I. INTRODUCTION

Smart electric power for process intensification is a challenging research field that integrates power engineering, chemistry and green technology. Conventional chemistry is one of the interesting target areas to be served by more efficient methods. Conventional chemistry is huge in energy consumption and waste production, costly in feedstock consumption, complicated in control and often needs high pressure, high temperature. Combustion is another area where huge gain is possible by introducing smart electric power with a smart interface. The main task is simple: couple the electric power efficiently and effectively into the process. It must be done in a smart way, be efficient in energy, be efficient in feedstock, and be very safe and cost effective. The interface between power and process is the crucial ingredient. A pulsed plasma is an ideal tool because it offers a controllable load to the electric circuit and a manageable source of chemical actors to the process. The power modulator is the source of electric power, the atmospheric plasma a convenient interface and the process is the final target. The two interfaces, power modulator to atmospheric plasma and the other one, the plasma to the process, are vitally important. Matching at the interfaces is a special research focus area. Here we can refer to the work in [1-4] and further in references like [5-14] to point out the importance of this subject.

II. MATCHING POWER SOURCE TO PLASMA: IMPEDANCE MATCHING

An elegant solution for impedance matching between pulse source and plasma is a transmission line transformer (TLT). Its advantages are: impedance control, voltage multiplication or current multiplication and DC path to ground [5,7,16-19]. Controlling the plasma impedance is the other issue. Fig. 2 shows the measured impedance of the streamer channels before complete...
transit [4, 15]. The ratio of measured load voltage to load current is shown. To simplify the interpretation, the contribution of the capacitive reactor current is subtracted from the experimental data. The results clearly reveal a constant impedance phase. The transition into the constant value platform occurs at the moment when the primary streamers reach the outer electrode. These moments have been indicated with cross markers in the figure. The impedance during the primary phase is a series connection of streamer resistance and remaining gap capacitance. To determine only the plasma resistance of the primary streamer channels we took the ratio of calculated voltage drop along the streamer and measured plasma current (excluding the measured capacitive current). The voltage drop along the streamers was calculated as the product of measured streamer length during transit and measured electric field (gap-average) \(E_{\text{gap}}\) upon arrival. It is assumed that this field was constant during transit of the streamers.

An example of the results of this calculation is shown in Fig. 3. The resistance of the primary and secondary streamers channels is constant. If the low value of \(E_{\text{cr}}\) of \(5\) kV/cm would be used to perform the calculations, the plasma resistance during the primary streamer phase would show a lower value (see Fig. 3). Nevertheless, even though the resistance of the primary streamers is constant, matching can only be optimized during for the secondary streamer phase. The modulator sees the complete impedance of the load: during the primary phase this includes the capacitance of the gap between the streamer heads and the plate electrode.

In Fig. 4 the results of a large collection of impedance measurements is shown [4]. The value of the constant resistance level as function of the applied voltage for various pulse conditions is plotted. As can be seen, independent of pulse width, pulse rise time and DC bias voltage, the plasma resistance tends to become equal to the output impedance of the source (200 \(\Omega\)) for increasing total reactor voltage. Apparently, the plasma matches automatically to the source if sufficient voltage is applied.

**III. MATCHING PLASMA TO PROCESS: ENERGY AND SPATIAL DISTRIBUTION**

The next step is matching the plasma power to the process. The plasma itself and the power source provide the tools. Two important parameters of the plasma are energy distribution and plasma spatial distribution. For smart activation we need to create a tunable electron cloud with energies in the range 1-10 eV i.e. electron energies tuned to the target process, or in case of plasma catalysis, tuned to vibrational excitation levels. Tuning is facilitated by controlling the plasma.

A result of an approach to tuning the electron energies in an atmospheric streamer discharge is given in Fig. 5. These data originate from the PhD study by Winands [4] and the later journal publication [9]. In this work the pulse width, rise time and voltage levels were varied. The resulting plasma parameters were recorded: electric energy input into the discharge, voltage levels, streamer dimension and number of streamers (CCD camera). The radical yield was derived from the measured ozone production by applying a kinetic model and a fitting procedure. The final results indicate that primary streamers have a higher O-radical yield than
secondary streamers.

It is generally assumed that primary streamers have high electric fields at their tip. These fields are higher than those of secondary streamers. High electric fields are causing high electron energies which explains the higher yield. Finally the effect of spatial distribution on processing is analyzed. For this specific purpose all possible complex chain reactions and branchings are approximated by the three single step reactions approach of the global chemical kinetic model proposed by Yan [2,13]. Multiple radical propagation and branching reactions are simplified by a one-step pollutant removal process. Radical generation is simplified by one production process. Various types of radical terminations are simplified by one linear termination process. It should be noted here that these are severe simplifications of the detailed processes that can occur, see e.g. [20] for the cases of toluene and limonene that we investigated. However, the application of the present simplified model to the cases of toluene and propane shows a good fit to experiments under a wide range of conditions. The simplified global model consists of one radical formation process and two general reaction processes: radical production R1, pollutant removal reaction R2 and radical linear termination reaction R3. Non-linear radical termination, unlike in Yan, is not considered here.

Radical production, $k_1 \quad M + \text{corona} \rightarrow Y$ (R1)

Pollutant removal reaction, $k_2 \quad C + Y \rightarrow B$ (R2)

Radical linear termination, $k_3 \quad M + Y \rightarrow D$ (R3)

where Y, C, B and D and M are radical, pollutant, by-products, and bulk gas compounds, respectively; $k_2$ and $k_3$ are reaction rate constants; $k_1$ is the initial radical production efficiency or radical yield in terms of power density, which is defined as ratio of input power during the pulse and plasma volume. The basic assumptions are:

1. A disk or slab of gas across the reactor (from wall to wall) is considered that moves through the reactor.
2. A small plasma region occurs in the slab during a short time, the pulse.
3. The ratio of the volumes of plasma region and slab, during one pulse, is defined as a.
4. We accept the simplification of homogeneous concentrations over the volume of the plasma regions inside the slab.
5. The production rate during the pulse in the plasma region is $k_1.p$ radicals per unit volume per second, where p is the constant power density in the plasma region during the pulse.

6. The radical concentration decays to zero before the next pulse starts.
7. In the inter-pulse period reaction products and gas compounds are uniformly redistributed over the slab.

Two scaling parameter are introduced: $\gamma = k_3M/k_2 = k_1\beta$ and $\beta = k_3M/(k_1k_2)$. After scaling all concentrations except M with this parameter $\gamma$, the set of equations for the dimensionless concentrations of radicals and pollutants in the plasma volume can be written as:

$$\frac{dY}{dt} = \frac{k_1p}{\gamma} - k_3 \frac{M Y}{C Y} \quad \text{(radical production and termination)}$$

$$\frac{dC}{dt} = - k_2 \frac{C Y}{\gamma} \quad \text{(pollutant removal)}$$

The analytic model further uses the notation: N as number of pulses after complete transit of the slab, $X = E/\beta$ as the scaled energy density received during complete transit, $\alpha = N.a$ as the ratio of repetitive plasma volume over reactor volume (i.e. after complete transit). Next, these momentary kinetic equations, as an average over the volume of a small plasma region are considered. Solving (1) and (2), integrating the result over the pulse duration and letting the concentrations redistribute from the plasma volume into the entire slab we can derive the following relation for the change in the relative pollutant concentration $\Delta Z_j = Z_j - Z_{j-1}$ in the slab after the $j$th pulse (Z is the redistributed C):

$$\Delta Z_j = aZ_{j-1} \{ \exp[-X/\alpha + N\Delta Z_j/\alpha] - 1 \}$$

Although this equation is implicit in the unknown $\Delta Z_j$ it can easily be solved in a simple numerical procedure. This procedure should be repeated for N pulses. The results show the behavior of the pollutant removal as function of global parameters like relative energy density $X = E/\beta$, overall filling ratio $\alpha$ or initial relative concentration $Z_0$. We can make a 3D surface plot of the pollutant decrease as function of $\alpha$ and $X$. The density $Z_0$ must be a given constant for such a plot. An example is given in Fig. 7. For purpose of estimation, we would like
to obtain some simple working formulas that describe the global behavior. We distinguish three limiting cases. The first case occurs for large $X/\alpha$. This condition simplifies (3) and allows repeating it for $N$ pulses. If $N$ is large, which mostly is true, we arrive at:

$$Z_N/Z_0 = \exp(-\alpha) \quad (4)$$

The next cases concern situations for small $X/\alpha$ ($\Delta Z_j$ will be small anyway). (3), after integration over $N$ pulses, leads then to the following expression:

$$Z_0 - Z_N + \log Z_0/Z_N = X \quad (5)$$

We distinguish the two sub cases:

Case 2 concerns situations with 'small $Z_0$ or large removal':

$$Z_N/Z_0 = \exp(-X) \quad (6)$$

Case 3 concerns situations with 'large $Z_0$ or small removal':

$$Z_N/Z_0 = 1 - X/Z_0 \quad (7)$$

This is the well-known expression for linear processing behavior. Turning to real concentration $S = Z/\gamma$ and real energy density $E = X/\beta$ and $\Delta S_N = S_N - S_0$, (7) reads:

$$-\Delta S_N = k_1 E \quad (8)$$

Pollutant removal data at large $Z_0$ or small $X$ can be easily used to find $k_1$ using this equation.

Summarizing:

At relatively low homogeneity ($X/\alpha > 1$) $\Rightarrow Z_N/Z_0 = \exp(-\alpha)$, i.e. the global filling ratio determines it all.

For higher levels of homogeneity ($X/\alpha < 1$) $\Rightarrow$ either $Z_N/Z_0 = \exp(-X)$ (at small $Z_0$ or large removal ratio) or $Z_N/Z_0 = 1 - X/Z_0$ (at large $Z_0$ or small removal ratio)

Fig. 7. Homogeneity offers huge gain in processing efficiency: outcome of the full model according to (3). Removal ratio $Z_N/Z_0$ is plotted vertically. The three plots represent typical examples of the three approximations.

IV. APPLICATION TO PULSED CORONA PROCESSING DATA

A data set on pulsed corona conversion of toluene and propane and 4 other gasses was analyzed as test of the applicability of the model. The data were obtained in a 3 meter long wire-cylinder reactor of 25 cm diameter. The power source to the reactor [6] has the following parameters: 100 - 1000 Hz repetition rate, 70 – 120 kV peak voltage, 100 – 200 ns pulse width, 0.2 – 1.5 kW average power. The pulse energies were measured with a fast D/I system mounted on the input to the reactor [7]. The pollutant concentrations were measured using a Gas Chromatograph with FID or TCD detector [7]. Standard flow and temperature detection were included for the reactor flow.

The analysis starts with plotting the measured values of $E/\Delta S_N$ versus $Z_N$ for each pollutant. Since, according to the model, $E/\Delta S_N$ will approximate $1/k_1$ at large values of $S_N$ (8), we can obtain an estimate for $k_1$ from these graphs. The graph for propane is shown in Fig. 8. The value $\gamma$ is obtained from the product of this $k_1$ with the fitting parameter $\beta$ ($\gamma = k_1 \beta$). In a next step $\beta$ will be used as fitting parameter for matching calculated removal to measured one. During all calculations the value for $\alpha$ was fixed at 0.002 (roughly in agreement with later CCD data; $\alpha$ is not a very sensitive parameter). The final results for propane and toluene are shown in Figs. 9, 10. Plotted are the measured and model pollutant reduction versus energy density. Each data point has two occurrences: the measured item and the model item. The correspondence is indicated when not clear. To quantify the agreement calculated pollutant removal is plotted versus measured pollutant removal. Ideally this should
give a line x=y. The deviations are shown in Fig. 11 for the case of toluene. The obtained prediction is excellent for four of the tested pollutants (R² is 0.98, 0.95, 0.87 and 0.86 for pentane, toluene, butane and propane) and good for ethylene and trichloroethane (R² is 0.74 and 0.73). These predictions are much better than predictions based on the simple formulas of case 2 or case 3 would be.

Real processes are very complex and specific as e.g. we show in [20]. But the present simple model based on formula 3, is capable of reproducing quite well the experimental data over a range of initial pollutant densities, energy densities and flow velocities or number of pulses.

REFERENCES


[18] P.W. Smith, Transient Electronics, John Wiley & Sons Ltd, 2002
