Ozone generation in the Practical exercises of applied plasma chemistry course

František Krčma, Zdenka Stará
Institute of Physical and Applied Chemistry, Faculty of Chemistry, Brno University of Technology, Purkyňova 118, Brno, CZ-612 00, Czech Republic

Introduction

Plasma chemistry is a relatively new scientific discipline that became a part of university study programs relatively recently. This discipline can be studied from two rather different points of view. The plasma chemistry courses for physicists are naturally focused on the basic phenomena in plasmas, the courses for chemists focus more on the use of plasma as an instrument. In both of these conceptions, the plasma chemical technologies plays only a minor role, although a huge increase of plasma chemical technologies has been observed during the last years. Usually, the practical exercises complement the lectures. The practical exercises at universities are normally focused on the basic processes and basic phenomena (studies of DC glow discharge etc.) and on some plasma diagnostic methods. At technical universities, the practical exercises are usually in the form of plasma technology demonstrations without active participation of students.
The study programs at our university contain a course in applied low temperature plasma chemistry where students can obtain the basic information about the theoretical description of plasmas and later on about some plasma chemical technologies. This conception raises a serious problem how to present modern plasma chemical technologies to our students because there is only a small chance to see the technologies in specialized laboratories or in industry except during excursions. Due to this fact we prepared a special practical course focused on the applications of low temperature plasma processes.
The exercises include various technologies, such as surface treatment, thin layer deposition or decomposition of molecules and also some basic tasks, such as calibration of the measuring devices and characterization of final products. Plasma diagnostics and fundaments of vacuum physics that are not included in any other course at our university are included in our course as well. The diagnostic methods use the apparatus available in our laboratories, so the students can obtain also information about other devices. Finally, most of the experimental plasma devices used in the practical course can be used also during the work on the students' master and doctoral thesis. This allows in return the continual enlargement and improvement of the exercises.
The interesting point of experimental plasma devices used in our course is that these apparatuses are mostly very cheap and also safe to be used by students having more or less no experience with high voltage devices. The study of ozone generation is one of the most complex exercises and thus it is a subject of this contribution. The survey of the other exercises is given below at the end of contribution.

Exercise: Study of ozone generation

The ozone generation in the low temperature plasma is one of the oldest plasma chemical processes. The experimental set up shown schematically in Fig. 1 uses the silent discharge reactor that is very similar to the original Siemens one. The gas flow through the ozonizer is adjusted by non calibrated flow meter (with the range of 1 Slm), so the first step of the task is its calibration from the known time for filling the given volume at different rotameter marker positions. Both oxygen and ambient air can be used for the ozone generation study.
The own ozonizer uses the coaxial configuration with metallic inner cylinder of 27 mm in diameter, the outer graphite electrode is as a surface layer on a Pyrex glass tube (the inner diameter of 30 mm). The total length of the ozonizer is 40 cm with the active part of 30 cm. The power supply constructed in our laboratory uses the car-starting coil giving the voltage amplitude of 10 kV at the frequency of 50 Hz. The input power supply current can be continuously varied between 16 and 34 mA. Due to the use of high voltage, the ozonizer itself is installed in the centre of a Perspex box (10 x 10 x 50 cm). The power regulation is at the low voltage part and therefore it can be placed outside this box.

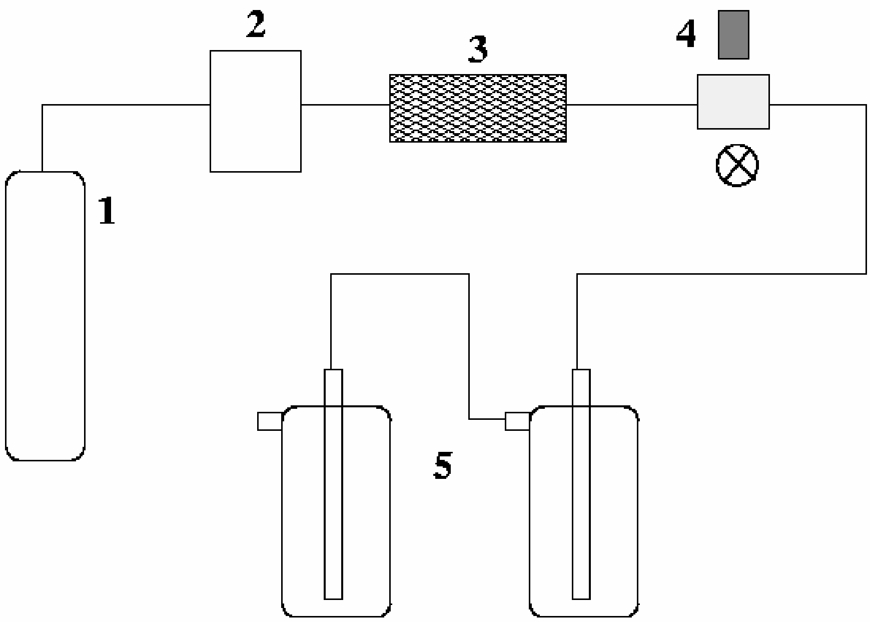

Figure 1: Simplified scheme of the experimental set up. 1 – oxygen bottle or high pressure ambient air source; 2 – rotameter; 3 – ozonizer; 4 – UV absorption measuring unit; 5 – KI double bubbler.

The determination of the amount of the generated ozone can be done by two different methods – by UV light absorption and by iodometric titration. The ozone absorption has a wide band in the range of 200 – 300 nm with the maximum at about 250 nm [1]. Due to this fact, the best source of UV light is a low-pressure mercury lamp. The standard side window photomultiplier with an appropriate home made non adjustable high voltage power supply is used as a light detector. The interference filter passable at the mercury line of 253 nm is placed just before the input window of photomultiplier. The signal form photomultiplier is measured by multimeter Metex connected to the PC with rate of 1 sample per second. The UV light absorption is done in the quartz cell with length of 10 cm. Because no imaging is necessary in our case, the cell was made by our glass blower and we don't use silica windows.
Of course, the ozone detection unit is not calibrated so another method which is absolute must be used for the calibration. The best one is iodometric titration that is based on the following reaction:

$$2\,KI + O_3 + H_2O \rightarrow I_2 + 2\,KOH + O_2.$$

We use the 0.2 M KI solution. The 2 M solution of HCl is added in the amount of 10 ml/100 ml of KI solution. Titration is done by a 0.05 M $Na_2S_2O_3$ solution. 1 ml of 0.05 M $Na_2S_2O_3$ solution is equal to 1.2 mg of ozone [2].
In our case, the generated ozone bubbles in the KI trap for 5 minutes if the generation is done from oxygen or for 10 minutes if the generation is done from air because in this case not only ozone is generated. Due to this fact it is also necessary to calibrate the UV detection line separately in both cases. We use 100 ml of KI solution. The second trap is added mostly for security, only about 1% of generated ozone is destroyed in it. After ozone generation the standard titration is completed and the amount of the generated ozone can be established. As the UV light absorption is more or less linearly dependent on the ozone concentration, usually four points are sufficient for the calibration of UV light detection unit.
The ozone generation in the dependence on the discharge current, gas kind and its flow rate are measured by the UV absorption after completing all the calibrations. An example obtained from the students' laboratory record is given in Fig. 2.

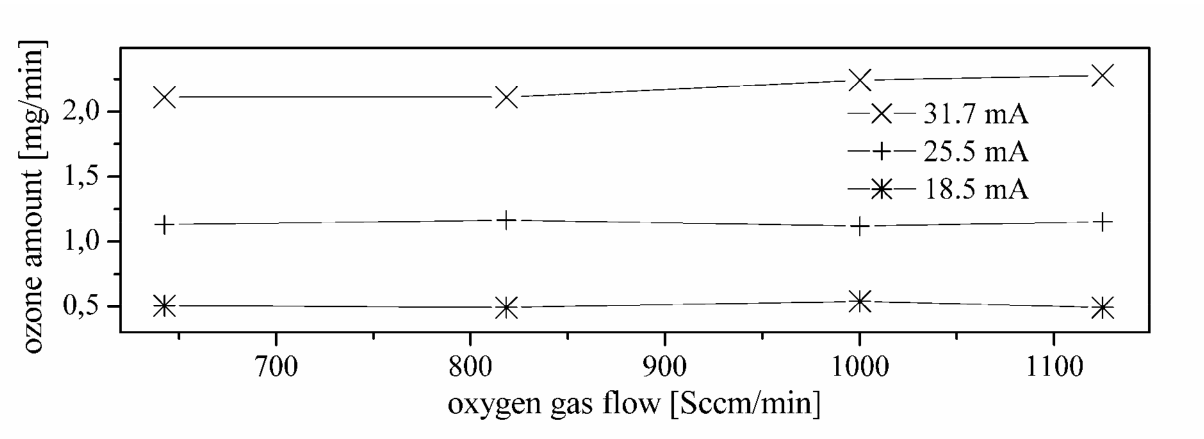

Figure 2: The ozone generation as a function of gas flow rate for three power supply currents.

Other practical exercises taking place at present

Besides the ozone generation another plasma chemical processes and technologies are included in our course. As they are not connected directly to ozone generation, they are only listed here with very short descriptions.

- *Calibration of pressure gauges*
  Calibration of Pirani gauge at two different operating temperatures; calibrations of an ionizing gauge in two different gases.

- *Optical emission spectroscopy*
  Identification of radiative particles – atoms and molecules; calculation of the rotational temperature; estimation of vibrational distribution or, if possible, the calculation of vibrational temperature. This work is done using two different DC discharge lamps. Study of the high voltage and influence of the slit width on the signal intensity and on the spectra resolution.

- *Changes of polymer materials wettability by surface discharge*
  Treatment of a thin polymeric foil (polypropylene, polyethylene, polystyrene) using the surface barrier discharge (UPS 100). The water wettability and surface energy changes are studied using the simple device for contact angle measurement and surface energy calculation (SEE System [3]) as a function of discharge conditions, mainly on the total discharge energy. Besides the direct surface activation by electrons, various radicals and UV radiation, the ozone generated by the discharge in air partially contributes to the surface processes. The influence of the surface ozonization should be added in the future.

- *Water permeability enhancement of non-woven textile materials*
  The non-woven polypropylene textile used for the agricultural purposes is treated using the same experimental device as above. The water permeability is measured by the permemeter constructed at Faculty of Science of Masaryk University. The permeability is studied as above as a function of discharge conditions.

- *Hydrogen peroxide generation by diaphragm discharge in liquids*
  Diaphragm discharge is generated using DC non-pulsed high voltage in water solution of selected electrolyte. Hydrogen peroxide formed by the discharge in water can be easily determined by colorimetric method (specific reaction with titanium reagent gives yellow complex which absorption intensity is directly proportional to H_2O_2 concentration). Students observe production of H_2O_2 in time and determine rate constant of H_2O_2 creation at particular discharge conditions.

- *Organic dyes degradation by diaphragm discharge in liquids*
  This task uses the same device as in the previous case. Moreover, selected organic dye is dissolved in the electrolyte solution and it is treated by the diaphragm discharge. Decrease of the dye concentration is determined by absorption spectroscopy. The dye decoloration is also well observed by the only eye.

- *VOC destruction in atmospheric pressure plasma*
  The simply single stage gliding arc reactor is used for the destruction of toluene as a typical example of volatile organic compounds (VOC). As the full analysis of the discharge products is very complicated and time consuming procedure the detector of simple low weight molecular

products is applied. The toluene destruction is measured as a function of discharge power, carrier gas composition and total gas flow through the reactor.

- *EPR spectroscopy of decaying plasma*
  The generation of nitrogen and oxygen atomic particles in the low pressure microwave discharge in pure nitrogen and oxygen is measured absolutely by in plasma science unique method of electron spin resonance spectroscopy. The absolute concentrations of atomic ground state species are determined in dependence on the discharge conditions as well as on the time during the post-discharge.

Conclusions

We have prepared a special practical course focused on applied low temperature plasma physical and chemical processes. The exercises include various technologies, such as surface treatment, thin layer deposition, decomposition of molecules; the exercises are connected with some basic tasks, such as the calibration of measuring devices and the characterization of final products. One of the most educative and complex exercises is focused on the study of ozone generation where students must complete calibration of flowmeter and UV absorption line that is used for the ozone detection. The plasmatic part of the exercises is mostly very cheap and thus the device can be simply installed anywhere.
We think the knowledge of the university graduates is not sufficient in the field of practical plasma chemistry. The international interaction and a new practical course can significantly increase the quality and adaptability of graduates in technological practice. Thus the acceleration and the progress in plasma chemical technology applications can be reached in the near future.

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