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PlasTEP - Standardisation and requirements: Methodology for comparison Part 1

1. Motivation

The idea of standardisation of plasma technologies for environmental protection is to attract the interest of potential industrial stakeholders to the advantages of the plasma-based technologies in comparison to alternatives. Therefore, the knowledge of how different plasma technologies work must be build up and the technologies must be compared to understand which of them is the most useful for a given problem.
Since there is a great variety of plasma technologies already available and also under investigation, it is necessary to focus on such a comparison with regard to the needs of the stakeholders. Their interest in cost efficiency and reduction needs to be within the scope of this standardisation. Therefore, the costs for investment and operation of the different technologies need to be taken into account. Primary values in this field are:

- Power consumption, per volume (exhaust flow)
- Warranty intervals, per operation time
- Consumption of additives, per amount of contamination
- Investment costs

But also from the scientific point of view it is interesting to compare the different plasma-based technologies. For this approach, the experiments require the same or at least very similar conditions. For the comparison the similarity parameters are of interest, as inter alia the specific energy density (SED, see next paragraph).

2. Parameters for comparison

G-value:

Baird et al. 1990 [1]: *The G-value refers to the number of molecules of a reactant consumed or products formed per 100eV of energy absorbed.*

Taken from radiation chemistry, results from the chemical reactions and stoichiometry are given as:

$$G(-A)= \beta_A \cdot p_A \cdot Q \cdot N_0 / (E \cdot R \cdot T)$$

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with –A being the removed species, β_A the percentage of destroyed A, p_A the partial pressure of A, Q the volume flow rate, N_0 the Avogadro constant, E the used energy (measured e.g. by calorimetry), R the gas constant and T the absolute temperature.

Penetrante et al. 1996 [2]: *The G-value is the number of reactions per 100 eV of input energy* calculated from:

$$G = 100 \cdot k / (v_d \cdot E/n)$$

with k being the rate coefficient, v_d the drift velocity of the electrons and E/n being the reduced electric field strength.

Since those definitions lack of the energy consumption for ignition and maintenance of the plasma, a factor for each plasma reactor should be included. This factor should provide the following features:

Residence time: Ratio τ of the capacity of a system V to hold a substance and the flow rate q of that substance into that system:

$$\tau = V / Q$$

Specific energy density (SED): The dissipated discharge power divided by the flow rate:

$$SED = P / Q$$

also: SEI (Specific Energy Input) or SIE (Specific Input Energy).

Energy yield:

1) The ratio of the electric energy which goes into the discharge rather than into an external circuit. [3]

2) The ratio of the concentration and the SED multiplied by the molecular weight of the gas compound:

$$EY = \Delta\, c[C] \cdot m / SED$$

Selectivity (chemical): The chemical selectivity S_X of one possible chemical product X is given by the ratio of its concentration (or number density of molecules etc.) and the sum of concentrations of all possible products of one reaction. For example:

$$S_{CO2}\,(\%) = c[CO_2] / (c[CO_2] + c[CO]) \times 100$$

Removal efficiency: The removal efficiency η_X states how many particles of a certain substance X were removed during the process. For example:

$$\eta_X\,(\%) = (c[X_{Inlet}] - c[X_{Exhaust}]) / c[X_{Inlet}] \times 100$$

to be finished with energy constant.

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3. Standard conditions for comparison of NTP processes

3.1 Gas standards

The standards are necessary for the comparison of the different processes and technologies. Since there are two different fields of application possible, the treatment of exhaust gases from engines and the treatment of off-air in VOC producing industries, two standards are advisable. This is due to the fact that the gas composition has a significant influence on the plasma chemistry. Nevertheless a simplification is useful.

Exhaust gases

For the exhaust gas the following compositions are possible and to be discussed:

<table>
<tr><th>Source</th><th colspan="2">Typical diesel exhaust composition Hammer [4]</th><th>Solid fuel (hard coal)[1] [5]</th><th>Liquid fuel (heavy fuel oil)[2] [6]</th><th>McAdams et al. Marine diesel [7]</th><th>Penetrante 1999 [8]</th><th>WTE[3] raw gas</th><th>WTE[4] clean gas (tail end SCR)</th><th>Filimonova et al. Simulation 2000 [9]</th></tr>
<tr><td>N_2</td><td colspan="2">Balance</td><td>75.75%</td><td>71.6%</td><td>Balance</td><td>90 %</td><td>Balance</td><td>Balance</td><td>80,24 %</td></tr>
<tr><td>O_2</td><td colspan="2">13%</td><td>9.95%</td><td>3.1%</td><td>15 %</td><td>10 %</td><td>6 %</td><td>7 %</td><td>17,86 %</td></tr>
<tr><td>NO</td><td>>80 %</td><td rowspan="2"><1000 ppm</td><td rowspan="2">682 ppm</td><td rowspan="2">230 ppm</td><td rowspan="2">1200 ppm</td><td>500 ppm</td><td rowspan="2">225 ppm</td><td rowspan="2">15-25 ppm</td><td>125 ppm</td></tr>
<tr><td>NO_2</td><td><20 %</td><td>-</td><td>75 ppm</td></tr>
<tr><td>SO_x (SO_2)</td><td colspan="2">-</td><td>1330 ppm</td><td>1500 ppm</td><td>0-1000 ppm</td><td>-</td><td>260 ppm</td><td>0-5 ppm</td><td>-</td></tr>
<tr><td>CO_2</td><td colspan="2">5 %</td><td>8.3%</td><td>11.25%</td><td>-</td><td>-</td><td>?</td><td>9 %</td><td>1,9 %</td></tr>
<tr><td>CO</td><td colspan="2"><1000 ppm</td><td>-</td><td>-</td><td>-</td><td>-</td><td>0</td><td>0</td><td>780 ppm</td></tr>
<tr><td>VOC</td><td colspan="2"><1000 ppm</td><td>-</td><td>-</td><td>Propene (7200 ppm)</td><td>(1000 ppm C_3H_6)[5]</td><td>-</td><td>-</td><td>100 ppm CH_2O</td></tr>
<tr><td>H_2O</td><td colspan="2">5%</td><td>6.0%</td><td>13.8%</td><td>0-5%</td><td>-</td><td>15 %</td><td>< 10 %</td><td>-</td></tr>
<tr><td>Temp.</td><td colspan="2">650 °C</td><td>140°C</td><td>224°C</td><td>250 °C u. 350 °C</td><td>300 °C</td><td>160 °C</td><td>60-70 °C</td><td>60 °C</td></tr>
</table>

Table 1 Gas compositions of experiment, simulation and industrial sites.

After discussion, the following project standard containing all main components and aspects was defined as given in table 2:

[1] Dust emission not listed (400 mg/Nm³).
[2] Dust emission not listed (170 mg/Nm³).
[3] WTE-Waste to Energy off-air; contains 750 ppm HCl, too.
[4] It contains less than 3 ppm HCl and less than 6 ppm NH_3, too.
[5] Different experiments, once with and once without HC.

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Component	Concentration
N_2	80 % / Balance
O_2	10 %
NO	400 ppm
NO_2	21 ppm
SO_2	-
CO_2	5 %
CO	100 ppm
VOC= C_3H_6	500 ppm
H_2O	5 %
Temp.	60 °C

Table 2 PlasTEP exhaust gas standard.

VOC enriched air

As the standard for off-air VOC treatment, synthetic air with an admixture of ethyl acetate and toluene in different concentrations is proposed. Toluene is a common VOC which is already studied under different conditions by different groups [10, 11, 12]. Ethyl acetate is known as the standard VOC in many applications and industrial sites [13] and used as a standard in industry (ethyl acetate guide value). Therefore, our suggestion would be a mixture of **90% ethyl acetate and 10% toluene** in synthetic air. Since it was already mentioned by the company Rafflenbeul [14], the off-air treatment with plasma-based technology is cost-effective compared to other technologies only for pollutant concentrations of total hydrocarbons (HC) of less than 1 gC_{org}/m^3. Thus, for the given mixture of the mentioned components the maximum of concentration is 225 ppm of ethyl acetate and 25 ppm of toluene. The odour threshold of toluene is at 2 ppm [15], the one for ethyl acetate is at 3.9 ppm [16] in air. More precisely, the minimum of toluene concentration should be higher than 2 ppm. Thus, the following three concentrations are suitable as standard:

	Maximum	Mean value	Minimum
Ethyl Acetate	200 ppm	100 ppm	30 ppm
Toluene	20 ppm	10 ppm	3 ppm

Table 3 Proposed VOC compositions.

As background gas synthetic air at room temperature should be used. The humidity should not exceed 2 % by vol. of H_2O.

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3.2 Mechanical standards

In any case, an important role is attributed to the spatial parameters of the reactors and the flow rate of the gas. Both the flow rate and the spatial parameters are still to be discussed. Nevertheless, they should be close to industrial standards. In the case of the dimensions of the reactors, the minimum size of the electron beam arrangement needs to be taken into account. Any other standard that needs to be regarded still needs to be discussed.

Diagnostic Requirements

For the comparison of the different technologies, the diagnostics of the laboratories also need to be standardised. This means that the diagnostics need to be performed in a comparable way. The main features are:

Electrical diagnostics

As electrical diagnostics two major and two minor values are necessary. For the scientific approach, the discharge power is necessary to characterise the plasma. This can be measured e.g. by Lissajous figures. Next to the discharge power, the applied voltage and the discharge current should be oscillographed. As an important value for the industry, the plug power is useful to know. Since these are parameters which cannot always be given for the electron beam flue gas treatment, a similar parameter for this special arrangement need to be found.

From these values and the knowledge of the flow rate, the specific input energy (SIE) can be calculated. In a similar way as already mentioned, a parameter for the EBFGT can be calculated.

Gas diagnostics

In addition to the electrical diagnostics of the plasma the diagnostics of the gas is also important. Next to the temperature, the gas components must be analysed, e.g. with an FTIR. But, here it is important to avoid cross sensitivity and the interference of different components. Furthermore, it has to be discussed if a special particle analysis should be done.

However, it still should not be forgotten to mention commercial solutions for a constant overall VOC measurement.

Data Analysis

In addition to the gas composition, the dimensions and the diagnostic, the data analysis should be also standardised. As already mentioned above, typical parameters for a standardised analysis are the SED value, the G-value calculation and similar parameters. As a first approach, the above mentioned parameters seem to be a good choice.

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