

## **Electronic Supplementary Information:**

### **CO<sub>2</sub> conversion in a dielectric barrier discharge plasma: N<sub>2</sub> in the mix as helping hand or problematic impurity?**

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#### **1. Detailed experimental results**

##### **1.1. CO<sub>2</sub> and N<sub>2</sub> conversion**

The experimental results presented here are first shown without correction for the gas expansion factor (i.e. raw data). The corrected experimental results are presented in section 1.1.2.

The experimental procedure consists of stabilizing the plasma for 30 minutes, followed by 5 consecutive measurements with the compact gas chromatograph (CGC), which take 2 minutes per measurement, and at the same time recording the peak-to-peak voltage and power, and finally a cool down and flush period of 20 minutes with the next gas mixture. The results shown below are thus the average of these 5 consecutive measurements. All measurements were performed at an applied frequency of 23.5 kHz.

The measurements were performed in three series: a) adding 0-10 % N<sub>2</sub> in steps of 1 %; b) adding 0-90 % N<sub>2</sub> in steps of 10 %; c) adding 90-98 % N<sub>2</sub>, again in steps of 1 %.

##### **1.1.1. Raw data**

The following tables give the CO<sub>2</sub> and N<sub>2</sub> flow rates in ml/min (1<sup>st</sup> and 2<sup>nd</sup> column), the corresponding CO<sub>2</sub> and N<sub>2</sub> percentages in the mixture (3<sup>rd</sup> and 4<sup>th</sup> column), the average peak-to-peak voltage (column 5), the average plasma power (column 6), the average CO<sub>2</sub> conversion with standard deviation (column 7 and 8), the average N<sub>2</sub> conversion with

standard deviation (column 9 and 10), the average energy cost per converted CO<sub>2</sub> molecule (column 11) and the obtained average energy efficiency (column 12).

**a) 0-10 % N<sub>2</sub>**

CO <sub>2</sub> (ml/min)	N <sub>2</sub> (ml/min)	CO <sub>2</sub> (%)	N <sub>2</sub> (%)	Vp-p (kV)	Power (W)	χ CO <sub>2</sub> (%)	σ CO <sub>2</sub> (%)	χ N <sub>2</sub> (%)	σ N <sub>2</sub> (%)	Energy Cost (eV/molec)	η (%)
611	0	100	0	11.67	121.9	4.88	0.30	-	-	37.4	5.1
605	6.1	99	1	11.73	123.1	6.21	0.27	3.06	1.44	29.7	6.4
599	12.2	98	2	11.75	121.4	6.04	0.36	8.15	3.98	30.9	6.2
593	18.3	97	3	11.74	122.8	6.14	0.30	5.04	1.01	30.7	6.2
587	24.4	96	4	11.79	122.7	6.15	0.32	2.55	1.20	30.9	6.1
580	30.5	95	5	11.80	124.7	6.42	0.28	3.19	1.85	30.0	6.3
574	36.6	94	6	11.86	125.6	6.47	0.30	2.10	1.36	30.1	6.1
567	42.8	93	7	11.87	126.8	6.70	0.31	2.12	1.31	29.3	6.2
562	48.9	92	8	11.88	125.8	6.75	0.33	2.77	1.22	29.5	6.3
556	55.0	91	9	11.91	125.7	6.79	0.30	1.91	1.28	29.6	6.2
550	61.1	90	10	11.93	126.9	6.81	0.28	2.99	1.80	29.8	6.1

**b) 0-90 % N<sub>2</sub>**

CO <sub>2</sub> (ml/min)	N <sub>2</sub> (ml/min)	CO <sub>2</sub> (%)	N <sub>2</sub> (%)	Vp-p (kV)	Power (W)	χ CO <sub>2</sub> (%)	σ CO <sub>2</sub> (%)	χ N <sub>2</sub> (%)	σ N <sub>2</sub> (%)	Energy Cost (eV/molec)	η (%)
611	0	100	0	11.73	122.8	4.74	0.03	-	-	59.1	4.9
550	61	90	10	11.83	123.5	6.77	0.20	2.96	0.22	46.3	6.3
489	122	80	20	11.89	124.2	6.98	0.25	2.08	0.67	50.7	5.7
428	183	70	30	11.93	123.5	7.66	0.28	2.67	0.59	52.6	5.5
367	244	60	40	12.00	121.5	8.51	0.26	2.38	0.54	54.3	5.4
305	305	50	50	12.05	122.0	9.42	0.27	2.36	0.43	59.2	4.9
244	366	40	60	12.05	120.7	10.72	0.31	2.35	0.36	64.4	4.5
183	428	30	70	12.14	122.1	12.43	0.23	1.97	0.31	74.9	3.9
122	489	20	80	12.22	118.3	14.95	0.24	1.84	0.32	90.4	3.2
61	550	10	90	12.07	116.9	19.07	0.20	1.21	0.34	140.1	2.1

**c) 90-98 % N<sub>2</sub>**

CO <sub>2</sub> (ml/min)	N <sub>2</sub> (ml/min)	CO <sub>2</sub> (%)	N <sub>2</sub> (%)	Vp-p (kV)	Power (W)	χ CO <sub>2</sub> (%)	σ CO <sub>2</sub> (%)	χ N <sub>2</sub> (%)	σ N <sub>2</sub> (%)	Energy Cost (eV/molec)	η (%)
61	550	10	90	11.75	116.7	19.19	0.21	1.16	0.34	138.9	2.1
55	546	9	91	11.67	114.2	19.55	0.32	1.29	0.31	148.2	2.0
49	562	8	92	11.65	115.4	20.18	0.27	1.16	0.35	162.7	1.8
43	568	7	93	11.55	116.2	20.91	0.32	0.99	0.31	180.1	1.6
37	574	6	94	11.51	114.6	21.58	0.30	0.95	0.31	200.1	1.5
31	580	5	95	11.42	110.6	22.22	0.34	0.71	0.31	224.0	1.3
24	586	4	96	11.40	111.1	23.52	0.26	0.73	0.30	274.3	1.1
18	592	3	97	11.25	110.8	24.34	0.40	0.18	0.31	352.5	0.8
12	599	2	98	11.51	109.9	25.72	0.39	0.45	0.35	496.5	0.6

### 1.1.2. Correction for gas expansion

In this section the obtained experimental results corrected for the gas expansion are presented; these corrected results are the data used throughout the manuscript.

In this work the corrected results are obtained by performing an iterative back calculation, with the following assumptions: (i) CO<sub>2</sub> is split into CO and ½ O<sub>2</sub>, so every converted CO<sub>2</sub> molecule gives rise to an expansion of the volume by a factor 1.5. (ii) On the other hand, for N<sub>2</sub>, due to its low conversion, we assume that the conversion of N<sub>2</sub> does not contribute to the gas expansion.

Based on these two assumptions we start from the “faulty” conversions obtained from our GC measurements. We know that the gas expanded and since we have a sample loop with a fixed volume, this means that the pressure increases. However, since our GC samples at atmospheric pressure, part of the gas is lost due to the depressurization in the GC system before injection, leaving less molecules in the sample volume than originally present in the outlet flow. Since there are now less (CO<sub>2</sub> and N<sub>2</sub>) molecules in the sample, the (CO<sub>2</sub> and N<sub>2</sub>) conversion will appear higher. To correct for this, we calculate X<sub>GC</sub> by solving the equation below for different values of X<sub>Real</sub> until X<sub>GC</sub> matches the (CO<sub>2</sub> or N<sub>2</sub>) conversion measured by the GC.

$$X_{GC} = 1 - \left( \frac{1 - X_{Real}}{1 + \alpha \left( \frac{X_{Real}}{2} \right)} \right) \quad (1)$$

This formula is used for both the CO<sub>2</sub> and N<sub>2</sub> conversion. The derivation of it, in case of CO<sub>2</sub>, is explained below. In this formula X<sub>GC</sub> is the calculated conversion, which we expect to be measured by the GC due to the gas expansion for a certain value of X<sub>Real</sub>, which is the real conversion.

This equation is derived, on one hand, from the expression to calculate the remaining fraction of (CO<sub>2</sub> or N<sub>2</sub>) in the output:

$$Fraction (output) = (1 - X_{Real}) \quad (2)$$

And on the other hand, from the expression for the gas expansion due to the CO<sub>2</sub> conversion:

$$Gas\ expansion = 1 + \alpha \left( \frac{X_{Real}}{2} \right) \quad (3)$$

In the latter expression, according to our first assumption,  $\alpha(X_{Real}/2)$  accounts for the gas expansion due to the CO<sub>2</sub> conversion, as this corresponds to the O<sub>2</sub> formed for a certain CO<sub>2</sub> conversion (X<sub>Real</sub>), where  $\alpha$  is the fraction of CO<sub>2</sub> in the initial (CO<sub>2</sub>/N<sub>2</sub>) gas mixture. Furthermore, according to the second assumption, the N<sub>2</sub> conversion does not give rise to further volume expansion.

Dividing expression 2 by expression 3 tells us how the output is normalized due to the depressurization in the CGC system, and subtracting this value from one, ultimately gives us the “faulty” conversion as obtained in the CGC under influence of the gas expansion. Thus by

doing this calculation for a range of different  $X_{\text{Real}}$  values and matching  $X_{\text{GC}}$  to the measured “faulty” conversion by the GC, we can determine the “real”  $\text{CO}_2$  conversion,  $X_{\text{Real}}$ .

After calculating  $X_{\text{Real}}$  for  $\text{CO}_2$ , we can calculate the “real” conversion for  $\text{N}_2$  following the same procedure. In this case,  $X_{\text{Real}}$  in expression 2 stands for the  $\text{N}_2$  conversion, while  $X_{\text{Real}}$  in expression 3 is the already calculated “real” conversion of  $\text{CO}_2$ .

The following tables give the  $\text{CO}_2$  and  $\text{N}_2$  flow rates in ml/min (1<sup>st</sup> and 2<sup>nd</sup> column), the corresponding  $\text{CO}_2$  and  $\text{N}_2$  percentages in the mixture (3<sup>rd</sup> and 4<sup>th</sup> column), the average experimental  $\text{CO}_2$  conversion before and after correction for the gas expansion (5<sup>th</sup> and 6<sup>th</sup> column), the average experimental  $\text{N}_2$  conversion before and after correction for the gas expansion (7<sup>th</sup> and 8<sup>th</sup> column), the average experimental energy efficiency before and after correction for the gas expansion (9<sup>th</sup> and 10<sup>th</sup> column).

**a) 0-10 %  $\text{N}_2$**

$\text{CO}_2$ (ml/min)	$\text{N}_2$ (ml/min)	$\text{CO}_2$ (%)	$\text{N}_2$ (%)	$\chi \text{CO}_2$ (%)	$\chi \text{CO}_2$ Gas exp (%)	$\chi \text{N}_2$ (%)	$\chi \text{N}_2$ Gas exp (%)	$\eta$ (%)	$\eta$ Gas exp (%)
611	0	100	0	4.88	3.30	-	-	5.1	3.5
605	6.1	99	1	6.21	4.24	3.06	1.02	6.4	4.3
599	12.2	98	2	6.04	4.14	8.15	-	6.2	4.3
593	18.3	97	3	6.14	4.22	5.04	-	6.2	4.2
587	24.4	96	4	6.15	4.24	2.55	0.57	6.1	4.2
580	30.5	95	5	6.42	4.44	3.19	1.15	6.3	4.3
574	36.6	94	6	6.47	4.49	2.10	0.03	6.1	4.3
567	42.8	93	7	6.70	4.68	2.12	-	6.2	4.4
562	48.9	92	8	6.75	4.72	2.77	0.66	6.3	4.4
556	55.0	91	9	6.79	4.77	1.91	-	6.2	4.4
550	61.1	90	10	6.81	4.80	2.99	0.90	6.1	4.3

**b) 0-90 %  $\text{N}_2$**

$\text{CO}_2$ (ml/min)	$\text{N}_2$ (ml/min)	$\text{CO}_2$ (%)	$\text{N}_2$ (%)	$\chi \text{CO}_2$ (%)	$\chi \text{CO}_2$ Gas exp (%)	$\chi \text{N}_2$ (%)	$\chi \text{N}_2$ Gas exp (%)	$\eta$ (%)	$\eta$ Gas exp (%)
611	0	100	0	4.74	3.21	-	-	4.9	3.3
550	61	90	10	6.77	4.77	2.96	0.10	6.3	4.4
489	122	80	20	6.98	5.09	2.08	0.09	5.7	4.2
428	183	70	30	7.66	5.79	2.67	0.70	5.5	4.2
367	244	60	40	8.51	6.67	2.38	0.42	5.4	4.2
305	305	50	50	9.42	7.68	2.36	0.49	4.9	4.0
244	366	40	60	10.72	9.10	2.35	0.58	4.5	3.8
183	428	30	70	12.43	10.99	1.97	0.36	3.9	3.4
122	489	20	80	14.95	13.78	1.84	0.49	3.2	3.0
61	550	10	90	19.07	18.33	1.21	0.31	2.1	2.0

c) 90-98 % N<sub>2</sub>

CO <sub>2</sub> (ml/min)	N <sub>2</sub> (ml/min)	CO <sub>2</sub> (%)	N <sub>2</sub> (%)	χ CO <sub>2</sub> (%)	χ CO <sub>2</sub> Gas exp (%)	χ N <sub>2</sub> (%)	χ N <sub>2</sub> Gas exp (%)	η (%)	η Gas exp (%)
61	550	10	90	19.19	18.45	1.16	0.25	2.1	2.0
55	546	9	91	19.55	18.86	1.29	0.45	2.0	1.9
49	562	8	92	20.18	19.55	1.16	0.38	1.8	1.7
43	568	7	93	20.91	20.34	0.99	0.28	1.6	1.6
37	574	6	94	21.58	21.08	0.95	0.32	1.5	1.4
31	580	5	95	22.22	21.79	0.71	0.16	1.3	1.3
24	586	4	96	23.52	23.18	0.73	0.28	1.1	1.0
18	592	3	97	24.34	24.07	0.18	-	0.8	0.8
12	599	2	98	25.72	25.53	0.45	0.20	0.6	0.6

## 1.2. NO<sub>x</sub> formation

To study the formation of O<sub>3</sub>, N<sub>2</sub>O and NO<sub>x</sub> compounds, we applied Fourier transform infrared spectroscopy (FTIR). FTIR bands corresponding to an IR active functional group of the gases are monitored in real-time. Figure 1 shows the spectrum for a 50-50 mixture CO<sub>2</sub>/N<sub>2</sub> with the different bands indicated.

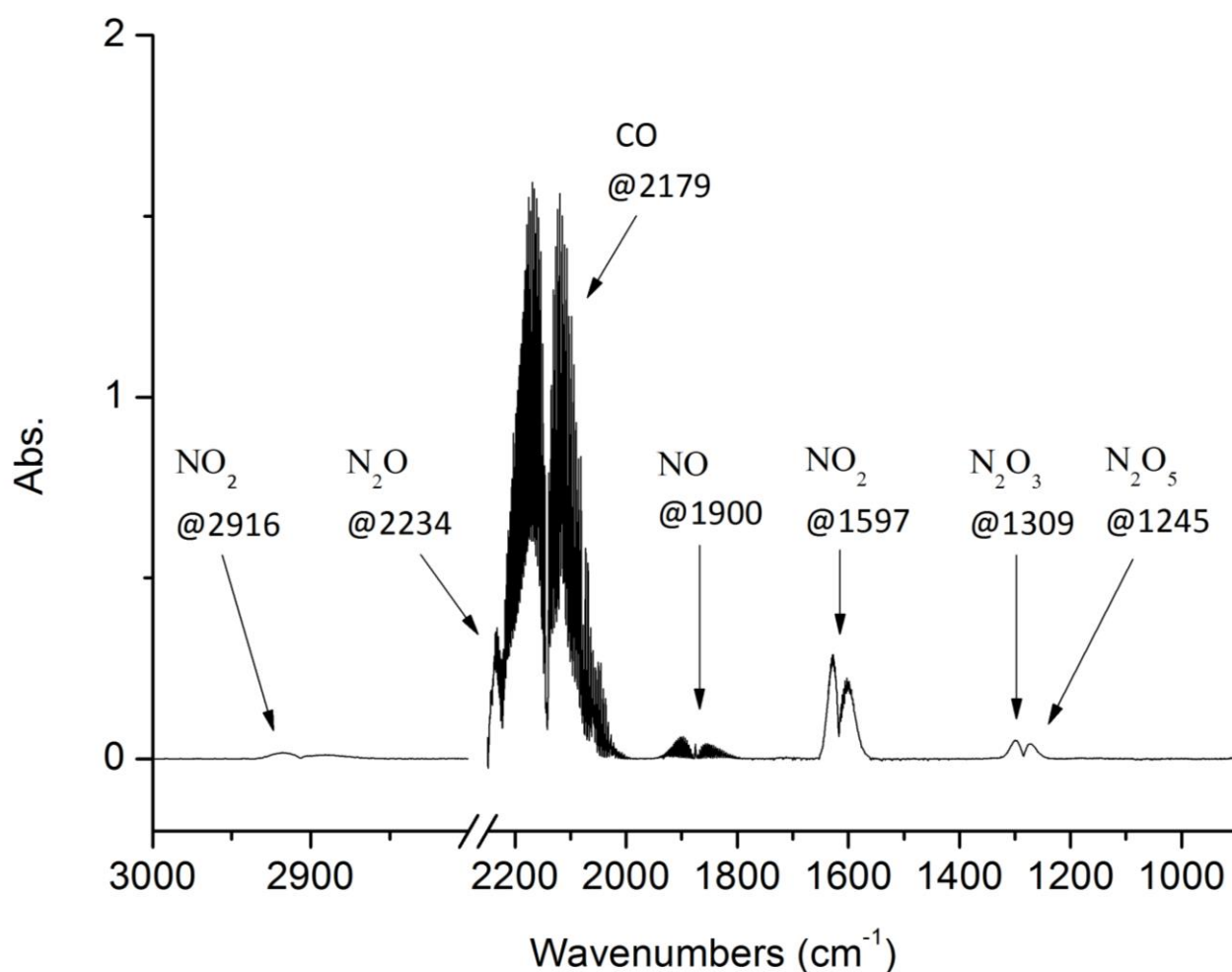


Figure 1. FTIR spectrum for a 50-50 mixture CO<sub>2</sub>/N<sub>2</sub>, indicating the different NO<sub>x</sub> (and N<sub>2</sub>O and CO) logging bands.

### 1.2.1. Raw data

The following tables give the CO<sub>2</sub> and N<sub>2</sub> flow rates in ml/min (1<sup>st</sup> and 2<sup>nd</sup> column), the corresponding CO<sub>2</sub> and N<sub>2</sub> percentages in the mixture (3<sup>rd</sup> and 4<sup>th</sup> column), the NO band ( $\nu$ NO) at 1900 cm<sup>-1</sup> (column 5), the NO<sub>2</sub> ( $\nu_{as}$ NO<sub>2</sub>) band logging at 1597 cm<sup>-1</sup> (column 6), the NO<sub>2</sub> ( $\nu_{as}$ NO<sub>2</sub> +  $\nu_s$ NO<sub>2</sub>) band logging at 2916 cm<sup>-1</sup> (column 7), the N<sub>2</sub>O band logging ( $\nu$ NN at 2234 cm<sup>-1</sup>) (column 8), the N<sub>2</sub>O<sub>3</sub> band logging ( $\nu_s$ NO<sub>2</sub> at 1309 cm<sup>-1</sup>) (column 9) and the N<sub>2</sub>O<sub>5</sub> band logging ( $\nu_s$ NO<sub>2</sub> at 1245 cm<sup>-1</sup>) (column 10). Note that all these results are in arbitrary units (a.u.). Ozone ( $\nu_s$  at 1054 cm<sup>-1</sup>) was never detected with the FTIR spectrometer.

#### a) 0-10 % N<sub>2</sub>

CO <sub>2</sub> (ml/min)	N <sub>2</sub> (ml/min)	CO <sub>2</sub> (%)	N <sub>2</sub> (%)	NO 1900 cm <sup>-1</sup> (a.u.)	NO <sub>2</sub> 1597 cm <sup>-1</sup> (a.u.)	NO <sub>2</sub> 2916 cm <sup>-1</sup> (a.u.)	N <sub>2</sub> O 2234 cm <sup>-1</sup> (a.u.)	N <sub>2</sub> O <sub>3</sub> 1309 cm <sup>-1</sup> (a.u.)	N <sub>2</sub> O <sub>5</sub> 1245 cm <sup>-1</sup> (a.u.)
611	0	100	0	-0.00253	-1.7E-05	7.34E-05	0.036386	-0.00041	-8.3E-05
605	6.1	99	1	0.012213	0.031595	0.002923	0.039362	0.000924	-0.00015
599	12.2	98	2	0.021533	0.039766	0.003497	0.043622	0.000685	-8.4E-05
593	18.3	97	3	0.029751	0.045549	0.003799	0.042921	0.000624	-0.00012
587	24.4	96	4	0.034032	0.049059	0.004175	0.039506	0.000466	-0.00012
580	30.5	95	5	0.041603	0.056878	0.004826	0.051976	0.000654	2.8E-05
574	36.6	94	6	0.047258	0.061017	0.005179	0.041416	0.00058	1.86E-05
567	42.8	93	7	0.055974	0.019795	0.001697	0.030233	-0.00044	-0.01203
562	48.9	92	8	0.060648	0.071408	0.005958	0.058815	0.000231	-0.00014
556	55.0	91	9	0.066247	0.075564	0.006115	0.051033	0.000674	-6.2E-05
550	61.1	90	10	0.066589	0.079807	0.006598	0.061262	0.000458	0.000105

#### b) 0-100 % N<sub>2</sub>

CO <sub>2</sub> (ml/min)	N <sub>2</sub> (ml/min)	CO <sub>2</sub> (%)	N <sub>2</sub> (%)	NO 1900 cm <sup>-1</sup> (a.u.)	NO <sub>2</sub> 1597 cm <sup>-1</sup> (a.u.)	NO <sub>2</sub> 2916 cm <sup>-1</sup> (a.u.)	N <sub>2</sub> O 2234 cm <sup>-1</sup> (a.u.)	N <sub>2</sub> O <sub>3</sub> 1309 cm <sup>-1</sup> (a.u.)	N <sub>2</sub> O <sub>5</sub> 1245 cm <sup>-1</sup> (a.u.)
611	0	100	0	-0.00253	-1.7E-05	7.34E-05	0.036386	-0.00041	-8.3E-05
550	61	90	10	0.066589	0.079807	0.006598	0.061262	0.000458	0.000105
489	122	80	20	0.11901	0.124921	0.010034	0.069467	0.002137	0.000209
428	183	70	30	0.130232	0.136295	0.011263	0.075507	0.003043	0.000378
367	244	60	40	0.166776	0.160221	0.013264	0.108849	0.006826	0.000638
305	305	50	50	0.169517	0.169624	0.014203	0.097302	0.005478	0.00081
244	366	40	60	0.154286	0.149847	0.012222	0.093913	0.005511	0.000601
183	428	30	70	0.13485	0.124089	0.009329	0.0964	0.006807	0.00071
122	489	20	80	0.121135	0.095289	0.007561	0.092582	0.007864	0.000922
61	550	10	90	0.060983	0.041701	0.003382	0.06438	0.006069	0.000389
0	611	0	100	0.000111	0.000234	-0.00034	0.031113	0.003044	-6.7E-05

**c) 90-98 % N<sub>2</sub>**

CO <sub>2</sub> (ml/min)	N <sub>2</sub> (ml/min)	CO <sub>2</sub> (%)	N <sub>2</sub> (%)	NO 1900 cm <sup>-1</sup> (a.u.)	NO <sub>2</sub> 1597 cm <sup>-1</sup> (a.u.)	NO <sub>2</sub> 2916 cm <sup>-1</sup> (a.u.)	N <sub>2</sub> O 2234 cm <sup>-1</sup> (a.u.)	N <sub>2</sub> O <sub>3</sub> 1309 cm <sup>-1</sup> (a.u.)	N <sub>2</sub> O <sub>5</sub> 1245 cm <sup>-1</sup> (a.u.)
61	550	10	90	0.060983	0.041701	0.003382	0.06438	0.006069	0.000389
55	546	9	91	0.039257	0.027067	0.00189	0.063275	0.006361	0.0005
49	562	8	92	0.029098	0.020959	0.001361	0.060787	0.00611	0.000613
43	568	7	93	0.025768	0.01792	0.001039	0.053	0.005325	0.000529
37	574	6	94	0.012127	0.013251	0.000913	0.062193	0.005806	0.00065
31	580	5	95	0.000514	0.000591	-0.00035	0.038054	0.003664	8.73E-05
24	586	4	96	0.000451	0.00084	-0.00031	0.039158	0.003677	0.00045
18	592	3	97	0.000275	0.000589	-0.00034	0.035147	0.003209	8.74E-05
12	599	2	98	0.000293	0.000568	-0.00046	0.034365	0.003356	0.000332

**1.2.2. NO and NO<sub>2</sub> conversion to ppm**

A ChemiLuminescence Detector (CLD) NO/NO<sub>x</sub> analyzer module (Emerson Process Management) was used to prepare a calibration curve for correlating the NO and NO<sub>2</sub> FTIR band intensities to NO and NO<sub>2</sub> concentrations in ppm. The CLD analyzer module determines either NO or combined NO and NO<sub>2</sub>. In this way it is possible to link the absorption height to the respective concentrations by using a calibration curve.

The following tables give the CO<sub>2</sub> and N<sub>2</sub> flow rates in ml/min (1<sup>st</sup> and 2<sup>nd</sup> column), the corresponding CO<sub>2</sub> and N<sub>2</sub> percentages in the mixture (3<sup>rd</sup> and 4<sup>th</sup> column), the NO band ( $\nu$ NO) at 1900 cm<sup>-1</sup> in arbitrary units (column 5), and in parts per million (column 6), the NO<sub>2</sub> ( $\nu_{as}$ NO<sub>2</sub>) infrared band logging at 1597 cm<sup>-1</sup> in arbitrary units (column 7) and in parts per million (column 8).

**a) 0-10 % N<sub>2</sub>**

CO <sub>2</sub> (ml/min)	N <sub>2</sub> (ml/min)	CO <sub>2</sub> (%)	N <sub>2</sub> (%)	NO 1900 cm <sup>-1</sup> (a.u.)	NO 1900 cm <sup>-1</sup> (ppm)	NO <sub>2</sub> 1597 cm <sup>-1</sup> (a.u.)	NO <sub>2</sub> 1597 cm <sup>-1</sup> (ppm)
611	0	100	0	-0.00253	-	-1.7E-05	-
605	6.1	99	1	0.012213	39.96	0.031595	9.97
599	12.2	98	2	0.021533	70.46	0.039766	12.54
593	18.3	97	3	0.029751	97.35	0.045549	14.37
587	24.4	96	4	0.034032	111.36	0.049059	15.48
580	30.5	95	5	0.041603	136.14	0.056878	17.94
574	36.6	94	6	0.047258	154.64	0.061017	19.25
567	42.8	93	7	0.055974	183.16	0.019795	-
562	48.9	92	8	0.060648	198.45	0.071408	22.53
556	55.0	91	9	0.066247	216.78	0.075564	23.84
550	61.1	90	10	0.066589	217.90	0.079807	25.18

## b) 0-100 % N<sub>2</sub>

CO <sub>2</sub> (ml/min)	N <sub>2</sub> (ml/min)	CO <sub>2</sub> (%)	N <sub>2</sub> (%)	NO 1900 cm <sup>-1</sup> (a.u.)	NO 1900 cm <sup>-1</sup> (ppm)	NO <sub>2</sub> 1597 cm <sup>-1</sup> (a.u.)	NO <sub>2</sub> 1597 cm <sup>-1</sup> (ppm)
611	0	100	0	-0.00253	-	-1.7E-05	-
550	61	90	10	0.066589	217.90	0.079807	25.18
489	122	80	20	0.11901	389.43	0.124921	39.41
428	183	70	30	0.130232	426.15	0.136295	43.00
367	244	60	40	0.166776	545.73	0.160221	50.54
305	305	50	50	0.169517	554.70	0.169624	53.51
244	366	40	60	0.154286	504.86	0.149847	47.27
183	428	30	70	0.13485	441.26	0.124089	39.14
122	489	20	80	0.121135	396.38	0.095289	30.06
61	550	10	90	0.060983	199.55	0.041701	13.15
0	611	0	100	0.000111	0.36	0.000234	0.07

## c) 90-98 % N<sub>2</sub>

CO <sub>2</sub> (ml/min)	N <sub>2</sub> (ml/min)	CO <sub>2</sub> (%)	N <sub>2</sub> (%)	NO 1900 cm <sup>-1</sup> (a.u.)	NO 1900 cm <sup>-1</sup> (ppm)	NO <sub>2</sub> 1597 cm <sup>-1</sup> (a.u.)	NO <sub>2</sub> 1597 cm <sup>-1</sup> (ppm)
61	550	10	90	0.060983	199.55	0.041701	13.15
55	546	9	91	0.039257	128.46	0.027067	8.54
49	562	8	92	0.029098	95.22	0.020959	6.61
43	568	7	93	0.025768	84.32	0.01792	5.65
37	574	6	94	0.012127	39.68	0.013251	4.18
31	580	5	95	0.000514	1.68	0.000591	0.19
24	586	4	96	0.000451	1.48	0.00084	0.26
18	592	3	97	0.000275	0.90	0.000589	0.19
12	599	2	98	0.000293	0.96	0.000568	0.18

## 2. Modeling details

### 2.1 Modeling the filaments/microdischarges in the DBD

We assume that every molecule has passed through a triangular microdischarge pulse of 30 ns every 100 half cycles, adopted from the work of Snoeckx et al.<sup>1</sup> For a residence time of 0.73 s and a frequency of 23.5 kHz, this means that the molecules pass through a microdischarge every 2.1 ms. The average power consumed per microdischarge is equal to the power inserted in the plasma divided by the total number of microdischarges through which the molecules pass. For each microdischarge, the power rises linearly towards a value equal to two times the average power consumed per microdischarge at 15 ns, and decreases again linearly towards zero at 30 ns. The electron density in every microdischarge is held between  $10^{12}\text{cm}^{-3}$  and  $10^{14}\text{cm}^{-3}$ .<sup>2-4</sup>

### 2.2. Modeling results

In this section the calculated results from the zero dimensional chemical kinetics model are presented. The same kinetic model as in reference<sup>5</sup> is used with some minor changes (as listed in the following table).



Reaction	Rate Constant ( $\text{cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ or $\text{cm}^6 \cdot \text{molecule}^{-2} \cdot \text{s}^{-1}$ )	Reference
$\text{N} + \text{O}_3 \rightarrow \text{NO} + \text{O}_2$	$5.0 \cdot 10^{-12} \cdot \exp(-650/T_{\text{gas}})$	6
$\text{NO} + \text{NO}_2 + \text{M} \rightarrow \text{N}_2\text{O}_3 + \text{M}$	$9.1 \cdot 10^{-33}$	7
$\text{N}_2\text{O}_3 + \text{M} \rightarrow \text{NO} + \text{NO}_2 + \text{M}$	$1.9 \cdot 10^{-7} \cdot (T_{\text{gas}}/300)^{-8.7} \cdot \exp(-4880/T_{\text{gas}})$	8
$2\text{NO}_2 + \text{M} \rightarrow \text{N}_2\text{O}_4 + \text{M}$	$1.4 \cdot 10^{-33} \cdot (T_{\text{gas}}/300)^{-3.8}$	9
$\text{N}_2\text{O}_4 + \text{M} \rightarrow 2\text{NO}_2 + \text{M}$	$1.3 \cdot 10^{-5} \cdot (T_{\text{gas}}/300)^{-3.8} \cdot \exp(-6460/T_{\text{gas}})$	8
$\text{N} + \text{O} + \text{M} \rightarrow \text{NO} + \text{M}$	$1.0 \cdot 10^{-32} \cdot (300/T_{\text{gas}})^{0.5}$	8
$\text{NO}_2 + \text{NO}_3 + \text{M} \rightarrow \text{N}_2\text{O}_5 + \text{M}$	$3.6 \cdot 10^{-30} \cdot (300/T_{\text{gas}})^{4.1}$	9
$\text{N}_2\text{O}_5 + \text{M} \rightarrow \text{NO}_2 + \text{NO}_3 + \text{M}$	$1.3 \cdot 10^{-3} \cdot (T_{\text{gas}}/300)^{-3.5} \cdot \exp(-11000/T_{\text{gas}})$	8,9
$\text{N}_2(\text{A}^3\Sigma_u^+) + \text{CO}_2 \rightarrow \text{CO} + \text{O}$	$6.25 \cdot 10^{-14}$	10

The following tables give the  $\text{CO}_2$  and  $\text{N}_2$  percentages in the mixture (1<sup>st</sup> and 2<sup>nd</sup> column), the calculated  $\text{CO}_2$  and  $\text{N}_2$  conversion (3<sup>th</sup> and 4<sup>th</sup> column), the calculated energy efficiency (column 5), the calculated  $\text{NO}$  concentration in parts per million (column 6), the calculated  $\text{NO}_2$  concentration in parts per million (column 7), the calculated  $\text{N}_2\text{O}_3$  concentration in parts per million (column 8), the calculated  $\text{N}_2\text{O}_5$  concentration in parts per million (column 9) and the calculated  $\text{N}_2\text{O}$  concentration in parts per million (column 10).

**a) 0-10 %  $\text{N}_2$**

$\text{CO}_2$ (%)	$\text{N}_2$ (%)	$\chi$ $\text{CO}_2$ calc (%)	$\chi$ $\text{N}_2$ calc (%)	$\eta$ calc (%)	$\text{NO}$ (ppm)	$\text{NO}_2$ (ppm)	$\text{N}_2\text{O}_3$ (ppm)	$\text{N}_2\text{O}_5$ (ppm)	$\text{N}_2\text{O}$ (ppm)
100	0	4.12	-	3.8	-	-	-	-	-
99	1	4.20	0.46	3.8	43.46	9.72	0.006	14.26	2.99
98	2	4.23	0.37	3.8	63.91	14.41	0.013	26.04	5.96
97	3	4.26	0.32	3.8	76.83	17.45	0.018	37.02	8.59
96	4								
95	5	4.33	0.27	3.7	91.86	21.17	0.026	58.29	13.39
94	6								
93	7								
92	8	4.45	0.22	3.7	102.81	24.20	0.034	90.36	19.88
91	9								
90	10	4.53	0.21	3.7	106.81	25.51	0.037	112.37	23.79

**b) 0-100 % N<sub>2</sub>**

CO <sub>2</sub> (%)	N <sub>2</sub> (%)	χ CO <sub>2</sub> calc (%)	χ N <sub>2</sub> calc (%)	η calc (%)	NO (ppm)	NO <sub>2</sub> (ppm)	N <sub>2</sub> O <sub>3</sub> (ppm)	N <sub>2</sub> O <sub>5</sub> (ppm)	N <sub>2</sub> O (ppm)
100	0	4.12	-	3.8	-	-	-	-	-
90	10	4.53	0.21	3.7	106.81	25.51	0.037	112.37	23.79
80	20	5.03	0.18	3.7	114.50	29.35	0.046	233.39	38.68
70	30	5.65	0.17	3.6	115.47	31.76	0.050	373.38	47.36
60	40	6.42	0.17	3.5	113.21	33.43	0.051	528.66	51.92
50	50	7.34	0.17	3.3	107.68	34.18	0.050	690.55	53.83
40	60	8.46	0.16	3.1	98.29	33.66	0.045	841.94	53.91
30	70	9.83	0.16	2.7	84.05	31.20	0.036	952.65	52.26
20	80	11.61	0.14	2.1	63.61	25.83	0.022	964.41	48.28
10	90	14.19	0.09	1.3	34.88	15.57	0.007	741.02	39.92
0	100	-	0.00	-	-	-	-	-	-

**c) 90-98 % N<sub>2</sub>**

CO <sub>2</sub> (%)	N <sub>2</sub> (%)	χ CO <sub>2</sub> calc (%)	χ N <sub>2</sub> calc (%)	η calc (%)	NO (ppm)	NO <sub>2</sub> (ppm)	N <sub>2</sub> O <sub>3</sub> (ppm)	N <sub>2</sub> O <sub>5</sub> (ppm)	N <sub>2</sub> O (ppm)
10	90	14.19	0.09	1.3	34.88	15.57	0.007	741.02	39.92
9	91	14.53	0.09	1.2	31.46	14.15	0.006	694.31	38.63
8	92								
7	93	15.28	0.07	1.0	24.35	11.04	0.004	580.31	35.58
6	94								
5	95	16.19	0.05	0.7	16.98	7.59	0.002	433.21	31.72
4	96								
3	97	17.38	0.03	0.5	9.63	3.91	0.001	244.68	26.62
2	98	18.29	0.02	0.3	6.12	2.22	0.000	135.13	23.38

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