“Efficient gas treatment for various applications with atmospheric non equilibrium plasmas”
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Abstract: A surface dielectric barrier discharge (S-DBD) is applied for the oxidation of volatile hydrocarbons (VOC). An aluminum reactor with one or more parallel electrodes is used to purify VOCs from the exhaust air of industrial processes and technical waste gases. The conversion of VOC can be up to 100%. Furthermore, the purification of coke oven gases is given as a second example. Besides hydrogen and carbon monoxide, these contain some oxygen which cannot be removed by pressure swing absorption. For this purpose, S-DBD based on the oxyhydrogen reaction is also used very successfully. Large volume flows can be managed by cascading and interconnecting several reactor units.

Keywords: VOC conversion, hydrogen cleaning, S-DBD reactor, quant. OES, Schlieren measurement

1. General: VOC Conversion

In recent years, the treatment of industrial and technical waste gases has become more and more important, as the limits of the various partly critical hydrocarbons (volatile organic compounds, VOCs) are being lowered more and more. The best example is formaldehyde, whose accepted concentration in exhaust gas has been lowered in 2016 by a factor of ten from 1 mg/m^3 down to 0.1 mg/m^3 by the European authorities.

To purify exhaust air from the aforementioned VOCs, a reactor system was therefore developed [1] that must satisfy several boundary conditions: First, it is important that VOCs are efficiently and ideally completely converted to carbon dioxide and water. Secondly, the system should be designed to be cascadable in order to be able to treat the completely different gas flows in industry, and thirdly, it is crucial that the pressure drop of the system during operation can be kept as low as possible, since a pressure drop at a given flow costs a lot of energy and money.

2. Surface-Dielectric Barrier Reactor (S-DBD Reactor)

For the above reasons, a dielectrically hindered surface discharge (S-DBD) was constructed on the basis of individual electrodes [1]. An electrode consists of an aluminum oxide plate (approx. 190 x 90 x 0.6 mm) with a metal grid of nickel applied on both sides by screen printing (Fig. 1). On each side there is a contact surface to which a small plug is soldered parallel to the surface. In this way, this electrode can be quite simply pushed into the reactor and electrically contacted in it.

The reactor itself is shown in Figure 1 (above) and consists of an aluminum housing with a quartz window at the top and bottom to allow the plasma to be characterized. In the case of the simple reactor shown here, the electrode is located exactly in the center with a wall gap of about 15 mm. When the high voltage is turned on at the electrode, the plasma ignites and the surface is illuminated along the grid lines (Fig. 1 bottom). In addition to the high voltage generator, a current probe and a voltage probe are needed to measure the electrical parameters with high dynamics and time resolution in the sub µsec range.

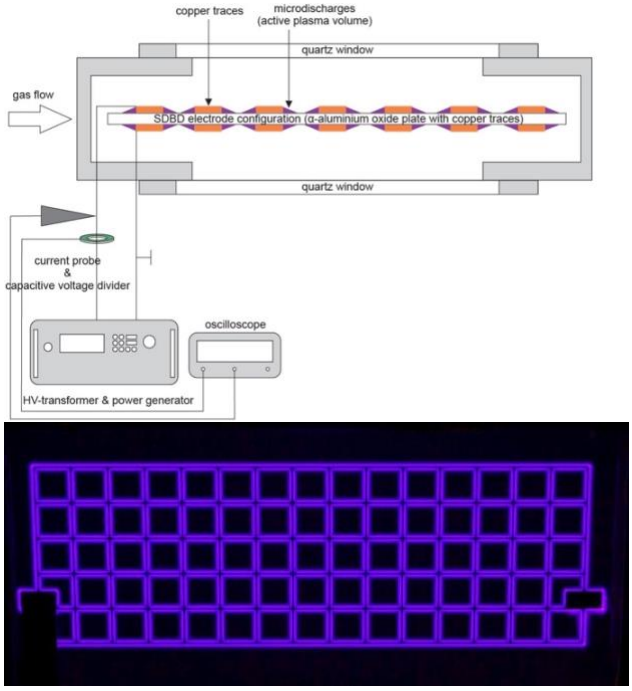


Fig. 1 Experimental Setup: Grid Electrode inside a reactor (top) equipped with a high voltage generator and electrical measurement devices; driven grid electrode with plasma ignited (bottom). The gas flow runs parallel along the surface of the electrode [1].

3. Plasma Characterization

To determine the electrical power dissipated in the plasma, current and voltage were detected. For this purpose, it is necessary to use an electrical equivalent circuit adapted to the real conditions. This equivalent circuit can then be used to determine the voltage dropping directly across the plasma and the corresponding current flowing through the plasma. The electrode is driven in pulse mode, i.e. a short voltage pulse from the generator excites the series resonance of the resonant circuit, which consists of the capacitance of the electrode and the inductance of the secondary winding of the high voltage transformer. This series resonance is about 86 kHz in the case of a single electrode. First, one determines the capacitance of the array without igniting the plasma. Then, the total current is

measured as the sum of the displacement current and the conduction current. From the determined capacitance and the measured derivative of the voltage (with respect to time), the displacement current is determined and subtracted from the total current. This then gives the electrical power shown in Figure 2 as a function of pulse frequency and voltage amplitude. It can be seen that increasing the pulse frequency results in an power increase [2]. The same is true for increasing the voltage. In both cases, more energy is added to the oscillating circuit. The limit at 1 kHz and 13 kV is formed by the limited power of the HV generator. It can be seen that the electrical power (in synthetic air) roughly ranges from a view up to several tens of watts per electrode.

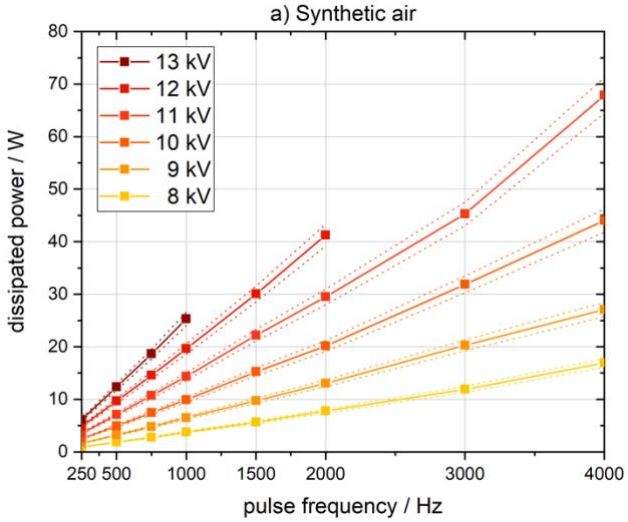


Fig. 2 Dissipated electrical power as a function of pulse frequency and pulse voltage amplitude

As another example of characterization, the electron density of the S-DBD plasma is shown as a function of gas mixing and pulse amplitude (Fig. 3). Since the individual filaments of the discharge are statistically distributed in location and time over the entire electrode area, this is a spatial and temporal rms value showing the global effect of the plasma for comparatively long times and **not** the electron density of a single filament over the filament lifetime.

The method for the determination of the electron density is based on a widely published method [2], for which on the one hand a collisional-radiation model (crm) of the molecular nitrogen is used. On the other hand, a Boltzmann solver is used in local approximation (i.e. without the transport term on the right hand side), where the force term is formed by the reduced electric field. The impact and radiation processes on the left-hand side are described by the crm. In the next step, one forms the (very strong field strength dependent ratio of the radiation of the first negative system (FNS) of N_2^+ at 391 nm and the second positive system (SPS) of N_2 at 337 nm). The electric field in the Boltzmann solver is then varied and the ratio of the two radiation contributions is calculated. If the experimental and calculated ratios agree, the distribution function (2-term approximation) is found as well as the reduced electric field [2]. The method is limited by excessively high reduced electric field strengths for which the 2-term approximation is no longer satisfied.

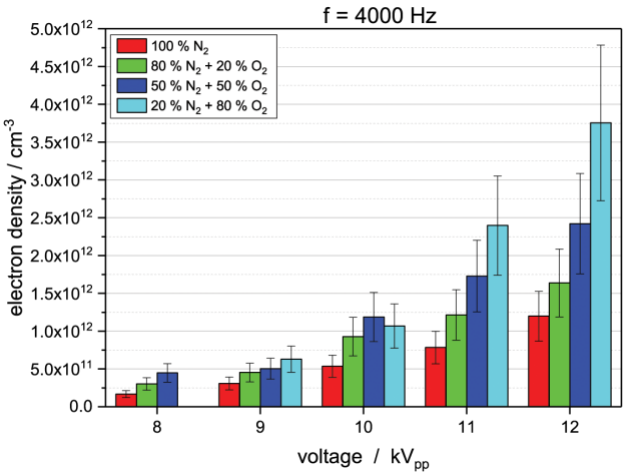


Fig. 3 "Effective" electron density @ 4 kHz as a function of amplitude and gas mixture

4. Conversion of VOCs

Butanol is selected as an example for the oxidation of a hydrocarbon. Figure 4 shows the conversion (right axis) of 50 ppm butanol in air for different pulse frequencies and voltage amplitudes. The measurement method here is based on two flame ionization detectors (FID), one FID is at the inlet to the reactor and one FID is at the outlet. It can be seen that complete oxidation of butanol is very possible at, for example, 1 kHz and 13 kV. However, this depends strongly on the particular molecule. For example, conversion at this setting is only 35% for n-butane, 95% for butoxyethanol, and 68% for ethyl acetate. In particular, alkanes with little or no oxygen content are more difficult to oxidize than other molecules [3].

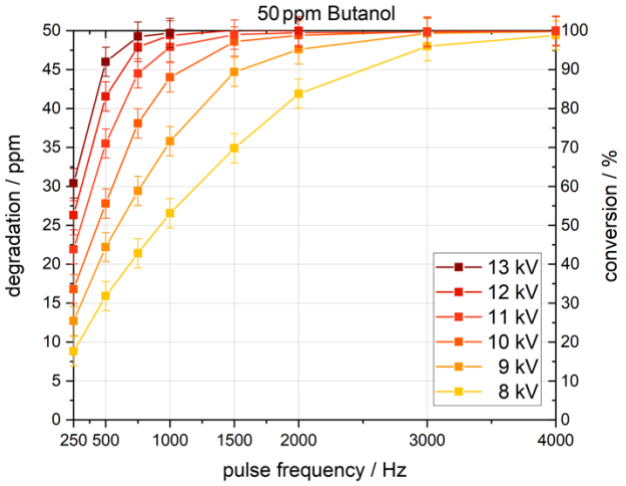


Fig. 4 Degradation (left) and conversion (right) of butanol as a function of frequency and voltage amplitude

5. Gas dynamics obtained with Schlieren measurement

If we look at the space filled by the S-DBD plasma, we see that at the distance of the electrode from the wall selected here, the free volume is very large. With a plasma height of less than one millimeter, at least 14 millimeters of the volume are free of plasma. At this point, therefore, the question arises as to the convincing effect of the plasma, although most of the volume flow seems to bypass the plasma. Schlieren measurements should provide information on this.

A Schlieren measurement [4] is shown in Fig. 5. This consists of visualizing refractive index fluctuations in the volume above and below the S-DBD with the gas volume stationary. It is clear that considerable, very nicely visible periodic oscillations of the refractive index occur in the free volume. This can also be visualized in the case of added gas flow. Directly on the electrode, the individual grid lines between the brightly illuminated streamers can still be seen. Further investigations show that the entire gas volume is regularly circulated. This is a fascinating mechanism that has already been recognized by research in the field of plasma actuators. At this point, it becomes clear that the gas dynamics above and below the electrode play a crucial role, causing the gas particles to be periodically transported into the plasma zone, where they undergo intense oxidation. In this way, if these dynamics are appropriately optimized and linked to the gas flow, an excellent effect can be achieved.

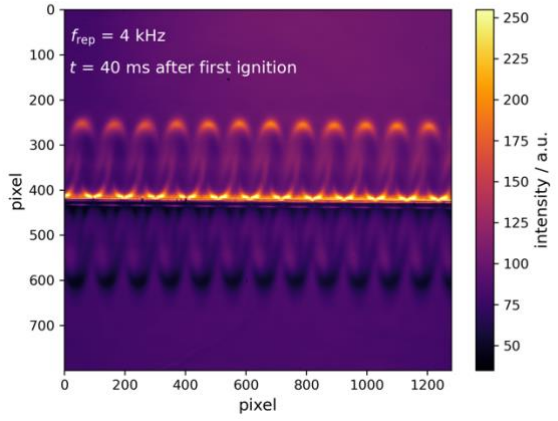


Fig. 5 Schlieren measurement above and below the electrode @ 4 kHz and 12 kV at stationary air (no flow)

6. Removing oxygen from coke oven gas

In Germany, steel production emits around 750 million tons of carbon dioxide (2020) [5]. At the same time, a large amount of hydrogen is produced in the coke oven for steel production, which together with the carbon dioxide makes it possible to produce fuels, plastics or even fertilizers.

Insofar, the second example on the subject of gas treatment is the purification of coke oven gas, which contains large proportions of hydrogen of about 63% in addition to other major components such as methane (≈ 22%), nitrogen (≈ 6%) and carbon monoxide (≈ 7%). One of the minor components is oxygen in the range of some 100 ppm. For hydrogen recycling, it is necessary to separate the hydrogen from all other gases in order to be able to use it further. This separation is done by means of pressure swing absorption (psa), which, however, does not work for oxygen, but on the contrary accumulates oxygen up to dangerous concentrations.

For this reason, the oxygen must be removed from this coke oven gas by other means. A non-equilibrium plasma on the basis of the aforementioned S-DBD reactor system is now available for this purpose, with which the conversion of oxygen to water functions very efficiently on the basis of the oxyhydrogen reaction.

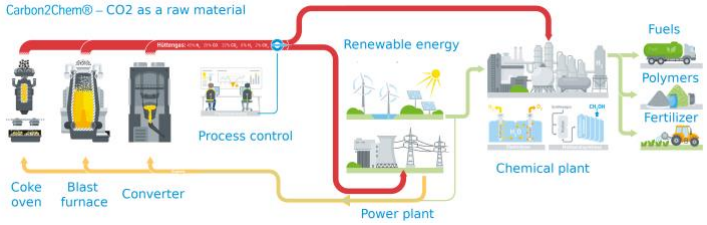
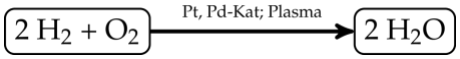


Fig. 6 CO_2 as raw material (Carbon2Chem) using hydrogen from steel production [5]

The oxyhydrogen reaction is well-known



and can be accomplished with both a catalyst (Pt) and a cold plasma. It is also possible to use both at the same time. In this case, the plasma lowers the operating temperature required for the catalyst and prevents catalyst poisoning.

Figure 7 shows the conversion using an S-DBD reactor from oxygen with hydrogen to water as a function of pulse voltage amplitude and oxygen concentration. It is clear that high conversion efficiencies are achieved.

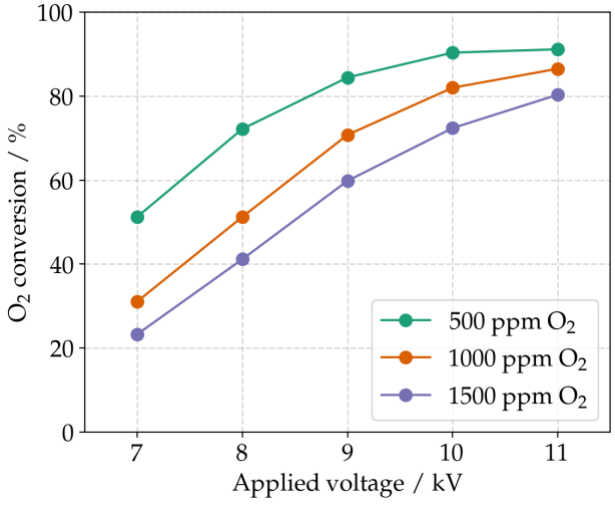


Fig. 7 Oxygen removal by S-DBD plasma for various oxygen concentrations and different voltage amplitudes

7. Upscaling a S-DBD reactor system

A major challenge is the large volume of coke oven gas to be purified. This would require reactors capable of handling thousands of standard cubic meters of gas volume. One solution to build S-DBD reactor system accordingly is to cascade the electrodes, combining 10 electrodes into one module each (Fig. 8 PM 10). Each individual module has full internal contacting of the individual electrodes as well as two connector plugs for the power supply. The electrodes are guided in PEEK (polyether ether ketone) rails and can thus be replaced quickly.

Fig. 8 Plasma module consisting of 10 electrodes (PM 10) with internal electrical contacts. The windows shown serve for plasma observation.

In Fig. 9, individual modules (with 10 electrodes each) are connected together to form larger units. The parallel connection makes sense if larger volume flows are to be treated. The series connection of the modules, on the other hand, makes sense if the gas flow velocity is very high and thus the residence time of the particles in the reactor becomes very short. In this case, the treatment distance must be extended.

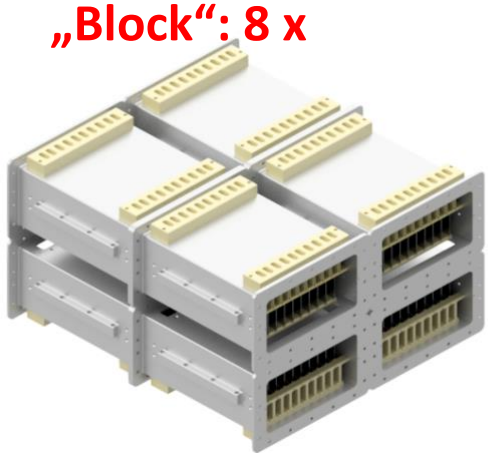


Fig. 9 Eight PM 10 in one “block” for 150 m^3/h @ 4 kW

8. Conclusion

An S-DBD reactor for gas treatment is presented. On the one hand, the characterization of the underlying plasma is briefly presented. This is based on quantitative optical spectroscopy, with which intensities of spectral lines and bands are measured in relative and absolute calibration. The measurements are coupled with simulations using a collisional radiative model and linked to a Boltzmann solver to obtain the plasma parameters. Furthermore, the S-DDB will also be measured electrically with precision to obtain the electrical power delivered to the plasma. The S-DBD plasma is used in the next step to remove volatile hydrocarbons (VOCs) from ambient air. The example of butanol and some other VOCs will be used to demonstrate this. The degree of oxidation depends very much on the particular molecule but also on the flow velocity and the plasma parameters.

Another example comes from steel production. Here, large quantities of carbon dioxide accumulate but also of hydrogen from the coke oven process, which is contaminated with various other gases. From both gases together, synthetic fuels, plastics and fertilizers are to be produced in the future. In particular, the oxygen contaminating the hydrogen mixture cannot be removed by pressure swing absorption and must therefore be converted to water with plasma together with hydrogen. This succeeds very well, but the large gas flows are a challenge. This is met by cascading the plasma electrodes. Ten electrodes are combined into one module. Multiple modules are also interconnected, with the serial arrangement increasing the dwell time if conversion is too low at large gas velocities. The parallel arrangement is needed to handle very large gas flows.

9. Acknowledgement

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10. References

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