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Thermodynamically based definition of limits for nitrogen oxide emissions of gas turbine plants

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Abstract

Thermodynamically Based Definition of Limits for Nitrogen Oxide Emissions of Gas Turbine Plants

The policy document of the Federal Government for an integrated energy and climate program represents the basis for the Regulation Concerning Assurance of Air Quality Standards (37. BImSchV) which comprises the revision of emission limits with consequences for gas turbines. After commencement of this regulation gas turbine plants of firing heat capacity > 100 MW with gases from public gas supply will be faced with tightened limits for nitrogen oxide emissions.

Because gas turbine technology has a relevant share in ecologically compatible and reliable energy supply, the authors show the necessary link of gas turbine efficiency to nitrogen oxide emission limits on the basis of thermodynamical considerations. Thus, a conflict of objective between climate protection and air pollution prevention and a discrimination of highly efficient gas turbines can be avoided. The “Eta algorithm” is a proper approach which does not privilege these plants at all. By its linear increase of the NO_x emission limit with the ratio of net efficiency to reference efficiency, this definition comprises the requirement of combustion technology advancement. It meets the thermodynamic principles much better than a limit definition which is only based on the exhaust gas flow rate for ISO reference conditions. That the “Eta algorithm”, which is already implemented in the existing document “13. BImSchV”, will also be adopted in the “37. BImSchV” can be considered as an achievement although this approach should be applied to combined-cycle plants as well.

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Introduction

The EU-NEC (NEC = National Emission Ceiling), which has set by the European Council of the Heads of States and Governments under German presidency in spring 2007, represents the approach for an integrated European climate and energy policy until 2020. This includes ambitious climate protection goals as well as goals for consolidating renewable energies and increasing energy efficiency. The goal agreed in spring 2007 envisages, among other intentions, to reduce the greenhouse gas emission throughout the European Union by 20 % of the 2005 value by the year 2020.

The national implementation of the European directive decision, which includes important German proposals, has been summarised by the Federal Government in the document "Policy for an integrated energy and climate programme" [1]. This document takes into consideration the statements of the government declaration dated April 3th, 2007 and the results of the energy summit conference dated July 3th, 2007. With regard thereto, the Federal Government has declared, among other announcements, that the envisaged economically efficient implementation of the individual measures of the policy paper will continue to be geared, within the scope of a continuous process, to the triple goal of "reliable supply, economic efficiency and environmental protection". In Section 5 "Clean power plant technology" of the policy paper consisting of 29 items, it is pledged to utilise the latest emission reducing facilities according to the best available technique (BAT) with the goal of significantly reducing as from 2013 the emissions of nitrogen oxides (NO_x) from new firing, garbage incineration and partial garbage incineration plants with more than 50 MW combustion thermal energy output, compared with the requirements in force.

For implementing these measures, the BMU (German Federal Ministry for Environment, Nature Conservation and Nuclear Safety) was commissioned to draw up on a relatively short term basis a corresponding regulation with tighter NO_x limits compared with the thirteenth regulations for implementing the federal immission protection statutes (13. BImSchV) [2]. In this 37. BImSchV "Regulations for ensuring fulfilment of the air quality requirements" [3], stationary gas turbine plants (GTP) in combined-cycle power plants, as well as simple cycle GTP for generating electric power and for mechanical drive, are taken into consideration. With regard to the mentioned BAT-status, the BMU recognises the need for acting in accordance with the BREF-documents (BREF = Best Available Technique Reference Documents) of the European Commission in Seville, which are part of the EU-IVU directive [4]. However, a perusal of the BREF-documents for gas turbines has revealed that important emission-relevant details with regard to parameter definition, operating conditions of the GTP as well as fuel properties [5, 6] have so far not been taken into consideration adequately.

Initial situation

By virtue of its advanced development status, gas turbine technology makes an important contribution to environmentally compatible, resources protecting and stable power supply.

Low pollutant emission rates result from the highly developed technology of lean premixing combustion, and low carbon dioxide (CO_2) emissions are achieved in particular by high pressure and temperature process parameters. For example, the heavy duty gas turbines frequently utilised for generating electric power achieve a net efficiency of approx. 38 % as the state of the art (Figure 1). The maximum electric power efficiencies of combined-cycle power plants are in the order of magnitude of 59 %. The development goals are ambitious. Further increase of process parameters offers the greatest potential for efficiency enhancement and thus also for lower specific CO_2 emissions related to effective work. GTP with turbine inlet temperatures significantly higher than 1400 °C achieve for net efficiencies of $\eta_e \geq 0.40$ for simple cycle GTP and of $\eta_e \geq 0.60$ for combined-cycle power plants, e.g. [7]. Aeroderivative gas turbines, which can also be utilised in solo operation as well as in combined cycles, nowadays come up to efficiencies of approx. 45 %.

For GTP with combustion heat performance ≥ 50 MW (thermal), the tolerated pollutant

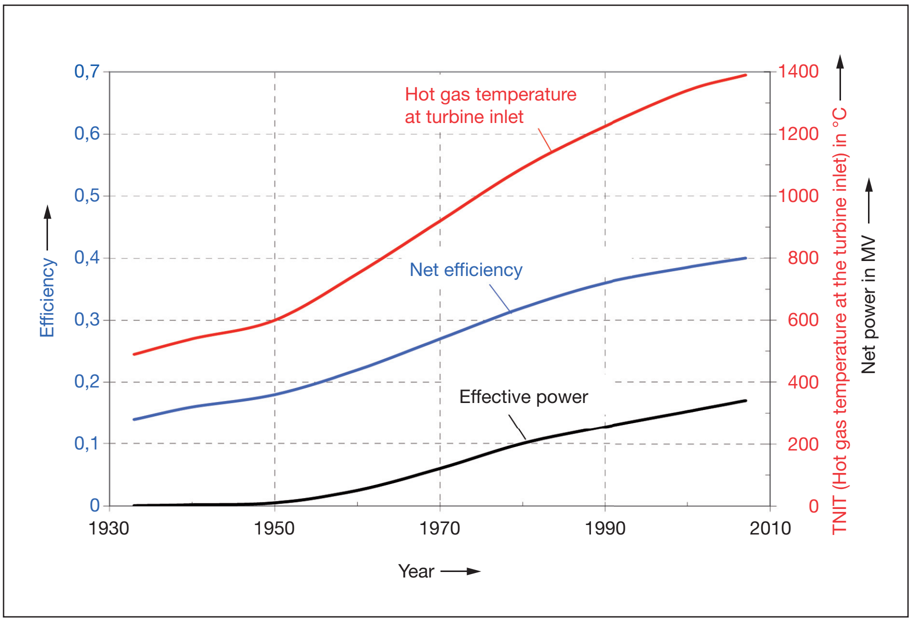


Figure 1. Parameter development for heavy-duty gas turbines.

emissions are at present determined by the thermodynamically based limits defined in the 13. BImSchV as reference [2]. It is remarkable that in §6 (3) at least for natural gas fired gas turbines for generating electric power in solo operation, the gas turbine efficiency is also taken into consideration for defining the NO_x emission limits, in that the tolerated emissions are increased above the basic value of 50 mg/m^3 (i. N.) by the corresponding percentage increase above a power efficiency factor of more than 35 % under ISO conditions ("Eta algorithm“). However, a NO_x emission limit of 75 mg/m^3 (i. N.) must not be exceeded.

A corresponding efficiency correction is also contained in the directive 2001/80/EC of the European Parliament and of the Council dated 23 October 2001 for limiting the pollutant emissions of large incineration plants into the atmosphere, as well as in the new draft of a directive for industrial emissions (integrated prevention and reduction of environmental pollution) dated 21 December 2007 recently presented by the European Commission.

The NO_x emission limits specified in the draft of the 37. BImSchV dated September 2007 were based on a level that cannot be maintained solely with firing side measures (primary measures). In addition the gas turbine net efficiency was not considered. The emerging technical and economical consequences of the new regulations has induced operators, manufacturers and univer sities to make a detailed study of nitrogen oxides production in combination with a reasonable definition of the limit values, within the scope of the enforcement process of these regulations.

The mechanism of nitrogen oxides production and the factors influencing the emission of nitrogen oxides

It is well known that the nitrogen oxides emissions during operation of GTP do not primarily originate from the fuel, but instead from the reaction of a share of nitrogen molecules in the air, depending on the combustion conditions and the available activation energy. The thermal production of NO_x, to which this paper is confined, is described by the elementary reactions determined by Zeldovich (Zeldovich mechanism).

$$N_2 + O \underset{k_2}{\overset{k_1}{\leftrightarrows}} NO + N \qquad \text{(Eq. 1)}$$

$$N + O_2 \underset{k_4}{\overset{k_3}{\leftrightarrows}} NO + O \qquad \text{(Eq. 2)}$$

$$N + OH \underset{k_6}{\overset{k_5}{\leftrightarrows}} NO + H \qquad \text{(Eq. 3)}$$

where: k_i (i = 1 to 6) = reaction rate coefficients determined from the ARRHENIUS ansatz.

In the following discussion of the production of nitrogen oxides in gas turbine combustion chambers (Equation 3) – the extended Zeldovich mechanism – is not taken into consideration, because the combustion takes place under air excess conditions (air excess number $\lambda > 1$).

On the basis of a simplified model consideration with

- the assumption that the combustion chamber is an ideal stirred reactor,
- the simplified consideration of natural gas as consisting of only methane CH4,
- the sole consideration of the NO emissions constituting the major fraction in NO_x,
- the assumption that the back reaction in (Equation 1) can be ignored,
- the assumption that the back reaction in (Equation 2) can be ignored,
- and the assumption that the reaction ½ O2 ⇆ O is in equilibrium,

the following equation is obtained for the production rate of NO:

$$\frac{dc_{NO}}{dt} \approx 4{,}7 \cdot 10^{13} \exp \frac{(-67837)}{T}\, c_{N2} \sqrt{c_{O2}}$$

$$\text{in } \frac{kmol_{NO}}{m^3{}_{\text{exhaust gas}}\ s} \qquad \text{(Eq. 4)}$$

whereby c_i are the concentrations of the substance i with i = NO, N_2, O_2

$$c_i = \psi_i \frac{p}{R_m T} \qquad \text{(Eq. 5)}$$

R_m is the universal gas constant and ψ_i are the mole concentrations, i.e. the number of mole of the respective substance i.

$$\psi_i = \frac{\text{Number of mole of the substance i}}{\text{Total number of mole}}$$

Evidently there are three significant factors influencing the NO-concentration c_{NO}:

- the combustion temperature,
- the pressure,
- and the residence time in the reaction zone

These relationships are shown in the Figures 2 to 4 and will now be discussed taking as example two GTP with very different design parameters, in order to draw conclusions regarding a thermodynamically based definition of the limits for the nitrogen oxide emissions. Thereby the NO-concentrations determined with (Equation 4) are converted to the standard state (ISO conditions) and related to 15 % of oxygen by volume in the dried exhaust gas. The following assumptions are made for the two GTP (Table 1).

For GTP 1 with the lower pressure ratio and the greater air excess an adiabatic combustion temperature of 1520 °C is determined and assumed to be the temperature in the

Table 1. Calculation boundary conditions for the GTP chosen as example.

	Compressor pressure ratio π_v	Air excess in the reaction zone	Residence time t in mss
GTA 1	16	1.92	30
GTA 2	24	1.66	30

combustion chamber (Figure 2). In contrast thereto, the GTP 2 has a much higher combustion temperature of 1700 °C. The consequences for the NO emissions resulting from the different pressures and temperatures are shown in Figure 3. In order to point out the significant influence of the residence time t on the NO emissions, in addition to the temperature and pressure dependent values for the residence time of 30 ms (annular combustion chamber), the NO emissions are also stated for 150 ms residence time (silo combustion chamber). With these model assumptions and the same combustion technology, the GTP 2, that is the gas turbine with the higher process parameters, has a NO emission greater by a factor of the order of magnitude of 10 compared with the GTP 1.

A plot of the NO emissions as a function of the pressure ratio or combustion chamber pressure (Figure 4) is also very informative and reveals that an increase of the combustion temperature by 50 K approximately doubles the NO emissions.

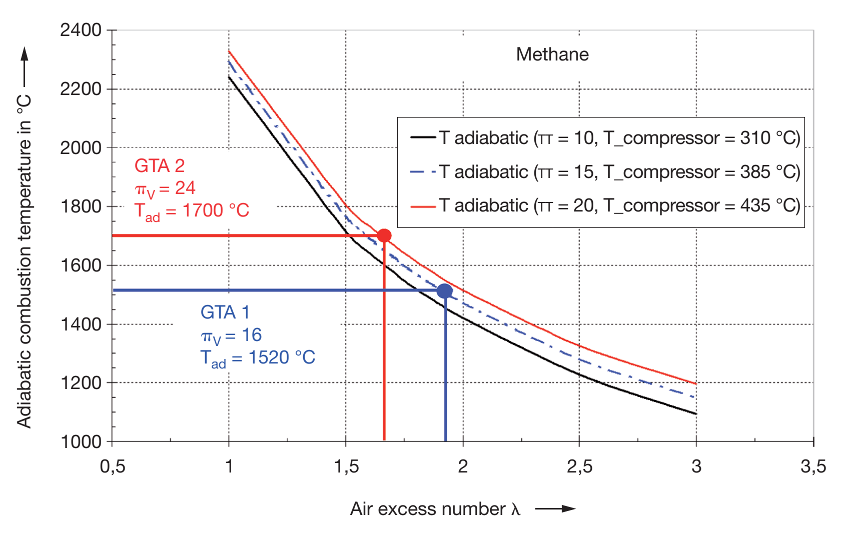


Figure 2. The influence of the air excess number on the adiabatic combustion temperature.

The parameters determining the efficiency and the CO_2 emissions of gas turbine plants, and their relationship to the nitrogen oxides emissions

Also for GTP and combined-cycle power plants, efficiency improvement and reduction of the specific CO_2 emissions will be achieved in future primarily by improving the process quality as a result of increasing the process parameters. Consequently, the efficiency of the real gas turbine process η_J will be taken as basis for further study of the inseparable relationship between the efficiency and the CO_2 emissions on the one hand and the nitrogen oxide emissions on the other hand. It is thereby assumed that an increase of the process efficiency η_J will increase the net efficiency η_e proportionally.

$$\eta_J = \frac{\Delta h_T - \Delta h_V}{h_3 - h_2} = \frac{\eta_{iT}\, \Delta h s_T - \Delta h_{sV} / \eta_{iV}}{h_3 - h_2} \qquad \text{(Eq. 6)}$$

Whereby:

Δh polytropic enthalpy difference of turbine (T) and compressor (V),

Δh_s isentropic enthalpy difference of turbine (T) and compressor (V),

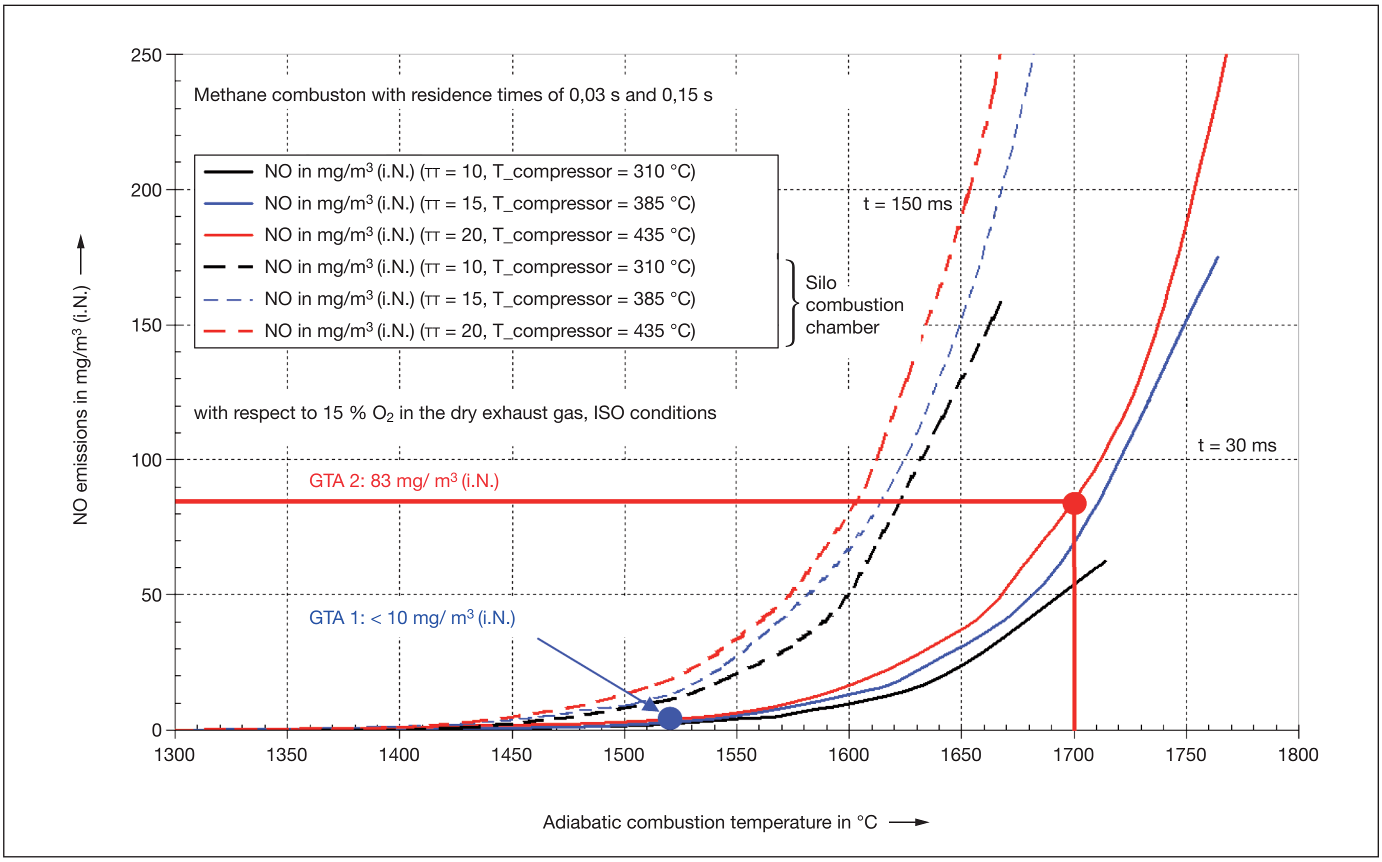


Figure 3. NO emissions as a function of the adiabatic combustion temperature, residence time and pressure.

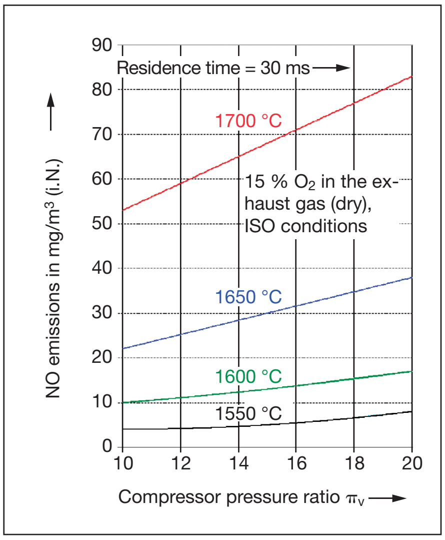
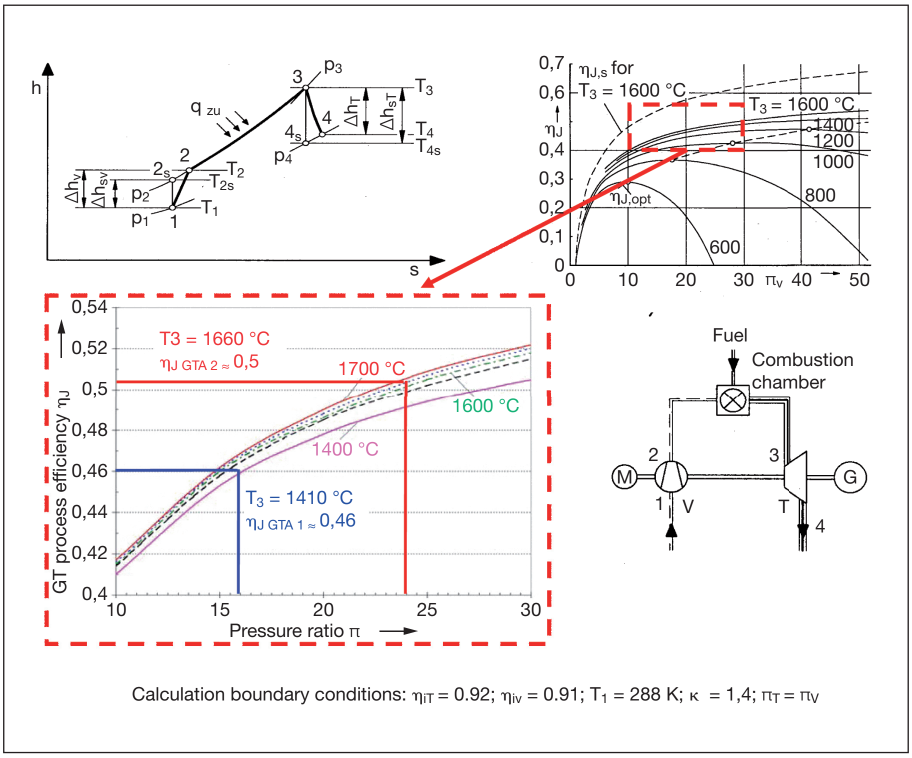


Figure 4. NO emissions as a function of the pressure with various combustion temperatures and residence time in the reaction zone of 30 ms.

$h_3 - h_2$ enthalpy difference between the combustion chamber outlet and inlet, assuming ideal gas as cyclic process fluid,,

$\Delta\eta_i$ internal efficiency of turbine (T) and compressor (V).

Using the equations for the isentropic changes of state in the turbine and compressor, the efficiency of the real gas turbine process can also be expressed as a function of the pressure ratios π in the turbine (T) and the compressor (V), and the temperature ratio of the Kelvin temperatures $\tau = T_3/T_1 = T_{max}/T_{min}$:



Calculation boundary conditions: $\eta_{iT} = 0.92$; $\eta_{iv} = 0.91$; $T_1 = 288$ K; $\kappa = 1,4$; $\pi_T = \pi_V$

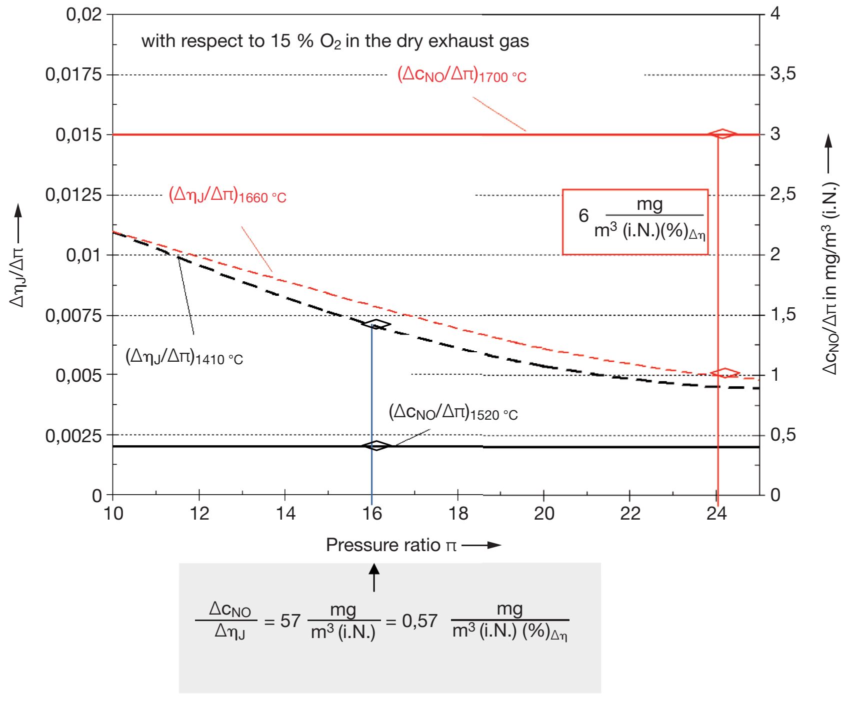
Figure 5. Efficiency of the real gas turbine process as a function of the pressure ratio and the upper process temperature.

$$\eta_J = \frac{\eta_{iT}\,\eta_{iV}\,\tau\,(1-\pi_T^{-m}) - (\pi_V^{m}-1)}{\eta_{iV}\,(\tau-1) - (\pi_V^{m}-1)} \qquad \text{(Eq. 7)}$$

where: $m = (\kappa - 1)/\kappa$ and $\kappa =$ isentropic exponent.

The graph of (Equation 7) is shown in Figure 5. The two GTP are also designated therein, but with their turbine inlet temperatures (T_3). The difference between combustion temperature (Figure 2) and turbine inlet temperature is explained by the mixing of the cooling air in the combustion chamber. Ambitious and visionary parameters were deliberately chosen for the GTP 2, in order to emphasise the differences and relationships. The GTP 2 with the higher process parameters and consequently also the greater nitrogen oxides emissions with the same combustion technology has, as expected, the higher process efficiency η_J with correspondingly lower specific CO_2 emissions.

Evidently the nitrogen oxides emissions and the specific carbon dioxide emissions always have a mutually inverse tendency in response to a modification of the upper process parameters. Whereas the discussion was based so far on different pressures and temperatures, it can be shown that even when the pressure ratio is increased alone, and thus the combustion chamber pressure is raised alone, the NO emissions increase more strongly than the process efficiency (Figure 6). Of course, increasing the pressure ratio increases the efficiency until the optimum for the respective turbine inlet temperature is reached, but the rise becomes smaller.



$$\frac{\Delta c_{NO}}{\Delta\eta_J} = 57\,\frac{mg}{m^3\,(i.N.)} = 0,57\,\frac{mg}{m^3\,(i.N.)\,(\%)_{\Delta\eta}}$$

For comparison:
According to the 37. BImSchV [3], when utilising natural gas for generating electric power with a simple cycle GTP with efficiency > 35 %, the emission limit value is increased according to the percentage increase of the power efficiency factor, i.e.

$$\frac{\Delta C_{NOx}}{\Delta\eta_e} = 1,0\,\frac{mg}{m^3\,(i.N.)\,(\%)_{\Delta\eta}}$$

Figure 6. Rise of efficiency of the real gas turbine process and NO emissions, depending on the compressor pressure ratio.

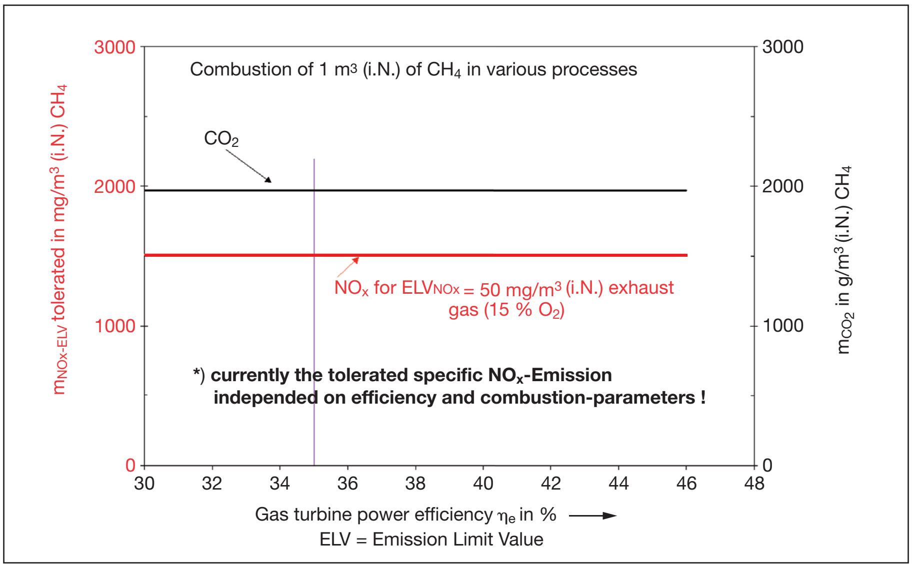


Figure 7. Specific CO_2 and NO emissions of GTP for a defined constant emission limit value ELV of 50 mg/m^3 (i. N.).

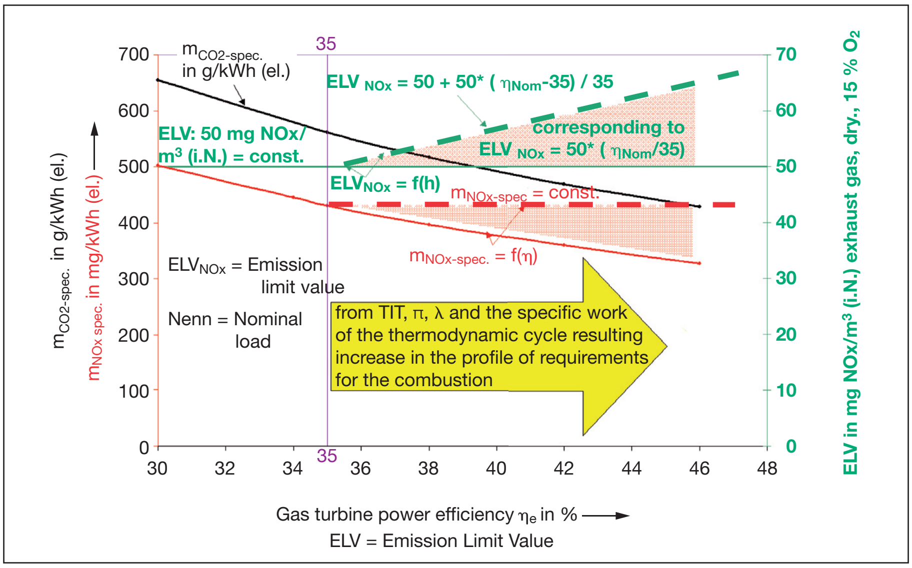


Figure 8. Specific CO_2 and NO_x emissions of GTP for applying the "Eta algorithm" (ELV_{NOx} = 50 mg/m^3 i.N.).

Compared therewith, the NO emissions increase in the considered parameter range almost linearly with the pressure (Figure 4), and over proportionally when the pressure and the temperature are increased.

Conclusions for a thermodynamically based definition of the limit values for nitrogen oxides

For same combustion technology, the more efficient GTP with higher process parameters inherently also have higher nitrogen oxides emissions. A thermodynamically based limit value definition has to take this fact into consideration. This means: The definition of an exhaust gas volume related NO_x limit value (expressed in mg/m^3 (i. N.)) has the consequence that for a high efficient GTP with reduced primary energy consumption and consequently smaller specific CO_2 emissions, compared with conservatively designed gas turbines, an additional reduction of the specific (i.e. effective output power related) NO_x emissions is required. These relationships are shown in Figures 7 and 8, taking as example a tolerated NO_x limit of 50 mg/m^3 (i. N., dry, 15 Vol. % O_2 by volume) and assuming combustion of pure CH_4.

A limit value definition in combination with the power efficiency of the GTP in the form of the so called "Eta algorithm" already implemented in [2] takes the a.m. requirements into consideration in a suitable manner:

$$ELV_{NOx} = ELV_{NOx,0} \cdot \eta_e / \eta_{Reference}$$

Whereby:

ELV_{NOx}	NO_x emission limit value,
$ELV_{NOx,0}$	defined NO_x base limit value,
η_e	Net efficiency with nominal load under ISO conditions,
$\eta_{Referenz}$	defined reference efficiency.

Thereby it is conservatively assumed that the NO_x emissions increase linearly with the efficiency. However, it has already been shown that the increase of the NO_x emissions in the parameter range of modern GTP with the same combustion technology is over proportional in relation to the power efficiency increase. Thus, such a limit value definition never leads to undue privilege for highly efficient GTP, but actually implies a demand for further development of the combustion technology in order to comply with the NO_x limit values.

The achieved level of the process parameters for high efficient GTP has no margin for further increasing the efficiency with simultaneous reduction of the NO_x emissions, because the required cooling air reduces the combustion air fraction and thus the air excess number. To avoid a conflict between the goals of climate protection and air pollution control, new or significantly modified GTP should make their contribution to environmental protection via the improved energy exploitation of the utilised fuel accompanying the efficiency increase.

As result of an intensive target oriented discussion between gas turbine operators, technical associations and legislative authorities, success has evidently been achieved for taking the "Eta algorithm" into consideration also in the 37. BImSchV [3], although so far only for simple cycle GTP. For combined-cycle power plants with high efficient gas turbines, an increased NO_x base value was defined instead of the "Eta algorithm".

Summary

The policy paper of the federal government for an integrated energy and climate programme constitutes the basis for the regulation to ensure fulfilment of the air quality requirements (37. BImSchV) with new definition of the emission limit values. The tolerated limits for NO_x emissions of GTP with a combustion power rating of more than 100 MW are redefined therein for using gas from the public supply gas network. When the new definitions come into force, they constitute stricter limits than those imposed by the present 13. BImSchV.

Since gas turbine technology makes an important contribution towards environmentally compatible, resources protecting and stable power supply, the authors wanted to show on the basis of a thermodynamic consideration that it is necessary to couple the limit values for nitrogen oxides emissions to the efficiency. This procedure can prevent a conflict between goals of climate protection and air purity control, and unfavourable treatment of highly efficient GTP. If, in contrast thereto, the emission limit value is defined on the basis of the normalised exhaust gas volume flow rate referred to its NO_x mass freight, this insinuates that, independently of the boundary conditions of the combustion process, for a certain quantity of fuel, a certain fixed amount of NO_x is tolerated. This does not correspond to reality. The "Eta algorithm" is a suitable approach which does not give highly efficient GTP undue advantage. The linear increase of the NO_x limit value according to the ratio of the net power efficiency to a reference efficiency is at the same time a formulation of the need for further development of the combustion technology. It can be considered as a successful achievement that as a result of the discussion with the legislative authorities, the "Eta algorithm" as thermodynamic based limit value definition will very probably be implemented also in the 37. BImSchV, although it would be appropriate to extend this approach also to GTP in combined-cycle power plants.

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