DECOMPOSITION OF HYDROCARBONS
BY BACK-CORONA DISCHARGES

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Abstract
Back-corona discharge has been successfully applied for decomposition of hydrocarbons. Back-corona discharge is generated in a needle-to-plate reactor, with a corona-counter electrode covered with a perforated mica plate. The results of laboratory experiments show that the back-corona discharge can be more efficient in decomposition of hydrocarbons than positive dc streamer corona discharges.

1. Introduction
Back-corona discharge is a type of gaseous discharge that take place from the corona-counter electrode when this electrode is covered with a dielectric layer which can be made of a porous material or a solid one with small holes in it [1]. The objectives of the studies of the back-corona discharge were mainly spurred by the detrimental effects caused by this type of discharge in electrostatic precipitators [2-5], or electrostatic coating [6,7]. However, no one has tested the back-corona discharge as a plasma source for technological processes, and specifically for conversion of acid- or green-house gases. It is important to note that despite many different methods applied there still exists an urgent need for more efficient methods of exhaust gas cleaning.

The back-corona discharge as a source of plasma for chemical reactions seems to be competitive to other corona discharges (pulsed or dc corona discharges) or other low temperature plasma assisted methods (for example: electron beam, gliding arc, ferroelectric pellet layer discharge, ac dielectric barrier discharge [8]).

The purpose of this paper is to report a new method of gas cleaning based on the back-corona discharge, either positive or negative polarity. This type of discharge can efficiently decompose hydrocarbons in air as a carrier gas. The results of the measurements of the products obtained in the gas mixture treated by the back-corona discharges are compared with the measurements obtained for dc streamer corona discharge of positive polarity. The comparison was made in terms of the time of gas treatment and the energy delivered to the discharges.

2. Experimental
The plasma reactions were carried out in a glass cylinder of volume of 156 cm$^3$ in which the back-corona or dc streamer corona discharges were generated between two electrodes: a stainless steel needle and a plate, spaced 20 mm. To generate the back-corona discharge the metal plate was covered with a mica plate 80µm thick. In this plate seven small pinholes 200 µm in diameter were made: a central one placed in the needle
axis, and six symmetrically placed around the central one, on a circle of radius of about 2 mm.

The diagram of the experimental set-up is shown in Fig.1. The mixture was prepared in a mixing chamber from the saturated vapors of extracted petrol obtained in the vaporizer, and diluted by air, used as a carrier gas, taken directly from the atmosphere. The flow rates of both gas streams were controlled as to obtain the required concentration of hydrocarbons of 3500 ±50 ppm. Next, the valves were closed and the voltage switched on. The extracted petrol of commercial standards was used in our experiments. The main compounds of the extracted petrol were n-hexane (38% - mass concentration), methylcyclopentane (13%), cyclohexane (10%), 3-methylpentane (10%), and 2-methylpentane (5%). Other components, mainly aromatic hydrocarbons, of concentrations below 5% were not identified. In the following, all compounds of the extracted petrol will be referred to as C_{x}H_{y}. The plasma processes were operated in stationary gas and near NTP.

The needle in the corona discharge reactor (CDR) or back-corona discharge reactor (BCDR) is connected through the resistor R=13.6 MOhm to a high voltage dc source.

The gas samples were analyzed by a Fourier-transform infra-red (FTIR) spectrometer PERKIN-ELMER 16PC-FTIR in the 1000-4000 cm\(^{-1}\) spectral range with 2cm\(^{-1}\) resolution. In order to determine the energy delivered to the discharge, the voltage across the electrodes was measured by a high voltage probe TEKTRONIX P6015A, and the current waveforms were measured by means of a current monitor PEARSON 2878. Both of these waveforms were recorded by a digital storage oscilloscope TEKTRONIX 2440.

3. Results

Typical photographs of back-corona discharges in space-streamer mode, generated in the hydrocarbons are shown in Fig.2a and in Fig.2b for positive and negative polarity of the needle, respectively. In the lower parts of the photographs, in the pinholes, the back-corona glow, forming a bright craters is visible.

The back-corona discharge for positive polarity of point electrode operated initially in the streamer regime. When hydrocarbons were decomposed almost completely the type of discharge changed to a pulseless glow, the craters in the holes in the mica layer became faint. For negative polarity of point electrode, the back-corona discharge in gaseous hydrocarbons started shortly as an arc discharge, next changed to the streamer mode, and finally, when the hydrocarbons were decomposed, the glow discharge was generated, similarly to the positive polarity. It should be mentioned that back-corona discharge for negative polarity of point electrode is unstable in hydrocarbons and sometimes quenches for a few seconds.

Typical FTIR absorption spectra before and after the gas treatment by three discharges tested are shown in Fig.3. The wave number 2969 cm\(^{-1}\), was identified as the absorption line of C_{x}H_{y}. The mixture of C_{x}H_{y} in the air atmosphere was converted mainly to CO\(_2\), and H\(_2\)O. The CO, NO\(_2\), NO, and N\(_2\)O products (wavenumbers 2110 cm\(^{-1}\), 1599 cm\(^{-1}\), 1903 cm\(^{-1}\) and 2237 cm\(^{-1}\), respectively) were also identified after the gas treatment. From Fig.3 can be concluded that the positive back-corona discharge
Fig. 1 Scheme of the experimental set-up for decomposition of hydrocarbons

Fig. 2. Photographs of the positive (a) and negative (b) back-corona discharges in hydrocarbons. Exposure 5s.
Fig. 3 FTIR spectrum before (a) and after gas treatment by dc corona discharge (b), positive (c), and negative back-corona discharge (d).
produces less NOₓ and CO than dc streamer corona. The final concentration of the hydrocarbons after the treatment time of 60 s is also lower, and equals (530 and 215) ppm for positive and negative discharges, respectively.

The concentration of hydrocarbons as a function of treatment time for different discharges tested is shown in Fig. 4. The decomposition rate is initially most faster for dc streamer corona discharge, however the final concentration of hydrocarbons after the treatment time of 60 s remains at higher level than for positive back-corona discharge. The energy per one molecule required for a given conversion is shown in Fig. 5. The energy delivered to the discharge was estimated from the time-resolved waveforms of the current and voltage pulses.
4. Conclusions

The back-corona discharge methods for decomposition of hydrocarbons provide a promising alternative to other plasma assisted methods. The obtained results lead to the following conclusions:
1. The vaporous hydrocarbons in the air used as a carrier gas can be converted to CO₂, CO and H₂O in the back-corona discharges. In the experiments, N₂O, NO and NO₂ as a final reactions products were also identified.
2. The final concentration of hydrocarbons for back-corona discharge of positive polarity of the point electrode is lower than for dc streamer corona discharge.
3. The general conclusion from this study is that the reaction processes in back-corona discharges are energetically competitive with other treatment methods.
4. The back-corona discharge operates at lower voltages than the dc streamer corona in the same geometry, and for the same electrical circuit.

The future investigations of the decomposition processes would enable to optimize of the reaction system with regard to the chemical reactions and energy consumption. The back-corona discharge itself requires also further experimental investigations specifically for more complex geometries with new goals of the studies aimed at its practical usefulness.

References