

Energy Storage and Transmission

PLATINUM CATALYSES CHEMICAL CLOSED-LOOP SYSTEM

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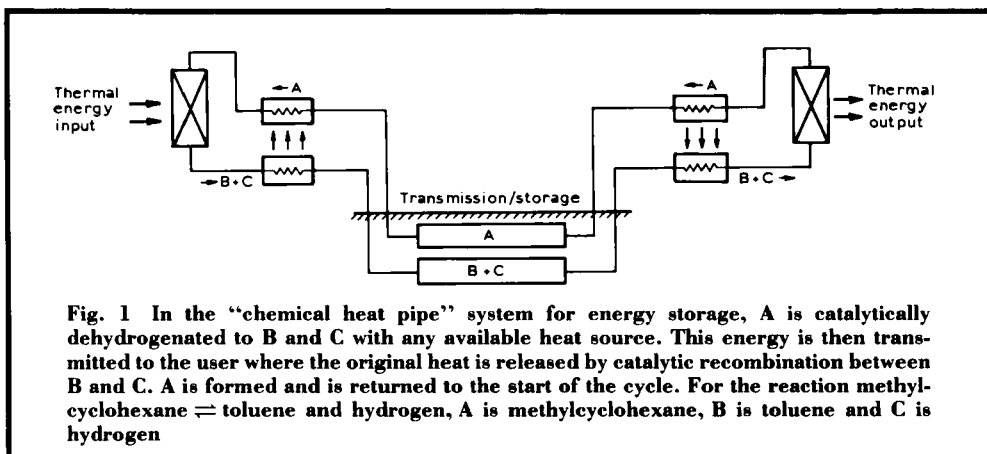
Increasingly the energy needs of society will have to be met from renewable resources. The use of these is limited at present by their location, the technologies available to harness them and the major problems associated with their storage. One possible solution to these difficulties has now been demonstrated, and is described here, while further development work is continuing. Hydrogen produced by any convenient means is used as a medium for energy storage and transmission. Close to its production site the hydrogen is catalytically reacted with toluene to yield methylcyclohexane; this is transferred safely by pipeline or container to the point of energy requirement where it is catalytically dehydrogenated. The hydrogen released is then available for use in a wide variety of ways, while the toluene is returned to the source for further hydrogenation, and the cycle is repeated.

The use of hydrogen as a fuel is not a new idea, having been proposed by J. B. S. Haldane in 1923 (1); however, the term "Hydrogen Economy" is more recent, being used first by John O'M. Bockris in 1971 (2). This concept relates to the possibility of using hydrogen as an energy medium. Appropriate technologies, including electrolysis, photovoltaic and thermochemical conversion are employed to produce hydrogen which is then used in conventional ways to produce thermal or electrical energy. It is evident that exploitation of renewable energy sources such as solar, wind or hydroelectric power by these means would be very dependent upon the location of the sources and the time they were available for energy generation. Consider, for instance, the climatological and geographical dependence of solar energy, the fluctuating character of the winds and the seasonal variations in the rainfall upon which hydroelectricity depends.

A prerequisite for these energy sources to be exploited successfully is the solution to the problems of hydrogen storage and transmission. An additional but no less important factor would be the availability of cheap land.

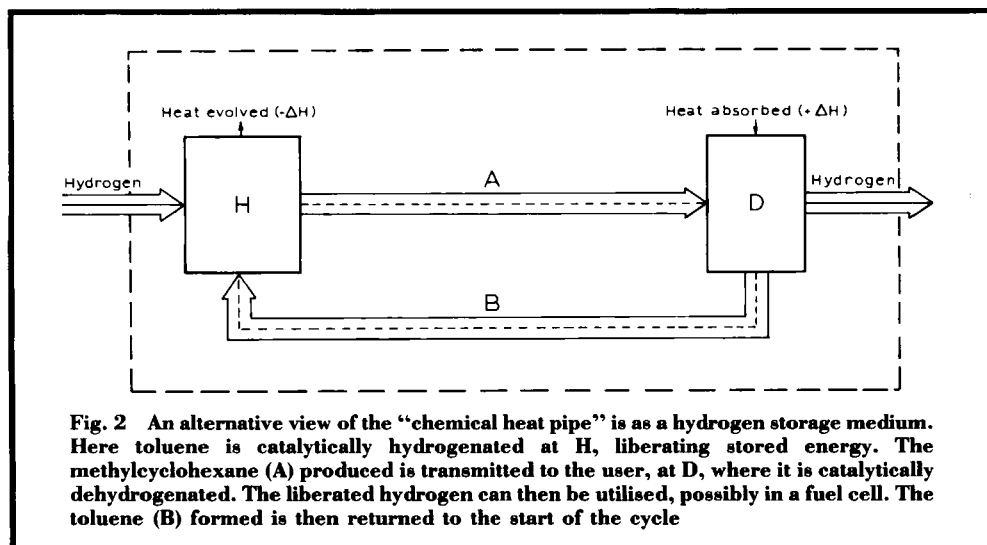
The ambitious goal of harvesting these dilute energy resources will require vast areas of desert where solar energy could be converted by thermal or photovoltaic means. Similarly the development of the huge unused sources of hydroelectric power would also require large areas for water collection and storage. These are available, but mostly in remote regions of the world, such as central Africa, central South America and northern North America; all at great distances from existing major energy users.

Although these problems belong to a future in which renewable energy sources will have to play an ever increasing role, finding more effective means for both storing and transmitting hydrogen could have important implications for everyday life. A solution to these problems would, in fact, have a bearing upon the many applications where hydrogen is currently used. At present transmission in liquid form may be restricted by hydrogen embrittlement which affects steel containment vessels and pipelines. As safety and energy density are paramount for any hydrogen utilisation programme, it is not surprising that great efforts are being made to



find alternatives to the presently available methods of storage and transmission, which are as a compressed gas in pressurised vessels or as a liquid in cryogenic containers. Recently the preferred approaches have involved the development of hundreds of metal alloys for possible use as hydrogen absorbing materials, and further investigations of cryogenic storage in the presence of hydrogen absorbing materials. However, while these could solve the problem of storage, it was only in the 1970s that the search for more convenient means of transmission achieved prominence. Liquid hydro-

genated molecules such as methyl alcohol or ammonia were first considered, but these were soon abandoned because of the difficulties associated with the gaseous nature of the constituents if they were to be used in closed-loop systems. The use of methylcyclohexane (MCH) as a liquid carrier of hydrogen to be used for automotive purposes was first reported by Sultan and Shaw (3). Later this concept was adapted for storing and transferring energy by Vakil (4, 5). His "chemical heat pipe" (CHP) concept involved the (de)hydrogenation of cyclohexane and methylcyclohexane and this



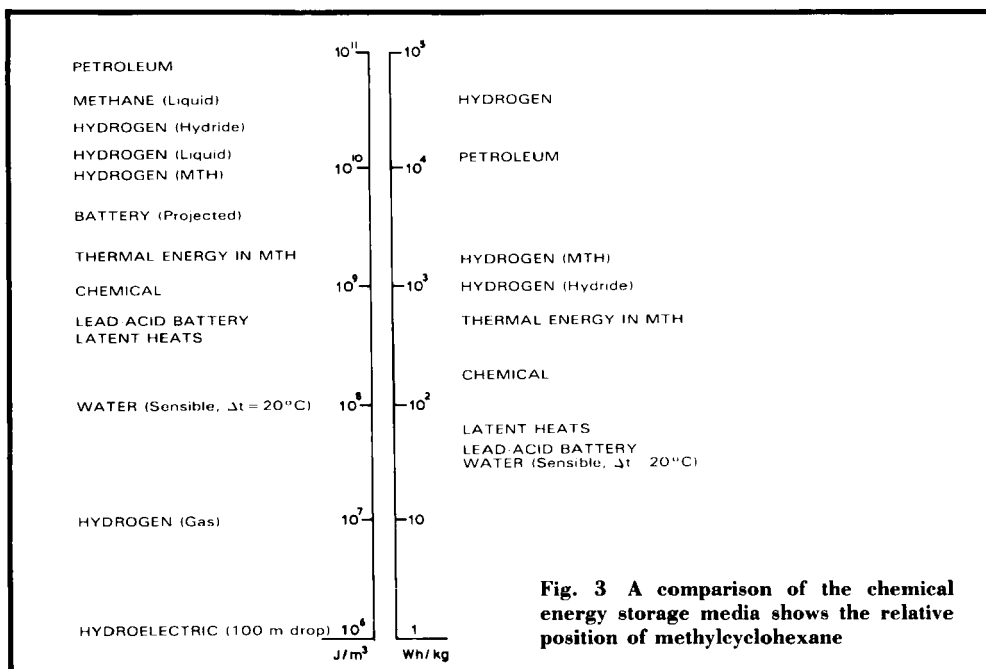
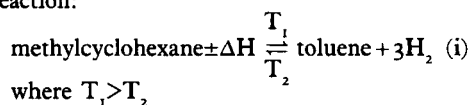


Fig. 3 A comparison of the chemical energy storage media shows the relative position of methylecyclohexane

was said to be the most suitable “model” reaction in a mid-temperature range.

To distinguish between the two concepts, consider the equilibrium of the catalysed reaction:



In the CHP concept for energy storage and transmission the process starts from the left, in Equation (i). Any available heat sources such as waste heat or solar energy are used to carry out the endothermic catalytic dehydrogenation reaction, to the right. The products formed are stored and/or transmitted to the location where the energy is required. Here the original heat is released by exothermic catalytic recombination, to the left. A conceptual scheme of this closed-loop cycle is shown as Figure 1. In the former idea, which relates to the storage of hydrogen, the same closed cycle is repeated but the starting point is different, see Figure 2. It starts with the hydrogenation of toluene and the methylcyclohexane formed is transmitted to the end-user, where it is decomposed. The

hydrogen released is consumed by any conventional means, or preferably in a fuel cell, and the toluene is sent back to the source for recycling.

Methylcyclohexane-Toluene-Hydrogen

Initial outlines of both concepts have been expanded in this Institute and elsewhere, to include engineering, catalytic and kinetic aspects, and techno-economic evaluation (6-23). Before going into details the main features of the methylcyclohexane-toluene-hydrogen cycle (MTH) will be summarised. First, MTH ranks amongst the best of the chemical storage media, even though these are poor when compared with fossil fuels; this is demonstrated in Figure 3. The ability to collect dilute quantities of energy is however a characteristic feature of chemical storage, in contrast to the depletive consumption of fossil fuels. With an energy storage capacity of 0.63 kWh/kg of methylcyclohexane (the heat of the hydrogenation reaction), 18 round trips of the methylcyclohexane-toluene-hydrogen cycle

store energy equivalent to 1 litre of oil. For hydrogen storage the MTH system offers definite advantages (energy density) over conventional systems, as shown by the data in Table I, and possesses the additional unique benefits of indefinite storage, ease of handling and transmission even over long distances. Furthermore the melting points of the components allow the system to be used under arctic conditions.

For these two closed-loop cycles to be cost effective, very stringent requirements have to be met. First the catalysts must possess long-life, high activity and the ability to catalyse both the dehydrogenation and the hydrogenation reactions completely, unhindered by even traces of by-products. In undertaking experimental work at this Institute it was accepted that even though the isolated (de)hydrogenation of cyclohexane and of methylcyclohexane are not used commercially they do form part of a series of reactions which are used industrially on a large scale for the catalytic reforming of naphthas to yield high

octane reformates. These reactions are catalysed by noble metals which therefore were also considered for our investigations. At the start, interest was focused on the cyclohexane-benzene cycle as a "probe" reaction. Although many platinum-based catalyst formulations were tested only a few attained 100 per cent selectivity, which was seen as a goal since even trace amounts of methylcyclopentane seriously affect the number of cycles necessary for a closed-loop system to be realistic. The superior performance attained over proprietary catalysts based upon honeycomb supported platinum encouraged extensive work at this Institute on all their inherent catalytic, structural and kinetic aspects. High turnover numbers comparable to those of conventional catalysts were found, with the added benefit of 100 per cent selectivities for both the forward and the reverse reactions. Typical conversion plots of conversion against contact time, W/F (where W is the weight of the catalyst and F the flow rate of the reactant), are shown in Figures 4, 5 and 6; the data being obtained as part of a

Storage system	Density, grams of hydrogen per litre	Theoretical weight per cent, grams of hydrogen per gram of saturated compound	Mass of non-saturated compound needed to store 1 kg of hydrogen, kg
Gaseous hydrogen P = 1 bar	0.09	100	—
P = 200 bar	18	100	—
Liquid hydrogen	70	100	—
Cryogenic storage with adsorbing material	16.9	4.76	20
Metal hydrides			
TiH ₂	150	3.8	25
FeTiH ₂	45.5	1.3	77
Reversible organic reaction			
C ₆ H ₆ + 3 H ₂ ⇌ C ₆ H ₁₂	56	7.19	12.9
C ₇ H ₈ + 3 H ₂ ⇌ C ₇ H ₁₄	47.4	6.16	15.2

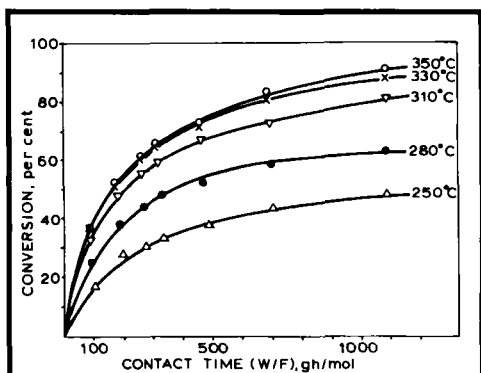


Fig. 4 The conversion of cyclohexane to benzene versus contact times at various temperatures, when the volume ratio of the reaction mixture $N_2 : CH$ is 5, N_2 serving as a carrier for the cyclohexane

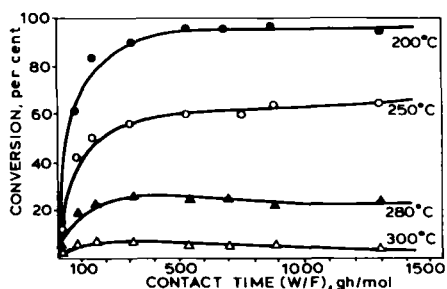


Fig. 5 The conversion of benzene to cyclohexane versus contact times at various temperatures, when the volume ratio of the reaction mixture $H_2 : benzene$ is three

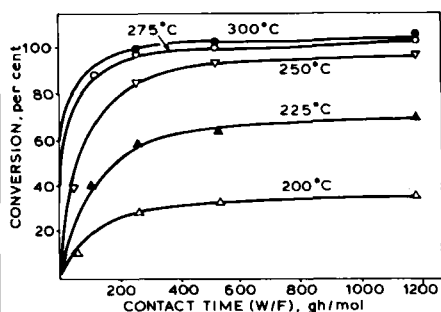


Fig. 6 The conversion of methylcyclohexane to toluene versus contact time at various temperatures, when the volume ratio of the reaction mixture $N_2 : MCH$ is five

continuing programme aimed at determining all parameters necessary for the scale-up, construction and testing of a pilot plant equivalent to a thermal power source of 6 kW (7). The geometry of the honeycomb monolith proved to be advantageous, the low pressure drop through it reducing the energy needed for pumping. Based upon extensive catalytic and kinetic information, some typical flow-sheets have been examined, and the one shown here as Figure 7 appears to offer the best compromise.

Relying upon a theoretical energy density of 0.68 kWh/kg of cyclohexane—for the chemical heat pipe concept of energy storage—and 2.4 kWh/kg of cyclohexane—for hydrogen storage—flow-sheets of this type have been adapted conceptually by us to fit the purposes of an ideal heat-storage plant of 1000 kW (7), or for the storage and transmission of 200 MW as hydrogen over a distance of 160 km (9), or the transmission of 10,000 MW electrical power as compared with the equivalent hydrogen energy as MTH, over distances of thousands of kilometres (12).

Supported Platinum Catalysts

Although details are not given here, we want to emphasise some essential points of the proposed processes. First, beyond any doubt the use of correctly tailored platinum catalysts is a

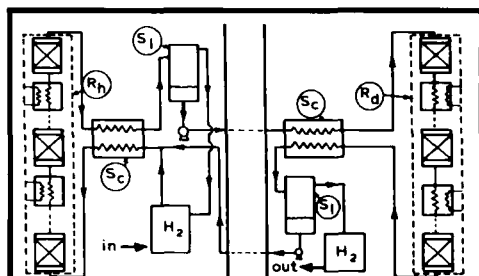
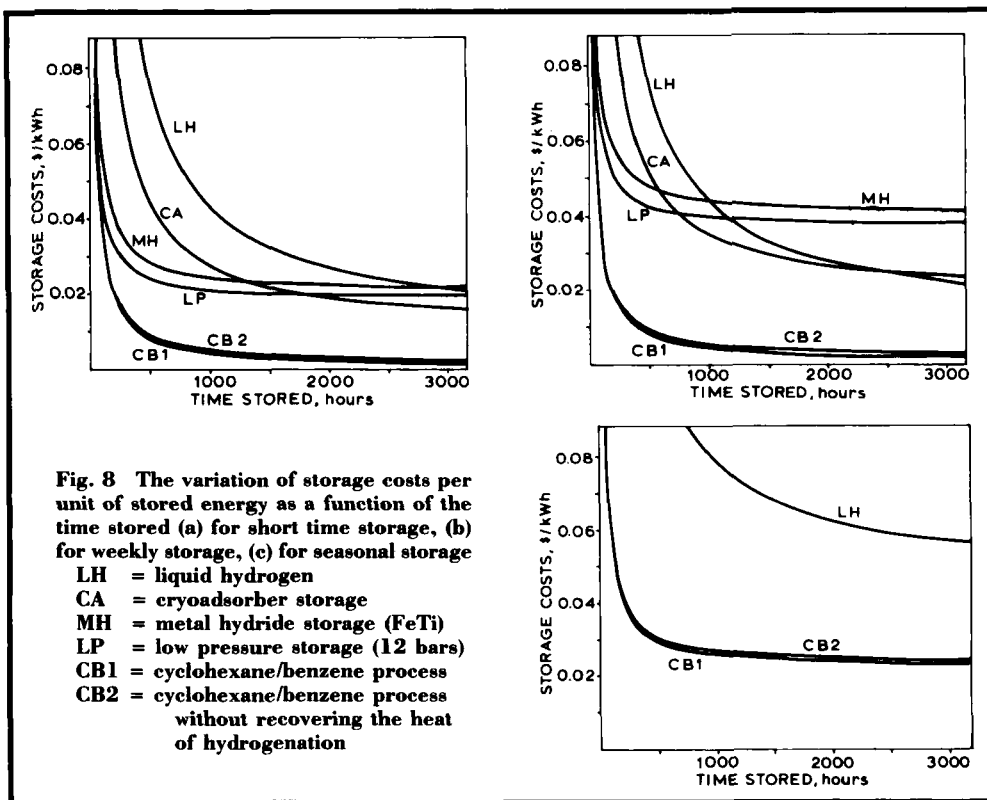


Fig. 7 This flow-sheet of a hydrogen storage and/or transmission system using a reversible chemical reaction has been selected as the best compromise

- R_h hydrogenation reactor
- R_d dehydrogenation reactor
- S_1 liquid gas separator
- S_c counter flow heat exchanger
- H_2 hydrogen tank



prerequisite, for they alone assure no losses of the recycled reactants and products. As the catalyst represents the heart of the process, further improvements to it are necessary, particularly for the MTH cycle where, at least under the most severe high temperature conditions of the dehydrogenation step, it suffers from a number of weaknesses, the most critical of which is a tendency to coking. Progress on this is likely to result from parallel work being

carried out on the catalytic reforming of naphthas, by which means 10^8 tons/year are processed using a platinum catalyst to increase the octane number. As deactivation by coking is the main difficulty we have recently focused our attention on the role of chlorine, which appears to be the key to this problem (23). If the limitation imposed by coking could be removed there is no doubt that the MTH cycle would have a great future. The way forward has

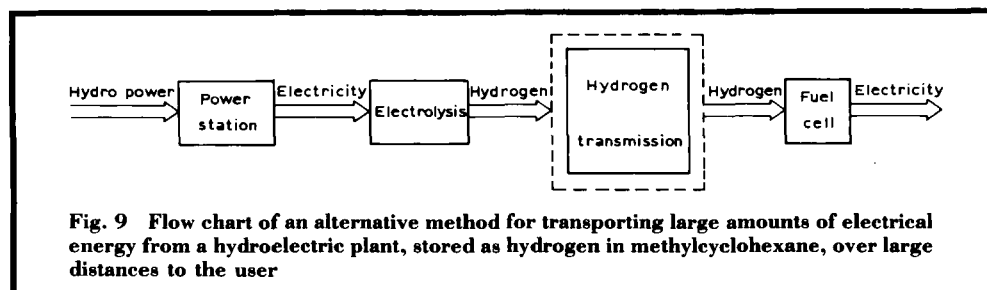
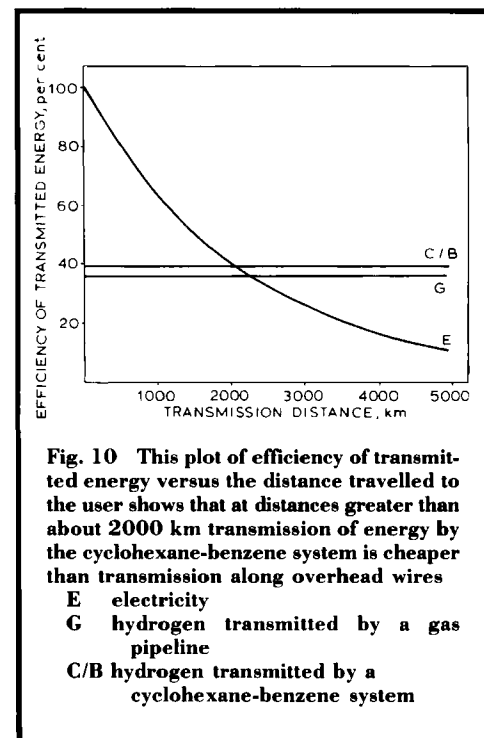


Table II
Characteristics of Two Projects Using the Cyclohexane Benzene Reaction to Store Hydrogen (CBH)

Hydrogen storage project	Outlet power of storage plant	Time, h	Stored hydrogen, kg	Storage Capacity		Efficiency of storage system, per cent	Reactor Characteristic	
				Amount of liquids to store hydrogen in CBH system, kg	m ³		Catalyst volume, m ³	Weight of platinum, kg
From wind energy (19)	72 kW(a)	30	146	2.5×10^3	3.3	32(b)	55×10^{-3}	0.14
From any source (9)	6×10^3 kg H ₂ /h	14 - 800	$84 \times 10^3 - 4.8 \times 10^6$	$1.24 \times 10^6 - 70.8 \times 10^6$	$1.6 \times 10^3 - 90.4 \times 10^3$	77(c)	56.3	141

(a) Electric power (b) Ratio between electrical energy released from the storage system and the electrical energy furnished to the storage system during the charge phase

(c) Ratio between the equivalent thermal energy of the hydrogen discharged from the storage system to the sum of the equivalent thermal energy of the hydrogen incoming into the storage system and the energy needed for the auxiliaries



already been prepared. A 17-ton truck with an engine producing 150 kW of mechanical power has been built and run successfully (21); even though improvements to the platinum-rhenium/alumina catalyst are still seen as a goal, this trial has demonstrated the readiness of the MTH closed-loop cycle to serve present needs while at the same time it is being developed for the future.

The ability of the MTH concept to serve in a future hydrogen economy has already been demonstrated and work carried out at this Institute has contributed to this. Catalyst formulations for the forward and the reverse reactions have been disclosed, and an adiabatic-type reactor which reduces capital costs has been proposed (7); this is illustrated in Figure 7. Computer optimisation of the main operating conditions and full heat- and mass-balance evaluations (9) have been established, to serve as the guidelines for future projects.

Estimation of thermodynamic efficiencies, reactor volumes and the other engineering

parameters—given in Table II—all contribute to the background information required to turn this process into a successful energy or hydrogen storage package.

The reader is reminded that only the MTH cycle meets the requirements for both storage and transmission of hydrogen, other conventional means being unsatisfactory for transmission. Unique advantages include the unlimited duration of storage, an energy density that is higher than that of any other reversible system, while there is no need for insulated vessels or pipes. All these factors, plus the extremely low cost of the starting materials, combine to make the cost of hydrogen storage and transmission at least one order of magnitude lower than that of any conventional process. This is demonstrated by the data in Figure 8.

Towards a Hydrogen Economy

Looking to the future, it is to be hoped that these lower costs and other considerations, such as pollution control and energy conservation, will attract the attention of sections of our industrial society. Of all the renewable energy resources, hydroelectricity is perhaps the source that could benefit first from this new technology, as unexploited resources amount to

4×10^9 tons of petroleum equivalent (TEP) per year; one TEP being 10^7 kcal and 11.6×10^3 kWh. This amounts to about 60 per cent of the present world consumption of fossil-fuel energy! Taking this as an example we have anticipated conceptually that it would be cheaper to transmit hydrogen produced by electrolysis over a distance of 2000 km from the source by means of the methylcyclohexane-toluene-hydrogen cycle than it would be to transmit it through overhead wires as electricity. Figures 9 and 10 show this. The feasibility of producing and consuming hydrogen from this renewable source is not in doubt; the electrolysis of water is a mature technique and fuel cells are poised for commercialisation. It is therefore to be hoped that in time, as fossil fuels are increasingly depleted, the needs of the hydrogen economy will match the prospects offered by the MTH process, like a cure in search of a disease.

Acknowledgements

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References

- 1 J. B. S. Haldane, in a lecture, "Daedalus, or Science of the Future", at Cambridge, 4 February 1923
- 2 J. O'M. Bockris, *Environment*, 1971, 13, 51
- 3 O. Sultan and M. Shaw, "Study of Automotive Storage of Hydrogen Using Recyclable Liquid Chemical Carriers", TEC 75/003 ERDA, Ann Arbor, Michigan, 1975
- 4 H. B. Vakil, "Energy Storage and Transmission by Chemical Heat Pipe", General Electric, Schenectady, N.Y., Technical Information Series No. 76CRD281, January 1977
- 5 H. B. Vakil and J. W. Flock, "Closed Loop Chemical Systems for Energy Storage and Transmission (Chemical Heat Pipe)", ERDA Contract EY-76-C-02-2676, U.S. Dept. of Energy, February 1978
- 6 N. Giordano, "Thermodynamic Analysis of Solar Energy Storage through Thermochemical Reversible Reactions", Complex, 18th Int. Conf. Solar Energy, New Prospects, Milan, 23-27 Sept. 1979
- 7 G. Cacciola, G. Restuccia and N. Giordano, Proc. Int. Conf. Energy Storage, Brighton, U.K., 29 April-1 May 1981, 1, pp. 73-89
- 8 G. Cacciola, *Tecnol. Chim.*, 1981, 1, (6), 56
- 9 G. Cacciola, N. Giordano and G. Restuccia, *Int. J. Hydrogen Energy*, 1984, 9, (5), 411
- 10 N. Giordano, G. Cacciola and A. Parmaliana, *Indian J. Technol.*, 1983, 21, (9), 398
- 11 G. Cacciola and N. Giordano, Proc. Fifth World Hydrogen Energy Conf., Toronto, 15-19 July 1984, 3, pp. 1232-1251
- 12 G. Cacciola, V. Recupero and N. Giordano, *Int. J. Hydrogen Energy*, 1985, 10, (5), 325
- 13 A. Parmaliana, C. Crisafulli, R. Maggiore, J. C. J. Bart and N. Giordano, *React. Kinet. Catal. Lett.*, 1981, 18, (3-4), 295
- 14 A. Parmaliana, A. Mezzapica, C. Crisafulli, S. Galvagno, R. Maggiore and N. Giordano, *React. Kinet. Catal. Lett.*, 1982, 19, (1-2), 155
- 15 A. Parmaliana, M. El Sawi, G. Mento, U. Fedele and N. Giordano, *Appl. Catal.*, 1983, 7, 221

- 16 A. Parmaliana, M. El Sawi, U. Fedele, G. Giordano, F. Frusteri, G. Mento and N. Giordano, *Appl. Catal.*, 1984, **12**, 49
- 17 M. El Sawi, F. Frusteri, A. Parmaliana and N. Giordano, *J. Chem. Technol. Biotechnol.*, 1985, **36**, 122
- 18 A. Parmaliana, O. S. Alekseev, G. A. Nesterov, Yu. A. Ryndin and N. Giordano, *React. Kinet. Catal. Lett.*, 1986, **31**, (2), in press
- 19 G. Moleti, R. Quagliata and G. Cacciola, "Studio di Fattibilità di Sistemi di Accumulo per Impianti Eolici", Intern. Rep., CNR Inst., Messina, 1983
- 20 F. Ippolito, "L'Energia" da L'Energia: Fonti e Produzione—Lecture da *Le Scienze*, Milano, 1976, pp. 13–25
- 21 M. Taube, D. Rippin, W. Knecht, D. Hakimifard, B. Milisavljevic and N. Gruenfelder, *Int. J. Hydrogen Energy*, 1985, **10**, (9), 595
- 22 A. Touzani, D. Klvana and G. Belanger, *Int. J. Hydrogen Energy*, 1984, **9**, (11), 929
- 23 A. Parmaliana, F. Frusteri, A. Mezzapica and N. Giordano, "Coking on Pt/Honeycomb Reforming Catalyst: Effect of Surface Acidity", *J. Catal.*, submitted

The Platinum Prints of Peter H. Emerson

At the turn of the century platinum was used extensively in photography, but the popularity of the platinum process declined prior to the First World War. Recently, however, the process has been revived, while early photographs have come to be recognised as valuable collector's items. Among the most sought after are the platinum prints of Peter Henry Emerson (1856–1936). His album "Life and Landscape of the Norfolk Broads" was illustrated with platinum prints, which demonstrated the wide tonal range that could be obtained with platinum. Another feature of the process was the permanency of the image, and today the condition of his platinum prints testifies to this.

Almost one hundred years after publication of this book, and fifty years after his death, an exhibition of his work is taking place at the Sainsbury

Centre for Visual Arts, University of East Anglia, Norwich, until 26th October 1986. The platinum prints that form part of this exhibition, which is sponsored by Norwich Union Insurance, could appeal especially to those who have previously regarded platinum solely as an industrial metal.

Later the display will move to the Royal Photographic Society, Bath (5th December 1986–17th January 1987), University of Warwick (21st February–21st March 1987), Impressions Gallery of Photography, York (27th April–31st May 1987), and the Walker Art Gallery, Liverpool (7th August–20th September 1987).

The image reproduced here, from an Emerson in the Johnson Matthey Collection, is featured in the exhibition.

