STUDY OF WATER PHOTOSONOLYSIS FOR HYDROGEN PRODUCTION

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ABSTRACT
This paper deals with an experimental investigation on water photosonolysis for hydrogen production. Water splitting is obtained by superposition of photolysis and sonolysis phenomena (photosonolysis) which are induced by the combined action of sunlight and ultrasounds. An experimental device was realized to investigate such phenomena; experimental tests were carried out: hydrogen production increases linearly with time; besides, hydrogen production dims as pressure increases.
Thus, the proposed method suggests further investigations focused to test improvements on ultrasound-water matching and sunlight catalyst; a new reactor will be designed which is characterized by innovative systems for hydrogen separation.

1. INTRODUCTION
Hydrogen production by the combined effect of sonolysis (which produce the water cavitation phenomenon) and photolysis was investigated. An experimental facility was realized to test the effect of ultrasounds and sunlight radiation on water. The facility is constituted by a reactor, an ultrasound generation system and a sunlight irradiation system. Sonolysis and photosonolysis experimental tests were carried out. The hydrogen production was verified; the dependence among hydrogen production, time and pressure was found.

2. PHOTOSONOLYSIS
Photosonolysis consists on molecular splitting by the combined effect of photolysis and sonolysis phenomena. Sonolysis is produced by mechanical waves which induce cavitation phenomena in the water; photolysis is due to the interaction between the water molecules and the sunlight radiation [1].
Water sonolysis is obtained by piezoelectrical transducers which may produce water splitting by generating mechanical waves with appropriate frequency. Energy is given by ultrasounds transmission in the water test sample; optima pressure and temperature conditions for hydrogen production are locally obtained by the cavitation phenomenon [2].
Water sonochemical reactions steps are the followings:

$$H_2O \rightarrow H\bullet + OH\bullet \quad (1)$$
$$H\bullet + H\bullet \rightarrow H_2 \quad (2)$$
$$OH\bullet + OH\bullet \rightarrow H_2O_2 \quad (3)$$
$$H_2O_2 \rightarrow H_2O + \tfrac{1}{2}O_2 \quad (4)$$
$$H\bullet + OH\bullet \rightarrow H_2O \quad (5)$$

Hydrogen and hydrogen peroxide are produced by the dimerization of their radicals (equations (2) and (3)). Hydrogen peroxide is unstable in standard conditions; thus, it splits into water and oxygen.
Ultrasounds are characterized by compression and expansion waves; they induce the acoustic cavitation phenomenon which gives the energy required for reaction (1). An heating process produces steam bubbles which are constituted by air molecules dissolved in the water. Bubbles vibrate quickly when they are mechanically stressed. Vibrations determine bubbles implosion at a 1,4 km/s speed; temperature increases up to 5000 K near the bubble implosion area. This is due to the bump waves produced by the bubbles which cross the other bubbles: an heating effect occurs which furnishes the energy for stripping the electrons from the atoms. Then, they collide, are caught and release the kinetic energy as heat [3].

The average intensity of a solar radiation outside the earth atmosphere is 1353 W/m^2. The intensity which hits the earth is affected by the atmosphere absorption and diffusion phenomena. The energy of a photon is given by:

$$E = h\upsilon \quad (6)$$

The O-H bond energy is 460 kJ/mol. Thus, the lowest wavelength suitable to split a water molecule into oxygen and hydrogen is 261 nanometers [4]; such wavelength is in the ultraviolet (UV) range. UV power is much lower than visible and infrared one in the solar spectrum; besides, ozone layer acts as a barrier for UV radiation. Thus, the available solar radiation for hydrogen production is very low on earth. However, cavitation phenomena induced by ultrasound application may increase the electromagnetic radiation absorption properties of the water [5].

3. THE EXPERIMENTAL FACILITY

The experimental facility is made by a reactor (where the water sample is inserted for the tests), the ultrasound generation system and a tool for the electromagnetic irradiation.
Piezoelectrical transducers lie on the reactor bottom side; the electromagnetic waves are produced by a xenon lamp which simulates the sunlight radiation. The system may be integrated with hydrogen separation systems (palladium membranes) and storage systems (metallic hydrides, carbon nanotubes).

3.1. Reactor

The reactor is the facility main component where the reaction of water photosonolysis occurs. The reactor frame (see figure 1) is realized in AISI 304 stainless steel; the upper side is closed by a quartz glass plate.

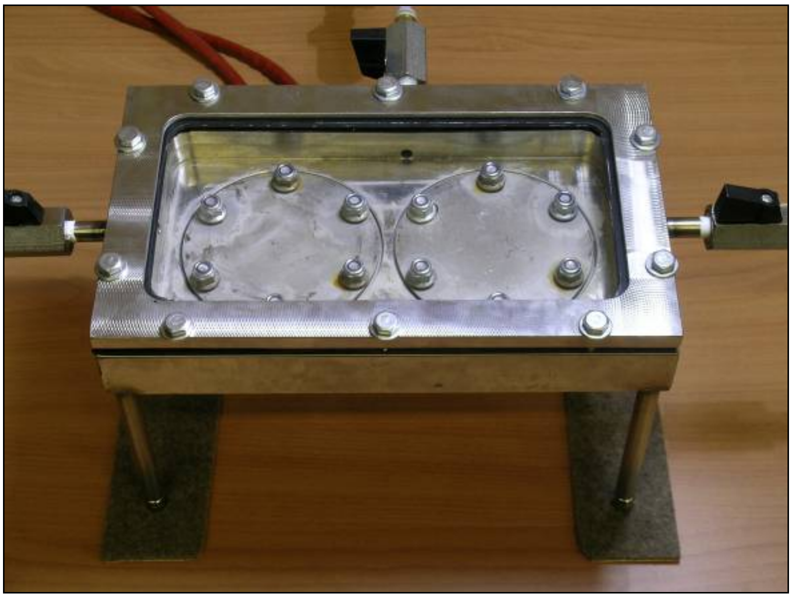

Fig.1. Photosonolysis reactor.

Three cylindrical ducts are connected to the reactor:

1. the inlet and outlet water duct;
2. a duct for output gas sampling, which is connected to a porous septa;
3. a duct for the reactor inertization through a washing with a vacuum pump and an inert gas.

3.2. Ultrasound Generation System

The cavitation phenomenon is produced in water by two piezoelectrical transducers connected to an amplified wave generator; it drives each transducer with a 22,5 kHz frequency and a 50 W power.
Each transducer is constituted by PZT electrostrictive elements (Piezoceramics-Zirconium-Titanium): a sandwich of two PZT rings is tightened by two metallic cylinders which constitutes mechanical amplifiers of the vibration amplitude (see figure 2).

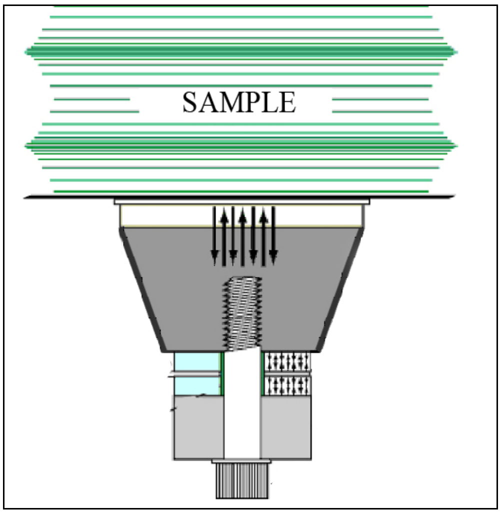

Fig.2. Piezoelectric transducer.

3.3. Sunlight radiation generation

The sunlight irradiation system is constituted by a lamp and an accumulator. The radiation is produced by a xenon lamp whose spectrum is very close to the sunlight one. The lamp is able to produce a 500 W/m^2 radiation on the reactor upper side at a 0.05 m distance.

The reactor upper side is made by an high purity quartz glass plate. The mechanical properties of this material are very close to a not-tempered normal glass; the optical transmittance properties are much different: quartz transmittance is high (over 60-70%) for a wavelength range much larger than the normal glass one (see figure 3).

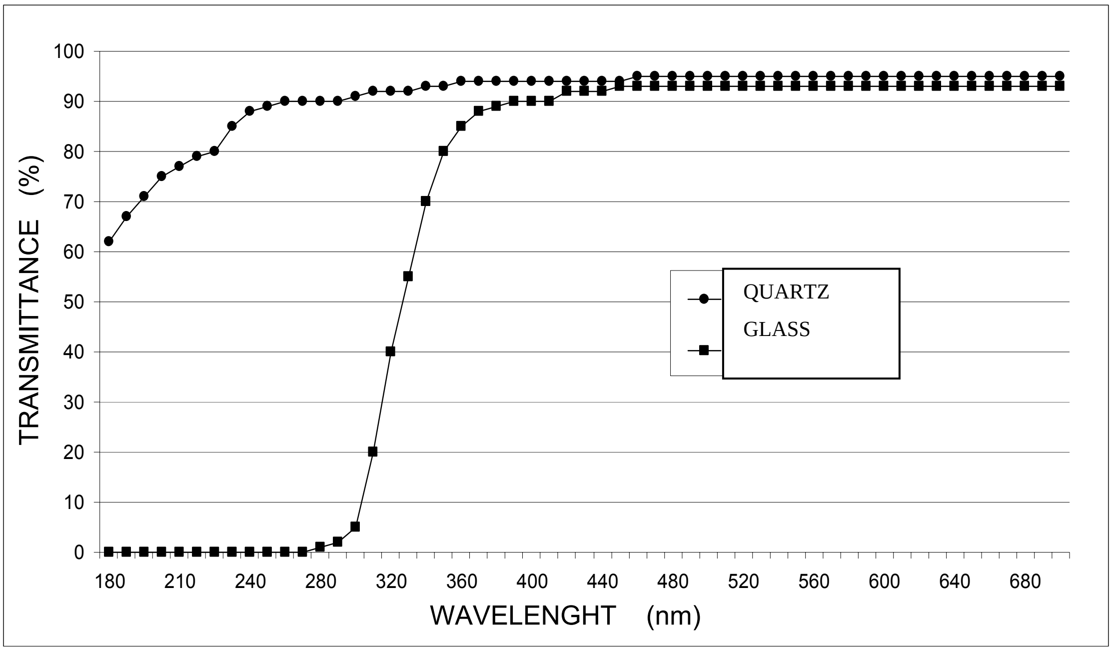

Fig.3. Transmittance: normal glass and quartz glass.

3.4. Sampling and cromatographical analysis

Gas sampling is made by a gastight syringe. Sampler is inserted into the reactor through a duct with porous septa in butilic rubber and teflon. The sample is injected in a gascromatograph able to separate, identify and evaluate its gas components.

Gas analyses were carried out by a Varian gascromatograph; the model is MicroGC CP-4900 with a molecular sieve column which enables the hydrogen, oxygen and nitrogen separation.

The thermal conductibility of the gases is evaluated by a TCD (Thermal Conductivity Detector) detector. The analysis of the thermal conductibilities (the chromatogram) allows the gas identification.

4. EXPERIMENTAL TESTS

Experimental tests were carried out by a 0,1 liters bidistilled water sample inside the reactor; air above the water surface was inertized.
The following tests were made:

1. water subjected to ultrasounds action (sonolysis);
2. water subjected to the combined action of ultrasounds and electromagnetic radiation (photosonolysis).

Both tests were carried out at the following pressure conditions:

- 1,0 atm;
- 1,5 atm;
- 2,5 atm.

4.1 Sonolysis Tests

Sonolysis tests were performed by ultrasonic waves produced by the piezoelectric transducers. Tests were made for different pressure conditions inside the reactor; figure 4 reports the results in terms of hydrogen production versus time. A linear behavior is shown.
Besides, results shows that hydrogen production is strongly affected by the air pressure conditions above the water surface.

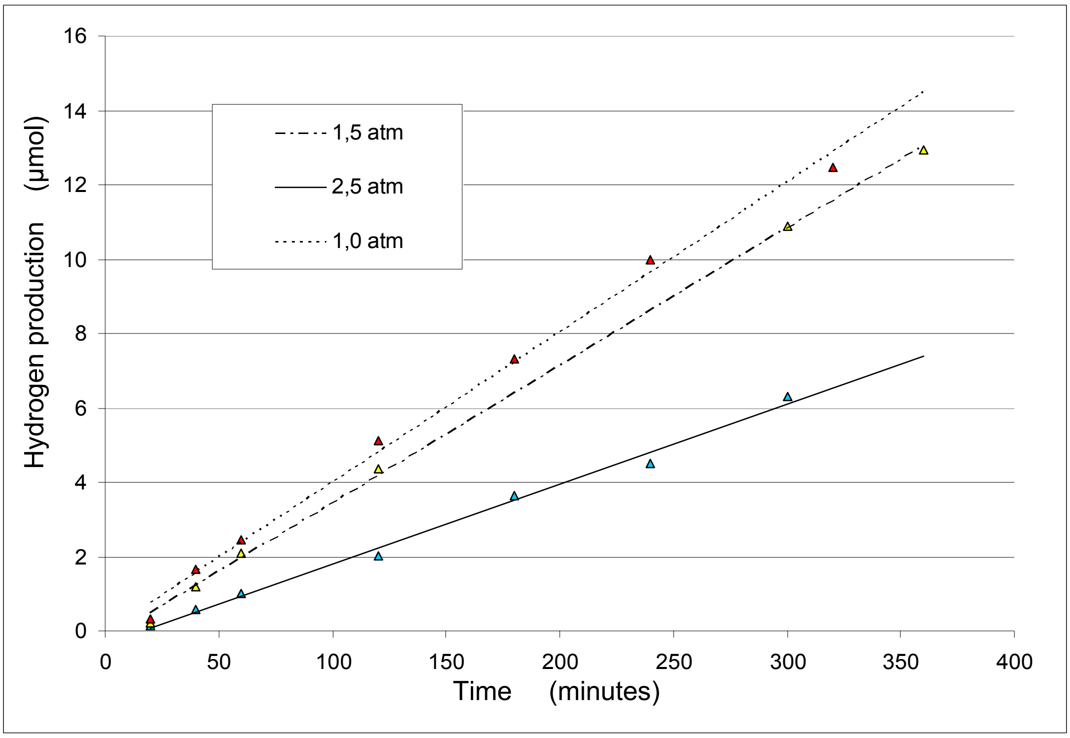

Fig.4. Hydrogen production versus time for different pressure conditions (sonolysis).

The highest production rate occurs for 1,0 atm pressure conditions; hydrogen production dims as pressure increases.

4.2. Photosonolysis Tests

Photosonolysis tests were carried out by supplying the reactor with mechanical and electromagnetical waves generators. Test configuration is similar to the previous one. Electromagnetic radiation is produced by a xenon lamp installed at about 0.4 m distance from the quartz glass (150 W/m^2 are measured on the reactor upper side).
A decrease of hydrogen production is shown when pressure increases (see figure 5); electromagnetic irradiation increases the hydrogen production with respect to sonolysis tests (see table 1, which is relative to three hours tests). A linear dependence is verified between hydrogen production and time also for photosonolysis tests.

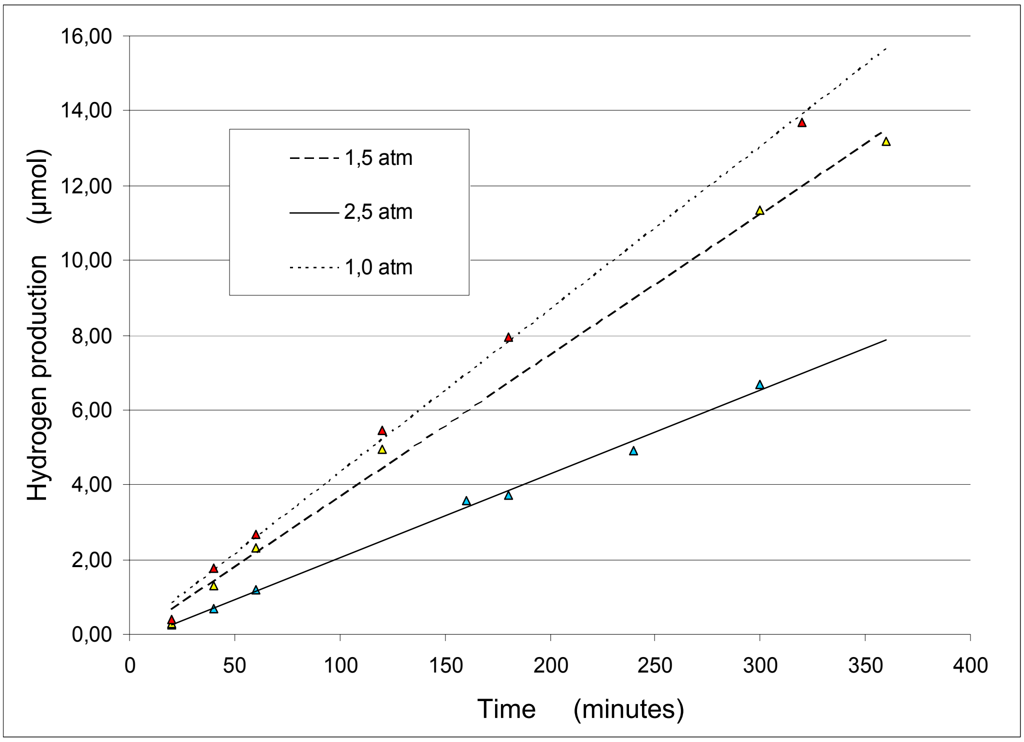

Fig.5. Hydrogen production versus time for different pressure conditions (photosonolysis).

Table 1. Hydrogen production after three hours.

H_2 PRODUCTION (3 hrs)		
Method	Pressure [atm]	H_2 production [μmol]
SONOLYSIS	1,0	7,32
SONOLYSIS	1,5	6,82
SONOLYSIS	2,5	3,65
PHOTOSONOLYSIS	1,0	7,69
PHOTOSONOLYSIS	1,5	7,03
PHOTOSONOLYSIS	2,5	3,71

A comparison between sonolysis and photosonolysis results is also shown in figure 6 relatively to 1 atm pressure tests (when the maximum hydrogen production occurs).

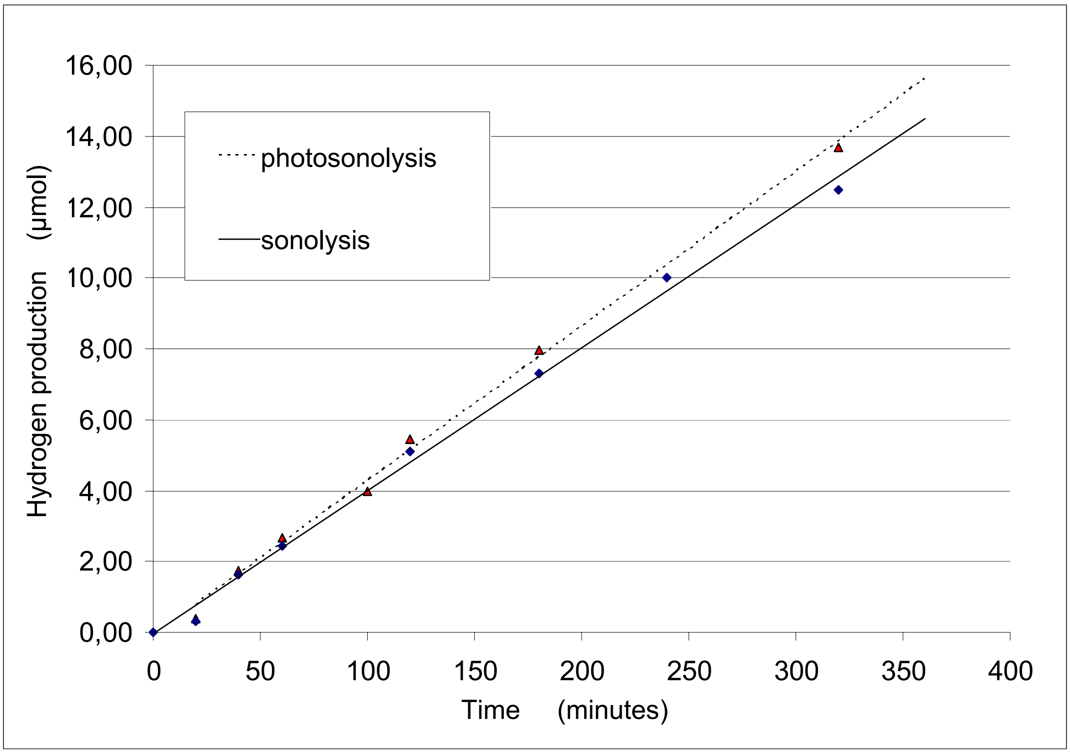

Fig.6. Comparison between sonolysis and photosonolysis test results (pressure = 1 atm).

CONCLUSIONS

Water sonolysis and photosonolysis were studied by experimental tests. A test facility was built; a measurement campaign was carried out to evaluate hydrogen production due to combined effect of ultrasounds and sunlight radiation.

Measurement results showed that hydrogen production due to sonolysis and sonophotolysis is linear versus time; besides, hydrogen production is higher for low pressure systems. Photosonolysis production is higher than sonolysis one.

Future developments are going on:

- the introduction of a photocatalyst able to enlarge and amplify the absorption spectrum;
- the study of innovative systems for hydrogen sieving and storage in water.

NOMENCLATURE

E energy, J

h Planck's constant, 6.6260693 × 10^{-34} Js

υ wave frequency, Hz

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