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Chemical engineering approach applied to non-thermal plasma reactors

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Abstract: In this article we apply chemical engineering concepts to describe the removal of atmospheric pollutants in non-thermal plasma reactors. We show that the removal efficiency is not only dependant on the so-called characteristic energy, but also on the relative importance of radical linear termination reactions and on the hydrodynamics of the reactor.

Keywords: non-thermal plasmas, chemical reaction engineering, VOC treatment.

1. Introduction

Non-thermal plasmas (NTP) are a promising solution for the treatment of volatile organic compounds and other atmospheric pollutants as NO_x or SO₂ [1-3]. Reactive species produced by non-thermal plasmas react with pollutant molecules to form less harmful products. For instance, volatile organic compounds may be oxidized by atomic oxygen produced by the plasma, yielding CO or CO₂.

Traditionally, most of non-thermal plasma reactors for such applications, based on corona or dielectric barrier discharges, have a channel shape. Inside the channel, a non-thermal plasma containing reactive species is produced. The treatment advances as pollutant molecules are exposed to the reactive species produced by the plasma and react to form other products. For example, figure 1 shows a surface dielectric barrier discharge used to generate a non-thermal plasma for the treatment of atmospheric pollutants.

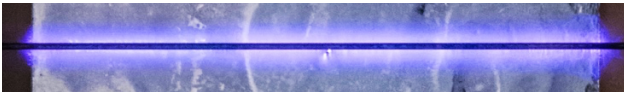


Fig. 1. Surface dielectric barrier discharge used to generate a non-thermal plasma for the treatment of atmospheric pollutants.

The reactor shape and dimensions will define how the gas will flow inside it and how the pollutants come into contact with the plasma reactive species. Therefore, geometrical aspects may have a major impact on the treatment efficiency. In spite of that, very few studies try to link the effect of hydrodynamics to the pollutant destruction efficiency of a given reactor.

This study tries to fill that gap. For that, we will use basic concepts of chemical reaction engineering. These concepts are well-established for classical homogeneous or heterogeneous reactors. They are an invaluable tool for the proper design and understanding of chemical reactors. Our goal is to apply them to plasma reactors, particularly in the scope of the treatment of atmospheric pollutants.

2. Basic chemical reaction engineering concepts

The following section is largely inspired from seminal work on chemical reaction engineering by J. Villiermaux [4]. The interested Anglophone reader will also find the concepts exposed here in the book by O. Livenspiel [5].

Chemical reaction engineering is a branch of process engineering dealing with the transformation and transfer processes taking place in reactors. And what happens in a reactor may be affected by:

- The nature of reactants, pressure, temperature, concentrations and flow rates at the inlet(s);
- Reaction thermodynamics and kinetics;
- Hydrodynamics, circulation and mixing;
- Heat, mass and momentum transfers;
- Reactor geometry.

All these may impact the conversion of reactants, as well as outlet products and their concentrations.

In order to simplify the approach to complex real reactors, ideal reactor configurations may be analysed. Three common ideal reactor configurations are:

- Batch reactor or well stirred reactor (WSR);
- Continuous stirred tank reactor (CSTR);
- Plug flow reactor (PFR).

The batch reactor is a closed reactor where a given quantity of mass reacts over time. Species concentrations and temperature are uniform inside the reactor. As there is no inlet or outlet flux, the species balance is written:

$$\frac{dn_j}{dt} = V\dot{\omega}_j \quad (1)$$

$$n_j(t = 0) = n_{j0} \quad (2)$$

where n_j is the number of moles of species j in the reactor, V the volume of the reactor and $\dot{\omega}_j$ the rate of production of moles of j per volume. $\dot{\omega}_j$ can be rewritten as:

$$\dot{\omega}_j = \sum_i \nu_{ij} r_i \quad (3)$$

where ν_{ij} is the number of moles of j produced (or destroyed if negative) per mole of reaction i , whose rate is r_i .

The continuous stirred tank reactor has an inlet and an outlet flow and works at stationary regime. As the batch reactor, the continuous stirred tank reactor also has uniform species concentrations and temperature, which are the same at the outlet. The species balance is written:

$$F_{j,in} + V\dot{\omega}_j = F_{j,out} \quad (4)$$

where $F_{j,in/out}$ are inlet and outlet molar fluxes of j .

In the plug flow reactor, the flow advances in a tube without axial diffusion. The species concentrations and temperature are supposed to be uniform in a given cross-section of infinitesimal thickness dx . In this case, the species balance is written:

$$\frac{dF_j}{dx} = S\dot{\omega}_j \quad (5)$$

where S is the cross-sectional area of the tube and:

$$F_j(x=0) = F_{j,in} \quad (6)$$

Further insight can be obtained for a single first-order reaction of type $A \rightarrow B$ with rate $r = kC_A$, where C_A is the concentration of A . In that case, the evolution of the concentration C_A can be obtained for each type of reactor according to equations 1, 3 and 4, respectively.

$$\text{Batch: } C_A/C_{A0} = \exp(-kt) \quad (7)$$

$$\text{CSTR: } C_A/C_{A,in} = 1/(1+k\tau) \quad (8)$$

$$\text{PFR: } C_A/C_{A,in} = \exp(-k\tau) \quad (9)$$

where $\tau = V/Q$ is the so-called space time (Q is the inlet flow rate).

Some important features of ideal reactors must be remarked at this point:

- I. A PFR of volume V is equivalent to an infinite number of CSTR of infinitesimal volume dV in series.
- II. A CSTR is equivalent to a PFR of same volume with infinite recirculation rate.
- III. A batch flow reactor and a PFR are analogous if there is no gas expansion. It means that results obtained with a batch reactor with time t can be transposed to results obtained with a PFR and residence time $\tau = t$.
- IV. The space time is only equal to the mean residence time if there is no gas expansion (or contraction) in the reactor.
- V. For a given reaction $A \rightarrow$ products of order n , optimal conversion of A is obtained with a PFR if $n > 0$, with a CSTR if $n < 0$. Conversions with PFR and CSTR are equal if $n = 0$.
- VI. For a first order reaction, $k\tau$ is the Damköhler number Da , which gives the ratio between the flow and the chemistry characteristic times. For a

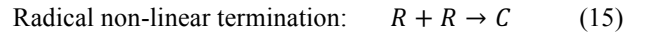
n -th order reaction, the Damköhler number is given by $Da = k_n C_{A,in}^{n-1} \tau$.

This last remark is of paramount importance. Whenever $n > 0$, a PFR configuration should be approached when designing a reactor. On the other hand, if $n < 0$, a CSTR configuration should be approached.

Thus, the kind of reactor used can greatly influence the conversion of a reactant A at a given space time $\tau = V/Q$, specially for high conversions. We can expect that the conversion of atmospheric pollutants in non-thermal plasma reactors may also be significantly affected by the reactor hydrodynamics.

3. Application to the treatment of atmospheric pollutants by non-thermal plasmas

In order to apply the concepts exposed above to non-thermal plasma reactors, we need an expression for the rate of reaction. For this, we use the four-reaction simplified kinetic model proposed by Rosocha and Korzekwa [6] and Yan et al. [7]:



For the sake of simplicity, we do not consider radical non-linear termination nor gas expansion in what follows. It can be shown that under certain assumptions, the pollutant removal rate is written:

$$\dot{\omega}_X = \frac{dC_X}{dt} = -\frac{k_X C_X G \bar{P}}{k_X C_X + k_M C_M} \quad (16)$$

where $\bar{P} = P/V$, with P the power dissipated in the plasma and V the reactor volume, k_X and k_M are the reaction rate constants for reactions 13 and 14, C_X and C_M the concentration of X and M , respectively, and G the number of radicals produced per energy unit.

Applying the species balance for a PFR (equation 5), and integrating from instant 0 to the space time τ , we can show that the concentration of X satisfies:

$$C_X - C_0 + \frac{k_M C_M}{k_X} \ln\left(\frac{C_X}{C_0}\right) = -G \bar{P} \tau \quad (17)$$

where C_0 is the initial pollutant concentration. This is the same equation obtained by Rosocha and Korzekwa [6]. On the other hand, if the species balance for a CSTR is applied (equation 4), it yields the algebraic equation:

$$C_0 \left(\frac{C_X}{C_0}\right)^2 + \left(\frac{k_M C_M}{k_X} + G \bar{P} \tau - C_0\right) \left(\frac{C_X}{C_0}\right) - \frac{k_M C_M}{k_X} = 0 \quad (18)$$

We then define:

$$\xi = C_X/C_0 \quad (19)$$

$$m = k_M C_M/k_X \quad (20)$$

$$\beta = (C_0 + m)/G \quad (21)$$

$$\bar{E} = \bar{P}\tau, \quad d\bar{E} = \bar{P}dt \quad (22)$$

The reader will remark that β and \bar{E} correspond respectively to the so-called characteristic energy and specific energy input (SEI). Equations 17 and 18 can be respectively rewritten as:

$$\frac{\xi-1}{m/C_0+1} + \frac{m/C_0}{m/C_0+1} \ln \xi + \frac{\bar{E}}{\beta} = 0 \quad (23)$$

$$\frac{1}{m/C_0+1} \xi^2 + \left(\frac{m/C_0-1}{m/C_0+1} + \frac{\bar{E}}{\beta} \right) \xi - \frac{m/C_0}{m/C_0+1} = 0 \quad (24)$$

We can see from equations 23 (PFR) and 24 (CSTR) that the removal of the pollutant X , given by $1 - \xi$, depends essentially on two non-dimensional numbers: \bar{E}/β and m/C_0 . The former is a Damköhler number, if we define the chemistry characteristic time as $\tau_c = \bar{P}/\beta$, and since the flow characteristic time is $\tau = \bar{E}/\bar{P}$. The number m/C_0 represents the importance of radical linear termination relative to radical loss by the pollutant removal reaction. Further, rewriting equation 16 according to equations 19-21, yields:

$$\frac{d\xi}{d\bar{E}} = -\frac{1}{\beta} \left(\frac{\xi + \xi m/C_0}{\xi + m/C_0} \right) \quad (25)$$

From equation 25 we can see that if $m/C_0 \gg 1$, the rate of pollutant removal with \bar{E} is of first order:

$$\frac{d\xi}{d\bar{E}} = -\frac{\xi}{\beta} \quad (26)$$

On the other hand, if $m/C_0 \ll 1$, we get a zero order rate:

$$\frac{d\xi}{d\bar{E}} = -\frac{1}{\beta} \quad (25)$$

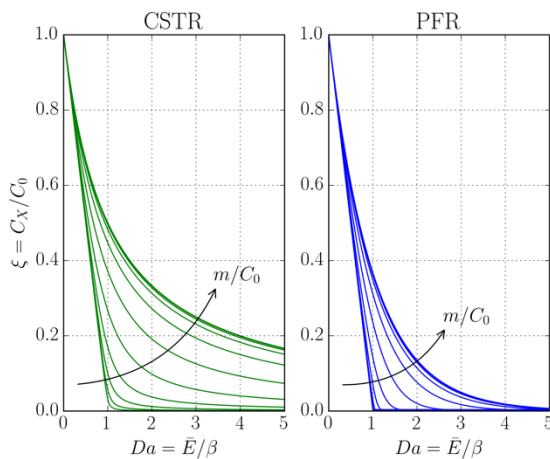


Fig. 2. Conversion of pollutant X as a function of the Damköhler number \bar{E}/β for a CSTR (left) and a PFR (right). Different curves on each side correspond to different values of m/C_0 , from logarithmically spaced from 10^{-3} to 10^3 and increasing in the arrows' direction.

Figure 2 shows the curves of ξ as a function of the Damköhler number $Da = \bar{E}/\beta$ for different values of m/C_0 for both CSTR and PFR reactors (equations 23 and 24, respectively). m/C_0 values are logarithmically spaced from 10^{-3} to 10^3 . The arrows indicate the direction of increase of m/C_0 . For $m/C_0 \ll 1$, curves for both CSTR and PFR approach the linear function $\xi = 1 - Da$, which corresponds to a 0th order reaction [4, 5]. On the other hand, when $m/C_0 \gg 1$, the curves approach the first order reaction laws given by equations 8 and 9 for CSTR and PFR, respectively. We can see that the higher the value of m/C_0 , the higher the differences of removal efficiency between PFR and CSTR. That is in accord with remark V of section 2.

4. Review of pollutant removal experimental data

In order to compare theoretical predictions from equations 23 and 24 for PFR and CSTR reactors, we collected 128 experimental datasets of pollutants removal by non-thermal plasmas. This collection includes several data on the removal of VOCs such as formaldehyde, ethanol, toluene but also of NO or NH₃. Non-thermal plasma generation methods include pulsed corona discharges or AC or pulsed dielectric barrier discharges, in both volume and surface configurations. Reactors' volumes, carrier gas composition, inlet temperatures and flow rates vary. The datasets have been obtained from figures available in a series of publications using *WebPlotDigitizer*, a free web application developed by Rohatgi [8]. The complete datasets in comma-separated values format (csv), including description and references are available at: <http://tinyurl.com/hvoy95w>.

The values of the initial concentration C_0 and of the characteristic energy have been obtained automatically. For this, the following algorithm was used:

- I. For each data set $(C_{Xk}, \bar{E}_k)_{k=1,\dots,N}$, select only values of k for which $C_{Xk} > 0.6 \times \max(C_{Xk})$. This is done because for high removal, the $C_X \times \bar{E}$ curve does not necessarily follows an exponential law. If the resulting length of (C_{Xk}, \bar{E}_k) is less than 4 after that filtering, consider the whole dataset instead.
- II. Fit the following function to each dataset:

$$C_X = C_0 \exp(-b\bar{E} + c\bar{E}^2) \quad (26)$$

This yields the value of C_0 .

- III. The value of the characteristic energy is then taken to be:

$$\beta = \bar{E}_{0.8} / \ln 0.8 \quad (27)$$

Where $\bar{E}_{0.8}$ satisfies:

$$0.8 = \exp(-b\bar{E}_{0.8} + c\bar{E}_{0.8}^2) \quad (28)$$

This method has several advantages. First, it allows us to obtain β automatically. Further, it takes into account small deviations from the exponential law $C_X = C_0 \exp(-b\bar{E})$ as \bar{E} increases. Indeed, we should expect

such deviations as seen in Figure 2. Finally, it avoids the estimation of asymptotical slopes when β is obtained from the logarithmic plot of $C_X \times \bar{E}$. Being so, this method could be used as a standard for the calculation of β from experimental data in future works.

In figure 3 we show the 128 analysed datasets with grey dots. Green and blue lines correspond respectively to CSTR and PFR at the first order reaction limit ($m/C_0 \gg 1$). Conversely, the black line corresponds to the zero order reaction limit ($m/C_0 \ll 1$). We see that most of the points remain roughly within the zero and first order reaction limits which have been described in section 3. Some other points find themselves above the CSTR first order reaction limit. That could be explained by some kind of fluid bypass in the reactor. As a whole, figure 3 encourages us to think that, beyond the Damkhöler number \bar{E}/β , the hydrodynamics of the reactor (PFR or CSTR) and the factor m/C_0 also determine the removal of an air pollutant by a non-thermal plasma reactor, specially for $\xi < 0.8$.

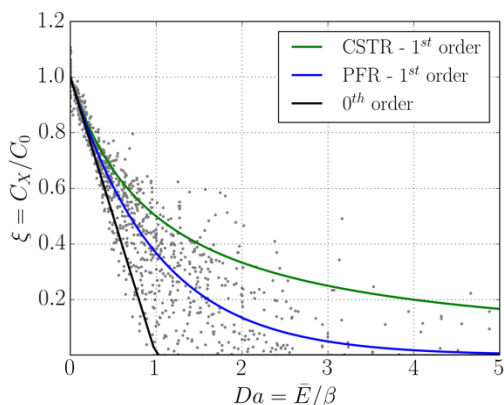


Fig. 3. Conversion of pollutant X as a function of the Damköhler number \bar{E}/β : comparison between 128 experimental datasets and theoretical predictions for CSTR and PFR ideal reactors, 1st order or 0th order reactions.

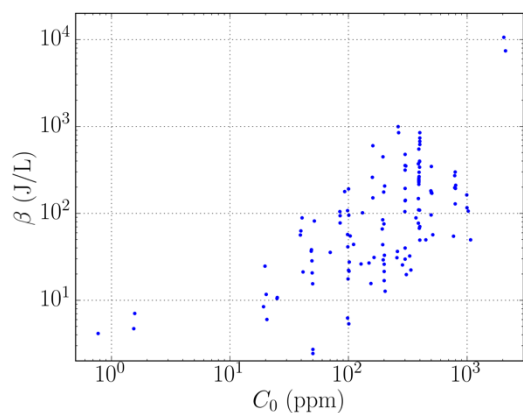


Fig. 4. Characteristic energy β as a function of the initial concentration for the 128 experimental datasets.

Figure 4 presents the values of β and C_0 for the 128 datasets. We can see that the values of β tend to increase with the initial concentration. However, for a given concentration β can vary by more than two orders of magnitude. This variation corresponds to different pollutants (which can be more or less easy to remove), background gases, inlet flow parameters and discharge characteristics.

5. Conclusions

In this work, we have firstly presented some basic chemical reaction engineering concepts. We have shown how the conversion of a given reactant may depend on the type of reactor, particularly for reaction orders different of zero. Secondly, we applied these concepts to the treatment of pollutants by non-thermal plasmas, using a simplified mechanism proposed by Rosocha and Korzekwa [6] and Yan et al. [7]. We show that the pollutant removal depends on a Damkhöler number defined as \bar{E}/β , on the factor m/C_0 which indicates the relative importance of radical termination reactions and on the type of reactor. Finally, we have compared theoretical predictions with 128 experimental datasets of pollutants removal by non-thermal plasmas ($C_X \times \bar{E}$ curves). Future work will include a more detailed investigation of each of these datasets in order to gain further insight into how can β and m/C_0 vary with experimental conditions, as well as how can reactor hydrodynamics different from CSTR and PFR ideal cases can impact the removal of a given pollutant.

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