

Hydrogen Production From Water Under UV Radiation with Carbon Dioxide Mediation

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Hydrogen production from water under UV radiation with carbon dioxide mediation

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Abstract

A simple method of hydrogen production through the decomposition of water subjected to UV radiation is presented. Water contained dissolved sodium hydroxide and the solution was saturated with carbon dioxide gas. During saturation, the pH value dropped from about 11.5 to 7-8. The produced bicarbonate and carbonate ions acted as scavengers for hydroxyl radicals, preventing recombination of hydroxyl and hydrogen radicals, and giving priority to the formation of hydrogen gas.

In the presented method, the production of hydrogen is combined with the utilization of carbon dioxide.

Keywords: Hydrogen production; carbon dioxide utilization

Introduction

The rapid development of the world economy and the growth of the number of people are related to the high demand for energy. According to the IEA, it is estimated that by 2040 energy needs will increase by 30% [1,2]. At the same time, the scenario is proposing to reduce more than 40% of CO₂ emission during 2015-2040 period. At present EU Commission reported that global fossil CO₂ emissions in 2019 still increased by 0.9 % to a total of 38 Gt CO₂. Also, CO₂ per capita emissions have increased by ca. 15% from 4.26 t CO₂/cap/year to 4.93 t CO₂/cap/year between 1990 and 2019 [3]. Therefore in order to reduce CO₂ emission, the search for new technologies with zero CO₂ emissions is still attractive. One of the directions is the splitting of water to obtain hydrogen as a fuel.

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The milestone was the experiment carried out by A. Fujishima and K. Honda, in which water was more effectively broken down into hydrogen and oxygen when a semiconductor p-type electrode with TiO₂ was irradiated with visible light radiation [4].

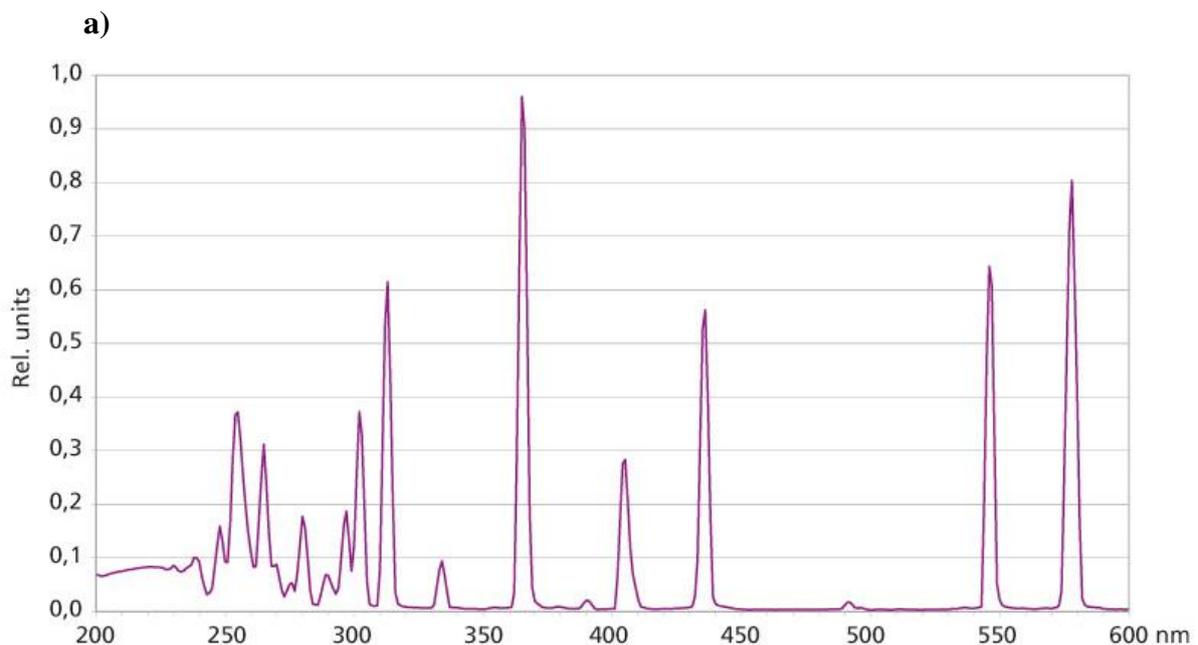
Since then, the photocatalytic direction of research related to the decomposition of water (water splitting) into oxygen and hydrogen has developed intensively. Then, the decomposition of water was combined with the reduction of CO₂ to obtain hydrogen, carbon monoxide, and useful hydrocarbons, as shown in the publication of T. Soltani et al. [5], where selective photocatalysts for hydrogen production with reduction of CO₂ were developed.

This work uses the fact that the energy of radiation with a wavelength in the UV range is sufficient to excite the H-OH bond in water, which is 498 KJ/mol. For example, a radiation quantum with a wavelength of 200 nm has an energy of about 590 kJ/mol [6,7].

Another fact of significant importance for these studies was the use of the inactivation capacity of OH· hydroxyl radicals. by HCO₃⁻ and CO₃²⁻ ions, formed during the saturation of water with carbon dioxide [8], which act as radical scavengers.

Methods

The experiments were carried out in a cylindrical quartz reactor with a working capacity of 766 cm³. A medium pressure mercury lamp TQ 150 (Heraeus, Germany) with a power of 150 W and UV-C radiation (or mercury lamp UV-A TQ 150 Z3 with lower UV-C component) was placed in a cooler located inside the reaction vessel. The spectra of lamps are given in Figures 1a) and 1b).



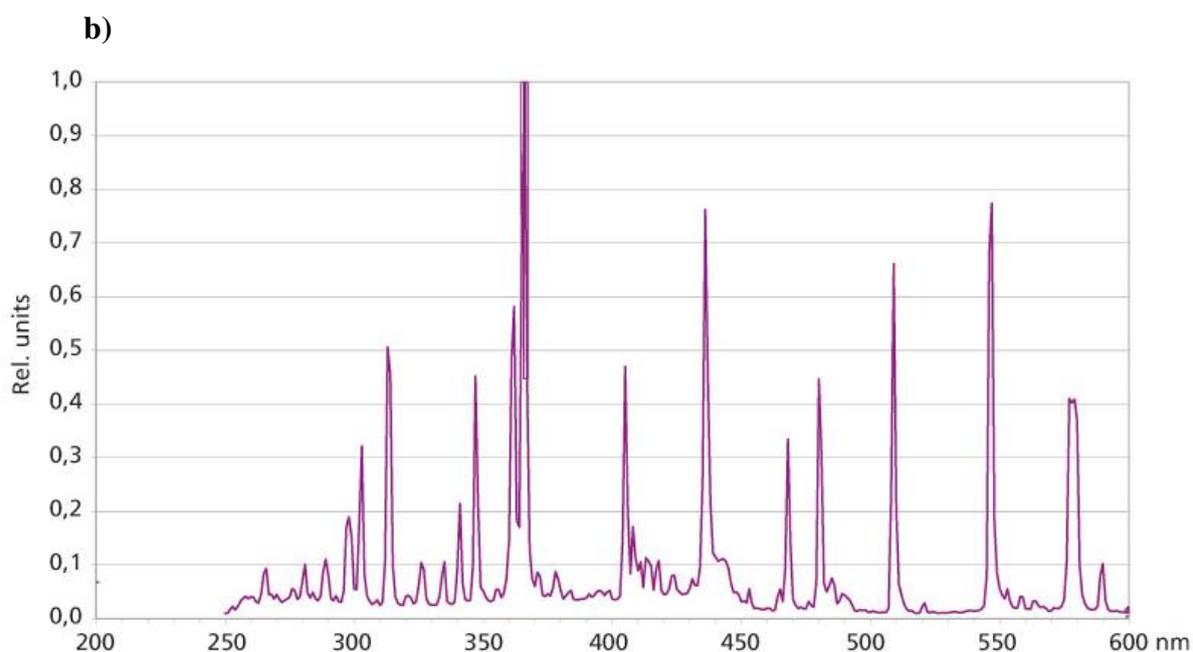


Figure 1. Spectra of used lamps: a) UV-C TQ 150; b) UV-A TQ 150 Z3

The cooler was supplied with water during the experiments. The reactor was closed in a thermostatic chamber in order to maintain stable temperature conditions and cut off any other light source. The scheme of the reactor is shown in Figure 2.

500 cm³ of distilled water or 500 cm³ of 0,2M sodium hydroxide solution (made from reagent grade NaOH; POCH, Poland) were poured into the reactor, and then the system was saturated with CO₂ by bubbling for 16 h. After this time, the reactor was tightly closed and the lamp, as well as the magnetic stirrer, were turned on. The content of the reactor was irradiated for 24 h. The gas phase from above the liquid surface was analyzed with gas chromatography after 0 h, 2 h, 4 h, 6 h, and 24 h.

All analyzes of the gas phase composition were performed by the chromatographic method using the SRI 310C gas chromatograph (SRI Instruments, USA), equipped with a Porapak Q 100/120 packed column and the HID detector (Helium Ionization Detector). The analyzes were carried out under isothermal conditions at 60°C. Helium was used

as the carrier gas. The gas flow through the column was $60 \text{ cm}^3/\text{min}$, while the volume of the tested gas sample was 1 cm^3 . The hydrogen content in the volume of the gas phase of the reactor in subsequent measurements was calculated based on the calibration curve.

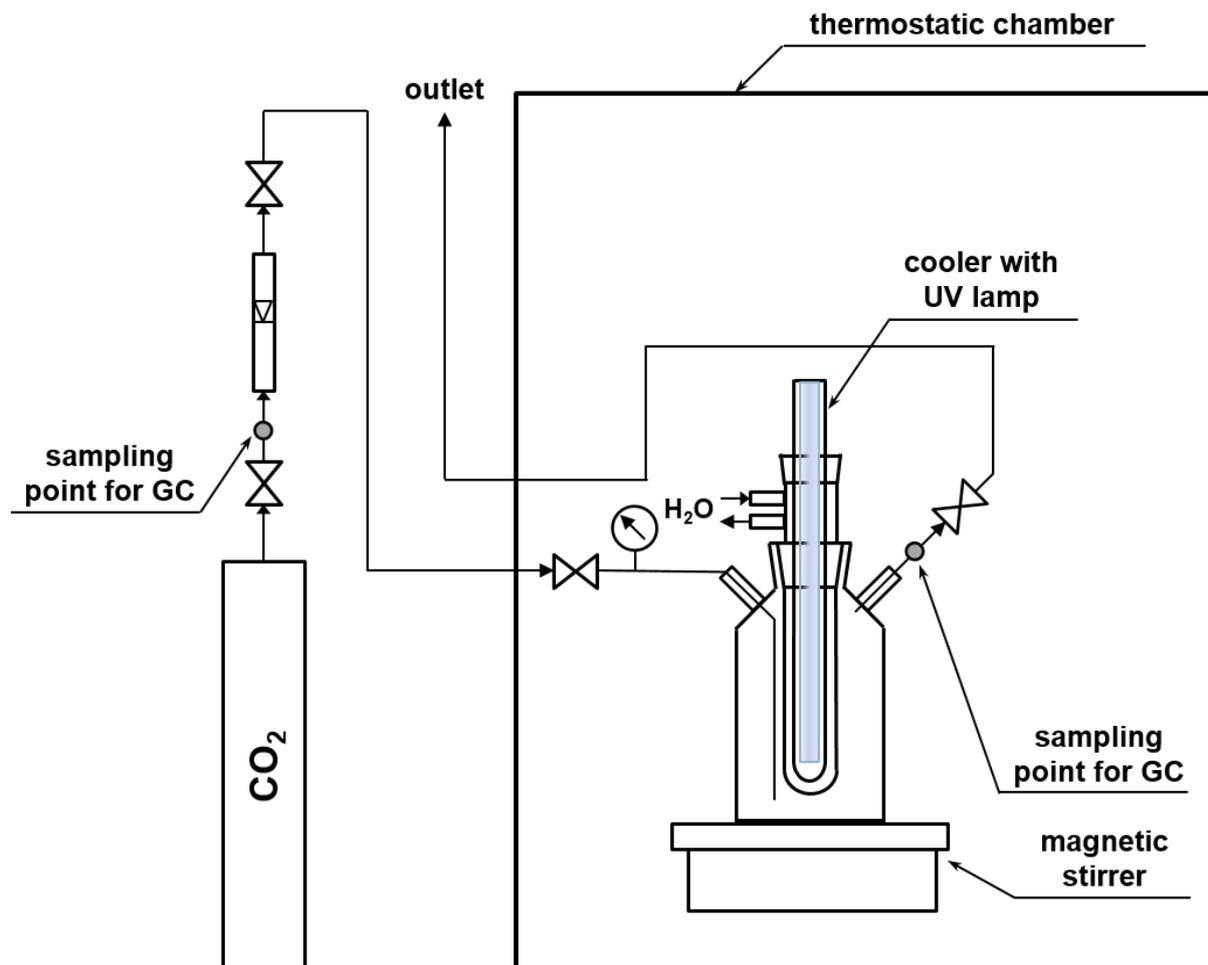


Figure 2. The scheme of the reactor for liquid phase processes

Results

We performed some preliminary and comparative experiments. In the first experiment, 500 cm^3 of water, which was not saturated with gaseous CO_2 , was placed in the reactor. Water was irradiated with a UV-C TQ 150 lamp. After 6 hours of irradiation, no hydrogen was found in the reactor.

In the second experiment, 500 cm^3 of water was saturated with CO_2 gas for 16 hours, and then the UV-C lamp was turned on. In the gas phase above the water surface, the content of hydrogen gas was analysed. The obtained results are shown below in Figure 3.

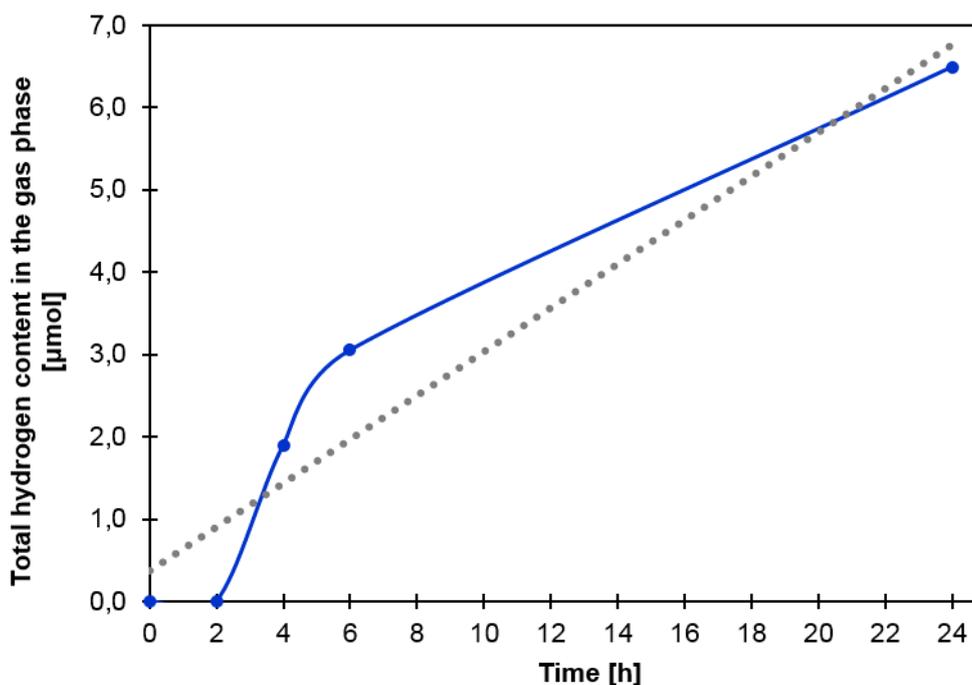


Figure 3. Hydrogen production from water saturated with CO₂ under UV-C TQ lamp radiation

The measured hydrogen content increased gradually and reached 6.4 micromoles after 24 h of irradiation. These changes are not rectilinear in the experiment period. At 2-6 hours of irradiation the rate of hydrogen formation increased to the level of 0.75 micromol/h and then dropped to ca. 0.2 micromol/h. The overall average reaction rate hydrogen production over 0-24 h may be estimated as 0.266 micromol/h.

The next step of the experiment was as follows: 500 cm³ of alkaline water containing 0.2 m NaOH was saturated with CO₂ for 16 h. During the UV-C irradiation with the TQ lamp, the hydrogen content in the gas phase above the solution was measured. The obtained results are shown in Figure 4. For comparison, an analogous experiment was performed with the use of UV-A TQ 150 Z3 mercury lamp with lower UV-C component (Figure 5).

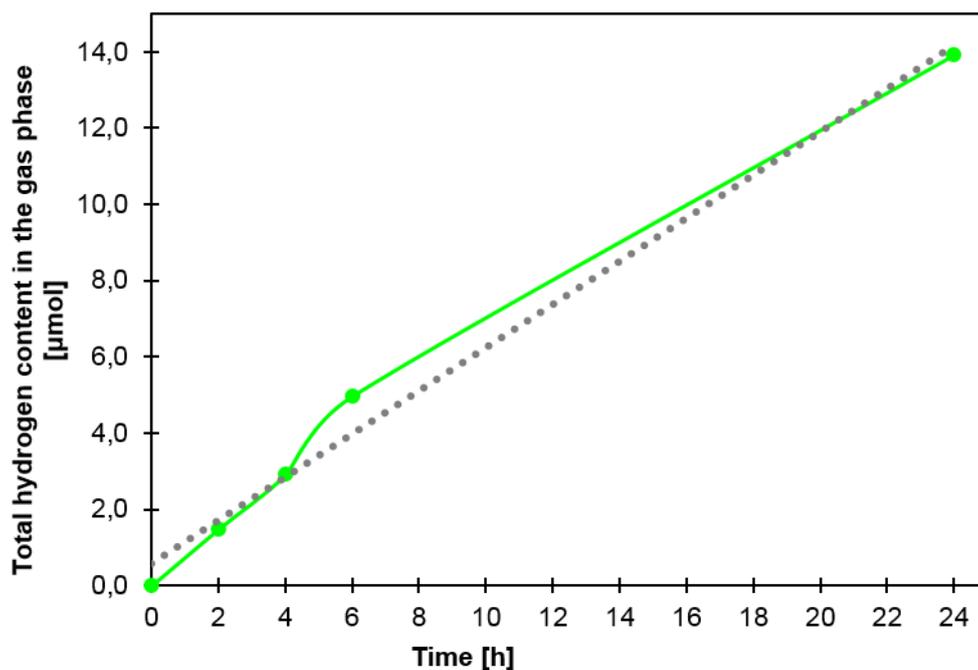


Figure 4. Hydrogen production by alkaline water (0.2 m NaOH) saturated with CO_2 under UV-C TQ lamp radiation.

The results presented in Figure 4 show almost a rectilinear dependence of hydrogen concentration on time, and the reaction rate can be estimated with a constant of about 0.6 micromol/h. In the first 6 hours of the process the rate was ca. 0.83 micromol/h.

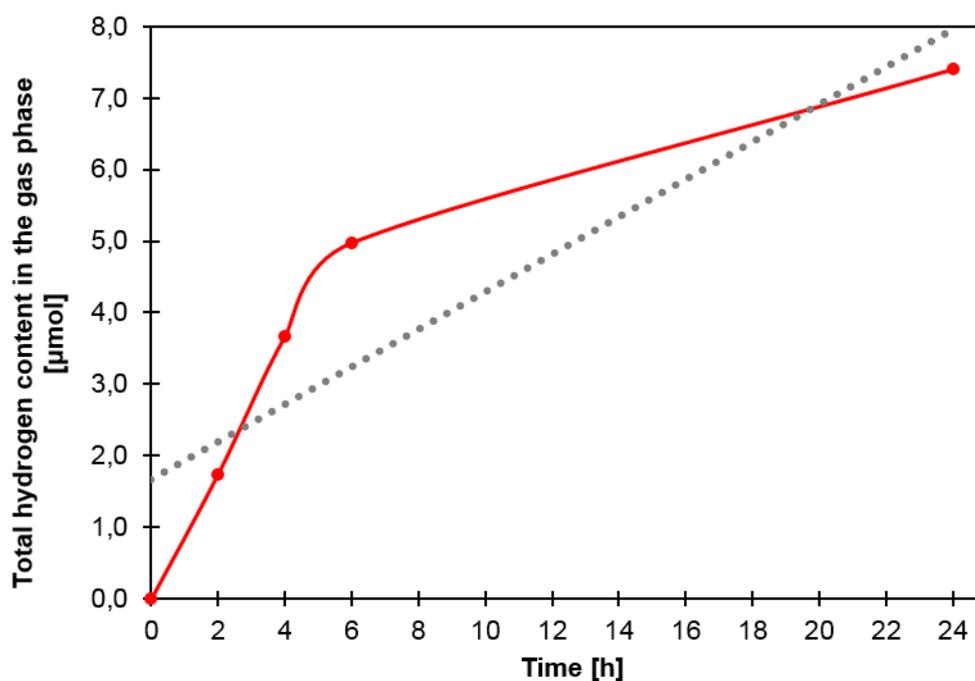


Figure 5. Hydrogen production from alkaline water (0.2 m NaOH) saturated with CO_2 under radiation of UV-A TQ 150 Z3 mercury lamp with lower UV-C component

The measured hydrogen content increased gradually and reached 7.4 micromoles after 24 h of irradiation. These changes are not rectilinear in the experiment period. At 0-6 hours of irradiation the rate of hydrogen formation increased to 0.83 micromol/h and then dropped to ca. 0.14 micromol/h. The overall average reaction rate hydrogen production over 0-24 h may be estimated as 0.31 micromol/h.

Discussion

It is well known that water is sensitive to solar radiation [9]. Products of this process are hydrogen and hydroxyl radicals:



Because of the short lifetime of radicals, the recombination of products occurs to produce water:



Another recombination ways that could be possible are as follows:



or



Reaction No. (2) is a support to explain why pure water without CO₂ saturation in the first experiment during UV-C irradiation did not generate hydrogen gas.

If we are interested in hydrogen production, the hydroxyl radicals OH[·] should be blocked to prevent the recombination to water according to the reaction No. (2). For this purpose, we used dissolved bicarbonate and carbonate ions formed following the mechanism presented below. Dissolution of carbon dioxide in water results in the formation of carbonic acid which is under equilibrium according to following reactions[8]:



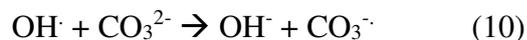
Reaction No 5. is dominating at the value of pH below 8.3, reaction No. 6 is occurring at a value of pH between 6-10, while reaction No. 7 from pH =8.3 to 11.

In our reactor the summarized saturation reactions are as follows:



Both bicarbonate and carbonate ions from reactions No. (6) and No. (7) respectively, are known as quick acceptors (scavengers) of hydroxyl radicals in water [10] with constant rate:

$k = 4.2 \times 10^8 \text{ mol}^{-1} \times \text{dm}^3 \text{s}^{-1}$ for CO_3^{2-} ions and $k = 41.5 \times 10^7 \text{ mol}^{-1} \times \text{dm}^3 \text{s}^{-1}$ for HCO_3^- ions, according to the following reactions:



In reactions No. (10) and (11) the reproduction of hydroxyl radicals is impossible. Hydroxyl ions OH^- could react with Na^+ to NaOH and again with carbon dioxide as was pointed out in reactions No. (8) and (9).

According to the above mechanism, the separated hydrogen radicals H^\cdot from reaction No. (1) can freely participate in reaction No. (4) to form gaseous hydrogen H_2 .

The use of sodium hydroxide increases the concentration of bicarbonate and carbonate ions during CO_2 saturation. The proposed mechanism of hydrogen formation with the capture of hydroxyl radicals acts like a pump extracting hydrogen from the water in a continuous manner.

Conclusions

In order to obtain hydrogen gas from water, a way to prevent the recombination of the hydrogen and hydroxyl radicals that arise in water during exposure to UV radiation is essential and depending on the UV-C radiation component. For this purpose, the best way is to use bicarbonate and carbonate ions, which are formed in an alkaline environment during the saturation of water with carbon dioxide. When the pH is lowered, the hydroxyl radicals react with bicarbonate and carbonate ions, with an irreversible inactivation of hydroxyl radicals.

In this way, the hydrogen radicals of H^\cdot combine to give hydrogen gas. The presented method is a simple method of producing hydrogen with the utilization of CO_2 as an “extracting pump” of hydrogen from water.

Acknowledgments

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