Plasma-assisted non-oxidative coupling of methane: A study on the effects of particle size distribution of glass beads and pressure on the product composition.

T. S. Larsen[1] , J. M. Christensen[1] , A. Fateev[1] , M. Østberg[2] , A. Bogaerts[3] , and A. D. Jensen[1,*]

[1] *Department of Chemical and Biochemical Engineering, Technical University of Denmark, Kgs. Lyngby, Denmark.*
[2] *Topsoe A/S, Kgs. Lyngby, Denmark.*
[3] *Research Group PLASMANT, Department of Chemistry, University of Antwerp, Wilrijk, Belgium.*

Abstract: Non-oxidative coupling of methane was conducted in a packed bed DBD reactor. The influence of parcticle size distribution (2000-5000µm, 900-1100µm, 425-600µm, 212-300µm, 150-212µm) of glass beads and operating pressure was investigated. The results showed a consistent increase in selectivity towards unsatured C_2 products (50%) in response to the utilization of the smallest glass beads. This tendency was attributed to a change in plasma dynamics, in particular the establishment of partial discharging.

Keywords: Plasma technology, DBD, non-oxidative coupling.

1. Introduction

The global society has been forced to direct more emphasis toward the development and implementation of green energy solutions as a consequence of the detrimental anthropogenic emissions of greenhouse gasses. However, the implementation of such energy conversion technologies into the existing energy infrastructure is extremely complex. The intermittent character of renewably produced electricity and fluctuating production capacity of these technologies impose a substantial need for efficient energy storage alongside a compelling need for a wide-ranging advancement of the electrical grid to maintain stability and resilience [1]. One possible solution that in recent years has been designated as an important contributor to the energy storage challenge of renewables is power to X (PtX). The preservation of renewably produced electricity surpluses into chemical energy carriers (methanol, ammonia, synthesis gas, hydrogen, etc.) is expected to increase considerably in the coming decades as a technology that efficiently equalizes the imbalance between energy supply and demand. One branch of industrial chemical reactions, in regard to PtX, that has attracted significant interest is the direct conversion of methane to value-added chemicals such as olefins and aromatics due to the economical upgrading potential and abundant supply [2]. Currently, the industrial utilization of methane proceeds via the indirect route producing synthesis gas as a precursor for Fischer-Tropsch or methanol synthesis. However, the indirect conversion of methane requires very energy-intensive process steps (reforming or partial oxidation). Therefore, significant research efforts have been devoted to investigating process conditions and catalysts that effectively enhance activation of the C-H bonds along with keeping a high selectivity towards desired C-C coupling reactions for non-oxidative coupling of methane (NOCM). However, the seemingly simple NOCM has proven to be challenging due to the inertness of the extremely strong C-H bonds where high-temperature conditions are required for activation causing severe catalyst deactivation [3]. Opposed to conventional approaches, a promising technology that has proven to overcome the thermodynamic and kinetic barriers of NOCM along with accommodating the substantial need for efficient energy storage of renewables is plasma-assisted processes [4]. In non-thermal plasmas (NTP), the energy transfer is based on the acceleration and collisions of charge carriers due to the strong externally applied electric field creating a very reactive environment consisting of free electrons, ions, radicals, and neutral species under mild reaction conditions. Different types of electrical discharge plasmas are categorized as NTP, however, the most common and widely applied configuration is the dielectric barrier discharge (DBD) often operated as a packed bed reactor (PBR). The application of PBR DBDs, so-called plasma catalysis, have in the recent decade been subjected to extensive research as a promising alternative gas conversion technology combining the advantages of both plasma and catalysis. This type of hybrid system has proven to result in enhanced process outcomes that would be unachievable by plasma or catalysis individually [5]. Such surplus effects frequently referred to as synergistic effects, are said to originate from the complex interplay between the plasma and the catalyst and vice versa. Until now, several investigations have aimed to elucidate the fundamental mechanisms of plasma-assisted catalysis combining both experimental work and modeling, however, inconsistent observations have been reported. Still, plasma catalysis as a new technology involves underlying complexities that need clarification to further advance and understand the inherently difficult co-dependency of the plasma and the catalyst. Irrespectively, previous research confirms and distinctly assigns the physical properties of the packing material, in particular, the dielectric constant but also surface area, porosity, and geometry, to have a prominent influence on the plasma dynamics. Changes in these properties can significantly alter the electrical properties, herein the streamer formation, propagation, and thereby the chemistry occurring [6].

In this work, a co-axial PBR DBD was used to study the performance of plasma-assisted NOCM. The influence of spatial confinement, by varying the particle size distribution of glass beads, and operating pressure on NOCM was investigated and evaluated in terms of methane

conversion, product composition, and energy efficiency. In addition, in-depth electrical characterization of the transitional behavior of the discharge regimes was elucidated by analysis of Q-V plots.

2. Experimental Setup and Operating Conditions

The experimental work, in this study, was conducted in a co-axial packed-bed DBD reactor. The configuration consists of five main components: a customized cylindrical quarts glass reactor acting as the dielectric barrier, two electrodes, and two end plugs. The high voltage electrode was a 5 cm long stainless steel mesh covering the outer surface area of the dielectric barrier. The inner electrode, working as the grounded electrode, was a stainless steel rod fixed at the center of the quartz reactor with a diameter of 10 mm. The quartz glass reactor had an inner and outer diameter of 19 mm and 22 mm, respectively, resulting in a dielectric barrier thickness of 1.5 mm and a discharge gap of 4.5 mm. A Trek 20/20C-HS-H-CE high voltage amplifier powered the high voltage electrode. A function generator from Tektronix was used to control the signal to the Trek amplifier by selecting the frequency and the peak-to-peak voltage. The electrical characterization was obtained by monitoring the output voltage from the amplifier, the total current, and the charge transfer in the reactor. These parameters were measured using a Tektronix high voltage probe (P6015A), a Rogowski coil (Pearson, 4100), and a ceramic monitor capacitor with a capacitance of 10 nF all connected according to the depiction in Figure 1.

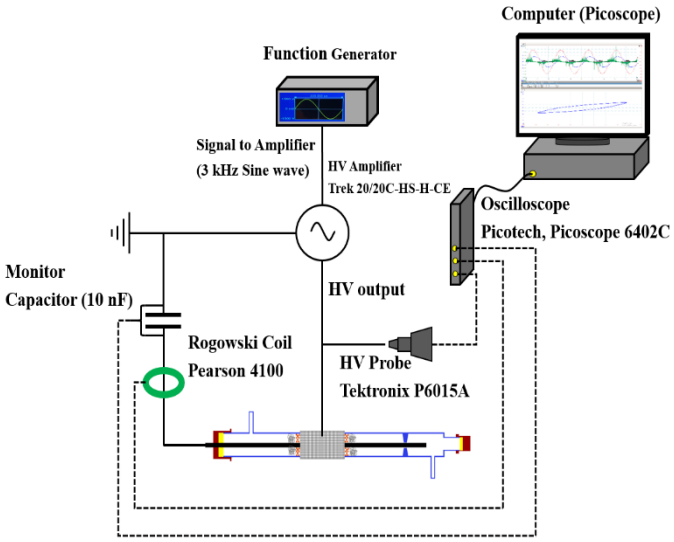

Figure 1 – Schematic diagram of the experimental setup.

The plasma power for the conducted experiments was kept at 30W and a frequency of 3 kHz. Upon ignition of the plasma, a stabilization period of 30 min was practiced prior to any measurements to ensure steady-state conditions. The gas, consisting of pure CH_4, was fed to the reactor at a volumetric flow rate of 50 Nml/min by Bronkhorst mass flow controllers. The experimental work is divided into two series, a low and high-pressure condition. The reaction environment of the low-pressure condition was equivalent to ambient conditions (**P=1.2 bar)** whereas the operating pressure in the high-pressure condition was slightly elevated (**P=1.7 bar**). The reactor pressure was monitored and manually regulated using a manometer and a needle valve placed right after the reactor exit. The product composition of the reactor effluent was analyzed using an online Thermo Fischer gas chromatograph (TraceGC 1300). The operating conditions and relevant geometric specifications are summarized in Table 1.

Table 1 – Overview of the geometric specifications and operating conditions.

Geometric Specification	**Value**
Discharge Gap [mm]	4.5
Outer Electrode Length [cm]	5
Plasma Zone Volume [cm^3]	10.3
Operating Condition	Value
Frequency [kHz]	3
Plasma Power [W]	30
Volumetric Flow rate, CH_4 [Nml/min]	50
Low-pressure condition [bar]	1.2
High-pressure condition [bar]	1.7

The packing materials tested in this work were glass beads of five different size distributions as seen in Table 2. The glass beads were tightly packed in the gap space between the glass barrier and the inner electrode. To restrict any movement of the packed glass beads, quartz glass wool was placed on each side of the plasma zone. After the packing procedure, the zone was slightly compressed to ensure a dense packing of the glass beads.

Table 2 – Overview of the five particle size distributions of glass beads and the corresponding packing efficiency.

Particle Size Distribution [µm]	**Packing Efficiency, V_{void}/V_{total}**
2000-5000	0.75
900-1100	0.45
425-600	0.41
212-300	0.41
150-212	0.36

3. Results and Discussion

The application of high dielectric constant packing materials in PBR DBDs is known to enhance local electric fields in the vicinity of the packing material, attributed to polarization effects. This can significantly affect the plasma dynamics, herein streamer formation, propagation,

and breakdown voltage [6]. However, the transitional plasma dynamics caused by the presence of the dielectric packing material and more importantly how the chemistry is dependent on the discharge regime, still need clarification. In this work, the plasma-assisted NOCM was carried out with an emphasis on how the discharge regimes can influence the chemical reaction routes and thereby affect the product composition. A very effective technique to explore the inherently complex character of the co-dependent behavior of the plasma and the utilized packing is through electrical characterization. For this purpose, the most commonly applied method is the so-called capacitor method, also used in this study as seen in Figure 1, allowing plasma power measurements along with in-depth electrical characterization by analysis of charge-voltage (Q-V) plots combined with a suitable equivalent circuit model. Detailed analysis of Q-V plots is increasingly utilized as a diagnostic tool, not only for power measurements, but also for measurements of gas gap charge transfer, reactor capacitance, and ignition voltage of the plasma, parameters that collectively quantify the reactor performance of a PBR DBD. However, Q-V plots for PBR DBD plasmas very often deviate from the ideal parallelogram shape, by having irregular forms, increasing the complexity of interpreting the reactor properties of PBRs as the classical DBD equivalent circuit model not directly can be applied. Figure 2 shows the obtained Q-V plots for the high-pressure condition, clearly displaying irregularities and deviations from the ideal parallelogram shaped Q-V diagram.

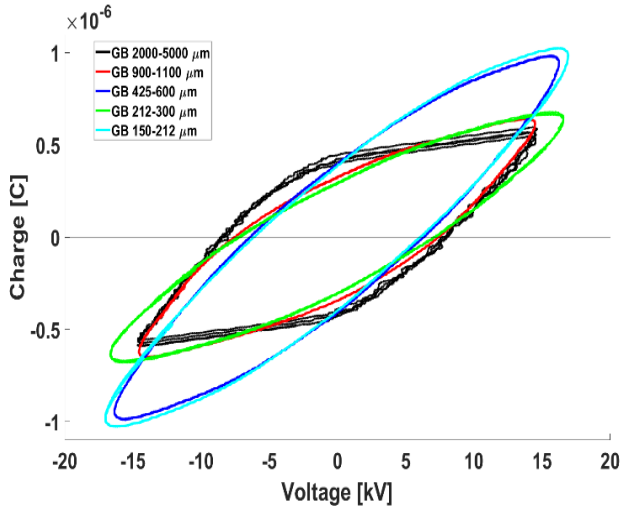

Figure 2 – Q-V plots for the high pressure condition.

Therefore, the different glass beads systems for both pressure conditions have been characterized in terms of the partial discharging formalism and their extended methods by Peeters et al. [7] and Butterworth et al. [8], respectively. The resulting partial discharge coefficients (α), describing the fractional area of the electrode which is not discharging, for the tested glass bead systems are provided in Table 3.

Table 3 – Resulting α value for the different tested conditions.

Size distribution,[μm]	150-212	212-300	425-600	900-1100	2000-5000
α, P=1.7 bar	0.94	0.88	0.85	0.84	0.30
α, P=1.2 bar	0.90	0.85	0.81	0.75	0.26

The value of α corresponds to different discharge regimes. A low value of α, <0.4, corresponds to a discharge regime dominated by streamers carryings a large charge, whereas a high value of α, >0.7, represents a discharge regime dominated by partial discharging, also termed as point-to-point discharges, where the charge transfer is incomplete between the electrodes [8]. The results of this study, shown in Figure 2 and Table 3, indicate that the value of α increases with decreasing particle size distribution of the glass beads for both pressure conditions. Consequently, the plasma dynamics and discharge regime changes from a stable streamer regime towards a partial discharging regime where every single bead increasingly acts as individual capacitors. Such partial discharge regimes are established when the applied voltage only marginally exceeds the breakdown voltage [8]. This affects the instantaneous capacitance of the discharging phases of a full cycle as it transiently changes which is in contrast to the DBD equivalent circuit model. This behavior of the plasma is reflected in the transition of the Q-V plots towards the non-ideal almond shape, which becomes more prominent with decreasing size of the glass beads. Furthermore, the α value is observed to be larger for the high-pressure condition which is ascribed to the slightly elevated pressure increasing the degree of partial discharging along with the breakdown voltage. Changes in the plasma behavior, herein streamer dynamics, influence the reaction enabling mechanisms associated with the electron density and energies [6]. This directly changes the reaction conditions and thereby the chemistry occurring in the PBR DBD. The transitional behavior of the discharge regime was found to significantly influence the CH_4 conversion and selectivities of the products for the conducted NOCM experiments as shown in Figure 3.

Figure 3 shows the CH_4 conversion and product selectivities of the five tested glass bead systems for both pressure conditions. The results show a decreasing conversion of CH_4 with decreasing particle size distribution of the glass beads for both pressure conditions. This trend is found to be more prominent for the high-pressure condition. The main products obtained in this study were a mixture of saturated and unsaturated C_2 and C_3 species. According to the selectivity plot in Figure 3, an increase in selectivity towards unsaturated C_2 products was obtained for decreasing particle sizes of the glass beads for both pressure conditions. This tendency resulted in a decreasing selectivity towards C_3 products.

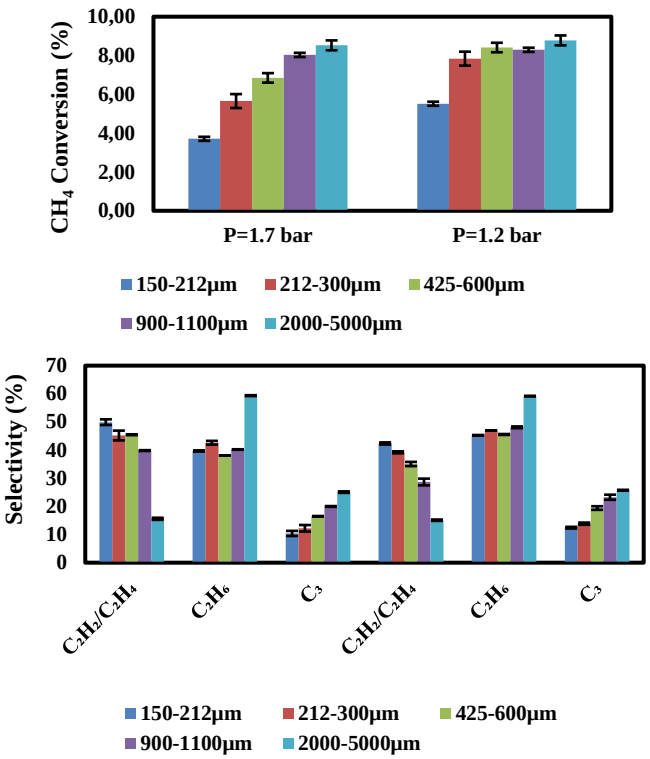

Figure 3 - CH_4 conversion and selectivity of the products for the tested glass bead systems.

Another observation to highlight is, that the high-pressure condition consistently enhances the selectivity towards unsaturated C_2 products for all the tested glass bead distributions, except for the largest glass beads (2000-5000µm). The highest selectivity towards unsaturated C_2 species for the low and high-pressure condition was obtained to 50% and 42%, respectively. This shift in the product composition is attributed to the transitional behavior of the discharge regime changing from a stable streamer regime for the largest glass beads towards a discharge regime increasingly dominated by partial discharging with the utilization of smaller glass beads. The increasing value of the partial discharging coefficient, α, and thereby partial discharging, was found to enhance the formation of unsaturated C_2 products along with decreasing the degree of conversion of CH_4 for both pressure conditions. Moreover, the plasma dynamics was found to significantly change character, from a stable streamer regime towards an increasing degree of partial discharging, for the different tested glass bead systems due to variations in the spatial confinement and operating pressure. The results presented in this study illustrate how the plasma dynamics itself determines the dominating chemical reactions of NOCM, however, an appropriate selection of packing material can be used to tune the plasma towards desired products such as light olefins.

4. Conclusion

Plasma-assisted non-oxidative coupling of methane was conducted in a co-axial packed bed DBD utilizing glass beads as the packing, belonging to five different particle size distributions. The tested glass bead systems were conducted under two pressure conditions. The performance was evaluated in terms of the CH_4 conversion and product composition, and explained by analyzing Q-V plots as a diagnostic tool for electrical characterization of the resulting plasma behavior. The results showed a significant increase (~15%) in unsaturated C_2 products with decreasing sizes of the glass beads for the low and high-pressure conditions. This was attributed to the change in the discharge regime, which was quantified by the partial discharging coefficient α.

5. References

[1] O. Smith, O. Cattell, E. Farcot, R.D. O'Dea, and K.I. Hopcraft, The effect of renewable energy incorporation on power grid stability and resilience, Science Advances, 2022 **8** (9).

[2] P. Schwach, X. Pan, and X. Bao, Direct Conversion of Methane to Value-Added Chemicals over Heterogeneous Catalysts: Challenges and Prospects, Chemical Reviews, 2017 **117** (13) 8497-8520.

[3] T. Zhang, Recent advances in heterogeneous catalysis for the nonoxidative conversion of methane, Chemical Science, 2021 **12** (38) 12529-12545.

[4] K. Ollegott, P. Wirth, C. Oberste-Beulmann, P. Awakowicz, and M. Muhler, Fundamental Properties and Applications of Dielectric Barrier Discharges in Plasma-Catalytic Processes at Atmospheric Pressure, Chem. Ing. Tech., 2020 **92** (10) 1542-1558.

[5] A. J. Zhang, A. M. Zhu, J. Guo, Y. Xu, and C. Shi, Conversion of greenhouse gases into syngas via combined effects of discharge activation and catalysis, Chemical Engineering Journal, 2010 **156** (3) 601-606.

[6] E. C. Neyts and A. Bogaerts, Understanding plasma catalysis through modelling and simulation - A review, J. Phys. D. Appl. Phys., 2014 **47** (22).

[7] F.J.J. Peeters and M.C.M van de Sanden, The influence of partial surface discharging on the electrical characterization of DBDs, Plasma Sources Sci. Technol., 2015 **24** (1).

[8] T. Butterworth and R.W.K. Allen, Plasma-catalyst interaction studied in a single pellet DBD reactor: dielectric constant effect on plasma dynamics, Plasma Sources Sci. Technol., 2017 **26**.