Hydrogen, key to the energy market

Nowadays nuclear energy is used primarily in the form of electricity. Why not also use it to produce hydrogen — a clean and versatile form of energy?

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Up to now practically the only source of primary energy available to man has been the sun. Plants convert it into chemical energy by breaking down water and combining the hydrogen with carbon dioxide taken from the air. This chemical energy goes to feed the biosphere where it is ultimately transformed into heat, apart from a small amount which is accumulated in deposits in the form of coal or oil. Our civilisation would be inconceivable if the crumbs from this great feast of energy indulged in by the sun and the green plants had not been kept for us for millions of years by these precious deposits. We should still be crossing the oceans in sailing ships and using wind or water power to drive our industry.

Enter the atom

The discovery of the fission of the uranium atom, however, opened up for mankind a vast reservoir of energy which was completely independent of the sun/green plants/biosphere cycle and which was potentially very economical. When breeder reactors have proved themselves commercially, for instance, a gram of uranium will produce about the same amount of energy as a ton of oil. The important thing is that the cost of the raw material will be negligible and the energy price will therefore be governed essentially by considerations of nuclear reactor technology. But the history of technological processes shows that their cost decreases in time according to exponential laws. There will therefore come a time—we are in fact already there—where the descending curve representing the price of nuclear heat will intersect the curve representing the cost of heat produced by conventional fuels—coal and oil—the latter having stayed constant in recent years.

The structure of the energy market

On the other hand, in one respect nuclear energy is highly inconvenient compared with the standard forms of energy—it lacks flexibility. It is produced in the form of heat and, to keep down the cost, it is produced in large plants. Furthermore, heat cannot be transported over great distances and the majority of uses to which energy is put (as, for example, in the propulsion of an aeroplane or car) involve a large number of small, separate units.

An intermediate product therefore has to be found which is adapted to the market situation.

For this reason the projects related to the development of the peaceful uses of nuclear energy have up to now been concentrated almost solely on the conversion of this heat into electric current. This is an almost ideal intermediate since it is produced in large units and has a highly ramified distribution network. But electricity can only meet about 20% of the energy needs of a technologically developed society, which limits the role nuclear energy can play in the total energy supply.

Having been especially struck by this fundamental problem, we set out, three or four years ago, on an attempt to find the technological means whereby this nuclear heat could be put into a "package" which was suitable, at least partially, for the remaining 80% of the energy market.

The intermediates

The conclusions arrived at in this study, which are shortly to be published, are that hydrogen can be an extremely flexible intermediate which would make it possible to penetrate the whole of the market without any sudden changes in technology being necessary. In certain cases the substitution is a straightforward matter; town gas, for example, already contains 50-90% hydrogen. In other cases it would seem to be a more complex operation, but in keeping with the normal course of technological development.

In the United States, for example, in an attempt to avoid atmospheric pollution the firm of *Allis Chalmers* is carrying out a study on electric automobiles driven by ammonia batteries. These seem to be quite a promising proposition—from an economic point of view as well. Ammonia can be produced very easily from hydrogen and air. Another point to be noted is that it was hydrogen that was used as the fuel to take man to the Moon. It would be surprising if the spin-off from space technology could find no useful application in the field of air transport.

Hydrogen's gradual penetration of the energy market is, of course, a fascinating problem, but this would be too lengthy to discuss here. Instead, let us look at the position as it exists

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at the moment. Hydrogen already has a large market, corresponding, broadly speaking, to half that for electricity (on the basis of the primary energy necessary for the production of both products). On the other hand, this market is essentially tied in with the production of ammonia and the hydrogenation of oil products and is therefore concentrated in large units which in their turn warrant hydrogen production in large units.

If, taking the calorie as the reference unit, a comparison is made between the price of hydrogen for the uses mentioned above and that of the heat produced by a large nuclear reactor, it can be shown that there is a factor of about five in favour of the nuclear calorie. The price situation is given in Table I.

To "package" thermal energy in the form of hydrogen naturally involves investment costs and also losses, but this factor of five, which is in fact tending to increase, provides a very effective incentive. This is why, about two years ago, our ideas and analyses were concentrated on one fundamental question, namely that of how this hydrogen was to be produced.

The present production method consists of either reducing water by means of coal or by partially oxidising and cracking oil products. The most important reactions are shown in Table II. The reactions here use not only the reducing power of coal, i.e. the strong tendency of oxygen to combine with the carbon in the coal to form CO_2, but also the energy released by combustion. The reactions taken as a whole are endothermic and a certain quantity of energy is necessary for the running of the plant.

A simple and obvious solution consists in using a nuclear reactor to provide the necessary heat, this being possible at a very advantageous price. In this way the difference is gained between this price and the price of the fuel that would have had to be burned to produce the heat by normal methods. This possibility has already been dealt with in this journal by Siebker and Martin (see *euro-spectra* Vol. VIII (1969) No. 2 pp. 34-38).

We wanted to go beyond this possibility, for two reasons:

1) The quantity of nuclear heat which can be introduced into the systems under consideration is fairly low —15 to 20% depending on the system. The low cost of nuclear heat therefore has only a slight influence on the price of the product and any advantage gained can easily be cancelled out as the result of small variations in the price of conventional fuels (see Table III).

2) With this system one has always to rely on classical sources of energy and there is thus no hope of nuclear energy gaining anything more than a very thin slice of that challenging 80% of the market.

If this way is ruled out then, there is in fact only one other course left open: the decomposition of water.

The decomposition of water

It is in fact precisely this process which nature uses to obtain chemical energy from solar energy so that the biosphere (and our civilisation) can function. In the first place the water is broken down by light energy picked up by chlorophill. Oxygen is liberated and the hydrogen "hydrogenates" carbon dioxide and thus triggers off the chemical cycle.

The decomposition of water can be seen as a very elegant process for the

Table I: *Illustrative prices of heat.*

	mills/Mcal
Nuclear heat	1.0 (1)
Natural gas	1.7 (2)
Coal	2.1 — 3.0 (3)
Heavy fuel oil	1.2 — 1.6 (4)
Hydrogen (conventional process)	5.2

(1) For a plant of the order of 2,500 Mwth.
(2) Price of Dutch natural gas, January 1970.
(3) Community price of flaming coal, March 1970.
(4) Community price of heavy fuel oil, February 1970.

Table II: *Two reactions by which hydrogen is at present produced: the reduction of water by carbon and the oxidation of methane.*

$$\left\{\begin{array}{l} C+H_2O \rightarrow CO+H_2 \\ C+\tfrac{1}{2}\,O_2 \rightarrow CO \\ CO+H_2O \rightarrow CO_2+H_2 \end{array}\right.$$

$$CH_4+\tfrac{1}{2}\,O_2 \rightarrow CO+2H_2$$

accumulation and transfer of energy, these, as we have seen, being our main aims.

Water can be found practically everywhere at prices which in general are very reasonable; transport costs for hydrogen are the same as those for methane. Another point: combustion gives just one end product—water. This holds out the prospect of a radical solution to the problem of pollution which has resulted from the intensive use of conventional fuels: there will be no acute poisons produced such as CO, or chronic ones such as SO_2, or "secular" ones such as CO_2. This is not to mention the host of products—possibly carcinogenic and at all events very unpleasant—which industry passes off to the atmosphere through the incomplete combustion of coal and oil.

However, all this lyricism about clean air must not blind us to the hard facts of economic life.

"Direct" processes

Our water must be decomposed in a way which is economical, i.e. competitive. This fact eliminates the simple solution to the problem—electrolysis. This process, although technically perfected, has unfortunately the disadvantage of wasting energy because of the numerous transformations which the latter has to undergo in changing from its primary state as heat into its chemical form. Furthermore each of these transformations requires equipment involving high investment costs. The difference in price between the hydrogen calorie and the nuclear calorie (represented by the factor of five mentioned above) is to a great extent cancelled out by these two facts.

It should be noted that electrolysis can still play a role in the use of off-peak energy produced by nuclear power plants but it must also be remembered that our aim is more ambitious, namely to decide the technical methods necessary to cater satisfactorily for the whole of the energy market. Off-peak energy constitutes only a fraction of the electrical energy produced, which, as we have seen, will in any case cover only 20% of primary energy consumption.

We thus arrive at the crux of the problem: how can we decompose water as "directly" as possible so that the price of the nuclear heat is not multiplied by a factor any greater than our factor of five (unless a convenient way of selling the oxygen can be found, to steelworks for example, in which case the factor can be increased to around seven)?

The water can be directly broken down by thermal cracking by heating it to an appropriate temperature. Unfortunately the necessary temperature is rather high—of the order of 2,500—3,000°C. The reactors designed for

Table III: *Illustrative costs of hydrogen production by different processes.*

	Conventional process	Methane + nuclear heat	Nuclear heat + Mark 1 process
Methane	2	1.6	—
Nuclear heat	—	0.2	2
Oxygen	0.7	—	−2
Capital and running costs	(2.5)	(2.5)	(2.5)
Total in mills/Mcal	5.2	(4.3)	(2.5)
Total in mills/Nm^3	13	(10.8)	(6.3)

For the first two processes a yield of 100% is assumed (an optimistic hypothesis); for the third a yield of 50% is anticipated (the theoretical yield being 75%).

Price of the primary energy: methane: 2 mills/Mcal; nuclear energy: 1 mill/Mcal.

Price of the oxygen: 11 mills/Nm^3.

The running and capital costs are taken as being equivalent for the three processes. Even if the production costs for the third process were to double, they would still only be about the same as for the other processes.

space rocket propulsion which are now being developed in the United States can reach temperatures of around 2,000°C. The same temperatures can be attained with the reactors which are to feed thermionic converters.

From a technical viewpoint it is not a simple problem to get over these remaining 500-1,000°C, but, apart from this, the price of the calorie produced by these reactors does not seem to be sufficiently low for the application contemplated here. Nevertheless it is worth while paying careful attention to their development.

Another possibility, which is very tempting, is to use the heat produced in fusion reactors, for it would be incredible to think that after having been able to produce fusion at 100,000,000°C it was not possible to find a way of obtaining 3,000°C, somewhere in the system, in order to decompose water vapour.

In view of the foregoing, the real key to the problem in the case of fusion lies perhaps in the possibility of transferring the energy using the fast neutrons produced. The latter would carry the energy to a specific place in the chemical plant.

A very important advantage of cracking water at 2,500-3,000°C is that theoretically its yield is unity. This advantage has economic repercussions and also means that there is no problem of heat loss. This problem can be collossal in the case of the plants envisaged, which would produce tens of thousands of thermal megawatts.

Of the nuclear reactors the *HTR* type now produces heat at the highest temperature. The fuel is graphite-clad, the coolant used is helium and the outlet temperature reaches about 800°C.

Not wishing to pursue futuristic methods, we therefore set ourselves the task of attempting to solve the problem by using heat available at temperatures lower than 800°C. What a heuristic approach would suggest under the circumstances was quite straightforward: to decompose water in two stages, each of which can be activated thermally at temperatures below 800°C.

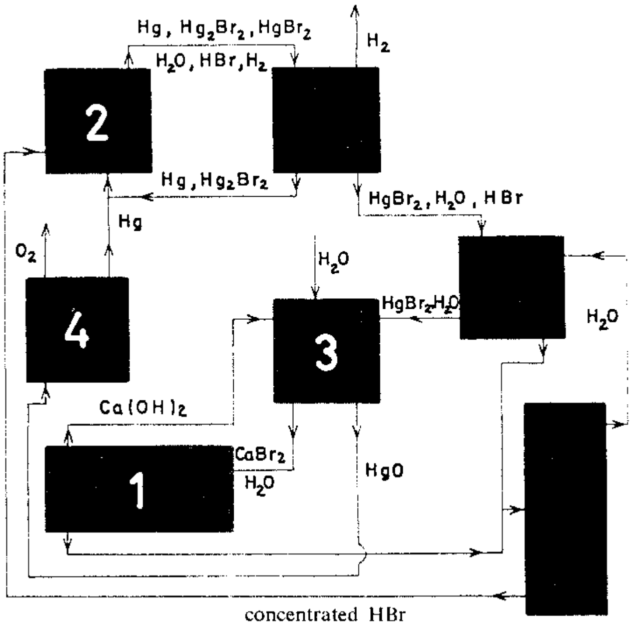

Figure 1:
Mark 1 process: flow diagram.

According to the laws of thermodynamics this is theoretically possible and the total yield of the operation, using heat between 500 and 800°C, will be close to 75%.

The Mark 1 process

After several months of research at Ispra a process, christened Mark 1, was found which satisfied these conditions. The main reactions of the process are shown in Table IV. A block diagram of the sequence of operations is given in Figure 3.

What are the advantages of this type of process?

1) The only raw materials it uses are water and nuclear heat.

2) The energy is transformed into its final state without any intermediate stages, as is the case with electrolysis —a fact which has a beneficial effect on both efficiency and investment.

3) Another substance, namely oxygen, is produced, which can play an important role, as we shall see later.

The Mark 1 process was discovered about two years ago. In the meantime research has been carried out on the reactions given in Table IV. These are fairly uncommon reactions and consequently the information on them in the literature is very limited.

The kinetics and equilibrium values shown in the results appear very promising for application on an industrial scale. The materials used will, however, present difficult problems in view of the fact that aggressive compounds have to be handled at high temperatures.

Other possible cycles

Obviously there was nothing against carrying out parallel research on other possible processes, either by sticking to the 800°C limit or by raising it. It is anticipated that the development of *HTR* reactors will result in the use of higher temperatures, especially if development of the gas turbines associated with these reactors is stepped up.

One of these processes, which employs iron and coal as its working materials, is shown in Table V. The materials are not used up but are continually recycled. It appears to be a

Table IV: *Essential reactions in the Mark 1 process.*

1) $CaBr_2 + 2\,H_2O \rightarrow Ca(OH)_2 + 2\,HBr$	at	730°C
2) $2\,HBr + Hg \rightarrow HgBr_2 + H_2$	at	250°C
3) $HgBr_2 + Ca(OH)_2 \rightarrow CaBr_2 + H_2O + HgO$	at	100°C
4) $HgO \rightarrow Hg + \frac{1}{2}\,O_2$		

simple process and uses cheap materials but it, too, presents problems, one being the temperature of 1,400°C needed for the partial decomposition of the iron oxide.

These new possibilities were set out and discussed at a meeting held at Ispra on 12 December 1969. Present were representatives of several major constructors of hydrogen production plant, firms specialising in the problems of transporting hydrogen and certain chemical firms using hydrogen.

The meeting resulted not only in a fruitful exchange of information but also in a discussion on the best means of implementing concrete industrial projects. Now that the value of the new potential offered by hydrogen has been generally recognised it only remains to establish the main lines to be followed by a research and development programme in the next few years and to find the best way of dividing up the work involved between the Ispra Research Establishment and industry.

The part coal plays

We shall now try to answer a question asked above: what is the best use for the oxygen produced at the same time as the hydrogen? In the case of existing industries there will be no difficulty provided they are well situated. Steelworks, in particular, consume very large quantities of pure oxygen in the production of steel by the lance-process and also in blast-furnaces. But there is another proposal which is worth putting forward. A century ago, Mendeleieff suggested winning coal by gasifying it immediately in the mine itself. However, the process never gained a foothold because if air is blown in as an oxidising agent the product has too low a calorie content as a result of the nitrogen which dilutes it. If, on the other hand, oxygen is blown in, the product is too expensive because of the cost of the oxygen. But oxygen obtained as a cheap by-product could make this unusual method of exploiting the Community's mining resources an economic proposition.

As we have seen, the Mark 1 process could make it possible in the near future to develop and perhaps even totally revolutionise the energy market by using hydrogen.

A certain amount of research still remains to be done to make the process industrially viable. From the data now available, however, we have reason to believe that this research should be a profitable investment.

Finally it must not be forgotten that, besides the economic prospects, this gradual introduction of the use of hydrogen holds forth the hope of a totally pollution-free atmosphere.
EUSPA 9-7

Table V: *Essential reactions in a hydrogen production process using iron and carbon as catalysts.*

1) $C + H_2O \rightarrow CO + H_2$	at	700°C
2) $CO + 2\,Fe_3O_4 \rightarrow C + 3\,Fe_2O_3$	at	250°C
3) $3\,Fe_2O_3 \rightarrow 2\,Fe_3O_4 + \frac{1}{2}\,O_2$	at	1,400°C

Literature: Luxembourg patent No. 60,372 dated 18.2.1970. Inventor: Gianfranco de Beni.