri.	Coal	Elect.	Oil and Nat.Gas	Trans.	Indus.	H_2	Final Demand	Gross Output
Agri.							-	Y_{F1}	X_{01}
Coal							*	Y_{F2}	X_{02}
Elect.							*	.	.
Oil and Nat.Gas							*	.	.
Trans.				a_{ij}			-	.	.
Indus.							*	.	.
H_2	-	-	* (in far term)		*	*		Y_{F7}	X_{07}

One important feature of hydrogen as a 'clean fuel', however, cannot be explicitly or quantitatively treated using this model, unless it indcludes the environment submodel.

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PERSPECTIVE, PROBLEMS AND PROMISES FOR TRANSITION TO HYDROGEN ENERGY

PANEL REPORT

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New Delhi

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Dr. K.V.C. Rao
Vikram Sarabhai Space Centre
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Consultant
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Banaras Hindu University
Varanasi

R. P. Dahiya (ed.), Progress in Hydrogen Energy, 231–233.

In the final session of the Workshop, a panel discussion was held on the theme: Perspective, Problems and Promises for Transition to Hydrogen Energy. Initiating the panel discussion, Dr. Gururaja, the panel moderator, emphasised the need for a planned and systematic approach to the development of an infrastructure for research in all aspects of hydrogen energy. He drew attention to the need for defining the programme in terms of realities, keeping in view the expertise and financial resources available and taking input from the Workshop. The Workshop was informed of the Seventh Five Year Plan proposal that a sub-group has made in this area. The deliberations of the Workshop were highlighted by the panelists (Figure 1).

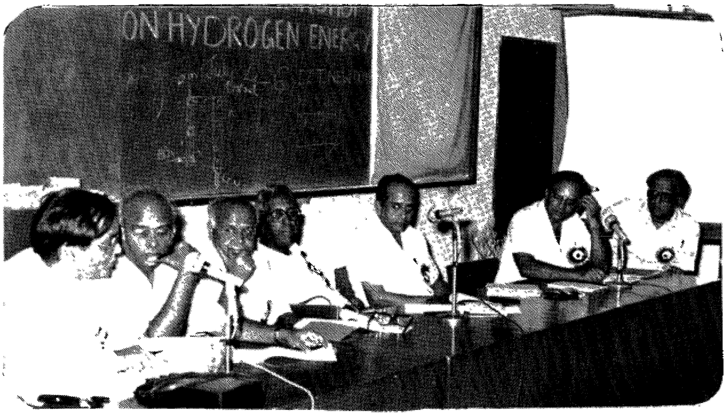

Figure 1. Panelists presenting their view points during panel discussion.

After considering the views of the speakers in the Workshop and taking into account the perspective, problems and promises for transition to hydrogen energy, the panel made the following recommendations:

(1) There is a definite need to support short and long term Research and Development programmes on hydrogen energy in national laboratories, IITs and universities. Industry should be encouraged to adopt knowhow generated and to use hydrogen as a fuel wherever possible.

(2) The Research and Development programmes in this area should be periodically reviewed to assess their progress and to chalk out new directions for research.

(3) Since the opportunity provided by holding the Workshop had been extremely useful for exchange of scientific information and reviewing the status of the work, a workshop should be organised at least once in two years.

(4) Hydrogen energy should be identified as a "Thrust Area" in the Seventh Plan. Sufficient resources should be allocated for the development of hydrogen energy technology.

(5) Research and Development work should be sponsored on the various aspects of hydrogen energy, i.e. production, storage and transportation, utilization, safety, economy and system analysis. The areas identified for immediate attention with regard to financial support from the government sources are given below:

- (a) Production of hydrogen using non-conventional energy sources:
  - (i) electrolysis method
  - (ii) photolysis, photo-thermal, photo-biological and photo-electrochemical methods
  - (iii) thermochemical methods
  - (iv) hydrogen generation by micro-organisms.
- (b) Storage and transportion using:
  - (i) metal hydrides
  - (ii) hydrogen liquefaction
  - (iii) cryogenic storage and transport vessels
  - (iv) high pressure storage gas
  - (v) pipeline transportation method.
- (c) Utilization of hydrogen for:
  - (i) industrial burners, furnaces and combustors
  - (ii) residential and commercial purposes
  - (iii) I.C. engines for automobile and agricultural use
  - (iv) fuel cells
  - (v) MHD power generation.
- (d) Safety aspects:
  - (i) instrumentation and control devices
  - (ii) codes and standards.
- (e) Environmental aspects.
- (f) Public education on hydrogen energy.

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SUBJECT INDEX