modular two-phase plasma catalyst reactor for the functionalization of liquids for ISPC25 21-26 May 2023, Kyoto, Japan

Alexander Alfred Zyla[1]

[1] *Graduate, Technical University of Dresden, Germany*

Abstract: Low temperature atmospheric plasma offers a good opportunity to catalytically excite multiphase reactions. In order to increase the yield , a new process was developed and implemented and validated in a prototype. The developed prototype has many advantages due to its design and functionality. In particular, the system offers a wide range of possibilities for development processes or scientific investigations of more complex reactions. The prototype of the ZPPK reactor system can be used and modified at low cost.

Keywords: plasma catalysis, multiphase reactions, plasma activated water, portable reactor

1. Motivation

Despite its enormous potential to save energy and expensive catalysts the use of atmospheric plasma as a catalyst for multiphase reactions remains very limited. A major obstacle to the use of atmospheric plasmas is the difficulty of transferring a laboratory-proven process to industrial processes in a meaningful way. Scientific papers use a variety of different plasma sources, plasma excitations, and plasma reactors [1–4]. The results of such studies are therefore difficult to compare and therefore do not provide a good basis for industrial application. To facilitate access for industry and academia, a system with increased resilience needs to be established. A cost-effective solution for this is the modular two-phase plasma catalytic reactor (**ZPPK reactor**, german: *Zwei-Phasen-Plasmakatalysereaktor*).

The system can be used for validation of further fields of application and for scientific investigations.

Through technology transfer, the knowledge of the application will be brought to universities worldwide and made available to creative people and interested students from various disciplines. Due to its versatility, the ZPPK reactor offers interdisciplinary application and development possibilities [5].

2. Introduction

The ZPPK reactor is a reactor in which an atmospheric plasma is used to catalytically excite chemical reactions in a liquid fluid. The reactants can come from the liquid phase, from the plasma phase itself or from the gas phase. The special feature of this reactor lies in its process control. In the process principle used, a liquid phase is introduced into a turbulent reactor chamber and atomized there. This reactor space is in an energetic non-equilibrium when the liquid enters. This means that the reactor chamber is filled with various free charge carriers. As the droplets penetrate the reactor chamber, the droplets encounter these charge carriers and can react with them. If these charge carriers possess the energy required for a reaction, a chemical reaction occurs. Since atmospheric plasma is involved, these reactions take place almost without any change in temperature [5, 6].

In order to prove the functionality of the process in initial trials, plasma-activated water (**PAW**) was to be produced using a ZPPK reactor prototype. For the production of chemical substances that have to be manufactured over several reaction steps, ZPPK reactors can be combined. The easy combinability allows multi-stage and more complex systems.

3. Detailed concept of the prototype

3D printing (FDM) was chosen as the main manufacturing method to achieve rapid protyping. 3D printers are cheap to buy and easy to use. 3D printing processes make it possible to produce replacement parts or implement modifications quickly and easily. The default 3D printed parts are made of PLA. The other components are made of copper, glass and silicone.

For the development of the prototype, a barrier discharge was chosen as the plasma excitation. More precisely, a planar capacitive plasma discharge configuration with dielectric on both sides has been chosen. Various planar DBD configurations are shown in **Fig. 1**. The numbers in the drawing indicate 1 the current source, 2 the dielectric barrier/dielectric, 3 the high voltage electrode, 4 the discharge gap/discharge region and 5 the ground electrode.

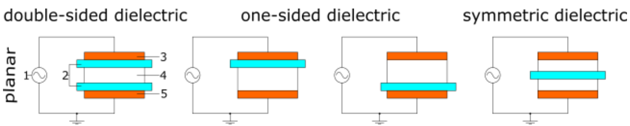

Fig. 1. DBD configuration in planar design of the electrodes and with double-sided, single-sided or symmetrical dielectric. [5, 7, 8]

The geometry of the electrodes is the same on both sides and has been varied in different prototypes. The chosen configuration serves to generate an electric field that is as homogeneous as possible. A homogeneous electric field allows a more uniform excitation of the plasma field and should enable the provision of a homogeneous non-thermal atmospheric pressure plasma [7]. **Fig. 2** shows a classification of usable plasma states in a one-sided symmetric DBD discharge. In the extreme case, it is either filamentary plasma or homogeneous/diffuse plasma. In between are mixed states of both states.

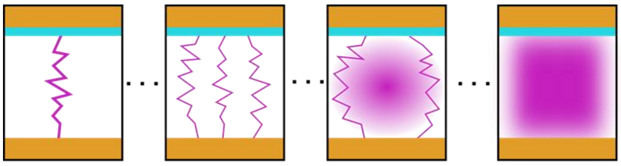

Fig. 2. Classification of usable plasma states: filamentary plasma on the left and homogeneous/diffuse plasma on the right. [6, 7]

Fig. 3 shows the ZPPK reactor prototype. It is a two-chamber system. In the first chamber, the process gas is pretreated and converted to the plasma state. The liquid to be treated is fed into the bottleneck between the two chambers. In the second chamber, when the liquid enters, a plasma is already ignited and the phases are dispersed. The treated liquid is then ejected from the reactor system together with the process gas.

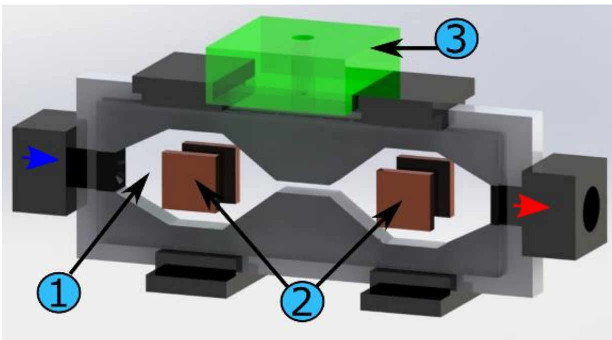

Fig. 3. ZPPK reactor: blue arrow: inlet (process gas); red arrow: outlet; (1) first reactor chamber; (2) square electrodes; (3) inlet/access (liquid).

4. Experimentell Section

Fig. 4. shows the schematic diagram of the electric production system using a ZPPK reactor. The compressed process gases are dry and come from gas cylinders. The liquid is distilled water which is fed into the reactor by a pumpsystem. The plasma module consists of the low temperature atmospheric plasma reactor (ZPPK reactor), a high voltage power supply, flow switches, a pumpsystem to control the liquid flow and central electronic control units.

A high-voltage pulse generator (AC) serves as the current source. Frequencies between 10-180 kHz and peak voltages from 2.5 to 26.5 kV were investigated.

The fluid was supplied via a syringe pump system. The system allows flow rates and duration of a continuous flow to be arbitrarily set and programmed. The flow rate was 0.9-1.8 ml/min.

Mass flow controllers were used to control and monitor the gas flow. Gas flow rates from 2.0 to 28.0 slm were investigated in the performed studies.

The influence of different control parameters on plasma ignition, plasma state and reactor behavior could be investigated. Required minimum ignition voltages could be determined.

Subsequently, investigations of the treated water were carried out batchwise via test strip systems or pH value measuring probes.

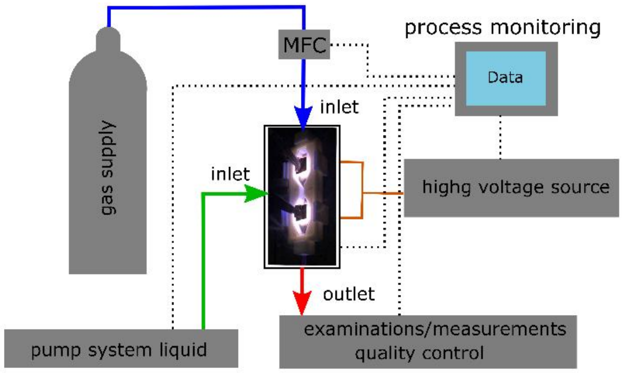

Fig. 4. Experimental schematic diagram of the ZPPK reactor system for the treatment of a liquid with various gases

5. Results and Discussion

PAW activated water consists of various reactive species. Essential for the application of PAW species are peroxide, nitrate and nitrite (reacitve oxide and nitrogen species, RONS) [1]. They are mainly responsible for the fact that a pH reduction occurs in PAW [2]. After treatment in the reactor, the reactive species were detected in the treated water using test strips. The relationship between the species formed can be seen in **Fig. 5**. Peroxide is formed independently of nitrate and nitrite. The nitrate and nitrite concentrations show a clear dependence. This is essentially due to the fact that nitrite is an intermediate product in the formation of nitrate. Argon or an argon-air mixture served as the main process gas for these illustrated results.

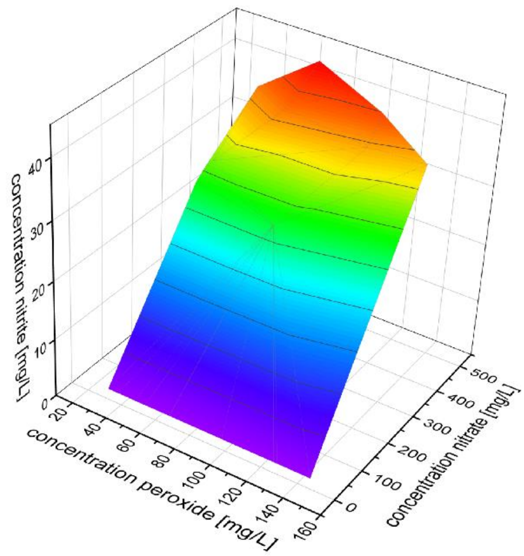

Fig. 5. Relationship of the detected species (peroxide, nitrate, nitrite) in the produced PAW.

Since the test strips used reached their detection limits, a pH value measurement was carried out for a further experiment. A mixture of helium, argon and air was selected as the process gas. The results of the pH value measurement can be seen in **Fig. 6**. SIE is the Specific Input Energy, which is the ratio of the energy introduced into the reactor to the gas flow. SIEL is the Specific Input Energy Liquid, which is the ratio of the electrical energy introduced into the reactor to the treated liquid.

Various attempts have been made to increase the yield. The atomizing rate in the reactor could be optimized by means of laser diffraction spectroscopy. To optimize the plasma state, the setting parameters for different gas compositions were optimized.

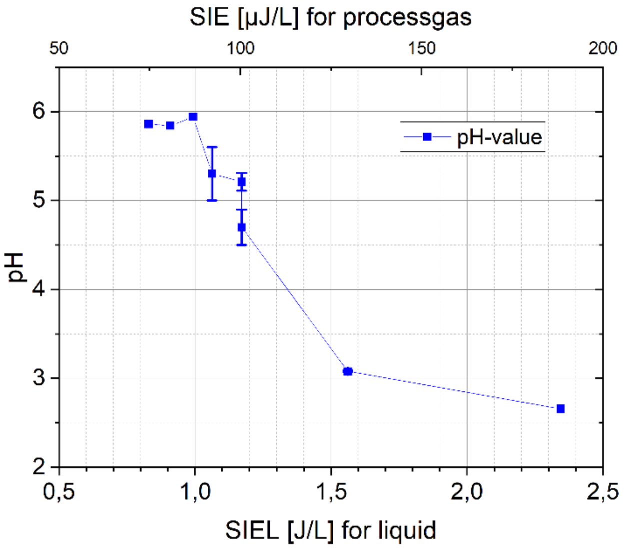

Fig. 6. pH value of the treated water as a function of SIE [µJ/L] and SIEL [J/L]

6. Fields of Application

The ZPPK reactor system offers the possibility for various scientific investigations. Special phenomena in atmospheric plasmas and interaction processes between plasma and liquid can be investigated. Results can be transferred and reproduced very easily. The integration of measuring instruments is very well possible due to the design of the ZPPK reactor.

Optimized reactor variants are very easy to implement for industrial applications. Smallest quantities can be produced independent of location. For scale up, several reactor systems can be connected in parallel or the conversion can be increased by increased energy input.

The technology provides easy access for interdisciplinary applications in the fields of **process industry**, **water treatment**, **agriculture**, **food and consumer goods industry** and **medical technology** [5]. Developers, scientists or users do not need in-depth knowledge to set up, operate and use the system or even multi-stage systems.

7. Future Challenges

In order to further simplify access to the technology, interdisciplinary work is required to further simplify the entire production system (see **Fig. 4.**). The pump systems, the gas flow controller and the high-voltage sources should be available pre-validated, thus facilitating the combination and integration. At the same time, costs are to be further reduced.

If the system is used for more scientific work, the collected data can be combined via BigData analyses. The findings obtained from this will make it possible to derive initial applications even before the first series of tests. Necessary parameters can thus be narrowed down in advance and development processes accelerated.

8. Conclusion

The process could be implemented well in the new reactor type. PAW could be produced and, due to optimized process data, the yield of the reactive species could even be increased disproportionately. Due to its compact form, the reactor can be very easily integrated into various investigation tools. In the event of defects or malfunctions, faults can be identified and rectified very quickly. Required spare parts can be produced directly at the laboratory using 3D printing technology. The geometry of the reactor offers many possibilities for modification without having to change the entire basic design. This ensures good comparability between different configurations and results can be processed and transferred more easily in terms of data technology.

The reactor offers a good alternative to previous reactor systems and, thanks to its modularity, also makes it possible to investigate more complex multi-phase reactions or to increase the turnover. **[3]**

9. Acknowledgements

Special thanks to the Fraunhofer Institut IST (Schicht- und Oberflächentechnik) in Braunschweig, Germany. After my honor to my theoretical work at the ak-adp research competition in 2021 they gave me the possibility to implement my work into reality [9, 10].

10. References

[1] Y.-M. Zhao, A. Patange, D.-W. Sun und B. Tiwari, „Plasma‐activated water: Physicochemical properties, microbial inactivation mechanisms, factors influencing antimicrobial effectiveness, and applications in the food industry", 2020, doi: 10.1111/1541-4337.12644.

[2] R. Zhou *et al.*, „Plasma-activated water: generation, origin of reactive species and biological applications", 2020, doi: 10.1088/1361-6463/ab81cf.

[3] S. Sasaki, K. Takashima und T. Kaneko, „Portable Plasma Device for Electric N2O5 Production from Air", *Industrial & Engineering Chemistry Research*, Jg. 60, Nr. 1, S. 798–801, 2021, doi: 10.1021/acs.iecr.0c04915.

[4] J. Golda *et al.*, „Corrigendum: Concepts and characteristics of the ‘COST Reference Microplasma Jet’ (2016 J. Phys. D: Appl. Phys. 49 084003)“, 2019, doi: 10.1088/1361-6463/aae8c8.

[5] Alexander Alfred Zyla, „Machbarkeitsstudie für einen Zwei-Phasen-Plasmakatalysereaktor zur Funktionalisierung von Flüssigkeiten“. theoretical study, Technical University of Dresden, Dresden, 2022.

[6] Alexander Alfred Zyla, „Experimentelle Untersuchungen zur kontinuirlichen Herstellung von Plasmaaktiviertem Wasser unter Verwendung des neuartigen Verfahrensprinzips eines Zwei-Phasen-Plasmakatalysereaktors“. Diplomarbeit/thesis, Technical University of Dresden, Dresden, 2023.

[7] U. Kogelschatz, „Filamentary, patterned, and diffuse barrier discharges“, S. 1400–1408, 2002, doi: 10.1109/TPS.2002.804201.

[8] U. Kogelschatz, „Dielectric-Barrier Discharges: Their History, Discharge Physics, and Industrial Applications“, *Plasma Chemistry and Plasma Processing*, Jg. 23, Nr. 1, S. 1–46, 2003, doi: 10.1023/A:1022470901385.

[9] Stephan Stern, *Preisträger Wettbewerb #ZukunftADP | ak-adp: Anwenderkreis Atmosphärendruckplasma.* [Online]. Access under: https://www.ak-adp.de/preistraeger-wettbewerb-zukunftadp/ (Access at: 24.10.2022).

[10] *Schichten und Oberflächen für zukunftsfähige Produkte und Produktionssysteme.* [Online]. Access under: https://www.ist.fraunhofer.de/ (Access at: 20.02.2023).