

A study of a singlet-oxygen generator with a twisted aerosol flow

A.A. Adamenkov, B.A. Vyskubenko, S.P. Il'in, I.M. Krukovskii

Abstract. The results of a study of a singlet-oxygen generator (SOG) with a twisted aerosol flow are presented. The output parameters of the generator obtained in experiments exceed the corresponding characteristics reported earlier in the literature. The maximum chemical efficiency of the reactor amounts to $\sim 70\%$. The flux density of the electron energy stored by the excited oxygen molecules in the reaction zone is above $1.5 \text{ kJ cm}^{-2} \text{ s}^{-1}$. The measured singlet-oxygen yield is $\sim 60\%$ at a pressure of 100 Torr. Adding a buffer gas (N_2) to chlorine ensures an increase in the outlet pressure up to 250 Torr without a decrease in the singlet-oxygen yield. The utilisation of chlorine under such conditions exceeds 95%. The SOG design with a twisted flow ensures atmospheric pressure of the waste solution at the reactor outlet, thus significantly simplifying the development of a system for liquid recycling.

Keywords: singlet oxygen, oxygen–iodine laser, chemical laser.

1. Introduction

Technological applications of oxygen–iodine lasers (OILs) are a subject of active discussions in the recent decade [1–4]. An interest in the development of an industrial OIL is determined by a number of its positive features. The main features are a high power of laser radiation with a good beam quality and the possibility of delivering the intense OIL radiation to remote working areas almost without losses using silica optical fibers. A purely chemical technique used to pump the laser medium makes it possible to create a high-power self-contained industrial laser setup. These and other unique properties guarantee a certain advantage of OILs over other industrial lasers, especially when they are used to disassemble nuclear plants with completed operational terms or to eliminate the consequences of accidents [2–5].

A key element of an OIL is a singlet-oxygen generator (SOG), in which the chemical energy is converted into an energy stored at the electronic levels of oxygen molecules. In

this paper, we analyse a conventional SOG, in which singlet oxygen $\text{O}_2(^1\Delta)$ is produced in a chemical reaction of gaseous chlorine with an alkaline solution of hydrogen peroxide.

At the moment, a jet SOG that was designed and investigated in detail at the Samara Branch of P.N. Lebedev Physics Institute [6–8] is the most efficient generator among those described in the literature. A maximum outlet gas pressure of 100 Torr (for the yield of singlet oxygen of up to 60% and chlorine utilisation of 80%) was achieved in experiments with a jet SOG. The gas velocity in the reaction zone reaches 37 m s^{-1} . In these laser experiments, the gas pressure and velocity at the reactor outlet are noticeably lower than the maximum possible values. This is associated with the emergence of aerosols at the reactor outlet at the output parameters obtained.

Note, however, that an increase in the total pressure in the OIL gas system provides a number of doubtless advantages of this laser [7, 9, 10], which can be implemented, for example, in the ejection method for preparing the OIL active medium [11]. The published data of OIL investigations show that, at present, the main element limiting an increase in the singlet oxygen pressure in the OIL gas system is the SOG. For an efficient operation of the SOG at a pressures of > 100 Torr, the gas velocity in the reactor must be increased in order to reduce relaxation losses of singlet oxygen $\text{O}_2(^1\Delta)$. An increase in the gas pressure and velocity is limited by the escape of the liquid from the reaction zone.

Based on these requirements, a scheme of a SOG with a twisted aerosol flow was developed at the All-Russian Research Institute of Experimental Physics [12]. The studies performed have shown that this design is promising [13–15]. This work generalises the results of investigations of a twisted-flow SOG and presents the results of the latest experiments.

2. Design of a SOG with a twisted aerosol flow

A structural scheme of a twisted-flow SOG is based on the concept of an aerosol SOG proposed in [16], in which aerosol and chlorine flows moving in the same direction in the reaction chamber were used. The aerosol was separated from the produced singlet oxygen downstream of the flow in a special separator in a twisted flow. A specific feature of the twisted-flow SOG is that the flow is twisted from the very beginning already in the reaction zone in order to separate the aerosol from the gas flow as early as possible.

A schematic of the SOG with a twisted aerosol flow is shown in Fig. 1. The reactor is a cylinder 51 mm in diameter and 200 mm high, on whose axis a rotating hollow screw is

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located. The screw has helical blades (the pitch of screw is 100 mm) and 0.3-mm-diameter holes for the liquid. The total number of holes is 4800. The screw is rotated by a motor at a rate of ~ 50 rps. The length of the working zone occupied by jets is 120 mm along the reactor axis, which corresponds to a 190-mm length of the trajectory along the helix. The cross section of the gas flow inside the SOG is 7.8 cm^2 (the cross section of the gas flow perpendicular to the reactor axis is 12.8 cm^2).

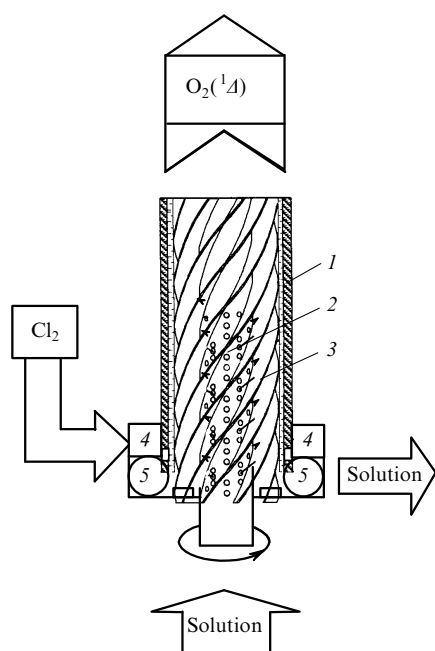


Figure 1. Schematic of the SOG with a twisted aerosol flow: (1) cylindrical housing of the reactor; (2) holes for feeding the liquid to the reactor; (3) eight-blade screw; (4) chlorine collector; and (5) channel for removing the spent liquid.

The working solution is injected into the reactor normally to the cylinder axis through the holes between the screw blades. Chlorine passes along helical channels between the screw blades and interacts with the dispersed solution, producing singlet oxygen. In the field of centrifugal forces, oxygen gets free of droplets of the solution, which are thrown to the cylinder wall and screw blades. During its rotation, the screw scrapes off the solution from the cylindrical surface of the reactor housing and removes it to a special collector, where, using a centrifugal wheel, the pressure of the spent solution is raised up to atmospheric pressure and the exhausted liquid is removed from the SOG volume.

Hence, chlorine interacts with a fresh cooled solution (a typical lifetime of a droplet of the solution in the SOG is ~ 3 ms) over the entire length of the reaction zone. This favours a more complete utilisation of chlorine and helps maintain a low temperature in the reaction zone, which results in a reduced content of water vapours in the gas flow. In this case, an efficient aerosol separation in the reactor is ensured by centrifugal forces (the centrifugal acceleration reaches a value of several thousands g), and the efficient utilisation of chlorine at an arbitrary gas velocity is provided by selecting a necessary length of the reaction zone.

3. Measurement scheme

The parameters of the output flow of the twisted-flow SOG were measured in a measurement section located immediately behind the chemical reactor. The measurement scheme is shown in Fig. 2. In order to simulate the operating conditions of the SOG as a component of an OIL, a nozzle, in which a supersonic pressure difference was maintained, was positioned at the end of the measurement section. After the passage through this section, the gas was discharged into a vacuum vessel with a 5-m^3 volume. Varying the gas pressure and the size of the flow-rate orifice in the chlorine pipeline and also the cross section of the supersonic nozzle provided the control of the gas pressure and velocity in the reactor.

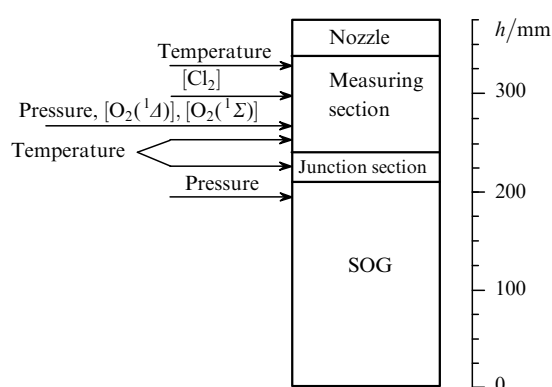


Figure 2. Scheme of measurements of the parameters of the SOG output flow.

The concentration of chlorine that had not reacted in the SOG was determined from the data of radiation absorption measurements at $\lambda = 0.334 \mu\text{m}$. The emission with the required wavelength was selected from the emission spectrum of a mercury lamp by an MDR-4 monochromator. The accuracy of the residual-chlorine concentration measurements depends on the chlorine concentration in the gas flow. The relative error of such measurements was 10%–20% at residual chlorine pressures of 1–3 Torr and within 10% at pressures above 3 Torr. The sensitivity of this technique was 0.3 Torr.

The concentration of singlet oxygen $[\text{O}_2(^1\Delta)]$ was determined from the intensity of spontaneous emission at $1.27 \mu\text{m}$, which was measured with an FD-10G germanium photodiode. The photodiode was calibrated using the method described in Ref. [17]. The error of this calibration method was determined mainly by the error of temperature measurements in the flow and was evaluated by us at $\sim 25\%$. The singlet oxygen yield $Y = [\text{O}_2(^1\Delta)]/[\text{O}_2]$, where $[\text{O}_2]$ is the total concentration of oxygen molecules, was calculated from the measured concentration $[\text{O}_2(^1\Delta)]$.

The concentration of water vapours was estimated from measurements of the spontaneous emission intensity at the $\text{O}_2(^1\Sigma) - \text{O}_2(^3\Sigma)$ transition at $0.762 \mu\text{m}$. Because in flows of singlet oxygen containing water vapours, the $[\text{O}_2(^1\Delta)]$ value is proportional to $[\text{O}_2(^1\Delta)]^2/[\text{H}_2\text{O}]$, the ratio of the squared emission intensity at $1.27 \mu\text{m}$ to the emission intensity at $0.762 \mu\text{m}$ is proportional to the concentration of water vapours [6]. Comparing the water content in the gas flow

determined by this method to the water content in a sample, which was determined by freezing out the water in a sampler, has shown their satisfactory agreement. Measurements have shown that the partial water pressure in the flow corresponds to the vapour pressure at the solution temperature (1.1–1.3 Torr at $-15... -17^\circ\text{C}$).

The temperature of the gas flow was measured by thermocouple sensors at the points indicated in Fig. 2, and the gas pressure was measured by IKD-27 inductive transducers located in the bottom part of the reactor, at the outlet of the twisted-flow SOG, and in the measurement sections.

4. Experimental results and discussion

At the initial stage, we carried out a cycle of experimental studies of the efficiency of a twisted-flow SOG for various input parameters of the gas and solution and varied the dimensions and screw rotation rates in order to determine their optimal values. A summary of the main results is as follows.

The screw rotation rate. A change in the screw rotation rate causes a change in the efficiency of liquid removal from the reactor working zone and may affect the pressure difference between the SOG input and output.

The experiments have shown that, for each liquid flow rate, there exists a threshold rotation rate below which the screw cannot cope with the liquid removal. The necessary screw rotation rate was within 60 rps at matched cross sections of removing channels for all liquid flow rates up to 2 L s^{-1} . When the screw rotation rate reaches a value sufficient for removing the liquid from the SOG active zone, its further increase weakly affects the aerosol separation in the SOG. This is clear in view of the fact that, when the gas flow moves along the helical channel of the screw, its rotation rate changes between 350 and 1000 rps depending on the gas velocity. The screw proper rotation rate within the range of 10–150 rps studied has a slight effect on the pressure difference between the SOG input and output. The experimental results presented below were obtained at a screw rotation rate of 50 ± 5 rps.

Reaction zone length. The reaction zone length of the SOG reactor has an effect primarily on the degree U of chlorine utilisation. As this length increases, the concentration of residual chlorine decreases. At first sight, this must result in an increased singlet oxygen flow from the SOG. However, an increase in the length of the SOG reaction zone leads to a longer time of the presence of singlet oxygen in the reactor volume, which causes additional relaxation losses and a decrease in the singlet oxygen yield. Therefore, an optimal length of the reactor active zone depends on the required degree of the chlorine utilisation and on the gas velocity in the reactor. This is illustrated by the plots in Fig. 3.

Solution flow rate. The problem of determining an optimal combination of the active zone length and the liquid flow rate was solved experimentally. The dependence of the SOG output parameters on the flow rate of the working liquid was studied for various lengths of the reaction zone and gas velocities. The experimental results have shown a slight increase in the singlet oxygen yield Y and a significant rise of the degree of chlorine utilisation U , as the flow rate of the working liquid increased from 250 to 1000 mL s^{-1} . These data made it possible to determine a flow rate of the

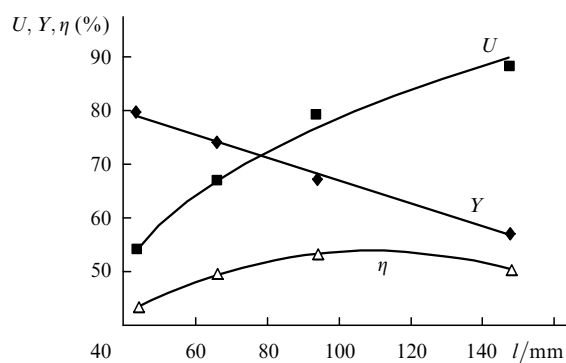


Figure 3. Output characteristics of the SOG (degree of chlorine utilisation U , SO yield Y , and SOG efficiency $\eta = YU$) versus the length l of the interaction zone (the chlorine flow rate is 60 mmol s^{-1} , the output pressure is $p_{\text{out}} = 35\text{ Torr}$, the flow velocity is 1.8 m s^{-1} , the gas velocity is 50 m s^{-1} , and $[\text{KOH}] = 2\text{ mol L}^{-1}$).

solution per unit screw length, which was close to the optimal value for the given geometry: $100\text{ mL s}^{-1}\text{ cm}^{-1}$.

Composition of the working solution. The SOG prototype was optimised using rather diluted working solutions which are cheaper and simpler in use. As a rule, a solution with a concentration of the alkali $[\text{KOH}] = 2\text{ mol L}^{-1}$ was used. At the final stage, in order to obtain the best output parameters of the SOG, the investigations were performed using a solution with $[\text{KOH}] = 5\text{ mol L}^{-1}$. The result of such changes in the KOH concentration is clearly displayed in Fig. 4. Note that the difference between the solutions is more significant at a gas pressure of $\sim 40\text{ Torr}$ and higher. This is probably explained by the fact that, at elevated pressures in the reactor, the surface liquid layer, in which singlet oxygen molecules are produced, is depleted more rapidly.

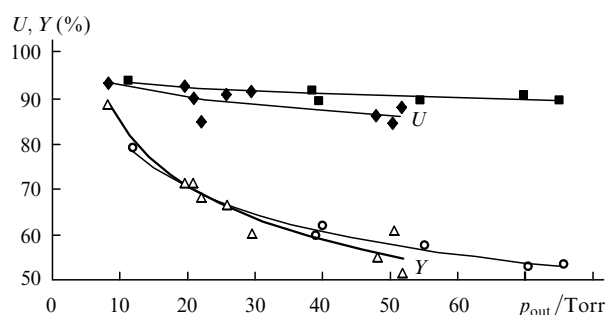


Figure 4. Degree of chlorine utilisation U and singlet-oxygen yield Y as functions of pressure p_{out} at $[\text{KOH}] = 2$ (filled diamonds, open triangles) and 5 mol L^{-1} (filled squares, open circles).

The reactor geometry. The pitch of the screw helix may have an effect on the efficiency of the aerosol separation inside the SOG, on the pressure difference between its input and output, and on the rate of the liquid removal from the reactor working zone. Comparing two screws with equal lengths and different pitches of the screw helix (14 and 10 cm) revealed no significant differences in the pressure difference in the SOG or in the rate of the solution removal from the working zone. However, a reduction of the pitch from 14 to 10 cm has led to an appreciable rise of the aerosol separation efficiency inside the SOG. A further

decrease in the screw pitch (the number of blades remains constant) leads to a significant decrease in the cross section for the gas passage, which appreciably increases the pressure difference in the SOG (especially at a high gas velocity). It follows from estimates of the reactor geometry that the screw with a 10-cm pitch is close to an optimal one for the selected transverse size of the reactor. Therefore, further experiments were carried out with this pitch of the screw helix.

A special series of experiments was devoted to determining the boundary parameters for the region of stable SOG operation, when the output flow is free of aerosols. These experiments were performed with the gas mixture composition $N_2 : Cl_2 = 2 : 1$ passing through the SOG. The presence of the aerosol in the gas flow emerging from the reactor was monitored visually (one wall of the measurement section was transparent) and by readings of thermocouples located in the gas flow (the temperature significantly fell upon appearance of the aerosol). When a working solution ($[KOH] = 5 \text{ mol L}^{-1}$) was pumped at a flow rate of 1.2 L s^{-1} , the following maximum total gas flow rates in the SOG, at which the aerosol was absent at the SOG output, were obtained: 660 mmol s^{-1} at $V_{out} = 60 \text{ m s}^{-1}$ ($p_{out} = 250 \text{ Torr}$) and 450 mmol s^{-1} at $V_{out} = 110 \text{ m s}^{-1}$ ($p_{out} = 120 \text{ Torr}$) (V_{out} and p_{out} are, respectively, the gas velocity and pressure at the SOG output).

Fig. 5 presents the main parameters of the SOG (U , Y , and SOG efficiency η) as functions of pressure at the reactor output in experiments without chlorine dilution by a buffer gas. Along with the experimentally measured chlorine utilization and SO yield, Fig. 5 also shows estimates Y_{calc} calculated from the relation [18]

$$Y_{calc} = (1/Y_0 + k_d[O_2]\tau)^{-1}, \quad (1)$$

where k_d is the pooling reaction; τ is the transport time of $O_2(^1\Delta)$ molecules; and Y_0 is the initial singlet oxygen yield.

The values of θ and $[O_2]$ were calculated from the experimentally measured parameters, k_d was assumed constant and equal to $3 \times 10^{-23} \text{ m}^3 \text{ s}^{-1}$, and Y_0 was selected from the best fit between the calculated and experimental Y values. It follows from (1) that, as the gas velocity increases, the dependence of Y on the gas pressure becomes weaker (the same effect was observed experimentally). The maximum chlorine flow rate in these experiments was 200 mmol s^{-1} . A further increase in the chlorine flow rate was useless, because the flow temperature in the measurement section rose above 700 K , which hindered the singlet oxygen concentration measurement because of the thermocouple burning.

The experimental dependences shown in Fig. 6 were measured with chlorine diluted by nitrogen. Adding N_2 to Cl_2 allows for a decrease in the temperature of the output flow to room temperature. This is important for obtaining an efficient generation of an OIL at elevated pressures. Note that a certain improvement of the SOG output parameters was observed at such a dilution (Fig. 7). This is explained by both a decrease in the singlet oxygen quenching with falling temperature and an increase in the velocity of the gas flow diluted by the buffer gas. The output gas velocity as a function of degree of chlorine dilution by nitrogen is shown in Fig. 8. This experimental dependence shows that the gas velocity in the reactor rises from 70 to 100 m s^{-1} , when nitrogen is added to chlorine in a ratio of $2 : 1$. This is associated with a decreased temperature in front of the nozzle.

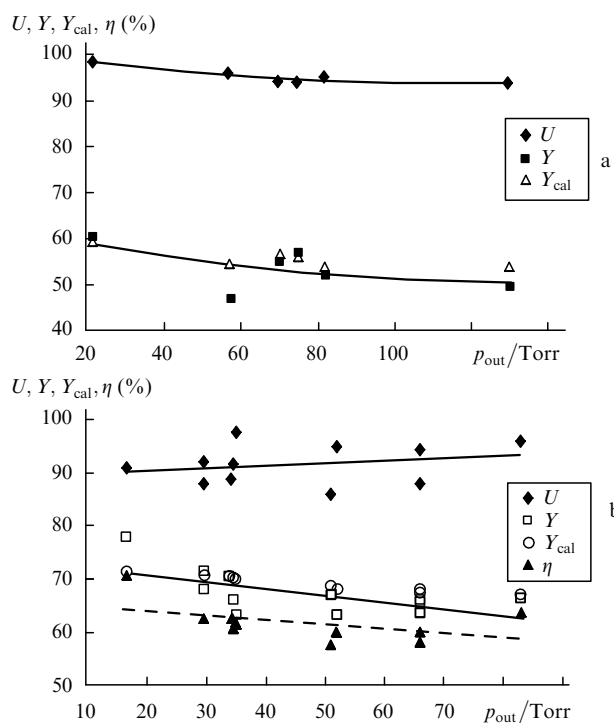


Figure 5. Basic SOG characteristics (U , Y , Y_{calc} , η) as functions of the gas pressure p_{out} at the reactor output obtained without chlorine dilution by the buffer gas at a gas velocity in the reactor $V_{out} = 60$ (a) and 100 m s^{-1} (b) and $Y_0 = 63$ (a) and 75% (b).

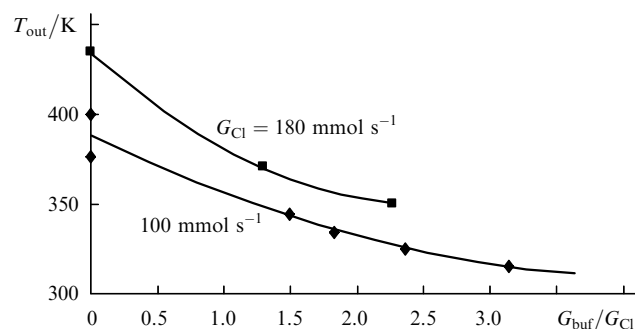


Figure 6. Gas temperature T_{out} at the SOG outlet as a function of the degree of chlorine dilution by the buffer gas G_{buf}/G_{Cl} ; G_{buf} and G_{Cl} are the flow rates of the buffer gas and chlorine.

Chlorine diluting with nitrogen at the SOG input leads to a significant improvement of the output parameters and an appreciable increase in the total gas pressure at the input to the OIL nozzle. Figure 9 presents the dependences of the SOG output characteristics on the gas pressure at the reactor output for a mixture composition $Cl_2 : N_2 = 1 : 2$. We see that the use of a SOG helps reach an output pressure of up to 250 Torr at a 95% degree of chlorine utilisation and the singlet oxygen yield of $\sim 60\%$.

As is known, in order to include the SOG into a closed loop of a recycling liquid system, a pump is necessary, which pumps the partially utilised solution to a technological

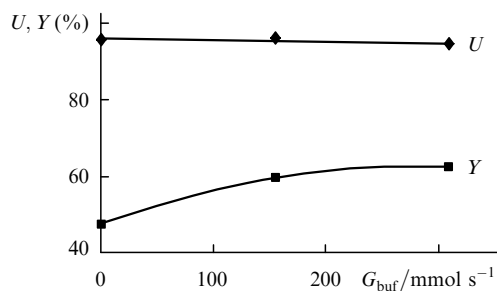


Figure 7. Degree of chlorine utilisation U and the SO yield Y as functions of the buffer-gas flow rate G_{buf} .

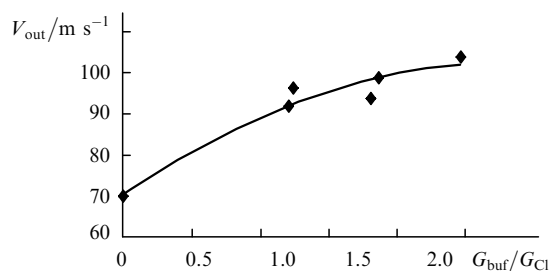


Figure 8. Gas velocity at the SOG output versus the degree of chlorine dilution by the buffer gas.

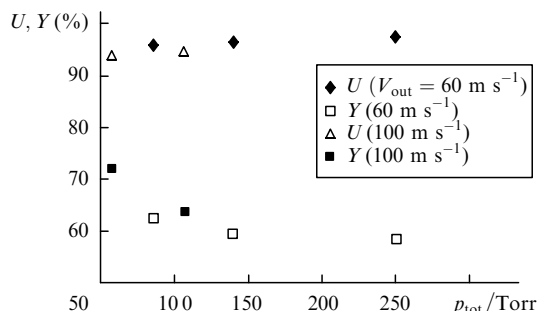


Figure 9. Degree of chlorine utilisation U and the SO yield Y as functions of the total pressure p_{tot} for chlorine dilution by nitrogen in a proportion of 1 : 2 and various gas velocities V_{out} .

vessel for cooling and regenerating the consumed reagents, which results in larger dimensions of the setup. This problem was solved by equipping the outlet collector of the SOG liquid by a centrifugal wheel. Tests have shown that such an improvement of the model ensures a pressure of the solution at the SOG output at a level above atmospheric pressure. This SOG model was tested in the regime of a closed loop without an additional pump for liquid circulation in runs when the working solution was displaced by atmospheric pressure. The duration of the experimental runs was 0.5 min (it was limited by the volume of the vacuum system and the heating of the working medium). The SOG output characteristics do not degrade in this case.

5. Conclusions

The use of a twisted-flow SOG scheme ensures a stable operation of this generator without a removal of the aerosol within wide gas pressure and velocity ranges at the output

of the reaction zone. In this case, the achieved output characteristics are as follows: the chemical efficiency of the reactor is $\sim 70\%$; the singlet oxygen yield is above 60% at a gas pressure at the reactor outlet of ~ 100 Torr and a gas velocity of 100 m s^{-1} ; the degree of chlorine utilisation in the reactor is $> 95\%$; the flux density of the electron energy stored by the excited oxygen molecules in the reaction zone is $> 1.5 \text{ kJ cm}^{-2} \text{ s}^{-1}$; the pressure at the reactor output is up to 250 Torr (when chlorine is diluted by a buffer gas (chlorine) at the reactor input).

The reactor can be connected to the nozzle directly without flow throttling between the SOG and nozzle. The SOG design makes it possible to obtain a pressure of the utilised solution at the reactor output exceeding atmospheric pressure, which significantly facilitates the arrangement of the solution recycling.

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