Inhomogeneous feed gas processing in industrial ozone generation
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ABSTRACT
The synthesis of ozone by means of dielectric barrier discharge (DBD) is extensively used in industry. Ozone generators available on the market differ in ozone production capacities, electrode arrangements and working parameters, but operate with a uniformly distributed filamentary discharge plasma pattern.

In the presented work the benefits of inhomogeneous feed gas processing are explored. Causality between power induction, production efficiency and working parameters are investigated. Different electrode arrangements, evenly distributed within a given space parameter, were designed, simulated, manufactured and tested on a representative scale. A finite element model was utilized to simulate an inhomogeneous power induction pattern along the ozone generator tube. The simulation yielded the local power density, the local gas temperature gradient and the relative DBD packing density.

Results show that the degree of filamentation turns out to be decisive, indicating a new potential by means of plasma tailoring. An arrangement with a pronounced power induction at the inlet of the ozone generator revealed several advantages over homogeneous plasma processing arrangements, for which an increase in robustness and a reduction in electrical power consumption are achieved.

Key words | DBD plasma, discharge filament, generation efficiency, ozone, power induction

INTRODUCTION
The nature of available ozone generator technology has recently been reviewed by Kogelschatz (2005). The so-called dielectric barrier discharge is used in almost all possible regimes of gaseous breakdown to enrich ozone within an oxygen-containing feed gas. The typical operation with adjacent plates or concentric cylinders relies on Townsend-like streamer discharges, which might be used in a continuous mode to produce a pronounced filamentary discharge pattern or, in a pulsed mode, to produce a homogenous discharge pattern.

Generators differ in diameter, length and arrangement of the tubular electrodes, type and support of the dielectric material and in the character of the applied micro-discharges. Nevertheless, for all available generators the discharge gap and the dielectric layer are designed to achieve a uniformly distributed filamentary DBD plasma pattern along the ozone generator tube and, therefore, homogeneous feed gas processing.

Since ozone generators work in different ranges of ozone concentrations, production levels, and cooling conditions, wide spread efficiency values were found. Lang et al. (2005) reported the optimum electrode arrangement for such operating conditions, which was obtained from a large number of measurement campaigns.

In this work the causality between electrode arrangement, ozone generator properties and efficiency of feed gas

1 In this work the efficiency or the power efficiency is defined as the ratio between the difference of the binding energy of O₂ and O₃, equal to 0.82 [kWh/kg] and the specific energy consumption Eₛ [kWh/kg] of applied power.
processing in DBD ozone generators is investigated for the case of inhomogeneous feed gas processing. Therefore, the following three different power induction patterns were investigated and compared with a homogeneously distributed power reference arrangement designed in accordance with the parameters found by Lang et al. (2005): power linearly increasing from the inlet to the outlet, power linearly decreasing from the inlet to the outlet and power inhomogeneously distributed.

For the sake of completeness, other approaches for the investigation of causality have to be mentioned. Eliasson et al. (1986) and Pitchford & Sciamma (2005) followed a bottom-up strategy and implemented a computational model, which was used to simulate the transients in the ozone synthesis of a single discharge and the build-up of higher ozone concentrations through the DBD plasma processing. Due to the nature of the bottom-up approach, such models would reproduce phenomena as far as included in the code and ignore unknown higher-order effects. The strength lies in the ability to explain phenomena, while it may be of limited help for process optimization purposes.

CALIBRATION OF FREE PARAMETERS AND SELECTION OF ELECTRODE ARRANGEMENTS

For a concentric cylindrical DBD electrode arrangement the electrical power induced into “n” slices can be calculated by the extended Manley formula (Manley 1943; Kogelschatz & Müller 1982):  

\[ P = \alpha \cdot 4 \cdot \sum_{i=1}^{n} C_{D,i} \cdot \frac{1}{1 + \beta_i} U_{\min,i}(U_{\text{peak}} - U_{\text{min,i}}) \text{[kW]} \]  

(1)

where “i” is the slice index, “n” the number of slices per cylinder, “U_{\text{peak}}” the peak voltage [V], “U_{\text{min,i}}” the minimum voltage for the “i”th slice [V], “f” the frequency [Hz], “C_{D,i}” and “C_{g,i}” the capacitance of the dielectric and the feed gas for the “i”th slice [F], “α” the adjustable parameter and “β_i” = C_{g,i}/C_{D,i}.

The α parameter was introduced by Kogelschatz & Müller (1982) to account for partial activation of the available discharge area at the lowest electrical loads, especially with the presence of mechanical tolerances in an experimental electrode arrangement. In a more general approach, the α parameter can be considered as the adjustable parameter, to match the measurement data. This can be justified by a comparison of two different electrode arrangements (with n = 1), which are operating at an identical power density, outlet ozone concentration, average cooling water temperature, cooling water temperature gradient, average gas pressure and identical discharge gap arrangements, but with different thickness of dielectric layers. Since the degree of filamentation increases with increasing thickness of the dielectric layer (Hirth et al. 1983), then the α parameter also increases after the adjustment of the C_{D}, β, U_{\text{peak}} and U_{\text{min}} quantities in Equation (1).²

The information about the measured power must be retrieved from measured data through a regression model (Montgomery 2001), expressed as a function of typical conditions in the plasma (ozone concentration, power density, average pressure, average cooling water temperature and frequency). For this work, power efficiency, rms-voltage, rms-current, power factor and pressure loss were determined for each electrode arrangement with non-linear regression models.

To focus the investigation on the most promising electrode arrangement geometry a so-called Takagi-Sugeno Fuzzy regression model (Babuska 1998) was used (Vezzù 2005). The regression analysis indicated a cone-shaped discharge gap, between 0.3 mm and 0.4 mm from inlet to outlet, as the most promising arrangement. This result is in agreement with the work presented by Lang et al. (2005), for which a discharge gap of around 0.3 mm was used at 12 weight percent in ozone concentration.

EXPERIMENTAL

According to the results of calibration of the free parameters of electrodes, seven different arrangements were selected, manufactured and tested. The electrode arrangements used, including information about the size of the discharging gap and the capacitance of the dielectric, are shown in Table 1.

² N.B.: This effect exceeds deviations in efficiency. Hence, the interpretation of α as packing density of the spatial distribution of filamentary micro-discharges is consistent with its original interpretation.
Each position, from 1 to 4, represents a tubular ceramic-coated electrode of approx. 0.5 m length and 0.056 m diameter, which is inserted into a stainless steel tube. For each arrangement the four electrodes were connected in series, and acting therefore as one system.

The Reference arrangement consists of four identical electrodes, for which a homogeneous power induction pattern is assumed. For marketing purposes the reference arrangement is known as AT98. It is a classical representation of a homogeneous feed gas processing ozone generator, which is used for oxygen-fed plants and high ozone concentrations. Arrangements B to G are designed to yield an inhomogeneous power induction pattern.

The experimental setup utilized for measurements complies with the ISO 9000 and Degrémont Technologies’ Quality Assurance system (Vezzu et al. 2007). For the different experimental arrangements the following parameters were measured: ozone concentration, mass flow of oxygen and nitrogen feed gas, and water and gas temperature at the inlet and outlet of the generator. The outlet current, voltage and the frequency from the power supply unit, as well as the ratio between $U_{\text{peak}}/U_{\text{min}}$ were also acquired.

### FINITE-ELEMENT MODEL

The spatial resolution of locally induced power is achieved by a finite element approach. The finite element simulation is calibrated with real measurement data, which is a prerequisite to project the intrinsic properties of the investigated plasma physics into estimated model parameters.

### Table 1

| The electrode design parameters ($c$, $p$, $U_{\text{peak}}$), data of electrode arrangements (gap_1..4, $C_{D_1..4}$), fractions of locally applied power $f_{q_1..4}$ and the average filament packing density $\alpha$ are summarized. Indices: 1 indicates the inlet and 4 the outlet position. |
|---|---|---|---|---|---|---|
| $c$ [wt%] | 12 | 12 | 12 | 12 | 12 | 12 |
| $p$ [bar a] | 2.2 | 2.2 | 2.2 | 2.2 | 2.2 | 2.2 |
| $U_{\text{peak}}$ [V] | 4981 | 5479 | 5479 | 5229 | 5130 | 5140 |
| $\alpha$ | 0.97 | 0.84 | 0.94 | 0.92 | 1.14 | 1.25 |
| gap_1 [mm] | 0.052 | 0.038 | 0.038 | 0.038 | 0.035 | 0.035 |
| gap_2 [mm] | 0.032 | 0.036 | 0.036 | 0.036 | 0.035 | 0.035 |
| gap_3 [mm] | 0.032 | 0.034 | 0.034 | 0.034 | 0.032 | 0.032 |
| gap_4 [mm] | 0.032 | 0.032 | 0.032 | 0.032 | 0.032 | 0.032 |
| $C_{D_1}$ [nF] | 11.41 | 15 | 9 | 10.63 | 10.63 | 10.63 |
| $C_{D_2}$ [nF] | 11.41 | 11.3 | 9.6 | 10.21 | 9.31 | 8.41 |
| $C_{D_3}$ [nF] | 11.41 | 9.2 | 10.2 | 9.82 | 8.41 | 7.8 |
| $C_{D_4}$ [nF] | 11.41 | 7.8 | 10.9 | 9.46 | 7.8 | 7.8 |
| $b_1$ | 0.219 | 0.140 | 0.233 | 0.198 | 0.215 | 0.215 |
| $b_2$ | 0.219 | 0.196 | 0.231 | 0.217 | 0.245 | 0.297 |
| $b_3$ | 0.219 | 0.255 | 0.230 | 0.239 | 0.297 | 0.320 |
| $b_4$ | 0.219 | 0.320 | 0.229 | 0.264 | 0.320 | 0.320 |
| $q_{1}$ [kW/m$^2$] | 3.54 | 5.18 | 3.26 | 3.88 | 4.31 | 4.56 |
| $q_{2}$ [kW/m$^2$] | 3.51 | 3.69 | 3.43 | 3.62 | 3.68 | 3.35 |
| $q_{3}$ [kW/m$^2$] | 3.48 | 2.84 | 3.57 | 3.36 | 3.15 | 3.05 |
| $q_{4}$ [kW/m$^2$] | 3.47 | 2.29 | 3.75 | 3.13 | 2.87 | 3.04 |
| $f_{q_1}$ [%] | 25.3% | 37.0% | 23.3% | 27.7% | 30.8% | 32.5% |
| $f_{q_2}$ [%] | 25.1% | 26.4% | 24.5% | 25.8% | 26.3% | 23.9% |
| $f_{q_3}$ [%] | 24.9% | 20.3% | 25.5% | 24.0% | 22.5% | 21.8% |
| $f_{q_4}$ [%] | 24.8% | 16.3% | 26.7% | 22.4% | 20.5% | 21.7% |
The electrode arrangement is sliced into “n” pieces, as in Equation (1), or “n” equal volumes respectively, which need to account for the local discharge gap size, local dielectric capacitance and the local $U_{\text{min}}$. The following assumptions to estimate the local $U_{\text{min}}$ were made.

Throughout experiments the local breakdown voltage increase can be estimated as 100 V per weight percent of ozone. Since the ozone build-up profile can be enveloped by a linear and an exponential curve, a third order regression is selected to fit two thirds of the outlet ozone concentration at one third of total applied power. The local $U_{\text{min}}$ is set to 60 percent of the local breakdown voltage, also if corresponding measurements (charge vs. voltage Lissajous plot) indicate even smaller values. For the local gas pressure a linear decrease from inlet to outlet was assumed. The total gas temperature increase between inlet and outlet of 5°C was split into the fraction of locally dissipated power. Several iterations are required to adjust $\alpha$ in Equation (1), in order to equalize the simulated induced power to the measured power.

This approach provides information including: distribution of locally induced power, profile of gas temperature increase and the determination of the average filament packing density of the electrode arrangement, which is going to be paired with the qualitative and quantitative properties of corresponding measurement results.

**RESULTS AND DISCUSSION**

In Table 1 information about the investigated electrode arrangements, such as the gap width (gap_{1..4}) and the electrode capacitance ($C_{D_{1..4}}$), with the experimental values and the data from the simulation are summarized. The estimate of the achievable resolution of locally induced power is a value around 1 percent on the absolute scale.

A comparison of the various arrangements revealed the following:

$U_{\text{peak}}$ varies with the size of the average discharge gap, obtained from the regression data models.

The average packing density $\alpha$ varies with the electrode arrangement. Values larger than 1 indicate an increased packing density compared to the reference arrangement used for the calibration of the model. The absolute value is influenced by $U_{\text{min}}$, which was kept at a constant 60 percent of the local breakdown voltage. The arrangement F has the highest $\alpha$ value and the lowest average capacitance $C_{D_{1..4}}$, whereas arrangement G has the highest discontinuity in the local power density. Arrangement B has the highest variation of the gap to dielectric capacitance ratio $\beta_{1..4}$, the higher local power density $q_{1..4}$ and the higher fraction of applied power $f_{q_{1..4}}$. The arrangement C is the only arrangement with an increasing fraction of applied power from the inlet to the outlet. The power induction pattern is found to be sensitive to changes of the design parameters displayed in Table 1. The highest local power induction is almost double the lowest local power induction (Arr. B).

**CAUSALITY BETWEEN POWER INDUCTION AND EFFICIENCY**

Figure 1 illustrates the simulated power induction patterns, $f_{q_{1..4}}$, for the different arrangements as summarized in Table 1. The complementary information about power efficiency $\eta$ relative to the reference electrode (Arr. Reference) is added to the axis with the letter of each arrangement. The following comments can be made.

Arrangement B is found to be too aggressive. Long-term operation is not possible, as the generator starts to pulse. Arrangement C is the only electrode arrangement with an increasing power induction pattern, but turns out to be less...
efficient than the reference arrangement. Arrangements D to G show a gradually increasing fraction of applied power at the generator inlet. An optimum seems to exist and this optimum is a power induction pattern close to arrangement F.

A simulation of arrangement F with 100 slices was performed and the results are summarized in Figure 2. The following can be determined.

The progress of the local power density is discontinuous. A high power density is applied at low ozone concentrations. The temperature profile indicates a favourable increased gradient at lower ozone concentrations. The high average filamentary discharge packing density of arrangement F is obviously due to the long section of smooth power induction.

In an attempt to summarize the results obtained, three major hypotheses can be considered:

1. The observed efficiency increase is due to the favourable temperature gradient at low ozone concentrations, achieved by a specific power induction pattern.
2. The observed efficiency increase is due to the balance and degree of discharge filamentation at low and high ozone concentrations.
3. The observed efficiency increase is due to a combination of both the above.

The decreased efficiency of arrangement G disproves the first hypothesis as the dominating effect. The balance and degree of discharge filamentation is obviously a substantial part of the obtained efficiency increase.

Therefore, discharge filament tailoring will increase the power efficiency and power induction pattern, which, adjusted to maximize robustness at all conditions of operation, leads to an ozone generator with amazing properties, as illustrated in Figure 3. The classical shape of an efficiency curve is represented by the dashed line. Due to increasing loss-terms, a nonlinear increase of $E_s$ is observed as the ozone concentration increases. The classical ozone generator has a limit concentration, which is related to a trade-off between ozone destruction and formation. The measured data fits the classical curve shape only in the low ozone concentration region, whereas an almost linear trend is evident in the high ozone concentration region.

An efficient and robust system is exclusively obtained from an optimized discharge arrangement. Test measurements were done on a large-scale ozone generator with a total active area of 112.7 square metres. With homogeneous feed gas processing and an ozone production capacity of approx. 60 kilograms per hour, 10 weight percent ozone concentration was achieved. Whereas, with a tailored degree of filamentation, obtained with an F-like dielectric arrangement, an ozone concentration of approx. 16 weight percent was achieved and could be maintained even at increased cooling water temperatures and high power densities, see monitor picture in Figure 3.

CONCLUSIONS

A tailored degree of filamentation at low and high ozone concentrations, due to inhomogeneous feed gas processing, benefits the ozone generation process in terms of reducing power consumption and increasing the range of ozone concentrations. The ozone synthesis in a DBD ozone generator may be summarized as follows:
- Inhomogeneous feed gas processing, with a proper
dielectric arrangement, can enhance ozone generation.
- Highly filamented DBD discharges are best suited to the
production of ozone in the range of 6 to 14 wt% concentration.
- Smaller than 0.3 mm discharging gaps require a thick
dielectric layer to maintain a good filamentation at
reasonable efficiency.

REFERENCES

Publishers.

Elleasson, B., Hirth, M. & Kogelschatz, U. 1986 *Ozone synthesis

Hirth, M., Kogelschatz, U. & Müller, J. 1985 Der Einfluss von
gemessenen Toleranzen auf den Wirkungsgrad von
Technical Report: KLR 83-104 B.

Kogelschatz, U. & Müller, J. 1982 Zündverhalten und
Leistungsaufnahme von Ozonisatoren. Baden, Switzerland:

Kogelschatz, U. 2005 *Industrial Ozone Generation: Historical
Perspective, Current Status and Future Prospects*. CDROM
Proceedings IOA 17th Ozone World Congress, Strasbourg F.

Lang, H. V., Vezzu, G. & Suter, M. 2005 Science and Experience-
based Improvements of Industrial Ozone Generators. CDROM
Proceedings IOA 17th Ozone World Congress, Strasbourg F.

Manley, T. C. 1943 The electrical characteristics of the ozonator

Montgomery, D. C. 2001 *Design and Analysis of Experiments*.

Pitchford, L. C. & Sciamma, E. 2005 Calculated excited and radical
populations in a DBD discharge in N2/O2 mixtures.
Dübendorf, Switzerland: Ozonia Ltd. Technical Report:
HKH108665.

Vezzu, G. 2005 Intelligent Gap System. Dübendorf, Switzerland:

Vezzu, G., Merz, R., Gisler, R., Müller, M., Paolini, B., Lopez, J.L.,
Freilich, A. & Becker, K. 2007 Evolution of Industrial Ozone
Generation. Proceedings of the International Congress of