

Unregulated Emissions with TWC, Gasoline & CNG

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ABSTRACT

Analysis of non-legislated engine-emission components, with different exhaust-gas after-treatment techniques, is an important air quality objective.

This paper reports the results for various nitrogen oxides, ammonia and differentiated hydrocarbons emitted at part load from a small 4-SI engine. It was operated with gasoline, with CNG *) and with two different three-way catalytic converters.

CNG produces less HC and less aromatics. But the HC conversion rate is insufficient. This is due to the lower exhaust gas temperatures, at part load with CNG, and due to the higher stability of light HCs.

CNG affects the λ -regulation window, of the investigated system, such that the NOx conversion rate is lowered.

In the rich domain of the λ -regulation window, the NO & NOx emissions after catalyst were lowest, while the NH3 formation was most intense, and vice versa.

The catalyst type: precious metal, and its content, influences the conversion rates and emissions of the investigated components during light-off.

INTRODUCTION

The potential of gaseous fuels to curtail engine emissions is, since many years, generally accepted. Lower emissions are mostly due to the much easier and consequently strongly improved gas mixture preparation.

Several investigations and engine developments have shown that compressed natural gas (CNG) is a cleaner fuel. Several manufacturers offer vehicle versions with CNG, mostly as dual-fuel design [1, 2, 3, 4, 5, 6]*).

*) References and Abbreviations: see at the end of paper

The electronic systems for multipoint gas injection are continuously refined. This enables further improvements of the mixture preparation, mixture distribution on the individual cylinders and Lambda regulation, [6, 7, 8, 9, 10, 11, 12, 13].

During the development of new exhaust gas after-treatment systems, as well as with the introduction of alternative fuels, there is concern about several non-legislated emission components. These are recognized as especially toxic. Expert groups propose these as candidate substances for future limitations.

The Swiss Federal Lab EMPA has a long tradition in the analyses of such substances for different national and international programs [14, 15, 16, 17, 18, 19].

This paper reports some results of collaboration between the IC-Engines Labs of the EMPA and of the University of Applied Sciences, Biel, Switzerland.

The tests were performed on a special research engine. It can be operated with gasoline and with CNG (both with MPI). The principal parameters, e.g. ignition- and injection timing and the air excess factor, can be varied by access to the ECU of the engine, [20].

The principal objectives of the study were to:

- Clarify the conversion behavior of different components, by varying the air excess factor λ in the lambda-window near to $\lambda = 1$.
- Investigate the cold start, warm-up and catalyst light-off with both fuels (gasoline & CNG) and with two different catalysts.

The on-line measurements of non-legislated substances like NO, NO₂, NH₃ and 7 differentiated hydrocarbons (see [appendix](#)) were done using the chemical ionization mass spectrometry (CI-MS) from EMPA.

TESTED ENGINE, FUELS, CATALYSTS

The engine used for investigations was a small 4-SI Lombardini LGW 523 OHC. [Fig. 1](#) shows the engine in the test cell. The most important data of this engine are:

Lombardini LGW	523 OHC
2-cylinder, B/S	72/62 mm
Displacement	505 cc
Compression ratio	8.7
Max. RPM	5000 rpm
Max. Torque	37 Nm at 2200 rpm
Rated power	15 kW (20.4 HP)
Idling	1100 rpm
Water cooling	
Multi-unit port injection	

The Lombardini LGW engine was equipped with the electronic engine control system for ignition, multipoint injection and λ -regulation, already in the previous projects of the IC-engine Lab at the University of Applied Sciences, Biel. This system was modernized and completed with a second separate system for the multipoint gas injection. To provide enough gas flow, two gas injectors per cylinder were installed.

The electronic engine systems enabled variability of spark timing, of sequential injection timing and of injection duration.

The fuels used in the investigations are: gasoline (Swiss market quality) and compressed natural gas (CNG) from the Biel city net. [Table 1](#) shows the most important data.

An example of the average composition of the Swiss city net-gas is given in [Table 2](#), [6]:

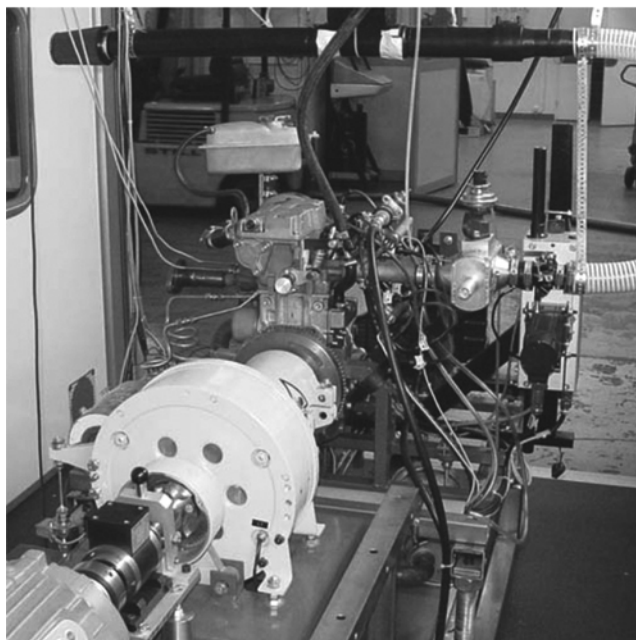


Fig.1. Lombardini LGW523 engine in the test cell

Table 1. Data of used fuels

Fuel	Gasoline	CNG
Density ρ_{nf} [kg/m ³]	735	0.78
Lower calorific value H_u [MJ/kg]	42.5	49
Air _{min} (kg _{air} /kg _{fuel})	14.44	16.35
c/h	6.1429	3.0742

Table 2. Average composition of city net-gas (Biel)

Component		Concentration [% vol]
CH ₄	Methane	93.97
C ₂ H ₆	Ethane	3.25
C ₃ H ₈	Propane	0.71
C ₄ H ₁₀	i-Butane	0.13
C ₄ H ₁₀	n-Butane	0.11
C ₅ H ₁₂	Iso-Pentane	0.05
C ₅ H ₁₂	n-Pentane	0.18
C _x H _y	Large HC molecules	0.12
N ₂	Nitrogen	1.29
CO ₂	Carbon dioxide	0.18
O ₂	Oxygen	<0.01

Two catalysts with different coatings were used, [Fig. 2](#).

The data are given in [Table 3](#).



Fig.2. Investigated catalytic converters

Table 3. Data of the investigated catalysts

Manufacturer	ECOTEC	ECOTEC
Number	18603	18604
Diameter [mm]	70	70
Length [mm]	74.5	74.5
Volume [mm ³]	0.29	0.29
Cells/in ²	350	350
Precious metals [g/dm ³]	1.77	3.18
Pr. metal ratio [Pt : Pd : Rh]	05:00:01	00:14:01
Symbol	Pt / Rh	Pd / Rh

MEASURING SET-UP & INSTRUMENTATION

Fig. 3 shows the scheme of the fuel system and the measuring set-up of this engine.

The instrumentation consists of:

- Schenck eddy current dynamometer W40
- Air flow: Degussa DegufLOW, Typ 8740
- Fuel consumption: Gasoline API-Com S.r.L. MP 324/R Gases - RHEONIK Remag RHM 015 GNT
- Pressure indication system: Kistler - DATAC-1, Pressure transducer Kistler Type 7061B
- Exhaust gas λ -measurement - Sonde λ NGK
- Exhaust gas components Horiba: infrared analyzers for CO, CO₂, HC_{IR}, Magnos for O₂, Flame ionization detector for HC_{FID}, Chemo-luminescent analyzer (CLD) for NO, NO_x
- Ambient conditions: pressure, temperature and humidity.

CHEMICAL IONIZATION MASS SPECTROMETRY

Mass spectrometric analysis of raw exhaust gas was performed at 180°C using a chemical ionization mass spectrometer (Airsense, V&F, Absam, Austria) in the low energy ionization mode with mercury as ionization gas (Hg⁺, 10.4 eV). The presence of ammonia, NO, NO₂, C₂H₄, C₃H₆, C₄H₆, C₄H₈, C₆H₆, C₇H₈, and C₈H₁₀ was tracked in the selective ion monitoring mode (SIM) recording cations at $m/z = 17, 30, 40, 28, 42, 54, 56, 78, 92$, and 106 amu respectively, at low ionization gas pressure. Calibration of the CI-MS was performed prior to every test run applying calibration gas standards in synthetic air.

Correction of chemical background, compensation of retardation effects and integration of the obtained emission profiles, were performed after the test run.

CI-MS measurements were validated with independent methods based on gas chromatography flame ionization detection (GC-FID) for hydrocarbons [16] and with fourier transformation infrared spectroscopy (FT-IR) and ion chromatography (IC) for ammonia [17]. As reported, correlation with these independent methods were convincing at comparable sampling methods. Raw gas sampling was strongly recommended for ammonia measurements [17].

<Figure 3 here>

TEST PROCEDURES

According to the objectives of the study, two types of test procedures were applied:

For the investigation of conversion of the gaseous components near to $\lambda = 1$, the engine was operated at two stationary operating points. These are: 2000 rpm / 2 bar and 2000 rpm / 4 bar [n/pme], which are generally recognized as representative for the average part load operation during city driving.

The objective was to investigate changes of reduction and oxidation near to $\lambda = 1$. Hence, the λ -variations in the λ -window were performed in small steps. The values of Lambda were estimated in two ways: by means of a continuous λ -sonde, and by calculating with the Brettschneider equation [21].

Investigations of the cold start & warm-up of the engine were done with the engine cooled down to the ambient temperature (approx. 20°C). Before cooling down, the engine was operated at the operating point 2000/ 2 [rpm/bar] with setting of α_z , λ and $\alpha_{throttle}$ for this point. These settings were kept for the cold start.

All the test series were performed with both fuels (gasoline & CNG) and with both catalysts (Pt/Rh & Pd/Rh).

RESULTS

EMISSIONS IN THE λ -WINDOW

Prior CNG investigations showed no conversion of NO_x with the activated λ -regulation (λ -regulation can be activated and deactivated by the ECU of this engine.) A careful variation of λ in small steps should clarify this.

Fig. 4 shows an example of NO_x-conversion rate, as a function of Lambda, for the two fuels and two catalysts at 2000 rpm / 2 bar. With the measured λ and CNG, richer λ -values are indicated, than the calculated λ (differences of Lambda are small 0.010 to 0.015). Nevertheless, this is enough to provoke too much leaning and the strong decrease of conversion rate with CNG (moving of the λ -window to the

rich side). The results were similar at the operating point 2000/4,.

After some repetitions and careful scrutiny of all possible error sources, the primary reason of the different behavior with CNG was identified. It is the change of λ -signal, due to the cross sensitivity of the λ -sensor against some of the CNG exhaust components. Buglass et al. [22] show that particularly H_2 has a significant influence in this respect. The influences of other possible reduction agents (CH_4 , aromatic HC, NH_3) are much weaker.

Depending on fuel and catalyst type, ammonia (NH_3) is produced, which depends on temperature and on the equivalence ratio λ . Fig. 5 shows the results of Lambda variations in the λ -window near to $\lambda = 1$. In the rich, reducing conditions, there is more formation of ammonia but no NO (which is reduced by ammonia). In the lean oxidizing conditions, this relationship is inverted: no ammonia, but much NO. With gasoline the ammonia production is more intense, due to higher exhaust gas temperatures.

$\alpha_z=40^\circ CA$ b. TDC, $\alpha_{throttle}=const.$

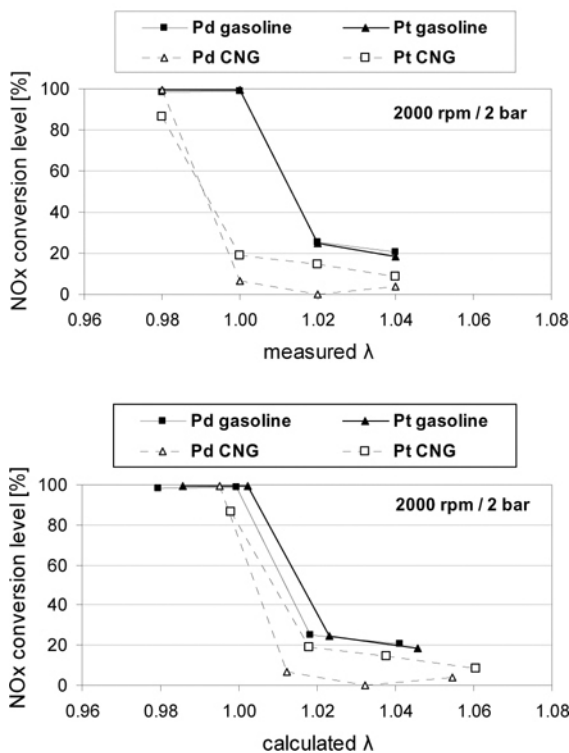


Fig.4. NO_x conversion efficiency in the λ -window with measured an calculated λ

$\alpha_z=40^\circ CA$ b. TDC, $\alpha_{throttle}=const.$

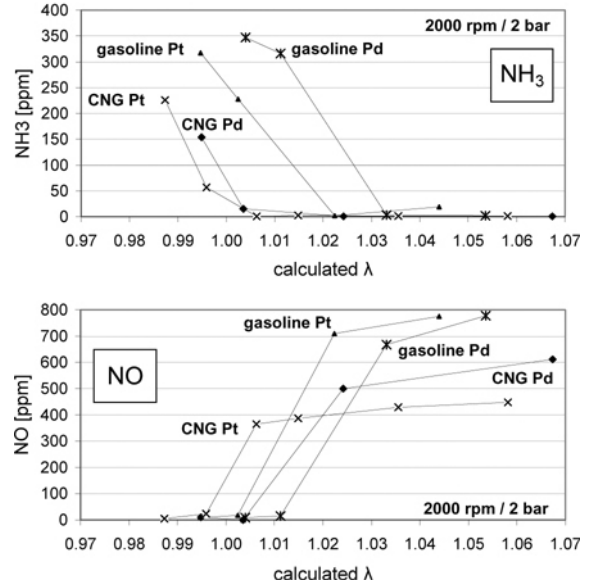


Fig.5. Emissions of NH_3 and NO in the λ -window with different fuels and catalysts

The Pt/Rh-catalyst shows increased NH_3 or NO production at slightly richer conditions ($\Delta \lambda \leq 0.01$), than the Pd/Rh-catalyst.

Fig. 6 shows the comparison of NO_x and NO_2 values measured with different methods at $\lambda = 1$. The NO_x values, obtained with CI-MS (Airsense), are generally comparable with those of CLD (except for CNG Pd). The correlation is good. The NO_2 -values with Pt-catalyst are higher, than with Pd-catalyst.