ISSN 0020-4412, Instruments and Experimental Techniques, 2006, Vol. 49, No. 1, pp. 132–134. © Pleiades Publishing, Inc., 2006.
Original Russian Text © S.B. Alekseev, V.A. Kuvshinov, A.A. Lisenko, M.I. Lomaev, V.M. Orlovskii, V.A. Panarin, E.A. Rozhdestvenskii, V. S. Skakun, V.F. Tarasenko, 2006, published in Pribory i Tekhnika Eksperimenta, 2006, No. 1, pp. 142–144.

PHYSICAL INSTRUMENTS FOR ECOLOGY, MEDICINE, AND BIOLOGY

A Photoreactor on the Basis of a Xe_2 Excilamp

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Received June 16, 2005

Abstract—A photoreactor developed on the basis of a Xe_2 excilamp with a power of ~10 W (with a power density of 15 mW/cm^2 emitted from a surface of ~700 cm^2), which can operate in liquids and gases at a pressure of up to 40 atm, and a multifunctional cell with an active volume of ~760 cm^3 is described. Data on water photolysis in a natural gas exposed to VUV radiation with $\lambda = 172$ nm are presented.

PACS numbers: 42.72.Bj

DOI: 10.1134/S0020441206010192

UV and VUV radiation sources based on a repetitively pulsed discharge in inert gases at pressures of a few hundred torr are used as fluorescent lamps in ozonizers; systems for cleaning and preparing semiconductor surfaces, removing polymers, cleansing photomasks, and etching various polymers; and in processes of photochemical water and air purification and synthesis of chemical compounds. Photolysis processes are conventionally conducted in combination with highly active oxidizers—oxygen, ozone, hydrogen peroxide, radicals–oxidizers, semiconductor oxides, etc.—thus allowing photoprocesses to be promoted considerably [1–4]. Excilamps based on xenon dimers [5, 6] are most suitable for stimulating numerous photoprocesses.

Xenon lamps have such specific features as a comparatively high efficiency (up to ~60% for physical efficiency and ~40% for engineering efficiency [5, 6]) and a high quantum energy of 7.2 eV, which is sufficient for breaking the chemical bonds of many molecules and, consequently, realizing various photostimulated physical and chemical processes. The high spectral density of the radiation energy, the comparatively high efficiency, the expanded surface of the radiators of Xe_2 lamps, and the possibility of performing irradiation in different media allow efficient structural transformations of gaseous hydrocarbons to be carried out [7, 8].

The objective of this study was to develop and test a photoreactor (PR) with a radiation power of ~10 W and an active surface of the radiator of ~700 cm^2.

Figure 1 shows a schematic drawing of the PR, which has a working volume of 760 cm^3 and allows irradiation of gaseous and liquid substances at different pressures (up to 40 atm) under substance-flow conditions. A single-barrier xenon excimer lamp is used as the radiation source. Structurally, it is sealed-off quartz tube *5* with an outer diameter of 22 mm, a length of 1100 mm, and walls 2.5 mm thick. The ends of the quartz tube have an almost spherical shape. This design of the lamp's bulb allows it to be arranged inside the reactor at a pressure of up to 40 atm. The reactor was tested at a pressure of up to 10 atm with the lamp's bulb sealed on the outside. In this case, the lamp surface is sealed using a set of alternating metal and rubber (or fluoroplastic) spacers placed in the pressure-separation unit, which allows loading with short-wavelength radiation to be minimized.

Cathodes nos. 1 or 2 could be installed inside the tube along its axis. Cathode no. 1 was wire coil *3* wound on quartz rod *4*. Cathode no. 2 was a zigzag-shaped flat wire structure with a width equal to the inner diameter of the lamp's quartz case. A voltage was applied to the cathode through a vacuum-tight lead-in. Grounded wire grid *2* arranged over the tube's exterior surface (the grid transparency was ≥75%) served as the anode. When a voltage was applied to the lamp's elec-

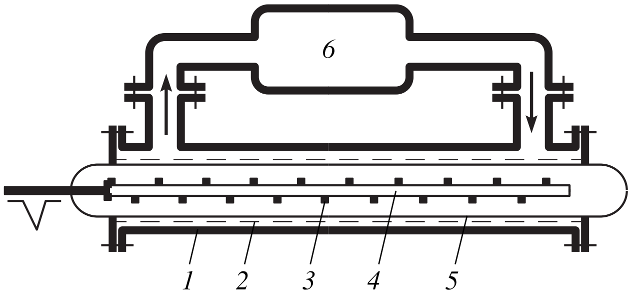

Fig. 1. Schematic drawing of the photoreactor: (*1*) reactor housing, (*2*) grid, (*3*) metal coil, (*4*) quartz rod, (*5*) lamp body, and (*6*) circulation system.

trodes, a discharge was initiated between the cathode and the interior surface of the quartz tube.

The power-supply unit has a traditional structure. It has an input noise-suppressing filter, a control circuit, a diode bridge, a device for limiting current surges during the discharge of a capacitive filter using a timer and an electromagnetic relay, a voltage changer based on a WARP2 half-bridge of IGBT-series fast transistors with built-in ultrafast soft-recovery diodes, and a high-speed current-protection device. A step-up pulse transformer forms negative-polarity voltage pulses of ~3.5 kV with a duration of ~1.0 μs and a repetition rate of 35–75 kHz. The average power of the power source was varied, depending on the excitation mode, between 150 and 300 W at an efficiency of ~85% by changing the pulse repetition rate.

The xenon pressure at which the radiation power reached its maximum was ~400 Torr for cathode no. 1 and ~210 Torr for cathode no. 2. When the pressure increased with respect to the optimal one, discharge contraction was observed; at a lower pressure, the discharge became more uniform but the radiation power decreased. The B–X band of Xe_2^* molecules ($\lambda \sim$ 172 nm) dominates in the discharge emission spectrum (Fig. 2); the second order of this band ($\lambda \sim 340$ nm) and broadband radiation in the visible spectral region ($\lambda \sim$ 510 nm) that can be attributed to emission from XeO molecules are also detected.

The mean radiation power was measured by a device produced by Hamamatsu that included a C8026 measuring unit and an H8025-172 photodetector. Measurements showed that the mean radiation power in the VUV region was ~12–17 mW/cm^2. The mean radiation power depended on the radiator temperature in such a manner that a decrease in the mean power corresponded well to an increase in the lamp temperature. The mean radiation power increased under forced cooling of the radiator. Note that, when the excilamp was turned on repeatedly after being cooled, the mean radiation power was restored to the initial value and then changed, depending on the radiator temperature.

The presence of a dielectric barrier in the form of the quartz bulb's wall forces one to use a pulse voltage and determines the capacitive–resistive character of the lamp as a load of the pulse generator. Oscillograms of voltage pulses at the lamp's electrodes and the discharge current, which are recorded at a mean excitation power of 200 W, show a slight delay of the voltage phase at the lamp's electrodes relative to the current phase, which is typical of a capacitive–resistive load. The presence of excitation-power modulation in time is also observed. Approximately 50% of the energy input for the entire period is deposited during the rise time of the voltage pulse. The remaining energy is transferred to the discharge plasma ~1 μs later through a discharge of the capacitance of the dielectric barrier.

The value of the excitation energy per period was calculated by two methods: (1) by integrating the excitation power and (2) using a voltage–coulomb figure [9]. Both methods yielded close results. In addition, using appropriate segments of the voltage–coulomb figure, capacitances of the gas gap C_g (~0.27 nF) and the dielectric barrier C_b were determined. It should be noted that the C_b value depends on the substance filling the reactor. For example, when the reactor was filled with a conducting liquid, C_b increased by ~35–40% as compared to the value for the gas-filled reactor (in the latter case, C_b was ~1 nF). Moreover, the conducting liquid on the exterior surface of the lamp's bulb can be used as a grounded anode, which correspondingly precludes the necessity of using a grid. In this case, radiation losses due to the absorption in the grid are absent.

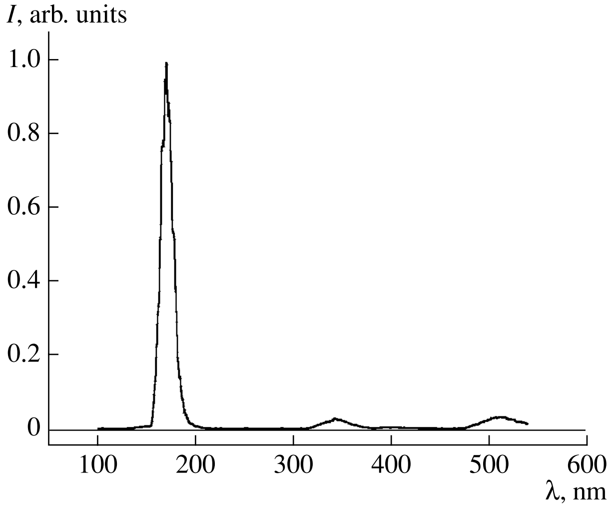

Fig. 2. Emission spectrum of a single-barrier lamp at a xenon pressure of 210 Torr.

This setup was used to study structural changes in the natural gas of the Myl'dzhinskii gas-condensate deposit in Tomsk oblast [7, 8]. Data on the structural changes and water photolysis in a natural gas at a pressure of 17.1 atm were obtained under its irradiation with VUV radiation at $\lambda = 172$ nm and a total energy emitted in one working cycle of ~10 J. The results of this study have shown that 172-nm VUV radiation allows water photolysis and changes in the structure of hydrocarbons to be performed efficiently and purposefully. The composition of stable products of the natural gas that were obtained after the irradiation of hydrocarbons was analyzed by the chromatography technique. The composition of the natural gas before and after (in parentheses) irradiation was as follows: methane, 92.34 (92.52); carbon dioxide, 0.39 (0.39); ethane, 3.48 (3.48); water, 0.27 (0.13); propane, 2.1 (2.04); i-butane, 0.57 (0.55); i-pentane, 0.16 (0.16); n-pentane, 0.11 (0.11); and C_6, 0.04 (0.1).

Figure 3 shows the dynamics of changes in the water concentration as a function of the irradiation time for the natural gas at a pressure of 17.1 atm. After 3-min irradiation, the water concentration falls by a factor of

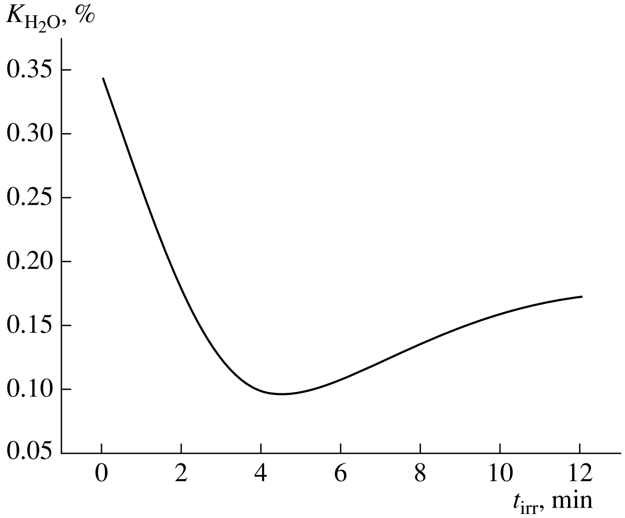

Fig. 3. Concentration of H_2O in a natural gas at a pressure of 17.1 atm as a function of the irradiation time.

>2 and then increases. In addition to water, the concentration of C_6 underwent the greatest relative change, by a factor of ~2.2.

Under the exposure to UV radiation, the main process occurring in natural gas that contains water vapors is water photolysis, with the formation of highly reactive radicals $^{\bullet}OH$ and $^{\bullet}H$ in the reaction

$$H_2O + h\nu \longrightarrow H_2O^* \longrightarrow {}^{\bullet}H + {}^{\bullet}OH.$$

The radicals then undergo chemical reactions with hydrocarbons [7, 8]. Hydrocarbon-dimerization and water-conversion processes are substantial under VUV irradiation. The dimerization mechanism is observed in reactions with hydroxyl radicals.

Hence, C_3 dimers and alcohols are synthesized. The most efficient processes in this system are water-reduction reactions in the interaction between hydroxyl radicals and C_{3+} hydrocarbons. The rate constants for these processes are two to three orders of magnitude higher than the rate constants for similar processes of interaction between $^{\bullet}OH$ radicals and methane and ethane molecules. Therefore, despite the low concentrations of C_3–C_6 compounds included in natural gas, a hydrogen atom is predominantly detached from such a molecule with the formation of a $^{\bullet}C_nH_{2n+1}$ radical. At the next stage, these radicals are dimerized or recombine with $^{\bullet}OH$, resulting in the synthesis of C_{6+} complex molecules with an isomeric structure and products of incomplete oxidation of alkanes (alcohols and aldehydes).

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