PRECEPT 6: Environmental impact of a power plants

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The object of the precept is to analyse the environmental performance of the steam cycle, whose flue gas composition and mass balances were computed in precept 1. We must analyse the emissions for two different type of fuel:

A) NATURAL GAS

- Concentration of NO_x in *dry* flue gases at the stack equal to 45 ppmvd at 3% of O_2 .

B) COAL

- Concentration of NO_x in *dry* flue gases at the stack equal to 90 ppmvd at 6% of O_2;
- Desulfurizer efficiency $\eta_{\text{desulfurizer}} = \eta_{SO_2} = 97.5\%$

For both plants A and B it is required to evaluate:

1. absolute emission of nitrogen oxides NO_x in $\frac{\text{kg}}{\text{s}}$ as equivalent NO_2;

2. NO_x mass concentration in dry flue gases;

3. absolute emission of CO_2 in $\frac{\text{kg}}{\text{s}}$;

4. ONLY for case B, check that concentration in flue gases of SO_2 respect the legal limit of $200\,\text{mg}/Mn_3$ with 6% of O_2.

Moreover it is required to compare the emission of NO_x and CO_2 with that produced by a *natural gas combined cycle* plant with the following data:

- net electric power $= 390\,\text{MW}$

- LHV efficiency $= 0.57\%$

- flue gases mass flow rate $= 650\,\frac{\text{kg}}{\text{s}}$

- NO_x concentration in dry flue gases $= 14$ ppmvd at 15% of O_2.

A   NATURAL GAS

From precept number 1 we have the following concentrations in flue gases;

Table 1: Composition of flue gases in natural gas plant

Molecule	CO_2	H_2O	N_2	Ar	O_2
Molar Mass (MM) [$kg/kmols$]	44.01	18.02	28.01	39.94	32.00
Molar Concentration (χ)	8.30 %	17.05 %	71.15 %	0.89 %	2.62 %
Mass concentration y	13.11 %	11.03 %	71.58 %	1.27 %	3.01 %

The theoretical model

Both in case of use of natural gas and coal, the text gives the fraction of NO_x (NO and NO_2) at the stack. The concentration of NO_x in ppmvd is referred to a certain % of oxygen in the dry flue gases. This means that the information regarding NO_x does not correspond to the real conditions of this pollutant in the flue gases, since the flue gases are humid and, a priori, with a different % of oxygen.

The legislation regulating the emissions from combustion power plants requires, for statistical elaborations and technical comparisons, that the flue gases flow is expressed on a dry basis, i.e. (virtually) purged of the humidity content, and normalized on a certain reference oxygen content, depending on the combustion system (The value chosen is usually close to the actual average value).
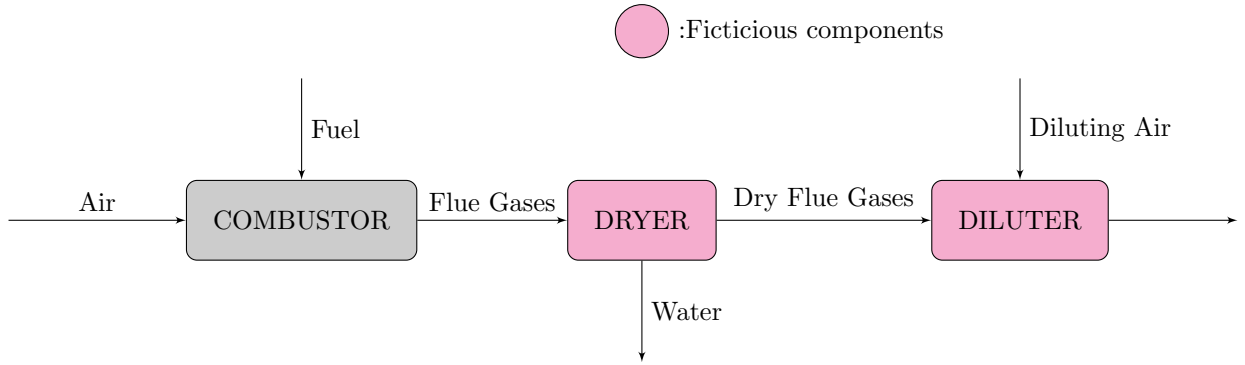

Figure 1: Scheme of the theoretical model.

These two corrections (dry flue gases and oxygen %) are applied in order to evaluate concentrations regardless of the random effects affecting the combustion process, such as:

- The excess air in the combustor. The plant control system acts on the inlet mass flow rate so that the oxygen is kept at a constant value in the flue gases. Nevertheless, because of changes in the chemical composition of the fuel, variations of load, etc... the oxygen content in the flue gases fluctuates over time;

- Condensation of water in the flue gases. In some processes (e.g. condensing boilers) water condenses reducing the flue gases mass flow rate at the stack. This would turn out in higher pollutant concentrations at the stack;

- Weather conditions. The mass flow rate of the combustion air inlet changes with air moisture.

Moreover, if the legislation would provide the limits for the pollutants without stating the reference oxygen content and the humidity = 0 in the flue gases, in order to comply with the limit it would be sufficient to dilute the flue gases with ambient air or steam.

Finally, the flue gases must be brought to normal reference conditions, as the gas density changes with the temperature and pressure. At these conditions (273.15 K and 101325 Pa) 1

kmol of gas occupies 22.414 m^3 (Nm^3). In order to derive the formula that expresses the relation between the actual concentration and the normalized concentration we assume a plant scheme with two fictitious components, defined *diluter* and *dryer*, respectively.

In a *real plant* there is no dilution of flue gases with ambient dry air (besides some eventual uncontrolled infiltrations of air in the depressed flue gases line), neither any drying.

From the *mass and concentration balance* between each section we can get a way to pass from one convention to the others for a generic molecule.

From FLUE GASES to DRY FLUE GASES

$$\chi_i^{\text{DFG}} = \chi_i^{\text{FG}} \cdot \frac{1}{1 - \chi_{\text{H}_2\text{O}}^{\text{FG}}} \tag{1}$$

where the coefficient $\dfrac{1}{1 - \chi_{\text{H}_2\text{O}}^{\text{FG}}}$ is constant and equals to 1.2072

From DRY FLUE GASES to NORMALIZED FLUE GASES

$$\chi_i^{\text{NORM}} = \chi_i^{\text{DFG}} \cdot \frac{\chi_{\text{O}_2}^{\text{NORM}} - \chi_{\text{H}_2\text{O}}^{\text{diluter}}}{\chi_{\text{O}_2}^{\text{DFG}} - \chi_{\text{O}_2}^{\text{diluter}}} \tag{2}$$

We just miss $\chi_{\text{O}_2}^{\text{DFG}}$ but we can get it with equation 1 applied for the oxygen:

$$\chi_{\text{O}_2}^{\text{DFG}} = \chi_{\text{O}_2}^{\text{FG}}/1.2072 = 3.15\,\% \tag{3}$$

The coefficient $\dfrac{\chi_{\text{O}_2}^{\text{NORM}} - \chi_{\text{H}_2\text{O}}^{\text{diluter}}}{\chi_{\text{O}_2}^{\text{DFG}} - \chi_{\text{O}_2}^{\text{diluter}}}$ now can be calculated and it constant and equals to 1.0088.

The diluter is simply ambient air, with an oxygen concentration of 20.7 %.

A.1   Absolute emission of NO_x as equivalent NO_2

We know the concentration of NO_x in dry flue gases with 3% of O_2 so reverting equation 2 we can get the concentration of NO_x in dry flue gases. From this value, using equation 1 we obtain their absolute concentration in original flue gases.

$$\chi_{\text{NO}_2}^{\text{FG}} = (1 - \chi_{\text{H}_2\text{O}}^{\text{FG}}) \cdot \chi_{\text{NO}_2}^{\text{DFG}} \tag{4}$$

$$= (1 - \chi_{\text{H}_2\text{O}}^{\text{FG}}) \cdot \frac{\chi_{\text{O}_2}^{\text{DFG}} - \chi_{\text{O}_2}^{\text{diluter}}}{\chi_{\text{O}_2}^{\text{NORM}} - \chi_{\text{H}_2\text{O}}^{\text{diluter}}} \cdot \chi_{\text{NO}_2}^{\text{NORM}} \tag{5}$$

$$= \frac{45 \text{ ppmvd}}{1.2072 \cdot 1.0088} = 37.00 \cdot 10^{-6} \tag{6}$$

The absolute emission of NO_x is computed as:

$$E_i \left[\frac{\text{kg}}{\text{s}} \right] = \chi_i^{\text{FG}} \cdot \text{MM}_i \cdot \dot{n}_{\text{FG}} \tag{7}$$

From precept 1 we know that the mass flow rate of flue gases is $445.34 \frac{\text{kg}}{\text{s}}$ and their mean molar mass is $27.85 \frac{\text{kg}}{\text{kmols}}$. From these values we can evaluate the molar flow rate of flue gases as

$$\dot{n}_{\text{FG}} = \frac{\dot{m}_{\text{FG}}}{\text{MM}_{\text{FG}}} = 15.99 \frac{\text{kmols}}{\text{s}} \tag{8}$$

We are now able to compute the absolute emission of NO_2.

$$E_{\text{NO}_2} \left[\frac{\text{kg}}{\text{s}} \right] = \chi_{\text{NO}_2}^{\text{FG}} \cdot \text{MM}_{\text{NO}_2} \cdot \dot{n}_{\text{FG}} = 27.23 \cdot 10^{-3} \frac{\text{kg}}{\text{s}} \tag{9}$$

A.2 NO_x mass concentration in dry flue gases

With the conversion coefficient between flue gases and dry flue gases it is not so difficult to evaluate the concentration of NO_2 in dry flue gases.

$$C_{NO_x}^{DFG} = \frac{\dot{n}_{DFG} \cdot \chi_{NO_2}^{DFG} \cdot MM_{NO_2} \cdot 10^6 \, \text{mg/kg}}{\dot{n}_{DFG} \cdot 22.414} = 91.56 \left[\frac{mg_{NO_2}}{Nm_{DFG}^3} \right] \tag{10}$$

A.3 Absolute emission of CO_2

To evaluate absolute emission of CO_2 we must apply equation 7.

$$E_{CO_2} \left[\frac{kg}{s} \right] = \chi_{CO_2}^{FG} \cdot MM_{CO_2} \cdot \dot{n}_{FG} = 58.40 \, \frac{kg}{s} \tag{11}$$

B COAL

The situation for the coal case is slightly different, in fact the flue gases encounter the desulfurizer before to exiting the plant. The desulfurizer is a component that remove the solphates as much as possible. The real operation consists making the sulphurous acid react with $CaCO_3$ with the following reaction:

$$H_2SO_3 + CaCO_3 \rightarrow CaSO_3 + CO_2 + H_2O \tag{12}$$
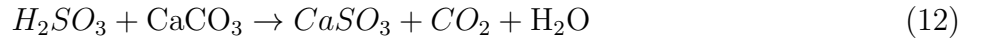
The reaction would introduce CO_2 and H_2O into the flue gases, but in our mathematical approach we consider the desulfurizer like a component that let us to remove SO_2 without changing any other molecule, with a certain efficiency defined as the SO_2 removed over the total SO_2 content in the flue gases. We can use the same theoretical model also in presence of the desulfurizer, drying and diluting the flue gases that come out from it.
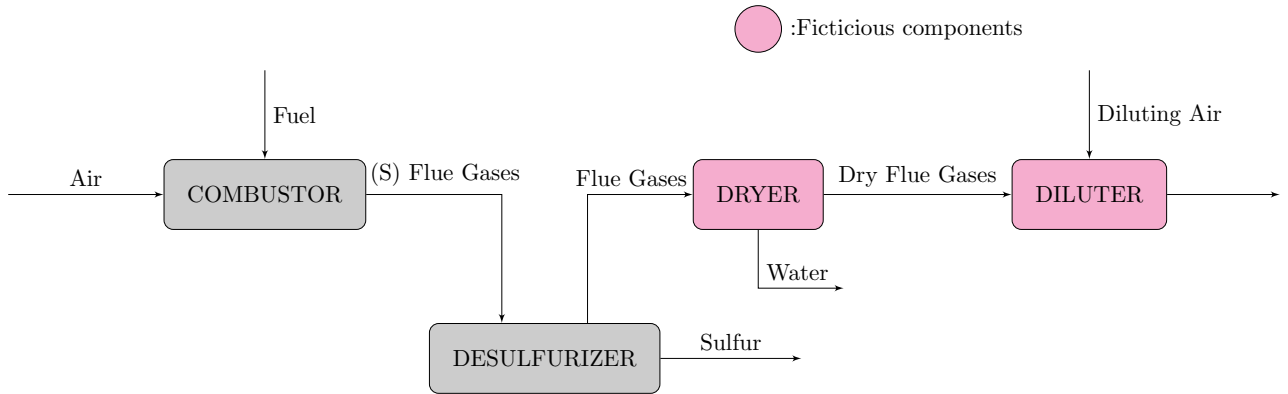

Figure 2: Scheme of the theoretical model with desulfurizer.

We just need to introduce a step before the dryer.

From SULFURIZED FLUE GASES to FLUE GASES For the concentration of SO_2 the equation that let to pass through the desulfurizer is equation number 13.

$$\chi_{SO_2}^{FG} = \chi_{SO_2}^{FG+S} \cdot \frac{1 - \eta_{FGD}}{1 - \eta_{FGD} \cdot \chi_{SO_2}^{FG+S}} \tag{13}$$

where the coefficient $\dfrac{1 - \eta_{FGD}}{1 - \eta_{FGD} \cdot \chi_{SO_2}^{FG+S}}$ is constant and equals to 0.0251. For any other substance the formula is slightly different because the SO_2 molar flow rate changes passing through the

desulfurizer while the mass and molar flow rates of the other molecules is constant. Therefore the correct equation is:

$$\chi_i^{\text{FG}} = \chi_i^{\text{FG+S}} \cdot \frac{1}{1 - \eta_{FGD} \cdot \chi_{\text{SO}_2}^{\text{FG+S}}} \tag{14}$$

where the coefficient $\dfrac{1}{1 - \eta_{FGD} \cdot \chi_{\text{SO}_2}^{\text{FG+S}}}$ is constant and equals to 1.0025.

The two following passages of the dryer and the diluter are exactly the same as the previous case. (Equations 1 and 2)

From FLUE GASES to DRY FLUE GASES

$$\chi_i^{\text{DFG}} = \chi_i^{\text{FG}} \cdot \frac{1}{1 - \chi_{\text{H}_2\text{O}}^{\text{FG}}} \tag{15}$$

We just miss $\chi_{\text{H}_2\text{O}}^{\text{FG}}$ but we can get it with equation 14 applied for the water:

$$\chi_{\text{H}_2\text{O}}^{\text{DFG}} = \chi_{\text{H}_2\text{O}}^{\text{FG+S}}/1.0025 = 8.48\,\% \tag{16}$$

The coefficient $\dfrac{1}{1 - \chi_{\text{H}_2\text{O}}^{\text{FG}}}$ is constant and equals to 1.0927

From DRY FLUE GASES to NORMALIZED FLUE GASES

$$\chi_i^{\text{NORM}} = \chi_i^{\text{DFG}} \cdot \frac{\chi_{\text{O}_2}^{\text{NORM}} - \chi_{\text{H}_2\text{O}}^{\text{diluter}}}{\chi_{\text{O}_2}^{\text{DFG}} - \chi_{\text{O}_2}^{\text{diluter}}} \tag{17}$$

We just miss $\chi_{\text{O}_2}^{\text{FG}}$ but we can get it with equations 14 15 and applied for the oxygen:

$$\chi_{\text{O}_2}^{\text{DFG}} = \chi_{\text{O}_2}^{\text{FG+S}}/1.0927/1.0025 = 4.82\,\% \tag{18}$$

The coefficient $\dfrac{\chi_{\text{O}_2}^{\text{NORM}} - \chi_{\text{H}_2\text{O}}^{\text{diluter}}}{\chi_{\text{O}_2}^{\text{DFG}} - \chi_{\text{O}_2}^{\text{diluter}}}$ now can be calculated and it constant and equals to 0.9257.

The diluter is simply ambient air, with an oxygen concentration of 20.7\,%.

B.1   Absolute emission of NO$_x$ as equivalent NO$_2$

We know the concentration of NO$_x$ in dry flue gases with 3% of O$_2$ so reverting equation 17 we can get the concentration of NO$_x$ in dry flue gases. From this value, using equation 15 we obtain their absolute concentration in flue gases that come out from the desulfurizer.

We know the concentration of NO$_x$ in dry flue gases with 15% of O$_2$ so reverting equation 17 we can get the concentration of NO$_x$ in dry flue gases. From this value, using equation 15 we obtain their absolute concentration in desulfurized flue gases. Finally we can pass from sulfurized flue gases to original flue gases with equation 14 instead of equation 13 because we deal with emission of NO$_2$.

$$\chi_{\text{NO}_2}^{\text{FG}} = (1 - \chi_{\text{H}_2\text{O}}^{\text{FG}}) \cdot \chi_{\text{NO}_2}^{\text{DFG}} \tag{19}$$

$$= (1 - \chi_{\text{H}_2\text{O}}^{\text{FG}}) \cdot \frac{\chi_{\text{O}_2}^{\text{DFG}} - \chi_{\text{O}_2}^{\text{diluter}}}{\chi_{\text{O}_2}^{\text{NORM}} - \chi_{\text{H}_2\text{O}}^{\text{diluter}}} \cdot \chi_{\text{NO}_2}^{\text{NORM}} \tag{20}$$

$$= \frac{90 \text{ ppmvd}}{1.0927 \cdot 0.9257} = 88.95 \cdot 10^{-6} \tag{21}$$

The absolute emission of NO_x is computed as:

$$E_i \left[\frac{kg}{s} \right] = \chi_i^{FG} \cdot MM_i \cdot \dot{n}_{FG} \tag{22}$$

From precept 1 we know that the mass flow rate of flue gases at the stack before desulfurizer is $525.35 \frac{kg}{s}$ and their mean molar mass is $29.57 \frac{kg}{kmols}$. From these values we can evaluate the molar flow rate of flue gases as

$$\dot{n}_{FG} = \frac{\dot{m}_{FG}}{MM_{FG}} = 17.77 \frac{kmols}{s} \tag{23}$$

We are now able to compute the absolute emission of NO_2.

$$E_{NO_2} \left[\frac{kg}{s} \right] = \chi_{NO_2}^{FG} \cdot MM_{NO_2} \cdot \dot{n}_{FG} = \chi_{NO_2}^{FG+S} \cdot MM_{NO_2} \cdot \dot{n}_{FG+S} = 72.52 \cdot 10^{-3} \frac{kg}{s} \tag{24}$$

B.2 NO_x mass concentration in dry flue gases

With the conversion coefficient between flue gases and dry flue gases it is not so difficult to evaluate the concentration of NO_2 in dry flue gases.

$$C_{NO_x}^{DFG} = \frac{\dot{n}_{\cancel{DFG}} \cdot \chi_{NO_2}^{DFG} \cdot MM_{NO_2} \cdot 10^6 \, mg/kg}{\dot{n}_{\cancel{DFG}} \cdot 22.414} = 199.47 \left[\frac{mg_{NO_2}}{Nm_{DFG}^3} \right] \tag{25}$$

B.3 Absolute emission of CO_2

To evaluate absolute emission of CO_2 we must apply equation 22.

$$E_{CO_2} \left[\frac{kg}{s} \right] = \chi_{CO_2}^{FG} \cdot MM_{CO_2} \cdot \dot{n}_{FG} = 99.24 \frac{kg}{s} \tag{26}$$

B.4 Concentration of SO_2 in flue gases

Concentration of SO_2 must be compatible with legal limit of $200 \, mg/Nm^3$ at 6% of O_2. To check the respect of this limit we must find the concentration of *soo* in flue gases.

$$C_{SO_2}^{NORM} = \frac{\dot{n}_{\cancel{NORM}} \cdot \chi_{SO_2}^{NORM} \cdot MM_{SO_2} \cdot 10^6 \, mg/kg}{\dot{n}_{\cancel{NORM}} \cdot 22.414} \tag{27}$$

We miss the molar concentration of sulphur dioxide, but we know how to pass through the desulfurizer with equation 13

$$\chi_{SO_2}^{NORM} = \chi_{SO_2}^{FG+S} \cdot \frac{1 - \eta_{FGD}}{1 - \eta_{FGD} \cdot \chi_{SO_2}^{FG+S}} \cdot \frac{1}{1 - \chi_{H_2O}^{FG}} \cdot \frac{\chi_{O_2}^{NORM} - \chi_{H_2O}^{diluter}}{\chi_{O_2}^{DFG} - \chi_{O_2}^{diluter}} = 67.19 \cdot 10^{-6} \tag{28}$$

So the final concentration of emitted SO_2 is $C_{SO_2}^{FG} = 191.84 \frac{mg_{NO_2}}{Nm_{DFG}^3}$ that respect the legal limit of 200

C Natural gas combined cycle

In order to compare the emissions of the steam boilers with those produced by the NGCC, it is necessary to compute the composition of the flue gas at the combustor outlet. From the net electric power and the total efficiency we can find the mass flow rate of fuel that we use to feed the combined cycle.

$$\eta_{CC} = \frac{\dot{W}_{net}}{\dot{m}_{fuel} \cdot LHV} \qquad \Rightarrow \qquad \dot{m}_{fuel} = \frac{\dot{W}_{net}}{\eta_{CC} \cdot LHV} = 14.67 \frac{kg}{s} \tag{29}$$

From the flue gases mass flow rate and the previous evaluated fuel mass flow rate we can get the air mass flow rate and consequentially also α, the air over fuel mass ratio.

$$\dot{m}_{air} = \dot{m}_{flue\ gases} - \dot{m}_{fuel} = 635.33\,\frac{\text{kg}}{\text{s}} \tag{30}$$

$$\alpha = \frac{\dot{m}_{air}}{\dot{m}_{fuel}} = 43.30 \tag{31}$$

We can write the chemical balance:

$$0.9\text{CH}_4 + 0.06\text{C}_2\text{H}_6 + 0.04\text{N}_2 + \beta_{O_2} \times \left(O_2 + \frac{\chi_{N_2}}{\chi_{O_2}}\text{N}_2 + \frac{\chi_{Ar}}{\chi_{O_2}}\text{Ar} + \frac{\chi_{H_2O}}{\chi_{O_2}}\text{H}_2\text{O}\right) =$$
$$a\text{CO}_2 + b\text{H}_2\text{O} + c\text{N}_2 + d\text{Ar} + e\text{O}_2 \tag{32}$$

We miss β_{O_2} but we can obtain in from α previously evaluated.

$$\alpha = \frac{\dot{m}_{AIR}}{\dot{m}_{fuel}} = \beta_{O_2} \cdot \frac{1}{\chi_{O_2}^{air}} \cdot \frac{\text{MM}_{air}}{\text{MM}_{fuel}} \tag{33}$$

$$\beta_{O_2} = \alpha \cdot \chi_{O_2}^{air} \cdot \frac{\text{MM}_{fuel}}{\text{MM}_{air}} = 5.38 \tag{34}$$

Balancing equation 32 we obtain the moles of chemical species in flue gases:

	a (CO_2)	b (H_2O)	c (N_2)	d (Ar)	e (O_2)
n	1.02	2.25	20.14	0.25	3.37

From that we easily get the concentration of each species in flue gases dividing the moles of each single species by the sum of all the species.

	a (CO_2)	b (H_2O)	c (N_2)	d (Ar)	e (O_2)
χ	3.77 %	8.32 %	74.50 %	0.93 %	12.47 %

A small amount of nitrogen does not bypass the combustion but it oxidises to NOx, 14 ppmvd at 15 % of O_2). Yet, we can neglect its presence in the calculation of the concentrations of the other products because it is really small for what that concern mass and energy, but it could be significant for environmental emission ($\chi_{O_2} \approx 0.0015\,\%$).

To calculate the emission we use the same procedure of the natural gas case.

C.1 Absolute emission of NO_x as equivalent NO_2

$$\chi_{NO_2}^{FG} = (1 - \chi_{H_2O}^{FG}) \cdot \frac{\chi_{O_2}^{DFG} - \chi_{O_2}^{diluter}}{\chi_{O_2}^{NORM} - \chi_{H_2O}^{diluter}} \cdot \chi_{NO_2}^{NORM} = 15.98\,\text{ppmvd} \tag{35}$$

$$E_{NO_2}\left[\frac{\text{kg}}{\text{s}}\right] = \chi_{NO_2}^{FG} \cdot \text{MM}_{NO_2} \cdot \dot{n}_{FG} = 16.83 \cdot 10^{-3}\,\frac{\text{kg}}{\text{s}} \tag{36}$$

C.2 NO_x mass concentration in dry flue gases

$$C_{NO_x}^{DFG} = \frac{\dot{n}_{DFG} \cdot \chi_{NO_2}^{DFG} \cdot \text{MM}_{NO_2} \cdot 10^6\,\text{mg/kg}}{\dot{n}_{DFG} \cdot 22.414} = 32.79\,\frac{\text{mg}_{NO_2}}{Nm_{DFG}^3} \tag{37}$$

C.3 Absolute emission of CO_2

$$E_{CO_2}\left[\frac{\text{kg}}{\text{s}}\right] = \chi_{CO_2}^{FG} \cdot \text{MM}_{CO_2} \cdot \dot{n}_{FG} = 38.03\,\frac{\text{kg}}{\text{s}} \tag{38}$$

C.4 Specific emission of NO_x per kWh

$$E_{NO_2}\left[\frac{mg_{NO_2}}{kWh}\right] = \frac{\chi_{NO_2}^{FG} \cdot MM_{NO_2} \cdot \dot{n}_{FG} \cdot 3600}{P_{net}^{electric}} = 155.35\frac{mg_{NO_2}}{kWh} \tag{39}$$

C.5 Specific emission of CO_2 per kWh

$$E_{CO_2}\left[\frac{g_{CO_2}}{kWh}\right] = \frac{\chi_{CO_2}^{FG} \cdot MM_{CO_2} \cdot \dot{n}_{FG} \cdot 3600}{P_{net}^{electric}} = 351.03\frac{g_{CO_2}}{kWh} \tag{40}$$