INTERACTION OF LASER RADIATION WITH MATTER. LASER PLASMA

Generation of hydrogen under laser irradiation of organic liquids

I.V. Baymler, E.V. Barmina, A.V. Simakin, G.A. Shafeev

Abstract. **The process of hydrogen generation under the action of pulsed radiation from an Nd : YAG laser with a peak intensity of ~ 10^{10} W cm^{-2} in the liquid on the chemically pure ethanol, isopropanol, isobutanol, and diethyl ether is studied. The rate of molecular hydrogen generation, characteristic for each sample of organic substance, is experimentally determined. The obtained results are interpreted basing on the analysis of the molecular structure of the studied samples of organic liquids.**

1. Introduction

At present, the search for an ecologically clean, high efficiency and cheap energy carrier becomes more and more urgent. This fact explains the interest in hydrogen as an alternative energy source. In using hydrogen, the pollutions are completely absent, since in the energy release the side products are only heat and water, which can be reused for other purposes. In spite of its simplicity and abundance, naturally hydrogen does not occur on Earth in free form. It either lifts to the upper layers of atmosphere, or participates in a chemical reaction with other elements, e.g., with oxygen forming water. Therefore, the only way to obtain hydrogen is to extract it from other substances using physical and chemical methods.

The most efficient method at present is the method of vapour conversion of the natural gas. Using this method 90%–95% of all hydrogen is produced. Other methods of hydrogen generation include the gasification of coal, using the atomic energy, water electrolysis, and hydrogen extraction from biomass.

In Ref. [1] an alternative version of hydrogen production using its generation under laser-induced ablation of aqueous solutions of iron and beryllium nanoparticles is discussed. It was found that plasma breakdowns also occur in pure water, but their number is much smaller than in the case of adding nanoparticles. In other words, nanoparticles play the role of a

seed: they provide the primary absorption of laser radiation and then give rise to plasma generation. Similar breakdowns in pure water apparently occur at impurities, accidentally introduced from environment, e.g., from air. The formation of hydrogen occurs also in the process of laser ablation of metallic targets in water [2, 3]. Hydrogen is produced both in the plasma torch above the target and in the breakdown plasma at the produced nanoparticles.

In Refs [4–7] the ethanol pyrolysis process at the temperatures 700–2500 K and the pressures 3–66 kPa was studied. The main products of these reactions are hydrogen, oxygen, and acetaldehyde. Based on the obtained results, one can expect that under irradiation of aliphatic spirits the main products will be hydrogen, glycols and aldehydes. Water, hydrogen peroxide and gaseous hydrocarbons are produced in small amounts. The primary reaction under irradiation is the reaction of dehydration, i.e., the rupture of C–H bonds. The formation of hydrogen peroxide and water manifest the rupture of C–O bonds. It was noticed that the presence of oxygen strongly enhances the aldehyde formation. In long molecules, probably, the influence of the OH group becomes weaker and the yield of aldehydes and glycols decreases [8].

For searching the most suitable substances, maximising the hydrogen production under laser irradiation, we propose to use pure organic substances, e.g., the spirits, containing more hydrogen than common water. We also expect that the generation of hydrogen will occur more intensely than in water. In the process of laser action on the spirits the reaction channels may open, different from those that occur during the pyrolysis.

2. Experimental technique

As organic liquids for studying the hydrogen generation rate under laser irradiation, we used the chemically pure ethanol (C_2H_5OH), isopropanol (C_3H_7OH), isobutanol (C_4H_9OH), and diethyl ether [$(C_2H_5)_2O$]. The studied sample having a volume of 8 cm^3 was placed in a cell with a transparent bottom. To prevent strong heating that occurs under the irradiation, the cell was cooled with water.

As a source of laser radiation, we used a Nd : YAG laser with the following parameters: $\lambda = 1064$ nm, the pulse duration 10 ns, the pulse repetition rate 8 kHz, the average power up to 20 W, the pulse energy 1.25 mJ. A schematic of the experiment is presented in Fig. 1.

To provide a homogeneous distribution of the energy density in the small cell volume, the laser beam was moved around the circle, lying in the plane perpendicular to the beam propagation direction and located within the cell volume. The choice of a circle for the scanning shape was caused by the necessity

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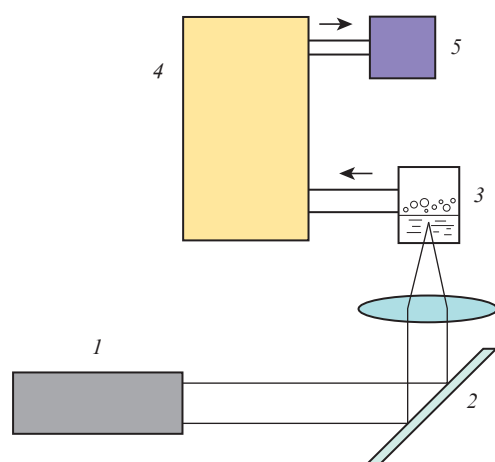
Figure 1. Schematic of the experimental setup for hydrogen generation in organic liquids:
(*1*) Nd:YAG laser; (*2*) 2D galvo mirror system for moving the laser beam (Ateko-TM); (*3*) cooled cell with the working liquid; (*4*) nitrogen trap; (*5*) AVP-02 hydrogen amperometric sensor.

to ensure equal conditions in the process of irradiation. If the beam is moved, e. g., along a square contour, there are stop points. Thus, choosing the circle, we ensure the constant velocity of the laser beam motion in the scanned volume of the liquid during the entire experiment.

The laser beam displacement was implemented by means of the scanning system of mirrors. The objective lens with the focal length $F = 9.5$ cm focused the radiation into the cell so that the produced plasma ring would be located at a distance of 3 mm from the entrance window to prevent its damage.

The hydrogen released in the process of the experiment was transported from the cell into the measurement volume via a system of pipes. The entire system volume V amounted to 230 ml. The hydrogen content in it was registered by means of an AVP-02 hermetically fixed portable hydrogen analyser (amperometric sensor). The air forced out by the generated hydrogen exited via a capillary sunken in water (waterlock). Thus, the pressure in the systems was kept close to the atmospheric one.

The sensor electrode was separated from the measured volume by a membrane made of lavsan or polyethylene, allowing only hydrogen to pass through. The operation of the AVP-02 analyser is based on the anode polarisation with respect to the auxiliary electrode and the measurement of depolarisation current arising as a result of hydrogen diffusion from the working liquid and subsequent electrochemical reaction of its oxidation. The signals of the sensor and the temperature meter are amplified in the pre-amplifier and after normalisation arrive at the ADC. After the calculation and introducing the automatic corrections both into the temperature dependence of the solubility coefficient of hydrogen in water and into the temperature dependence of the coefficient of hydrogen penetration through the gas-permeable membrane of the sensor, the signal generated in the measuring device is displayed on the analyser screen in the chosen measurement units. In the present paper in order to compare with the atmospheric pressure, it is most convenient to measure the partial pressure of hydrogen recorded by the sensor in Torrs. Besides that, it is possible to measure the hydrogen concentration (in mg L^{-1} or μg L^{-1}). The accuracy of measurement using the sensor was 5%.

In order to obtain correct data, we performed the calibration of the analyser zero point and the calibration using a reference gas mixture. As a sample with a zero content of hydrogen we used air, as a reference gas we used pure (99.995%) hydrogen from the GVCh-6 hydrogen generator (produced by electrolysis of pure water).

In the course of experiments, we noticed the influence of the products of spirits decomposition on the indications of the analyser sensor. After the completion of the experiment, the repeated calibration of the sensor with respect to the atmospheric pressure of pure hydrogen was carried out. In this process, the device showed the pressure values much lower than the atmospheric one, which indicated the change in the analyser sensitivity. To prevent this effect, a nitrogen trap was installed between the cuvette and the sensor, which prevented the appearance of the spirit decomposition products, except hydrogen, on the sensor. The nitrogen trap and the sensor were placed sufficiently far from each other, so that the analyser did not detect the temperature effect of the trap, and the produced hydrogen passed through the cold volume fast enough, having no time for considerable cooling. Thus, we can consider the sensor indications as corresponding to room temperature.

3. Results

In the framework of the experiment, we found the dependence of the hydrogen amount in the system on the laser exposure time for three different spirits and one ether (the typical dependence for ethanol is presented in Fig. 2).

In the process of further irradiation ($t > 40$ min), the slope of the curve decreases and the dependence tends to a constant value due to saturation of the system with hydrogen. As seen from Fig. 2, during the first 5 minutes of laser irradiation the dependence is nonlinear, which is related to the stabilisation. Then the dependence becomes close to linear. Small jumps of the partial pressure are due to evaporation and consequent addition of liquid nitrogen in the nitrogen trap. In this case, the cold part of the system volume increases and the pressure gradient appears directed towards the cold volume. The outflow of hydrogen from the measurement volume temporarily occurs with subsequent transition to the steady state.

The dependences of the hydrogen yield on the time of laser irradiation of organic liquids are presented in Fig. 3. One can
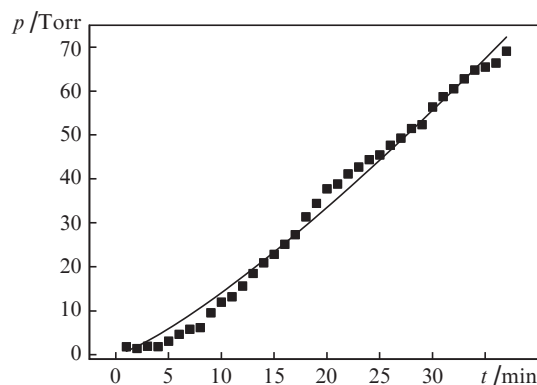

Figure 2. Dependence of the hydrogen pressure in the system on the laser exposure time of ethanol (the solid line is the result of approximation).
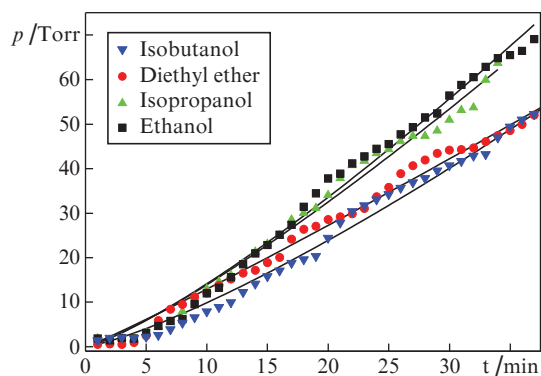
Figure 3. Dependences of the hydrogen pressure in the system on the duration of laser irradiation of organic liquids (solid lines are the approximation of the experimental data).

Figure 4. Photographs of optical breakdown plasma in ethanol after (a) 0.5 min and (b) 5 min of its laser irradiation.

4. Discussion of results

From the experimental results, it follows that the pressure of emitted hydrogen depends on the molecular structure of irradiated spirits, as well as on the number of carbon–carbon bonds in them. One can see from Fig. 3 that the most efficient hydrogen generation is possible from the spirits containing the minimal number of carbon–carbon bonds. In our experiments the ethanol (C_2H_5OH) appeared the most efficient substance, in which the ablation produced the greatest amount of hydrogen. It is worth noting that isobutanol and diethyl ether possess different structures, although the number of C–C bonds in them is similar. Thus, we can suppose that the structure of molecules of the used sample also plays a role in the process of molecular hydrogen generation.

4.1. Analytical description of the generation process

The dependences that characterise the hydrogen yield, obtained in the experiments, are obviously nonlinear. In order to define more precisely the values of the generation rate obtained from the linear approximation of these dependences, they can be rather simply described analytically using the analogy with the diffusion process and keeping in mind that the concentration of gas is proportional to its partial pressure.

The change in the hydrogen partial pressure in the system is described by the equation

$$dp/dt = -C_1 p + u, \qquad (1)$$

where the first term in the right-hand side of the equation describes the rates of hydrogen exit via the waterlock and the leakage of hydrogen in the system. The second term describes the rate of the hydrogen increase in the system due to its extraction from the spirit. This term is pressure-independent and is considered constant, which is not quite correct. Here we neglect these processes and assume that the hydrogen generation rate corresponds to that in the quasi-stationary state. The coefficient C_1 (c^{-1}) depends on the total volume of the system V, as well as on the rate of hydrogen supply u. For simplicity we assume that $C_1 = u/V$.

The solution of Eqn (1) with the initial condition $p(0) = 0$ (initially there is no hydrogen in the system) has the form:

$$p(t) = V[1 - \exp(-tu/V)]. \qquad (2)$$

see that both the quantity of generated hydrogen and its emission rate depend on the studied liquids.

For a primary estimate of the hydrogen generation rate, we used the slope of the straight line approximating a segment of the curve in the range 5–30 min. The approximate values of the hydrogen generation rate obtained in this way are presented in Table 1.

Table 1. Hydrogen generation rates obtained by linear approximation of experimental dependences.

Studied liquid	Generation rate /Torr min^{-1}
Ethanol (C_2H_5OH)	2.17 ± 0.03
Isopropanol (C_3H_7OH)	2.01 ± 0.03
Isobutanol (C_4H_9OH)	1.58 ± 0.02
Diethyl ether [(C_2H_5)$_2$O]	1.45 ± 0.02

In the process of irradiation of organic liquids, e. g., spirits, the laser radiation is absorbed by impurities, initially contained in the liquid or getting into the cuvette, e. g., from the surrounding air. The absorbed radiation ionises the impurity particles, which gives rise to surrounding plasma torches. In the case of ethanol, the dissociation of molecules occurs due to electron impact (by plasma electrons) and thermal processes taking place in the reactor. In the course of decay, the glassy carbon (disordered carbon) nanoparticles are formed in the liquid, which, in turn, absorb the radiation of laser and are ionised. This avalanche-like process leads to the formation of a plasma in the reactor, which then stops to develop, because the energy density, required for ionisation, falls on a limited region near the focal point. After the stabilisation of the plasma formation, its radiation leads to the appearance of molecular hydrogen and other products. Figure 4 presents photographs of the plasma appearing under laser irradiation of ethanol. It is seen that initially the plasma formations are separated from each other and the number of breakdowns is not great. Then this number increases, which is just due to the formation of new centres of absorption and plasma in the liquid.

The plasma ring visually observed as continuous actually consists of individual plasma formations. The vertical chains, consisting of a sequence of plasma formations arise during one laser pulse.
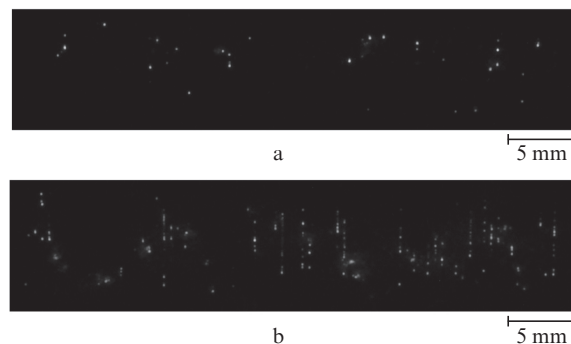
Figure 5 illustrates the comparison of experimental curves of the generated hydrogen pressure for different liquids with the corresponding approximation curves calculated using Eqn (2). Note that the difference of curves at the initial stage is caused by the transient processes in the measurement volume mentioned above and leading to the variation of hydrogen supply to the system. As a result, the approximating curves are shifted along the time axis with respect to the experimental ones. Equation (1) is seen to describe the process of hydrogen generation in the system well enough. The values of the hydrogen generation rates for the organic liquids, obtained by comparison of theoretical curves with experimental ones, and the generation rate for water [1] are presented in Table 2.

Table 2. Obtained values of hydrogen generation rates u_{H_2} and number of molecules N in the studied volume for the chosen samples and the corresponding data for water from Ref. [1].

Studied liquid	u_{H_2} /mmol L^{-1} min^{-1}	$N/10^{22}$	n_H
Ethanol (C_2H_5OH)	141.2 ± 2.8	8.27	3
Isopropanol (C_3H_7OH)	130.5 ± 2.6	6.29	2.66
Isobutanol (C_4H_9OH)	96.3 ± 2.1	5.21	2.5
Diethyl ether ((C_2H_5)$_2$O)	104.3 ± 2.1	4.64	2.5
Water (H_2O)	14.4 ± 0.3	26.8	–

N o t e : n_H – is the number of hydrogen atoms (with the OH group taken into account) per atom of carbon in the molecule.

4.2. Relation between the hydrogen generation rate and the molecular structure of the liquid

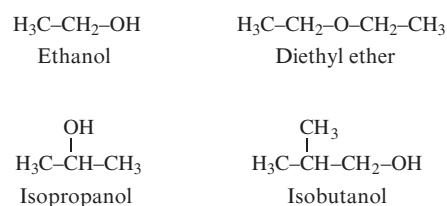Figure 6 presents the structural formulae of molecules of the chosen samples.

$$H_3C-CH_2-OH$$
Ethanol

$$H_3C-CH_2-O-CH_2-CH_3$$
Diethyl ether

$$\underset{\text{Isopropanol}}{H_3C-\overset{\overset{\displaystyle OH}{|}}{C}H-CH_3}$$

$$\underset{\text{Isobutanol}}{H_3C-\overset{\overset{\displaystyle CH_3}{|}}{C}H-CH_2-OH}$$

Figure 6. Structural formulae of the molecules of studied liquids.

Comparing the experimental results with the molecular structures, one can qualitatively substantiate the observed yield of generated hydrogen. Basing on the idea that due to the interaction of the sample molecules with the electrons of plasma the C–H bonds are broken first, we can assume that the amount of released hydrogen will depend on the number n_H. From Table 2 it follows that ethanol has the maximal number of hydrogen atoms per atom of carbon; isopropanol is the next after ethanol. For isobutanol and diethyl ether, these numbers are minimal. This is explained by the fact that in 'long' molecules the additional bonds of carbon atoms are used to bind other carbon atoms (like, e. g., in the isobutanol molecule). On the contrary, in the ethanol molecule more bonds are used to bind carbon atoms with hydrogen ones. Then, generalising this result, we can expect methanol (CH_3OH) to be the most efficient 'fuel' for hydrogen production. In methanol, four hydrogen atoms fall on one atom of carbon, including the OH group, in which the breakage of chemical bond can also occur.

Using the known values of density at room temperature (ρ [g cm^{-3}]), molar mass (M [g mol^{-1}]) and volume ($V = 8$ cm^3)
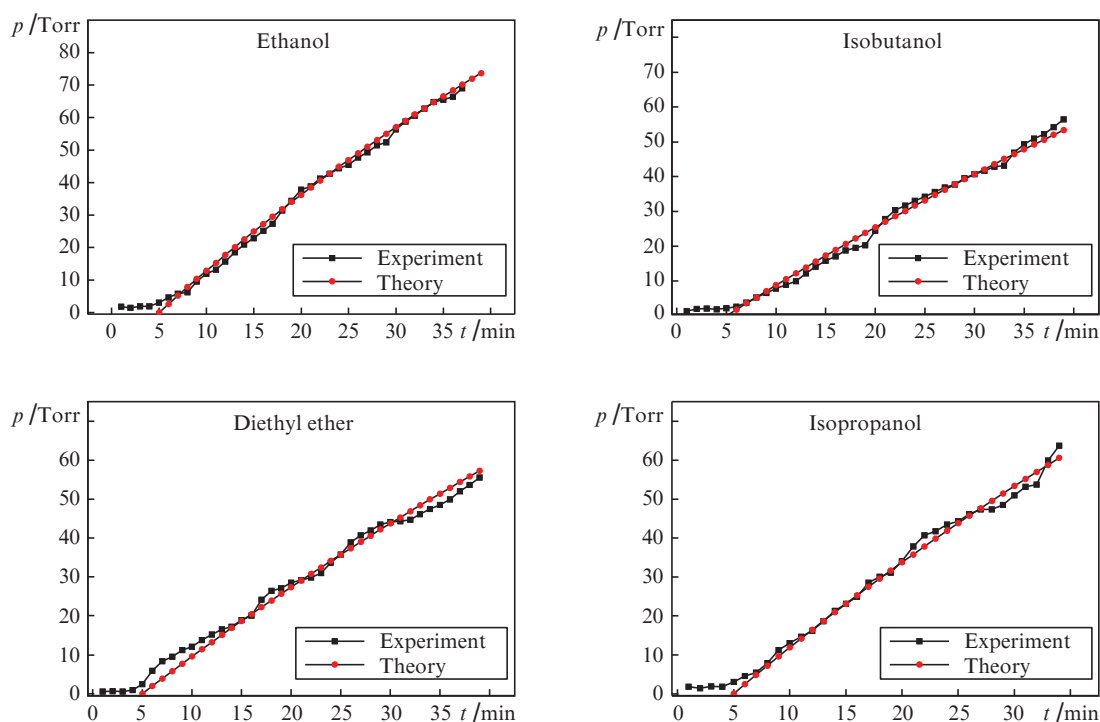

Figure 5. Experimental and approximating curves describing the process of hydrogen generation during laser irradiation of different organic liquids.

of the studied liquid it is easy to estimate the number of molecules by means of the expression

$$N = N_A \rho V/M,$$

where N_A is the Avogadro number. The values of N for the studied liquids are presented in Table 2.

Thus, in the given sample volume the number of spirit molecules is greatest for ethanol. The rates of hydrogen generation obtained in the experiment with different samples correlate with the number of molecules contained in them.

5. Conclusions

The values of hydrogen generation rates that characterise the productivity of different samples of organic liquids for producing molecular hydrogen were obtained. We studied pure ethanol, isopropanol, isobutanol, and diethyl ether. It was found that the hydrogen generation rate for them is by an order of magnitude higher than for water. It was established that with other conditions being similar, the hydrogen generation rate depends on the molecular structure of the liquid and correlates with the number of C–H bonds. Ethanol and isopropanol appeared to be the most 'productive' (the hydrogen generation rates being 141 and 130 mmol L^{-1} min^{-1}, respectively). It is easy to calculate that in the case of ethanol nearly 4.5 µL of produced hydrogen falls on a unit of laser radiation energy. Correspondingly, the production of 1 m^3 of hydrogen requires 220 MJ of energy. However, it is worth noting that not all the energy is absorbed by the medium, so that the real expenditures will be smaller.

To find the hydrogen generation rate, we developed an analytical model describing the variation of the gas amount in the system with its volume and gas supply rate taken into account. From the comparison of experimental and theoretical data, we found the averaged values of the molecular hydrogen formation rates. Probably, in the process of laser irradiation of the studied liquids other gaseous products, e. g., methane, are also formed. However, their detection and measurement of relative yield requires chromatographic determination of the gas composition above the liquid.

References

1. Barmina E.V., Simakin A.V., Shafeev G.A. *Chem. Phys. Lett.*, **655–656**, 35 (2016).
2. Zhang D., Goökce B., Barcikowski S. *Chem. Rev.*, **117**, 3990 (2017).
3. Kalus M.-R., Bärsch N., Streubel R., Gökce E., Barcikowski St., Gökce B. *Phys. Chem. Chem. Phys.*, **19**, 711 (2017).
4. Barnard J.A., Hughes H.W.D. *Trans. Faraday Soc.*, № 56, 55 (1960).
5. Freeman G.R. *Proc. Royal Soc. London. Ser. A*, **245** (1240), 75 (1958).
6. Rotzoll G. *J. Analytical Pyrolysis*, **9** (1), 43 (1985).
7. Park J., Xu Z.F., Lin M.C. *J. Chem. Phys.*, **118**, 9990 (2003).
8. Swallow A.J. *Radiation Chemistry of Organic Compounds* (Oxford: Pergamon Press, 1960).