

## HYDROGEN ENERGY – A CHEMICAL ENGINEERS VIEW

*The main idea of this letter and comments is to initialize discussion and promote chemical engineers to publish their research results regarding hydrogen technology and its further usage in many fields in the chemical Industry Journal (Belgrade).*

With the special issue about problems of hydrogen energy the Chemical Industry Journal in the previous year (No. 12) and in 2000 enters into world-wide discussions about one of the most important problems of mankind – how to fulfill fast growing energy needs without further depleting natural resources and destroying our environment and the planet itself. Solar energy and hydrogen as the most suitable energy medium and carrier seem to be optimal solutions, but there are tremendous obstacles to achieve either aims. I hope that my comments will help our starting discussion. The comments present some points which were not covered in the special issue last year (No 12) and cover one untapped renewable energy source, one method to convert solar energy into heat and further into electrical energy, one hydrogen carrier and structurally integrated processes to produce hydrogen based fuels.

### OSMOTIC ENERGY – a renewable energy source

Osmotic energy can be obtained by the appropriate mixing of fresh water with sea water or concentrated brines. As an example: the average power of the river Neretva, mixed with water from the Adriatic Sea is about 2000 MW and it would be feasible to practically use about 500 MW. The largest rivers such as the Amazon have powers of more than 100 GW. Using membrane techniques osmotic energy can be converted into mechanical energy, by pressure retarded osmosis (membranes for reverse osmosis), or directly into electric energy (ion-exchange membranes). According to the first method, a project was made in Israel for an electric power station of 10 MW, using the high potential of mixing water from the river Jordan with Dead Sea brine, and a preliminary project for power station of 100 MW was made by applying the electrochemical method

(Sweden) (mixing normal sea water with river water). Till now problems have involved efficient membrane systems and extremely large membrane surfaces.

### SOLAR PONDS – a low technology method to use solar energy

Solar ponds are ponds made of water impermeable materials, with surface areas of about 100 m<sup>2</sup> and depths of about 1,5 m. A solar pond is filled with a saturated brine of mixed natural salts and a layer of the same salts is placed at the bottom. The brine in the pond must be filtered and clear, so that the bottom is heated by sun rays. The heated water at the bottom dissolves more salts, so natural convection is reversed and a layer of hot saturated brine ( $t = 50\text{--}80^{\circ}\text{C}$ ) is formed near the bottom of the pond. Heat energy can be used directly, or converted into electricity, using cycles with suitable media. Due to rather large heat capacities of the hot brine, solar ponds can operate even at night. Such ponds have been built in Israel and in the Southern USA, but they can be built in many desert and other southern countries.

### AMMONIA – a suitable hydrogen carrier

The storage of hydrogen is one of the most serious problems of utilizing hydrogen as a fuel in moving vehicles. The use of liquid hydrogen is clearly the best solution, but its applications are practical only for large rockets or airplanes. Cylinders with highly pressurized hydrogen are heavy and dangerous to use. Hydrogen in metal hydrides appears as an optimal solution for cars and similar uses, but ratios of weight of hydrogen/weight of hydrate are low (0.0135–0.07 kg/kg).

Liquid ammonia, as a source of hydrogen has the net weight ratio of 0.176 and, even without refrigeration, rather low vapor pressure, so the tanks for ammonia should not be heavy. Ammonia is easily converted at elevated temperatures to a mixture of  $3\text{H}_2 + \text{N}_2$ , using

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porous iron or other metal catalysts. The reaction is not strongly endothermic ( $\Delta H = 46 \text{ KJ/Mol}$ ).

We have investigated ammonia as a fuel for liquid fuel rockets, where liquid ammonia was fed to the combustion chamber through porous walls composed of a catalyst. The walls were heated by the reaction hydrogen–oxygen ( $\Delta H = -285 \text{ KJ/Mol}$ ), and also, efficiently cooled by the evaporation of ammonia and the endothermic ammonia cracking, so it was possible to achieve high thermal loads of the chamber without overheating its walls.

Due to the nitrogen content, some nitric oxides are formed at high temperatures, so it is better to use ammonia as a source of  $\text{H}_2$  for processes at lower temperatures (fuel cells).

### STRUCTURAL INTEGRATION OF PROCESSES PRODUCING HYDROGEN FUELS

In the production of fuels with a lower emission of  $\text{CO}_2$  (ethanol and methanol), as well as in ammonia and hydrogen production, integrations of reactors or fermentors with separators of products into single units have multiple advantages (process efficiency, energy consumption, working pressures or temperatures, economy).

Ethanol fuel production, from agricultural raw materials, is economical only if a fermentor is coupled with a membrane pervaporation separator into one unit. In such a system the fermentation proceeds at lower ethanol concentrations (4–5%), with high efficiencies, and it is possible to obtain 99–99.5% pure ethanol, miscible with hydrocarbons.

Reactor–separator integration can be applied in the production of methanol and ammonia. In both cases the removal of the product from the catalyst enables low pressure syntheses. The produced methanol can be removed from the catalyst by an adsorbent in a trickling bed 3–phase reactor, or from the system in a chromatographic reactor. Both systems produce methanol yields of nearly 100%, even at low pressures.

For low–pressure ammonia synthesis we considered two integrated systems: membrane reactor–separators and reactors–simulated continuous chromatographs. A membrane reactor–separator consists of a catalytic membrane with synthesis gas on one side. The membrane is semipermeable for the ammonia produced.

The second system, consisting of 8 microcapillary catalytic reactor elements and 8 microcapillary chromatographic columns, connected into a circle, with inlets for synthesis gas and outlets for ammonia between the reactors and columns, was simulated. It was supposed that the residence times for ammonia in each column were longer than for the synthesis gas components and that the inlets and outlets were opening and closing in calculated time sequences.

Both systems could produce ammonia under low pressures and with high yields, but their realization is still far away, especially in a large industrial scale.

Water splitting into  $\text{H}_2$  and  $\text{O}_2$ , using high temperatures, is not practically feasible, since for substantial yields of the process it is necessary to apply temperatures higher than  $2000^\circ\text{C}$ . A reactor, structurally integrated with two membrane separators, of which one removes  $\text{H}_2$  and the other  $\text{O}_2$ , was simulated. It was shown that such a system could operate at lower temperatures, for which it is possible to find materials for the reactor and separation membranes, with high overall yields.

### CONCLUSION

Problems of hydrogen energy, especially connected with solar energy as a primary source, will be solved only step by step, by close multidisciplinary cooperation. My comments give only some ideas of one chemical engineer. Very broad technical, ecological, energy used and obtained and economical analyses will be necessary before these and other ideas are evaluated and even partial solutions found.

