Supporting Information – Reduction of NO_x emissions in nitric acid absorption during transient regimes

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Section S1: Description of the operational procedures during Bondalti's nitric acid startup

The Bondalti's nitric acid startup was analysed and most important operational procedures are presented concomitantly in Figure 1 by splitting the time interval. Different ramps corresponding to feed operations are noted. In Figure 1 the first plot corresponds to the inlet column's pressure, NP_T, the second one to the column's inlet water flowrate, $NL_{\mathrm{H_2O}}$, the third to the secondary air flowrate, $NG_{\mathrm{sec.air}}$ and the last one to the column's outlet $\mathrm{NO_x}$ pressures, $NP_{\mathrm{NO_x}}$. Our goal of splitting the time interval is to avoid discontinuities in the mathematical model.

The number of subintervals depends on the number of explicit discontinuities of the system and, in this case, 8 subintervals are specified. In more detail, the sequence of the operations is:

(i) $[t_0, t_1]$ - constant regime;

(ii) $[t_1, t_2]$ - increase the water flow rate;

(iii) $[t_2, t_3]$ - increase the inlet $\mathrm{NO_x}$ gas composition, decrease of the total absorption pressure and keep increasing the water flow rate;

(iv) $[t_3, t_4]$ - keep water flow rate constant;

(v) $[t_4, t_5]$ - decrease the inlet water flow rate;

(vi) $[t_3, t_6]$ - increase the total absorption pressure;

(vii) $[t_2, t_7]$ - increase the secundary air flow rate; and

(viii) $[t_7, t_8]$ - stabilize all variables until the steady state is reached.

The observation of $\mathrm{NO_x}$ emissions at the beginning of the start up procedure reveals an increase that lasts approximately 860 s. After this increase there are three peaks in the

NO_x pressure. Notice that the shape of the peaks is different for every analysed startup, see Ref. 1. We recall that the decrease of the NO_x pressure in the industrial data around 06:30 is caused by the EnviNO$_x$® reactor that was started and represents the end of the nitric acid startup. After this, the plant's production rate is increased to the desired value. From this point forward, there are no major concerns regarding the gas emissions since the NO_x are abated in the EnviNO$_x$® reactor. As a result, the NO_x emissions that the company pretends to reduce are those occurring until 3000 s.

To simulate the startup we set a reference schedule that are mathematical functions describing the inputs profiles captured from Figure 1. The reference was established in order to generate a proper sequence of operations that allows comparing the behaviour of the unit with the model predictions. Practically, we observed a relevant variability in the analysed startup procedures, indicating a certain degree of change in the basic disturbances induced on the unit. A deeper analysis led us to consider that the startup is formed by a sequence of eight stages identified in Figure 1. After this, we characterized each of the ramps forming the overall procedure, and noticed that four input variables change either simultaneously or individually:

- NO_x inlet molar flow rate the sequence is:
  - (i) increase with a ramp slope of 0.058 s^{-1} (normalized value) from t_1 to t_2; followed by
  - (ii) a constant value in the interval $[t_2, t_8]$.
- Column's inlet total pressure, we conceptualize the following sequence:
  - (i) decrease with a normalized ramp slope of 1.05×10^{-4} s^{-1} from t_2 to t_3;
  - (ii) increase with a normalized ramp slope of 6.73×10^{-5} s^{-1} from t_3 to t_6; followed by
  - (iii) a period where the value is kept constant, in the interval $[t_6, t_8]$.

- Column's inlet water flow rate, the sequence includes the:

  (i) increase with a normalized ramp slope of 0.023 s^{-1} from t_0 to t_1;

  (ii) a constant value in the interval $[t_1, t_4]$;

  (iii) decrease with a normalized ramp slope of 0.012 s^{-1} from t_4 to t_5; and

  (iv) a constant value in the interval $[t_5, t_8]$.

- Secundary air flow rate, the sequence is as follows:

  (i) increase with a normalized ramp slope of 6.3×10^{-6} s^{-1} from t_2 to t_7; and

  (ii) a constant value in the interval $[t_7, t_8]$.

Figure 2 shows the graphical representation of each modelled ramp.

Section S2: Dynamic process response – additional information

The effects of the lateral feed stream flow rate and secondary air flow rate during the column's startup are herein presented. Figure 3 represents the simulation results for the reference scenario and for a scenario where the flow rate is reduced by 30 %. The analysis of Figure 3 reveals that no considerable impact occurs when reducing the lateral feed stream flow rate by 30 %; specifically, a decrease of 1.3 % is observed at the peak. Figure 4 presents the nitric acid mass fraction profile at the beginning and end of startup. Observing the figure, we can conclude that decreasing the lateral feed stream flow rate will lead to an increase in the absorption rate in Zone 1, compared to the reference case, and consequently, the HNO_3 concentration is lower in the lateral feed tray. However this reduction is not significant and in Zone 2 the nitric acid profile is similar to that of the reference. Thus, low impact is observed in the NO_x gas stream leaving the column.

The impact of the secondary air flow rate was also analysed, by simulating an increase of 33.3 % with a normalized ramp slope of 1.6×10^{-5} s^{-1}, from t_2 until t_7, as opposed to the reference scenario where an increase of 13.4 % with a normalized ramp slope of 6.3×10^{-6} s^{-1} was used. After the ramp, the secondary air flow rate was kept constant for the remaining period. The comparison of the NO_x gas leaving the column between the reference case and this new scenario is shown in Figure 5. The dynamics do not show significant differences in the NO_x gas concentration leaving the column during the startup. The secondary air flow rate has an impact in the NO oxidation rate as it increases the oxygen content in the inlet gas stream. This increase induces a higher oxidation rate which promotes the increase of the NO_x absorption rate, verified in Figure 6 where the beginning and end of startup profiles are analysed.

Figure 6 shows the influence of increasing the secondary air flow rate along the column and, in this case, no difference is observed when compared to the reference. Consequently, the increase of the secondary air does not have a significant impact on the NO_x pressures leaving the absorption column. Notice that, in this case, the mass fraction in Zone 1 is above 0.3 not causing any safety problems.

References

(1) Vilarinho, I. Abatement of NO_x emissions in nitric acid plants during transient regimes. Ph.D. thesis, University of Coimbra, 2019.

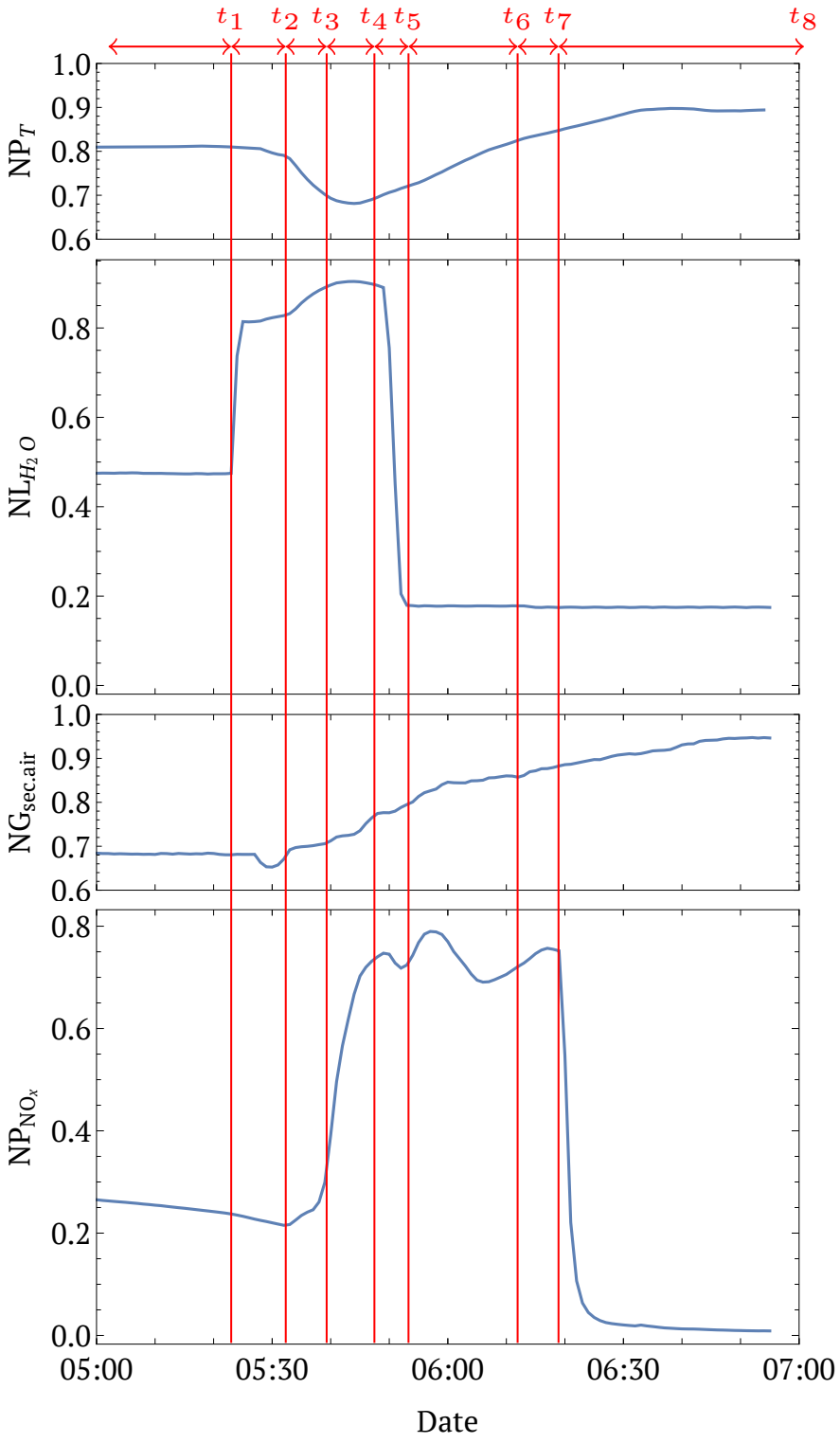

Figure 1: Sequence of the most relevant changes during one startup operation.

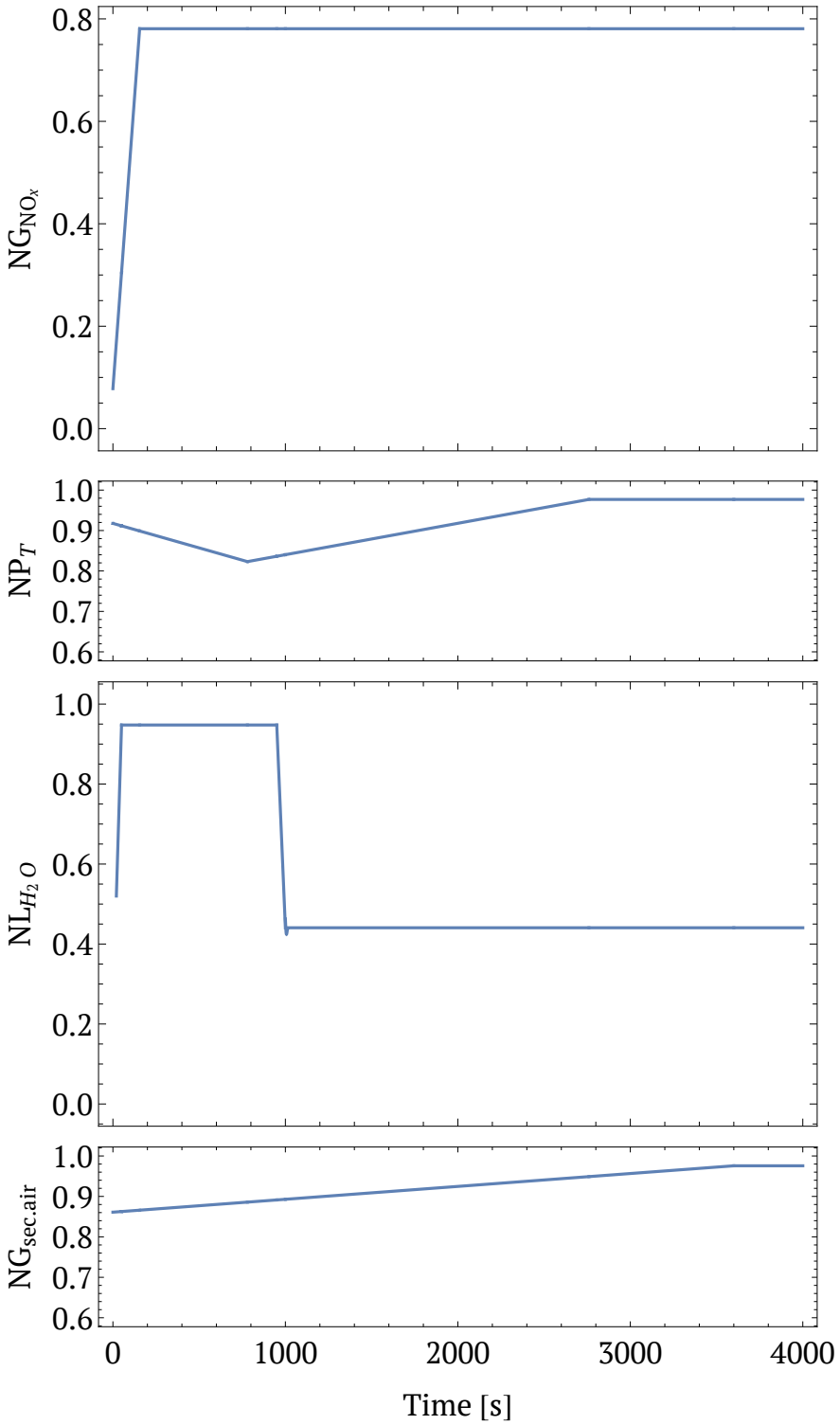

Figure 2: Sequence of ramps of the start-up procedure: the first plot corresponds to the column's inlet NO_x gas flowrate, NG_{NO_x}, the second to the inlet column's pressure, NP_T, the third to the column's inlet water flowrate, NL_{H_2O}, and the last one to the secondary air flowrate, $NG_{sec.air}$.

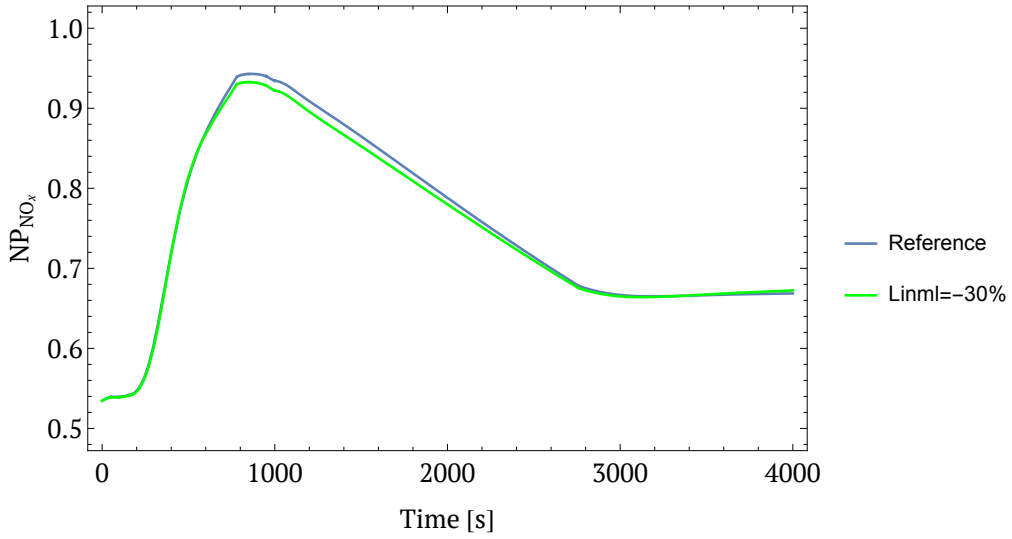

Figure 3: Comparison of the NO_x gas pressure leaving the column between the reference case and in case the lateral feed stream flow rate is reduced by 30 %.

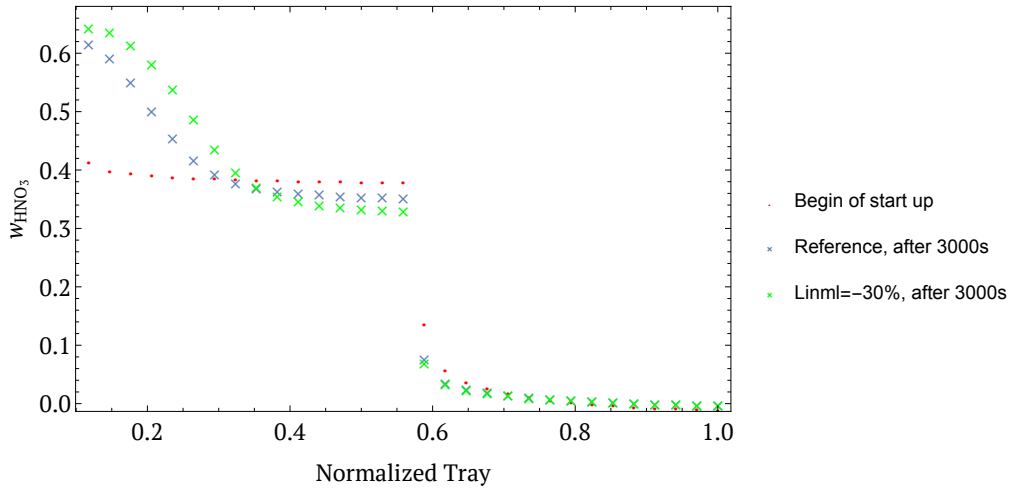

Figure 4: Nitric acid mass fraction profile in the beginning and end of startup in case the lateral stream flow rate is reduced by 30 %.

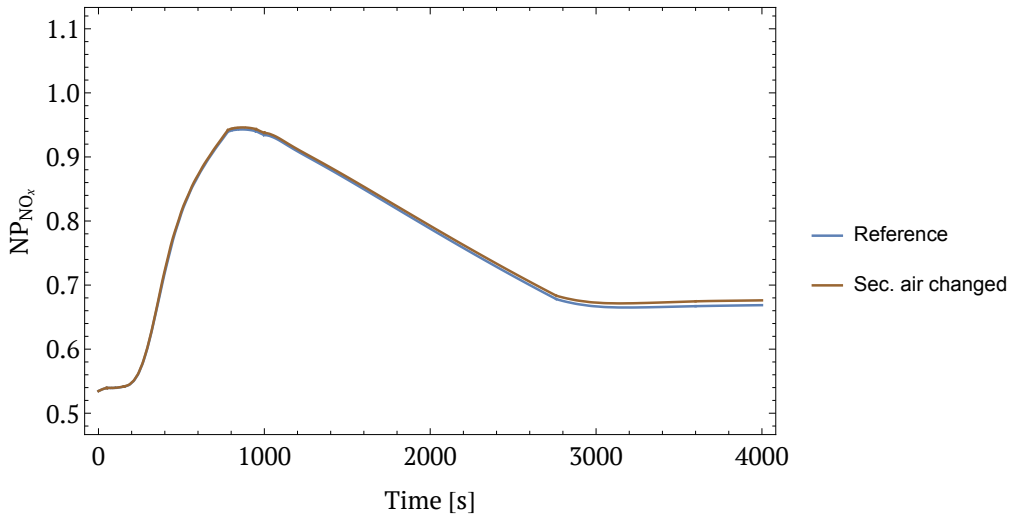

Figure 5: Comparison of the NO_x gas pressure leaving the column between the reference case and in case the secondary air has a different ramp profile.

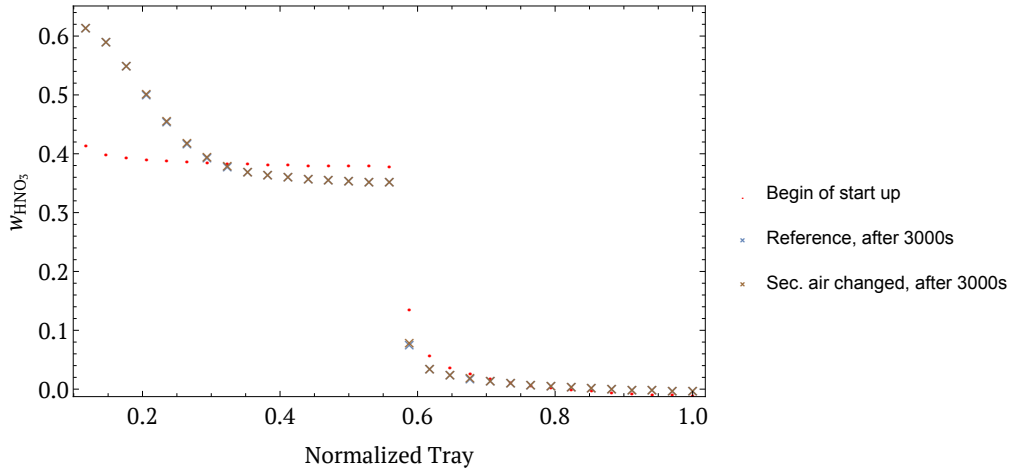

Figure 6: Nitric acid mass fraction profile in the absorption column at the beginning and end of startup in case the secondary air has a different ramp profile.