Pulsed electrical discharges in chemical processes intensification

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Abstract: Pulsed plasmas operating at atmospheric pressure can provide unique conditions to initiate various chemical processes. Among others, the plasma-initiated conversion of hydrocarbons is of particular interest for chemical industry electrification and transformation of the current paradigm based on the use of fossil fuels. Based on experimental results, chemical kinetics initiated by ns-duration plasma pulses are analyzed. It shows the importance of electron-impact driven pathways over other mechanisms in the initiation step of the process intensification.

1. Introduction

At present chemical industry is almost exclusively based on the use of fossil fuels leading to enormous CO_2 emissions above 900 Mt a year with an expected increase of 8% annually. Among the most energy-demanding chemical processes is natural gas reforming having also enormous CO_2 footprint. As such, decarbonization of the reforming process can provide a sustainable way of reaching the goal of the EU for 2050 on the reduction of fossil fuels and chemical industry electrification. On the way to achieve this challenging goal, a possible pathway is the use of electrical discharges. The advantages of plasma-intensification of chemical processes are (i) applicability at a low scale; (ii) use of electricity instead of fossil fuel; (iii) flexibility of the process and coupling with renewable electricity production; (iv) zero CO_2 footprint. Despite obvious advantages, hydrocarbon reforming was not yet implemented on an industrial scale as a deep understanding of the fundamentals behind plasma chemistry is still required at first. Here we discuss the kinetics of various species generated in plasma and compare the contribution of plasma with thermal effects appearing due to gas heating in the conditions of ns-pulsed discharges.

2. Methods.

The chemical process intensification is investigated in 10 ns pulsed discharge with MWs pulsed power in a pin-to-plate as well as pin-to-pin electrode arrangement. The plasma discharge generation process in CH_4 and CH_4/H_2 mixtures was studied by time-resolved emission spectroscopy, plasma imaging and laser scattering. Gas ionization in conditions of high-power pulses was investigated through time-resolved Stark broadening analysis of H_α line. Gas heating kinetics during the pulse was analyzed based on the detection of CH(A) and C_2 Swan bands appearing in the discharge spectra during the first 500 ns whereas gas temperature in the after-pulse phase was investigated by detection of Rayleigh laser scattering. The kinetics of primary active species was investigated by ns-laser induced fluorescence spectroscopy applied to study C_2, CH and H radicals and atoms.

2. Results and Discussion

The effect of gas pressure was investigated on selectivity and production of valuable hydrocarbons in high-power pulsed discharge at variable operational pressure from 0.5 to 3 bar. It was found that the discharge constriction strongly depends on the gas pressure. The plasma filament of 450 µm diameter was formed at 500 mbar that decreased to 150 µm at 1 bar which then stayed almost constant up to the highest tested pressure of 3 bar. Due to the high energy injected per pulse, the ionization degree in the discharge core could reach 0.5% or electron density of 1.8×10^{23} m^{-3} at 3 bar pressure and strongly depended on the pressure and admixing of H_2. The main phase of electron formation is observed during the current pulse whereas the recombination phase characterized by lower electron density can last till 900 ns, depending on operational conditions. The reason for long discharge decay has been attributed to mismatching of the impedance.

Next to electron kinetics, the gas heating kinetics was analyzed based on CH, C_2 emission and Rayleigh scattering. It showed that gas temperature strongly depends on operational pressure. The gas temperature rose during the discharge phase and after the pulse on µs time scale. Correspondingly, both electron-impact and thermal pathways can take place in reforming in conditions of ns-pulsed plasma. The heating kinetics was compared with the kinetics of CH and H species formation and also with 0D plasma kinetics model.

The integral approach, combining both experimental results and modelling, confirmed the importance of non-thermal processes in hydrocarbon reforming in conditions of pulsed high-power electrical discharges operating at a gas temperature below a critical value of 1300 K.

3. Conclusion

The kinetics of gas and electron heating coupled with the kinetics of primary active species reveals the significant role of electron-impact processes in intensifying hydrocarbons conversion in nanosecond pulsed plasmas. The contribution of electron impact processes in overall electrical energy transfer prevails at conditions of low gas heating below 1300 K.

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