Effect of gas mixture composition on tar removal process in a pulsed corona discharge reactor

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Abstract. Results of simulation of naphthalene removal from nitrogen and its mixture with water vapour by a sequence of corona discharge pulses are presented. A comparison of the data calculated on the basis of two approaches is presented: with approximate and detailed account of reactions involving charged species. It is shown that approximate account gives the efficiency of naphthalene removal close to that obtained basing on more detailed approach.

1. Introduction

The use of pulsed corona discharges is considered as a perspective method for gas cleaning from harmful admixtures [1]. In particular, it has been shown [2] that such discharges are effective tools for removal of heavy hydrocarbons (tars) from products of biomass gasification. In these works naphthalene removal by a sequence, including up to several thousands, of corona discharge pulses has been experimentally studied in pure nitrogen and its mixtures with H₂, CO, CO₂ and H₂O, at the initial tar content around 1000 ppm. The remaining tar molar fraction has been obtained as a function of the specific energy input.

In [3] the results of numerical modeling of naphthalene removal by pulsed corona discharges, for conditions close to those of experiment [2], have been presented. The simulation of the cleaning process included a description of two stages. The first, fast stage is generation of primary active species (radicals, ions, excited molecules and atoms) during the corona discharge pulses, the discharge having a structure of thin plasma filaments – streamers. The densities of primary active species obtained at streamer simulation were used as the input parameters for the modeling of the second, slow stage: the chain of chemical transformations triggered by the primary species.

For account of the role of ions as active species in the cleaning process an approximate approach was used in [3]: the ion-molecular reactions and electron-ion recombination processes were assumed to be infinitely fast. In this approach the reactions involving ions were accounted for as additional sources of primary neutral active species (atoms, radicals, excited molecules) and were not included to the kinetic scheme describing the chemical transformations at the second stage. In the given work for simulation of naphthalene removal in pure nitrogen and its mixture with water vapor a more rigorous approach is used, with explicit account of ion-molecule reactions and electron-ion recombination processes during the second, postdischarge stage of gas treatment. The modeling results based on these two approaches are compared with each other and with experimental data [2].

The consideration of more detail kinetics containing ions is aimed at more accurate account of reactions involving ions, as additional (to reactions between neutral species) effective channels of the
removal process, especially in strong electric field of pulsed corona discharge. The increased interest to the kinetic processes involving ions is noted also in other fields such as plasma assisted combustion and plasma medicine. The other aspect related with ion kinetics is associated with the role of electronegative gas admixtures in streamer start, propagation and branching phenomena [4].

2. Formation of primary active species during streamer propagation

The number densities of primary active species produced by the streamers are evaluated via corresponding G-values - the numbers of particles produced per 100 eV of input energy. For calculation of the G-values the method, based on streamer simulation, is used analogous to that described in [3]. At evaluation of the G-values for dissociation of nitrogen and water molecules the dissociation cross sections are taken from [5] and [6], respectively. The values $G_i$ for the production of active species of sort $j$ for a given mixture composition are estimated by weighting of partial G-values as

$$G_j = \sum_i X_i G_{ij}$$

where $X_i$ is the molar fraction of species of sort $i$, $G_{ij}$ is the partial G-value for production of species $j$ in the reaction of electrons with particles of sort $i$ (normalized to the molar fraction of species $i$ equal to unity). The partial G-values are assumed to be independent of the mixture composition, gas pressure, temperature, applied voltage and geometry of the discharge gap.

Obtained estimates for the partial G-values in nitrogen and its mixtures with water vapor are $G_{\text{OH}} = G_H = 1.4$, $G_{\text{N}(4S)} = G_{\text{N}(2D)} = 0.5$, $G_{\text{N}_2(A^3 \Sigma)} = 2.2$, $G_e = 0.7$. The G-value for production of $\text{N}_2(A^3 \Sigma)$ is estimated with account of cascade transitions from higher triplet and singlet states of nitrogen molecules. The dominating channel of nitrogen dissociation is assumed to be $\text{N}_2 + e \rightarrow \text{N}(4S) + \text{N}(2D) + e$ [7]. Note that some uncertainty exists concerning the G-values for $\text{N}_2$ and $\text{H}_2\text{O}$ dissociation. The effective dissociation cross sections are governed by competition of predissociation and collisional quenching and, hence, may decrease with growth of the gas density [8]. The cross section presented in [5] corresponds to low gas pressures, so that the evaluated, basing on this cross section, G-value for $\text{N}_2$ dissociation is an above estimate (in [3] twice lower G-value for this process was used). As for $\text{H}_2\text{O}$ dissociation, we assume, basing on the data given in [6], that its dominating channel is $\text{H}_2\text{O} + e \rightarrow \text{OH}^+ + \text{H} + e$. Note that in [9] another dissociation channel, $\text{H}_2\text{O} + e \rightarrow \text{O}^+(1D) + \text{H}_2 + e$, was taken as dominating.

The number densities $n_j$ of active species vary with the relative gas number density $\delta$ (the ratio of the gas number density to its normal value, $2.5 \times 10^{19} \text{ cm}^{-3}$, at the gas pressure of 1 bar and temperature of 300 K) as $\delta^2$. They are estimated as

$$n_j = \frac{G_j}{G_e} n_e \delta^2$$

where the evaluated G-value for generation of electrons is $G_e = 0.7$ and the number density of electrons $n_e$ is $5 \times 10^{14} \text{ cm}^{-3}$.

**Table 1.** G-values in pure $\text{N}_2$ (I, I a) and in 17.5%$\text{H}_2\text{O}$+82.5% $\text{N}_2$ mixture (II, II a).

|       | I  | I a | II   | II a |
|-------|----|-----|------|------|
| H     | –  | –   | 0.945| 0.245|
| OH    | –  | –   | 0.945| 0.245|
| $\text{N}_2(A^3 \Sigma)$ | 2.94| 2.24| 1.85 | 1.85 |
| N     | 0.5| 0.5 | 0.42 | 0.42 |
| $\text{N}(^2\text{D})$ | 0.5| 0.5 | 0.42 | 0.42 |
| $\text{N}_2^+$ | – | 0.7 | – | 0.55 |
| $\text{H}_2\text{O}^+$ | – | – | – | 0.15 |
| E     | –  | 0.7 | –   | 0.7  |
In table 1 the \( G \)-values are given in pure nitrogen and its mixture with \( \text{H}_2\text{O} \) for two approaches: the first approach, described in [3], (columns I and II) estimates contribution of ions approximately, the second one (columns Ia and IIa) is based on inclusion, to the kinetics scheme, of reactions involving ions. These data are used at the modeling of the postdischarge stage of the cleaning process.

3. Results and discussions

The simulations have been performed for the conditions of experiments [2]: at pressure of 1 bar and temperature of 200º C, other parameters are indicated in [3]. The results in [3] have been obtained for pure \( \text{N}_2 \) and mixtures 90%\( \text{N}_2 \)+10%\( \text{CO}_2 \), 80%\( \text{N}_2 \)+10%\( \text{CO}_2 \)+10%\( \text{CO} \) and 50%\( \text{N}_2 \)+20%\( \text{CO} \)+12%\( \text{CO}_2 \)+17%\( \text{H}_2 \)+1%\( \text{CH}_4 \). Here the modeling results for the mixture of nitrogen with water vapor 17.5%\( \text{H}_2\text{O} \)+82.5%\( \text{N}_2 \) are discussed and compared with results for pure nitrogen. The initial (just after streamer stage) gas composition for two mixtures is given in table 2, evaluated in accordance with \( G \)-values from table 1.

### Table 2. Initial concentration of components in pure \( \text{N}_2 \) (I, Ia) and in 17.5%\( \text{H}_2\text{O} \)+82.5%\( \text{N}_2 \) mixture (II, IIa).

| Components | I \( \text{cm}^{-3} \) | Ia \( \text{cm}^{-3} \) | II \( \text{cm}^{-3} \) | IIa \( \text{cm}^{-3} \) |
|------------|----------------|----------------|----------------|----------------|
| \( \text{N}_2 \) | 1.50\( \times \)10^{19} | 1.50\( \times \)10^{19} | 1.24\( \times \)10^{19} | 1.24\( \times \)10^{19} |
| \( \text{H}_2\text{O} \) | – | – | 2.63\( \times \)10^{18} | 2.63\( \times \)10^{18} |
| \( \text{C}_{10}\text{H}_8 \) | 1.33\( \times \)10^{16} | 1.33\( \times \)10^{16} | 1.24\( \times \)10^{16} | 1.24\( \times \)10^{16} |
| \( \text{H} \) | – | – | 2.52\( \times \)10^{14} | 6.53\( \times \)10^{13} |
| \( \text{OH} \) | – | – | 2.52\( \times \)10^{14} | 6.53\( \times \)10^{13} |
| \( \text{N}_2\text{(A}^3\Sigma) \) | 7.83\( \times \)10^{14} | 5.97\( \times \)10^{14} | 4.92\( \times \)10^{14} | 4.92\( \times \)10^{14} |
| \( \text{N} \) | 1.33\( \times \)10^{14} | 1.33\( \times \)10^{14} | 1.10\( \times \)10^{14} | 1.10\( \times \)10^{14} |
| \( \text{N}\text{(D) } \) | 1.33\( \times \)10^{14} | 1.33\( \times \)10^{14} | 1.10\( \times \)10^{14} | 1.10\( \times \)10^{14} |
| \( \text{N}_2\text{ }+\text{ } \) | – | 1.86\( \times \)10^{14} | – | 1.46\( \times \)10^{14} |
| \( \text{H}_2\text{O}^+ \) | – | – | – | 4.00\( \times \)10^{13} |
| \( \text{E} \) | – | 1.86\( \times \)10^{14} | – | 1.86\( \times \)10^{14} |

In figure 1 the remaining fraction of naphthalene is shown versus the specific energy input in pure \( \text{N}_2 \) and in the mixture of 82.5% \( \text{N}_2 \)+17.5% \( \text{H}_2\text{O} \). Two cases are considered: with approximate account of contribution of ions (I and II) and with inclusion of ion reactions in the kinetics scheme (Ia and IIa). One can see that the results are almost identical. Note that addition of \( \text{H}_2\text{O} \) increases the calculated cleaning efficiency, in agreement with experimental data, whereas the addition to nitrogen of such gases as \( \text{CO} \), \( \text{CO}_2 \) and \( \text{H}_2 \) decreases the removal efficiency [3].

![Figure 1. Naphthalene decomposition in mixtures versus the specific energy input in the gas. Symbols are experiments, lines are calculations; dash lines (I and II) are first approach, solid lines (Ia and IIa) are second one.](image-url)
The leading reactions in pure nitrogen are presented and discussed in [3]. In this case the main reactions for C\(_{10}\)H\(_8\) destruction are:

\[
\begin{align*}
N_2(A^3\Sigma) + C_{10}H_8 & \rightarrow \text{products}, \quad k = 1.6 \times 10^{-10} \text{ cm}^3\text{s}^{-1}, [10], \\
N'(2D) + C_{10}H_8 & \rightarrow \text{products}, \quad k = 3 \times 10^{-11} \text{ cm}^3\text{s}^{-1}, [10], \\
N_2(A^3\Sigma) + N_2(A^3\Sigma) & \rightarrow N_2 + N_2(B^3\Pi, C^3\Pi), \quad k = 4 \times 10^{-10} \text{ cm}^3\text{s}^{-1}, [10].
\end{align*}
\]

In the mixture of 82.5\%N\(_2\)+17.5\%H\(_2\)O other channels are added to the reactions mentioned above:

\[
\begin{align*}
\text{OH} + C_{10}H_8 & \rightarrow H_2O + C_{10}H_7, \quad k = 1.1 \times 10^{-17}T^2 \exp(-969/T) \text{ cm}^3\text{s}^{-1}, \\
\text{H} + C_{10}H_8 & \rightarrow \text{products}, \quad k = 1.4 \times 10^{-9} \exp(-2566/T) \text{ cm}^3\text{s}^{-1}, \\
\text{H} + C_{10}H_7O & \rightarrow C_{10}H_7OH, \quad k = 1.7 \times 10^{-10} \text{ cm}^3\text{s}^{-1}, \\
\text{O} + C_{10}H_8 & \rightarrow H + C_{10}H_2O, \quad k = 2.3 \times 10^{-11} \exp(-902/T) \text{ cm}^3\text{s}^{-1}.
\end{align*}
\]

The rate constants of these reactions were taken from [11] (see the discussion in [3]).

Below the processes involving charged species (electrons and ions) are considered. The chain of fast ion-molecule reactions transforms primary positive ions N\(_4\)\(^+\) and H\(_2\)O\(^+\) to more stable positive ions N\(_4\)\(^+\) and H\(_3\)O\(^+\).

\[
\begin{align*}
\text{N}_2 + N_2 \rightarrow N_4^+ + M, \quad k = 1.5 \times 10^{-26}T^{-1} \text{ cm}^6\text{s}^{-1}, [12], \\
\text{H}_2O + H_2O^+ \rightarrow OH + H_3O^+, \quad k = 1.7 \times 10^{-9} \text{ cm}^3\text{s}^{-1}, [13], \\
\text{H}_2O + N_2^+ \rightarrow N_2 + H_2O^+, \quad k = 2 \times 10^{-9} \text{ cm}^3\text{s}^{-1}, [14], \\
\text{H}_2O + N_2^+ \rightarrow N_2 + N_2 + H_2O^+, \quad k = 3 \times 10^{-10} \text{ cm}^3\text{s}^{-1}, [14].
\end{align*}
\]

The latter recombine with electrons with production of radicals:

\[
\begin{align*}
e + N_2^+ & \rightarrow N_2 + N_2(A^3\Sigma) \quad k = 6.0 \times 10^{-4}T^{-1} \text{ cm}^3\text{s}^{-1}, \quad \text{(*)}, \\
e + N_2^+ & \rightarrow N_2 + N_2(A^3\Sigma) + M \quad k = 9.35 \times 10^{-21}T^{-2.5} \text{ cm}^6\text{s}^{-1}, [14], \\
\text{H}_2O + e + H_2O^+ & \rightarrow OH + H + H_2 \quad k = 7.81 \times 10^{-8}T^{-4.5} \text{ cm}^3\text{s}^{-1}, [13], \\
e + e + H_2O^+ & \rightarrow H_2O + e \quad k = 2.4 \times 10^{-6}T^{-0.5} \text{ cm}^3\text{s}^{-1}, [14], \\
e + H_2O^+ & \rightarrow O + H + H \quad k = 3.0 \times 10^{-6}T^{-0.5} \text{ cm}^3\text{s}^{-1}, [14], \\
e + H_2O^+ & \rightarrow O + H_2 \quad k = 2 \times 10^{-4}T^{-0.5} \text{ cm}^3\text{s}^{-1}, [14], \\
H_2O + e + H_2O^+ & \rightarrow OH + H + H_2O \quad k = 2 \times 10^{-7} \text{ cm}^3\text{s}^{-1}, [16].
\end{align*}
\]

The evolution of concentrations of these ions in streamer trace is demonstrated in figure 2; the time of electron-ion recombination is about 10 ns. Note that in the previous approach [3] the influence of ions was estimated only through reaction (*)..

The evolution of produced radicals is shown in figure 3; the lifetime of O, OH and H radicals is around one millisecond, in contrast to excited nitrogen molecules, with lifetime about 10 \(\mu\)s. Due to the presence of water an additional quenching of the radicals most effective for removal, namely N\(_2\)(A\(^3\Sigma\)) and N\(^{(3)D}\), takes place in the reactions [10]:

\[
\begin{align*}
\text{H}_2O + N_2(A^3\Sigma) & \rightarrow OH + H + N_2 \quad k = 5 \times 10^{-14} \text{ cm}^3\text{s}^{-1}, \\
\text{H} + N_2(A^3\Sigma) & \rightarrow H + N_2 \quad k = 2.2 \times 10^{-10} \text{ cm}^3\text{s}^{-1}, \\
N(3D) + H_2O & \rightarrow NH + OH \quad k = 1.3 \times 10^{-11} \text{ cm}^3\text{s}^{-1}.
\end{align*}
\]

The decomposition of formed complex ions also gives the additional H and OH radicals:

\[
\begin{align*}
\text{H}_2O + H_2O^+ + M & \rightarrow H_3O^+(H_2O) + M \quad k = 9.6 \times 10^{-20}T^{-1} \text{ cm}^3\text{s}^{-1}, [13], \\
\text{H}_2O + e + H_2O^+ & \rightarrow OH + H + H_2O \quad k = 2 \times 10^{-13} \text{ cm}^3\text{s}^{-1}, [17], \\
\text{H}_2O + H_2O^+ + M & \rightarrow H_2O + H_2O^+(H_2O) + M \quad k = 4 \times 10^{-29} \text{ cm}^3\text{s}^{-1}, [17].
\end{align*}
\]

The decomposition of formed complex ions also gives the additional H and OH radicals:

\[
\begin{align*}
e + H_3O^+(H_2O)_2 & \rightarrow H + 3H_2O \quad k = 1.56 \times 10^{-1}T^{-0.2} \text{ cm}^3\text{s}^{-1}, [14], \\
e + H_3O^+(H_2O)_2 + M & \rightarrow H + 3H_2O + M \quad k = 7.79 \times 10^{-20}T^{-2.5} \text{ cm}^3\text{s}^{-1}, [14].
\end{align*}
\]
Figure 2. Evolution of ions in the mixture of 17.5% H$_2$O+82.5% N$_2$ in streamer trace.

Figure 3. Evolution of radicals in the mixture of 17.5% H$_2$O+82.5% N$_2$ in streamer trace.

The time dependencies of the densities of complex ions and electrons in the streamer trace in first tens of discharge pulses are presented in figure 4, where the data inside the streamer channels are shown. After averaging the concentrations inside and outside the channels (see [3]), the remaining in the reactor the ions OH$^-$(H$_2$O) and H$_3$O$^+$(H$_2$O)$_2$ have concentrations about 1·10$^9$ cm$^{-3}$. With the growth of NO$_2$ concentration the contribution of ion NO$_2^-$ (H$_2$O) in neutralization of positive complex ion H$_3$O$^+$(H$_2$O)$_2$ increases:

\[ \text{H}_2\text{O} + \text{OH}^- + \text{M} \rightarrow \text{OH}^-(\text{H}_2\text{O}) + \text{M} \]

\[ k = 2.5 \cdot 10^{-28} \text{ cm}^6\text{s}^{-1} \]

\[ \text{NO}_2^- + \text{OH}^-(\text{H}_2\text{O}) \rightarrow \text{OH} + \text{NO}_2^-(\text{H}_2\text{O}) \]

\[ k = 1.5 \cdot 10^{-11} \text{ cm}^3\text{s}^{-1} \]

\[ \text{NO}_2^-(\text{H}_2\text{O}) + \text{H}_3\text{O}^+\text{(H}_2\text{O})_2 \rightarrow 4\text{H}_2\text{O} + \text{HNO}_2 \]

\[ k = 5.0 \cdot 10^{-15} \text{ cm}^3\text{s}^{-1} \]

Besides chemical transformations in reactions with active species, the naphthalene experiences the thermal decomposition, both in the discharge reactor and in the inactive volume [2,3]. The more is the treatment time, the more amount of naphthalene is thermally decomposed. In the considered nitrogen-water mixture, at the initial C$_{10}$H$_8$ molar fraction of 825 ppm, during 18 min of treatment 10 ppm of C$_{10}$H$_8$ is thermally decomposed.

Note that the effect of formation of tar ions in ion-molecular reactions with participation of tar molecules may be neglected, because the time of this process is (at number densities of tar molecules
about $10^{16}$ cm$^{-3}$ and rate constants $\sim 10^{9}$ cm$^3$/s [18]) about $10^{-7}$ s, much larger than the time of dissociative recombination.

4. Conclusions

The comparison of two approaches to the modeling of tar removal in the pulsed corona reactor has been performed. In the framework of the first approach it is assumed that the ion-molecule reactions are infinitely fast and may be taken into account approximately at estimation of the G-values for primary neutral active species. The second one is based on the consideration of plasma-chemical kinetics with participation of ions and electrons. The results of calculations have shown that the difference between the values of removed C$_{10}$H$_8$ concentration obtained using these two approaches, both in pure N$_2$ and its mixture with H$_2$O, is weak. It follows that at simulation of cleaning process the effects related with charged species may be estimated approximately, as additional contributions to the G-values for primary neutral active species.

References

[1] van Veldhuizen E M (ed) 2000 Electrical Discharges for Environmental Purposes: Fundamentals and Applications (New York: Nova Science)

[2] Nair S A, Pemen A J M, Yan K, van Heesch E J M, Ptasinski K J and Drinkenburg A A H 2003 Plasma Chem. Plasma Process. 23 665

Pemen A J M, Nair S A, Yan K, van Heesch E J M, Ptasinski K J and Drinkenburg A A H 2003 Plasmas and Polymers 8 209

Nair S A, Yan K, Pemen A J M, van Heesch E J M, Ptasinski K J and Drinkenburg A A H 2005 Ind. Eng. Chem. Res. 44 1734

[3] Bityurin V A, Filimonova E A and Naidis G V 2009 IEEE Trans. Plasma Sci. 37 911

[4] Pancheshnyi S 2005 Plasma Sources Sci. Technol. 14 645

[5] Itikawa Y 2006 J. Phys. Chem. Ref. Data 35 31

[6] Itikawa Y and Mason N 2005 J. Phys. Chem. Ref. Data 34 1

[7] Zipf E C and McLaughlin R W 1978 Planet. Space Sci. 26 449

[8] Slovetsky D I 1980 Mechanisms of Chemical Reactions in Nonequilibrium Plasmas. (Moscow: Nauka)

[9] Yousfi M Bekstein A, Merbahi N, Eichwald O, Ducasse O, Benhenni M and Gardou J P 2010 Plasma Sources Sci. Technol. 19 034004

[10] Herron J T 1999 J. Phys. Chem. Ref. Data 28 1453

[11] NIST Chemical Kinetics Database on the Web, http://kinetics.nist.gov

[12] Gordiets B, Ferreira C M , Pinheiro M J and Ricard A 1998 Plasma Sources Sci. Technol. 7 363

[13] Bychkov V L and Yurovskii V A 1993 High Temp. 31 5 (Translated from Teplofiz. Vys. Temp. 31 8)

[14] Matzing H Tech. Report Kernforschungszentrum Karlsruhe, KfK 4494, 1989

[15] Cao Y S and Johnsen R 1991 J. Chem. Phys. 95 1991

[16] Viggiano A A, Ehlerding A, Hellberg F, Thomas R D, Zhaunerych V, Geppert W D, Montaigne H, Larsson M, Kaminska M and Osterdahl F 2005 J. Chem. Phys. 122 226101

[17] Popov N A 2010 Plasma Phys. Rep. 36 (Translated from Fiz. Plasmy 36 867)

[18] Midey A 1999 Sci. Report AFRL-VS-TR-2002- 610-1590