New concepts for NO_x emission measurement and limits - challenges for new fuels and fuel flexible systems

Dr.-Ing. Nico Schmitz

Department for Industrial Furnaces and Heat Engineering (IOB)
RWTH Aachen University
schmitz@iob.rwth-aachen.de

Outline

- Current NO_x emission regulations
- Challenges for future combustion systems
- Consequences for NO_x emission limits and measurement techniques

NO_x emission regulations at EU-level

- National Emission Reduction Commitments Directive (**NEC**) EU 2016/2284 defines five important air pollutants:
  - Nitrogen oxides (NO_x)
  - Non-methane volatile organic compounds (NMVOC)
  - Ammonia (NH_3)
  - Sulphur dioxide (SO_2)
  - Fine particulate matter ($PM_{2,5}$)
- The general framework for industrial production plants is built upon the Industrial Emissions Directive (**IED**) 2010/75/EU and refers to the best available techniques (**BAT**) in specific sectors.
- The BAT and the associated emission levels/limits are documented in the best available techniques reference document (**BREF**) and the **BAT conclusions**.
- Individual transfer of the IED and BREFs including specific emission limit values into national legislation

BREF Ferrous Metals Processing Industry

- Definition of BAT-associated emission levels for reheating furnaces defined in the BREF "Ferrous Metals Processing Industry" (FMP)
- Table 1.9 in the BAT conclusions "[…] feedstock heating in hot rolling":

Parameter	Type of fuel	Specific process	Unit	BAT-AEL (Daily average or average over the sampling period)	Indicative emission level Daily average or average over the sampling period)
NO_X	100 % natural gas	Reheating	mg/Nm³	New plants: 80–200 Existing plants: 100–350	No indicative level
		Intermediate heating	mg/Nm³	100–250	
		Post-heating	mg/Nm³	100–200	
	Other fuels	Reheating, intermediate heating, post-heating	mg/Nm³	100–350 (1)	

(1) The higher end of the BAT-AEL range may be higher and up to 550 mg/Nm³ when using a high share of coke oven gas or of CO-rich gas from ferrochromium production (> 50 % of energy input).

NO_x emission limit definition - today

- “Indicative emission levels for emissions to air […] refer to **concentration** (mass of emitted substances per volume of waste gas) under the following standard conditions: **dry gas** at a temperature of **273.15 K** and a pressure of **101.3 kPa**, and expressed in **mg/Nm³**.”
- Reference oxygen level is given for feedstock heating and drying: 3 vol-% (dry)
- For a measured NO_x concentration of 85 ppm @ 5 vol-% O_2 (dry) the emission value is calculated by:

$$Q_{NO_x,dry,ref}\left[\frac{mg}{m^3_{dry}}\right] = Q_{NO_x,dry}\left[ppmv_{dry}\right] \cdot \left(\frac{21 - Q_{O_2,ref,dry}\left[vol\%_{dry}\right]}{21 - Q_{O_2,dry}\left[vol\%_{dry}\right]}\right) \cdot \rho_{NO_2}$$

$$Q_{NO_x,dry,ref}\left[\frac{mg}{m^3_{dry}}\right] = 85\ ppmv_{dry} \cdot \left(\frac{21 - 3\ vol\%_{dry}}{21 - 5\ vol\%_{dry}}\right) \cdot 2{,}05\frac{kg}{m^3} = 196\ \frac{mg}{m^3_{dry}}$$

NO_x emission measurement - today

- Either continuous emission monitoring system (CEMS) or periodical measurements with portable analyzer systems are applied to quantify the NO_x emissions of reheating furnaces.
- Standard reference method for the determination of the mass concentration of nitrogen oxides: **chemiluminescence** (EN 14792)
- Gas analyzer systems have to fulfill a number of standards (EN 15267 1-4, EN 14181, EN 15259, …)
- Today, mostly **dry extractive gas analyzers** are used to measure NO_x and O_2 concentrations in the off-gas.

Challenge – future combustion systems

- **New fuels**:
  - Hydrogen (H_2), ammonia (NH_3), biofuels (e.g. DME), new top gases, blends of natural gas (NG) and these fuels...
- **New oxidizers:**
  - oxygen-enriched combustion, pure oxygen (O_2)
- **Fuel flexible operation:**
  - fluctuating availability of fuels

Challenge – future combustion systems

- Case study I: NO_x concentration of 180 $ppmv_{dry}$ @ 3 $vol.-\%_{dry}$ O_2

Basis	Unit	NG/air	H_2/air
measured NO_x level, dry off-gas	ppmv	180	180
Calculation acc. to BREF	mg/m^3 @ 3 vol-%	351	351
NO_x mass flow	**g/h**	**350**	**257**

- For a system retrofitted to hydrogen combustion or a fuel-flexible combustion system running from natural gas (NG) to hydrogen (H_2), the **NO_x mass flow** emitted through the stack **decreases by 26%** when switching from NG to H_2.
- **This results in lower NO_x emission limits for H_2 through the back door.**

Challenge – future combustion systems

- Case study II: NO_x mass flow (wet) per unit of energy: 110 mg/kWh @ 2 vol.-%$_{wet}$ O_2

Basis	Unit	H_2/air	H_2/O_2
NO_x amount in off-gas	mg/kWh	110	110
NO_x concentration (wet)	ppmv (wet)	182	567
NO_x concentration (dry)	**ppmv (dry)**	**265**	**28222**

- For a system running on pure oxyfuel combustion, the NO_x emission limit is not applicable[1].
- NO_x measurement technologies based on dry off-gas used today are not applicable for H_2/O_2 combustion (H_2O-concentration in the off-gas, NO_x-concentration in the dry off-gas)
- **Current NO_x limits and measurement techniques are not applicable to oxyfuel combustion with new and flexible fuel systems.**

[1] A calculation procedure to compare oxyfuel to air combustion for fossil fuels is formulated in the BREF FMP document. However, this is not applicable for H_2 as the basis is the CO_2-concentration in the off-gas.

Consequences – NO_x emission limits

- Current NO_x emission limits are only formulated for NG and ”other fuels” in the BREF FMP

- New definitions of NO_x limits must be established to allow a fair comparison between different fuels and oxidizers

→ Approach: limit definitions in ”mass flow per energy unit” (→ mg/kWh) are applicable and comparable for all fuels

→ Alternative: mass of NO_x per ton of product produced (→ kg(NO_x)/t(steel))

Consequences – NO_x measurement

- NO_x measurement based on dry extractive techniques is the most commonly used and is also applicable to new and different fuels with air combustion.
- Additional O_2 (mandatory today) and **H_2O** (not applied today) measurements are needed to allow comparable results.
- Due to the high water vapour concentration in e.g. H_2/O_2 combustion **(~98 vol-%)**, dry measurements of NO_x and O_2 with high accuracy are not possible.

→ Approach: emission measurement on a wet basis

- For a NO_x limit in mg/kWh, the fuel quality must be measured and transmitted to the emission monitoring system to calculate the LCV and the min. off-gas volume.

Summary and outlook

- Legislation is not ready for the widespread introduction of defossilized combustion systems and fuel-flexible industrial furnaces.
- Open topics:
  - NO_x limit definitions
  - Revision of BREF FMP to new limit definitions
  - Development of emission measurement system
  - Emission measurement standards
- Stay tuned:
  - IOB will shortly publish a paper describing the upcoming challenges for NO_x limits and measurement in detail.
  - IOB and many partners are working on NO_x emission measurement solutions for H_2/air and H_2/O_2 combustion systems in the HYINHEAT project (www.hyinheat.eu)

dissHEAT

Thank you for the attention!

Stay informed

www.dissheat.eu

Dr.-Ing. Nico Schmitz | Group Manager Combustion Technology
Department for Industrial Furnaces and Heat Engineering (IOB)
RWTH Aachen University
schmitz@iob.rwth-aachen.de | www.iob.rwth-aachen.de