Fuel Standardization Requirements for Compressed Natural Gas (CNG)

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CONTENT

- **Prospects of NG / Methane as Automotive Fuel**
- **Natural Gas / Methane Quality Requirements**
  - Catalyst Durability - Sulfur
  - Energy Content – Lower Heating Value & Wobbe Index
  - Knock Resistance - Methane Number
  - Steel Tank Safety – Hydrogen
  - Cleanliness –Siloxane (Si Content)
  - Cleanliness – Compressor Oil
- **European Standardization Status**
- **Summary & Conclusions**

Prospects of NG / Methane as Automotive Fuel

Source: ExxonMobil; Outlook for Energy, A View to 2040
http://www.exxonmobil.com/Corporate/energy_outlook.aspx

Higher NG reserves (200+ years) than oil reserves (70 years)

Worldwide CNG retail prices (status ~ 2013)

Source: Alternative Fuels Data Center,
http://www.afdc.energy.gov/fuels/prices.html accessed 03/2015

Worldwide lower CNG than gasoline price.

Total Number of NGVs Worldwide

Source: Alternative Fuels Data Center,
http://www.afdc.energy.gov/fuels/prices.html accessed 03/2015

17.7 million NGVs worldwide. Annual growth 2000 – 2012: ~ 25 %

Prospects of NG / Methane as Automotive Fuel

Well-to-Wheel View of Alternative Fuel Pathways

Renewable methane (bio-methane / power-to-gas-methane) can be blended with NG up to 100% (unlike ethanol/gasoline or biodiesel/diesel)

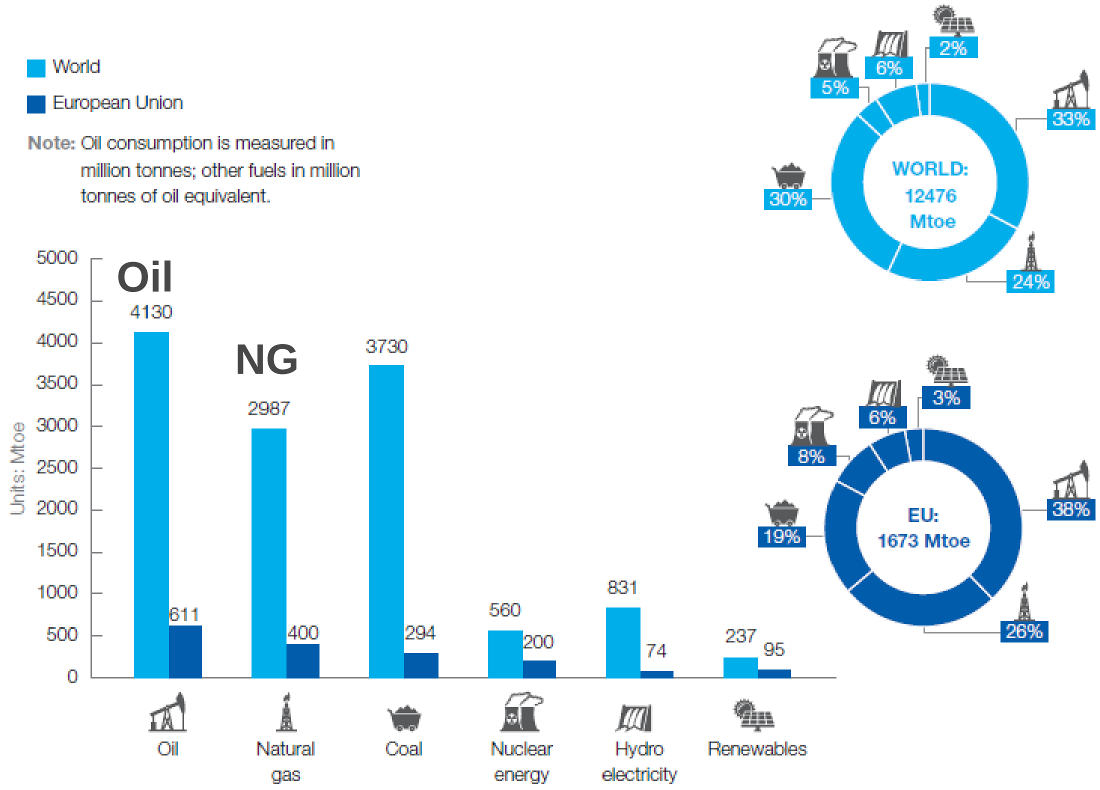
NG / Methane Advantages - Combustion

- More favorable C/H ratio than gasoline/diesel→ TtW CO_2 reduction: ~25%
- Low feedgas emissions: in particular no soot
- Very knock resistant → ideal fuel for boosted, downsized SI engines and dual fuel NG / diesel engines

Methane: interesting future automotive transportation fuel.

Prospects of NG / Methane as Automotive Fuel

Worldwide Energy Consumption by Fuel Type in 2012



Source: "Fuels Europe Statistical Report 2014"; www.fuelseurope.eu / BP Statistical Review of World Energy 2013

Worldwide:

NG consumption: 2987 Mtoe*

Oil consumption: 4130 Mtoe*

EU:

NG consumption: 400 Mtoe*

Oil consumption: 611 Mtoe*

*<u>*Mtoe</u>: Mega tonne of oil equivalent. 1 toe is defined as the amount of energy released by burning one tonne of crude oil. It is approx. 42 GJ*

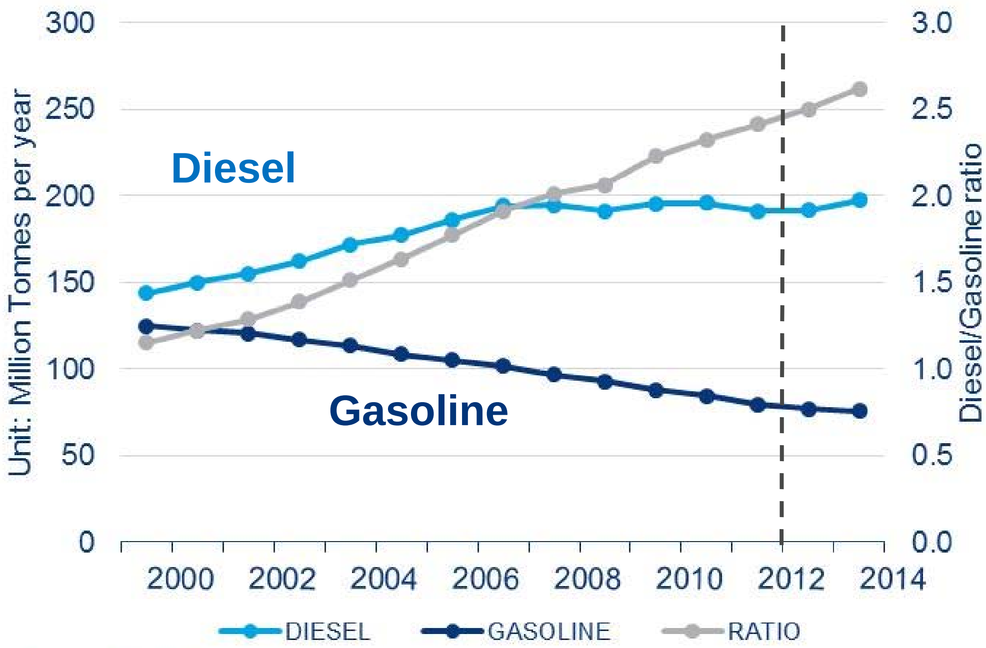
- **EU oil consumption = 1.5 x EU NG consumption**

Transition from oil based fuels to NG/methane as automotive fuel would increase the NG demand considerably.

Prospects of NG / Methane as Automotive Fuel

Road Fuel Demand in the EU

Sources: ‚Fuels Europe Statistical Report 2014, www.fuelseurope.eu / Wood Mackenzie



Source: Wood Mackenzie

2012

EU NG: 400 Mtoe/y

EU Oil: 611 Mtoe/y

EU gasoline:~ 80 Mt/y

EU diesel: ~ 200 Mt/y

EU total: ~ 280 Mt/y

- **If half [all] of the EU diesel/gasoline is replaced by NG** → approx. 140* Mtoe/y [280* Mtoe/y] additional NG demand → **35% [70%] increase of NG consumption**

Automotive Transportation has the potential to become the main NG customer.
→ NG quality standards must be aligned with automotive needs !

**Approximation:1 Mtoe is equivalent to 1 Mt of gasoline and 1 Mt of diesel*

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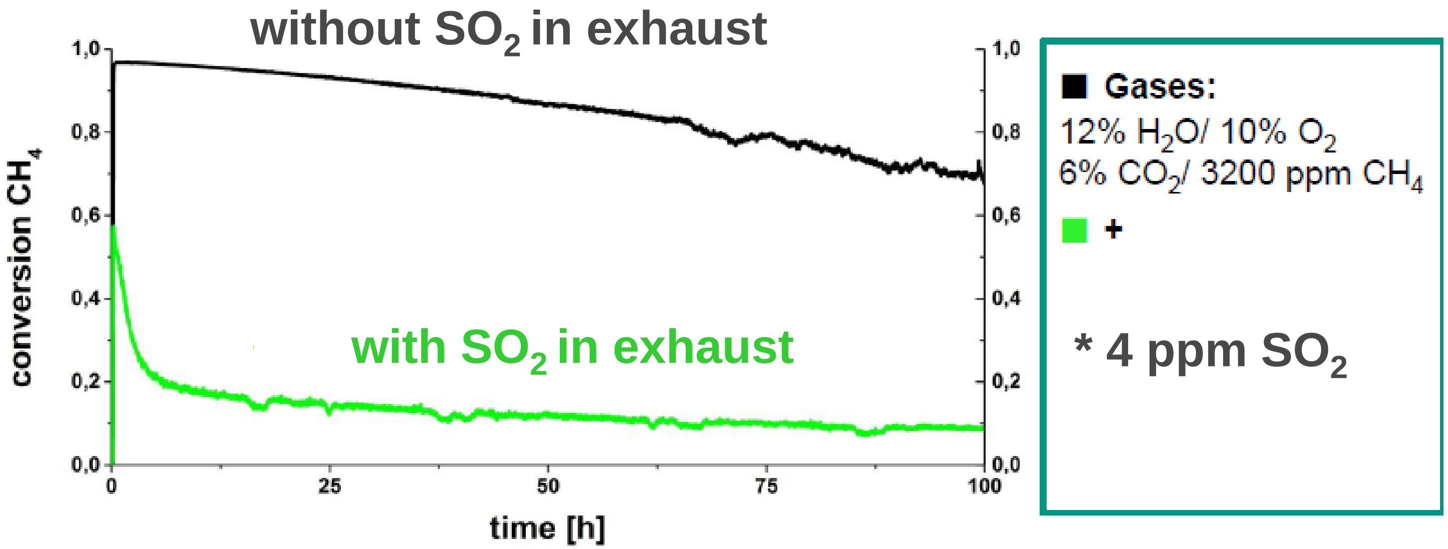
NG / Methane Quality Requirements

Catalyst Durability – Sulfur Effect on Conversion Efficiency

Test Rig Results of FVV Project 1134 (2014)

"[…] catalytic methane reduction"

Source: Investigation of mechanism of catalytic methane reduction; C. Schwarzer, U.Endruschat, A. Gremminger, O.Deutschmann, J.-D. Grunwaldt, KIT Karlsruhe; Final report, FVV-project No. 1134, FVV Spring Conference, Magdeburg, 27. March 2014



** 4 ppm in the exhaust gas is approx. equivalent to 30 ppm S in NG fuel*

- Strong deactivation of catalyst within 10 h in the presence of SO_2
- Only 9 % of methane converted after 100 h of operation at 450°C

<u>Research Catalyst</u>, required e.g. for future HD Dual Fuel applications (λ > 1):
91% reduced CH_4 conversion during 100 hrs aging in the presence of 4 ppm SO_2
→ Considerable loss in methane conversion efficiency (in particular lean burn)

NG / Methane Quality Requirements

Catalyst Durability – Sulfur Requirements

Maximum sulfur limit requirements as in other well established fuel quality standards:

- **10 mg/kg in German automotive NG standard** — **DIN 51624**
- **10 mg/kg in European gasoline standard** — **EN 228**
- **10 mg/kg in European diesel standard** — **EN 590**

=> Requirement:

- *** Maximum sulfur limit 10 mg/m³ required in European NG standards**

** [mg/m³] (used in European draft standards) instead of [mg/kg] is already a relaxation of existing limits*

NG / Methane Quality Requirements

Catalyst Durability - Sulfur Species and Origin

Source: Assessment on Sulphur Limitation in NG/biomethane as Automotive Fuels; Input for CEN/TC 408; NGVA Europe, 2013

- **2 Origins:**
  1. **Natural sulfur:** due to organic decomposition process → traces of sulfur → typically cleaned or processed close to the extraction points.
  2. **Sulfur additive for odorization**

     (as NG is an odorless product → safety).

- **Significant sulfur entry by conventional odorization.**

NG / Methane Quality Requirements

Catalyst Durability – Sulfur Occurrence

Source: Assessment on Sulphur Limitation in NG/biomethane as Automotive Fuels; Input for CEN/TC 408; NGVA Europe, 2013

Mean and maximum total sulfur levels observed in different EU member states
(non-odorized unless otherwise stated):

Country	Sulfur (mean) / mg/m³	Sulfur (max. observed) / mg/m³	Components	Odorization Status
Belgium	**2.7**	**8**	**Total Sulfur**	non-odorized
Germany	**1.5**	**5**	**H2S + COS**	non-odorized
Netherlands	**1.5**	**6**	**Total Sulfur**	non-odorized
UK	**3.3**		**Total Sulfur**	non-odorized
Italy	**25**	**35**	**Total Sulfur**	non-odorized
Spain	**11**	**25.7**	**Total Sulfur**	**odorized !**
Denmark	2.6		H2S	non-odorized
France	< 5	14	H2S	non-odorized

- **Non-odorized mean sulfur levels usually below 10 mg/m³.**
- **Peaks can be cushioned by NG conditioning at injection points.**
- **Sulfur free odorants are commercially available**
  (e.g. Germany*: 20…25%) **Source: http://www.dvgw.de/gas/gase-und-gasbeschaffenheiten/odorierung/*

NG / Methane Quality Requirements

Wobbe Index

Inferior Wobbe Index (WI):

- **Inferior calorific value, on a volumetric basis**, at specified reference conditions**, divided by the square root of the relative density** at the same specified metering reference conditions (dry air density)
- Measure of heat input to gas appliances derived from the orifice flow equation. ***Heat input for different natural gas compositions is the same if they have the same WI, and operate under the same gas pressure*** (see ISO 6976).

Source: ISO 15403:2008 Natural gas — Designation of the quality of natural gas for use as a compressed fuel for vehicles

Source: SAE Paper 920593, The Impact of Natural Gas Composition on Fuel Metering and Engine Operational Characteristics; Steven R. King; Southwest Research Institute

- **WI restriction beneficial for automotive usage.**
- **Net Wobbe Index (H-Gas): 41.9 - 49.0 MJ/m³**
- **Net Wobbe Index (L-Gas): min. 40.5 MJ/m³**

NG / Methane Quality Requirements

Lower Heating Value

Picture Source: erdgas mobil / Danny Kurz Photography

Lower Heating (Calorific) Value:

- Mass related Lower Heating Value [MJ/kg] (aka Lower Calorific Value) also usual for other automotive fuels like diesel and gasoline

- CNG is usually sold in “kg”
- Energy content of CNG determines vehicle range and value for money

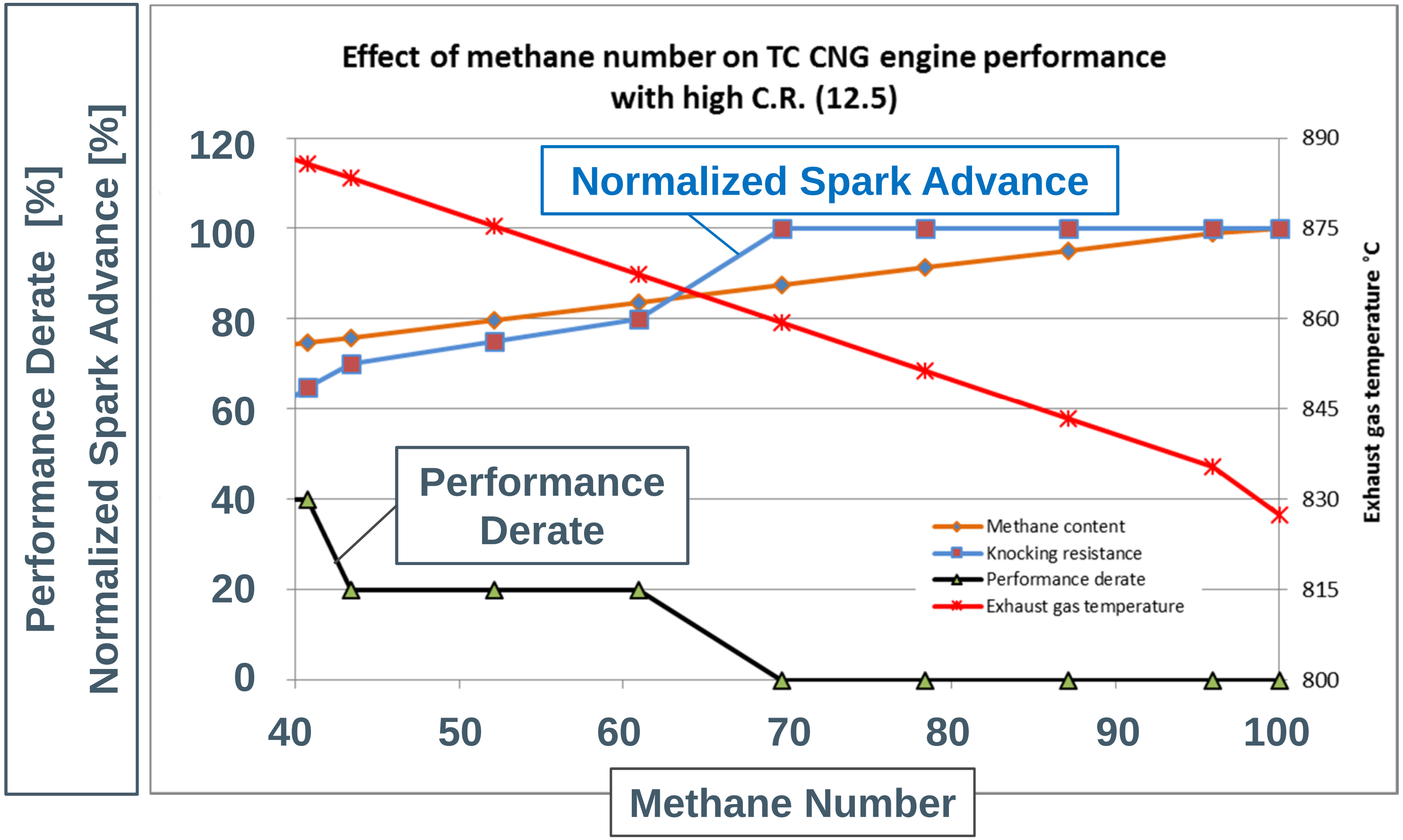
Required: Specification for Lower Heating Value, in addition to WI.
- **Lower Heating Value (H-Gas): min. 44 MJ/kg**
- **Lower Heating Value (L-Gas): min. 39 MJ/kg**

Specified for automotive CNG in Germany since 2008 (DIN 51624):
- Lower Heating Value (H-Gas): min. 46 MJ/kg
- Lower Heating Value (L-Gas): min. 39 MJ/kg

NG / Methane Quality Requirements

Methane Number (Boosted SI Engine with High Compression Ratio (CR))

Methane Number (MN) describes the knock resistance of NG

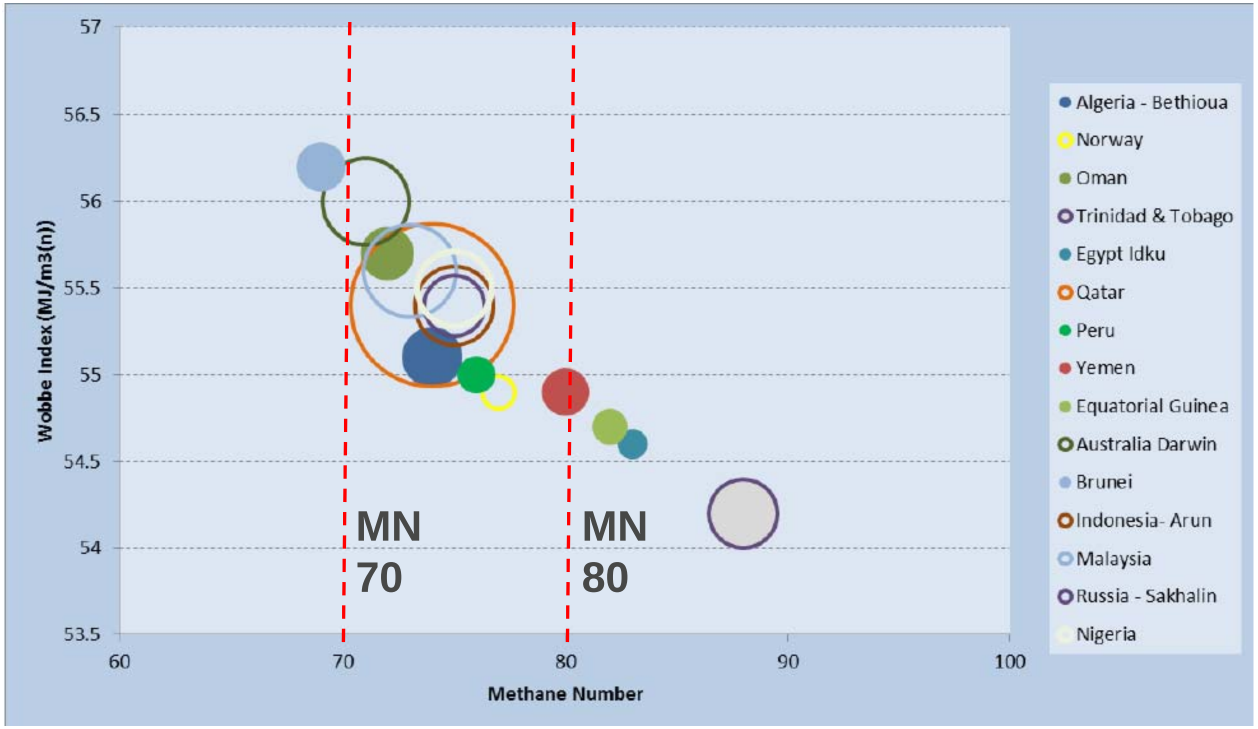


Source: Centro Ricerche FIAT S.C.p.A (CRF), 2014

- **Boosted CNG SI engine CR 12.5: MN 70 → 60: 20% performance derate**
- **Efficiency degradation below MN 70 → increased CO_2 emissions**

NG / Methane Quality Requirements

Methane Number vs. Wobbe Index for LNG Qualities



Source: GIIGNL (International Group of LNG Importers) Position paper on the impact of including methane number in natural gas regulation; 05/2015 http://www.giignl.org/system/files/mn-position-paper-giignl-v20150527-_rev.pdf

- **MN critical: LNG Markets only** (CNG is usually MN > 70, bio-methane MN > 80)
- "Bubble Size" proportional to liquefaction plant capacity

Methane number vs Wobbe Index of LNG from different countries and amounts exported worldwide (based on average composition for 2013 and MWM calculation method for MN).

- **The most MN critical NG is LNG**
- **LNG is only ~ 7% of the NG market** (directly used as LNG or re-evaporated to CNG)
- **Only 3 % of LNG underachieves MN 70 (→ 0.2 % of total NG)**

NG / Methane Quality Requirements

Hydrogen *Source: STATUS OF UNITED NATIONS REGULATION, ECE 110; UNIFORM PROVISIONS CONCERNING THE APPROVAL OF:*
I. SPECIFIC COMPONENTS OF MOTOR VEHICLES USING COMPRESSED NATURAL GAS (CNG) IN THEIR PROPULSION SYTEM;
II. VEHICLES WITH REGARD TO THE INSTALLATION OF SPECIFIC COMPONENTS OF AN APPROVED TYPE FOR THE USE OF COMPRESSED NATURAL GAS (CNG) IN THEIR PROPULSION SYSTEM

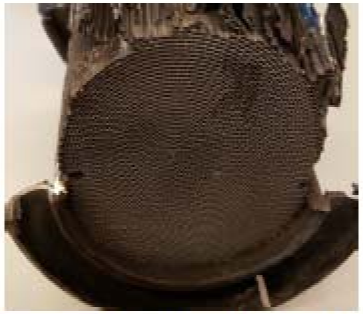
- **Hydrogen content critical for CNG steel tanks**, due to risk of Risk H_2 embrittlement.
- CNG steel tanks are usually designed in accordance to **ECE 110**
- **Maximum acceptable H_2 content:**
  - **Dry CNG: 2 % v/v**
  - Wet CNG 0.1 % v/v
- **Automotive CNG is usually dry:**
  - Dry means: < 32 mg/m³ water, pressure dewpoint -9° C at 20 MPa.

- **Steel tank safety issue -> embrittlement**
- **H_2 limit of max. 2% v/v required for existing and future NG vehicles**

NG / Methane Quality Requirements

Siloxane (Si Content)

- Siloxanes are introduced into NG by bio-methane blending (sources: landfill gases or defoamers used during bio gas production)
- Most sensitive components are catalysts and (switch type) lambda sensors (→ misalignment of fuel/air ratio).



Catalyst: front

Catalyst: back

DNVGL tests – Micro CHP (Combined Heat Power) engine: silica deposition (grey deposit) on front of catalyst:
20% degradation of NO conversion (10 g SiO_2) -> max. concentration in biogas: 0.26 mg Si/m3

Source: M. van Essen, P. Visser, Towards well-founded standards for siloxanes in bio-CNG, DNV GL report no. GCS.102568, July 2016

On λ probe

Micro CHP engine: deposits found on lambda sensor: Bosch recommends a max. Si content of 0.1 mg/m³.

Source: M. van Essen, P. Visser, Towards well-founded standards for siloxanes in bio-CNG, DNV GL report no. GCS.102568, July 2016

Source: Bosch 2015

NG / Methane Quality Requirements

Siloxane (Si Content)

- Currently no capable method agreed to determine the Si content in 0.1 mg/m³ range

- **Capable Si concentration determination method to be developed.**
- **Limit of 0.1 mg/m³ considered as safe limit → to be introduced as long as no relaxing data available.**

NG / Methane Quality Requirements

Compressor Oil

- Delay in injector closing with high compressor oil content reported.
- Impact of oil type (mineral / synthetic) not investigated
- Impact on pre-Ignition behavior not investigated
- No standardized test method available

Source: Influence of Oil Contamination on Injector for NGV and Development of Oil Trap Filter; Toshitaka Hachiro (Keihin Corporation); Presentation Congress "Gas Powered Vehicles", Potsdam 2012

Source: Einfluss von Verdichteröl aus Erdgastankstellen auf den Betrieb von CNG Fahrzeugen; Hans Jürgen Schollmeyer, Manfred Hoppe; Fachberichte Erdgasfahrzeuge, Jan./Feb. 2012, gwf-Gas

- **A capable compressor oil determination method is required.**
- **Limits to be determined with regard to injector functionality and pre-Ignition / knock tendency (on dedicated high CR NG engines).**

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European Standardization Status

Overview European of NG Standardization

Source: EN 16726:2015 E & prEN 16723-1:2014 E & prEN 16723-2:2014 E

- European NG standardization is fragmented and handled by different standardization groups:
  - CEN TC 234: Grid Standard
  - CEN TC 408: Bio-Methane Injection Standard and Automotive Standard

- Currently 3 different standards are proposed for Europe:
  1. Automotive CNG / methane fuel retail quality: prEN 16723-2:2014 E (TC 408)
  2. Quality of NG in the European grid: EN 16726:2015 (TC 234)
  3. Quality of bio-methane injected into the grid: prEN 16723-1:2014 E (TC 408)

Important automotive requirements are difficult to implement into standards because:

- **Fragmentation of NG standards**
- **Small fraction of NG consumed by the automotive sector today.**

European Standardization Status

Automotive CNG / methane fuel retail quality: prEN 16723-2:2014 E (TC 408)

Parameter	Unit	Min.	Max. Limit
Si	mgSi/m³	-	0.1 or 0.5
Hydrogen	% m/m	-	2
Hydrocarbon Dew Point	°C	-	-2 (as in EN 16726)
Oxygen	% m/m	-	1
H_2S	mg/m³	-	5 (as in EN 16726)
Total Sulfur	mgS/m³	-	[c]
Methane Number	Index	65 [d] (as in EN 16726)	-
Compressor Oil			
Dust Impurities			[e]
Amine			[e,f]
Water dew point			10 [g]

- No Wobbe Index.
- No Lower Heating Value.
- Si limit not agreed. No method agreed.
- No sulfur limit.

  Footnote "c": "[…] difference between the automotive industry needs for sulfur content (10 mgS/m3 including odorisation) and the values the gas industry can provide (30 mg/m3 including odorisation). […]"
- Methane Number 65 is too low.

  Footnote "d": "[…] only a small fraction of the distributed natural gas has a methane number below (MWM) of 70. "
- Compressor oil: No limit. No agreed method available.

Upgrade required: WI, LHV, Si, S, MN & Compressor Oil

Source: prEN 16723-2:2014 E; Natural gas and bio-methane for use in transport and bio-methane for injection in the natural gas network — Part 2: Automotive fuel specifications

<u>Source:</u> *DIN EN 16726:2016-04 ; EN 16726:2015; Gas infrastructure - Quality of gas - Group H*

European Standardization Status

Quality of NG in the <u>European grid</u> (1): EN 16726:2015 (TC 234)

Parameter	Unit	Min.	Max. Limit
Rel. Density	-	0.555	0.7
Total Sulfur	For sulfur in high pressure networks and on interconnection points the **maximum acceptable sulfur content for conveyance is 20 mg/m3,** where in high pressure networks non-odorized gas is current practice. However, for existing practices with respect to transmission of odorized gas between high pressure networks higher **sulfur content value up to 30 mg/m3 may be accepted.** NOTE On distribution networks the odorization is considered as a national safety issue. Some information about sulfur odorant content is given in Annex B.		
H_2S	mg/m³	na	5 [a]

- Sulfur: limit **before** odorization 20 mg/m³ already too high
- No sulfur limit after odorization.

Footnote: "[…] for existing practices with respect to transmission of odorized gas between high pressure networks higher sulfur content value up to 30 mg/m³ <u>may be accepted</u>"

- **Grid standard needs to ensure automotive NG quality in order to ensure adequate quality for connected filling stations !!!**
- **Desulfurization at retail stations is economically unrealistic.**
- **Upper sulfur limit must be after odorization. Should be 10 mg/m³.**

European Standardization Status

Quality of NG in the European grid (2): EN 16726:2015 (TC 234)

Parameter	Unit	Min.	Max. Limit
Mercaptan S	mg/m³	na	6 [a]
Oxygen	% m/m	na	0.001 or 1
CO2	% m/m		2.5 or 4
Hydrocarbon Dew Point	°C	na	-2
Methane Number	-	65	na

- No Wobbe Index.
- No Lower Heating Value.
- No Si (Siloxane) limit.
- No H_2: limit.
  Note in Annex E: "[…] admixture of up to 10 % by volume of hydrogen to natural gas is possible in some parts of the natural gas system […] steel tanks in natural gas vehicles: specification UN ECE R 110 stipulates a limit value for hydrogen of 2 vol%."
- Methane Number: 65 too low.
  Positive: in accordance to MWM method, which is sufficiently laid out in Annex A.

Source: DIN EN 16726:2016-04 ; EN 16726:2015; Gas infrastructure - Quality of gas - Group H

Upgrade required: WI, LHV, Si, S, H_2, MN

European Standardization Status

Quality of (bio-) methane injected into the grid: prEN 16723-1:2014 E (TC 408)

Parameter	Unit	Min.	Max. Limit
Si	mg / m³		0.1 ... 1 or 0.3 …1 [b]
Compressor Oil		[c]	[c]
Dust Impurities		[c]	[c]
Chlorinated Compounds		-	[d e]
Flourinated Compounds		[c]	[c]
CO	% m/m	-	0.1 [f]
PAHs			
NH3	mg/m³		10 [g]
Amine	mg/m³		10 [g]

- In general: responsibility for grid quality regulated in EN 16726.
- Double limit agreed to be in standard for Si. Above 0.1 mg/m³ required by AI.
- Accurate determination method pending

Source: prEN 16723-1:2014 E; Natural gas and biomethane for use in transport and biomethane for injection in the natural gas network — Part 1: Specifications for biomethane for injection in the natural gas network

- **None of the important automotive requirements (WI, LHV, Si, S, H_2 & MN) regulated adequately in injection standard.**
- **Since grid standard is not regulated properly, this can lead to NG quality inadequate for automotive applications in the grid**

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Summary & Conclusions

- NG (+ renewable methane) as fuel has a considerable green house gas (GHG) and cost reduction potential. Thus it is in the focus of many OEMs for future automotive transportation, in particular as fuel for dedicated, highly efficient NG engines. e.g. downsized SI engines for passenger car applications (→ Horizon 2020 GasOn EU project) and as dual fuel engines for HD long haul trucks
- Any significant shift from oil based fuels to NG/methane as automotive fuel would increase the NG/methane demand considerably.
- Automotive transportation has the potential to become the main NG/methane customer. Thus NG standards need to be aligned with automotive needs.
- European methane standardization is fragmented and handled by different standardization groups (CEN TC 234 and CEN TC 408).
- Currently 3 different standards are agreed or proposed for Europe: grid (EN 16726:2015), bio-methane injection (prEN 16723-1:2014 E) and automotive (prEN 16723-2:2014 E) quality.
- Automotive NG quality must be ensured in the grid.
- Upgrade with appropriate limits are required for: Wobbe Index, Lower Heating Value, Si, S, H_2, Methane Number, Compressor Oil
- **Inclusion of methane fuels in Fuel Quality Directive is recommended**

Recommendation

Parameter	Unit	Min	Max	prEN 16723-2	prEN 16723-1	EN 16726	Comment
Net Wobbe Index (H-Gas)	MJ/m³	41.9	49.0	Adopt parameter & limit	Adopt parameter & limit	Adopt parameter & limit	
Net Wobbe Index (L-Gas)	MJ/m³	40.5	-	Adopt parameter & limit	Adopt parameter & limit	Adopt parameter & limit	no upper limit → transition to H-Gas
Lower Heating Value (H-Gas)	MJ/kg	44	-	Adopt parameter & limit	Adopt parameter & limit	Adopt parameter & limit	
Lower Heating Value (L-Gas)	MJ/kg	39	-	Adopt parameter & limit	Adopt parameter & limit	Adopt parameter & limit	
Sulfur Total	mg/m³	-	10	Adopt limit	Adopt parameter & limit	Adopt limit	including odorization
Methane Number (regular grade)	MWM	70	-	Adopt limit	Adopt parameter & limit	Adopt limit	
Total Siloxanes (calculated as Si)	mg/m³	-	0.1	Adopt limit & new method	Adopt limit & new method	Adopt parameter, limit & new method	capable test method to be agreed
Hydrogen	% v/v	-	2	OK	Adopt parameter & limit	Adopt parameter & limit	according to ECE 110
Compressor Oil	mg/m³	-	tbd.	Adopt new method and limit	Not required	Not required	method and limits to be agreed

Thank you very much for your attention !

Dr. Ulrich Kramer

FORD *Research & Advanced Engineering*

Q U E S T I O N S ?

BACK UP

BACK UP

NG / Methane Quality Requirements

Wobbe Index Range - Europe

Source: Natural gas — Designation of the quality of natural gas for use as a com-pressed fuel for vehicles; ISO Fuel Standard, EN ISO 15403-1:2008

Group	Wobbe Index Range W_S / MJ / m³
L	39.1 – 44.8
E	40.9 – 54.7
H	45.6 – 54.7
Conditions: 288.15 K, 101.325 kPa	

- **Gas Industry normally uses Superior Wobbe Index (W_S)**
- **European Wobbe Index range (without exceptional LL-Gas): W_S = 39.1 …. 54.7 MJ/m³**
- **Better suited for automotive: WI (Inferior Wobbe Index)**

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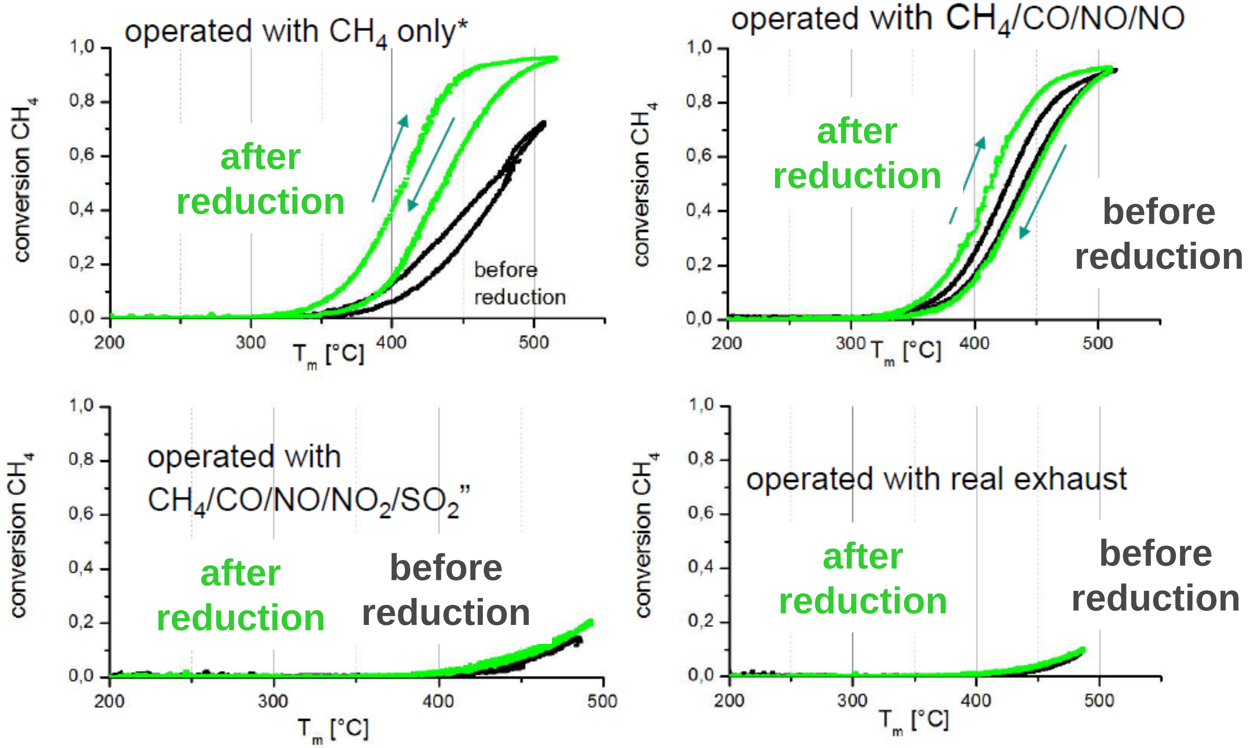
NG / Methane Quality Requirements

Catalyst Durability – Sulfur Effect on Regeneration of Aged Catalysts

Test Rig Results of FVV Project 1134 (2014)

“Investigation of mechanism of catalytic methane reduction”



Source: Investigation of mechanism of catalytic methane reduction; C. Schwarzer, U.Endruschat, A. Gremminger, O.Deutschmann, J.-D. Grunwaldt, KIT Karlsruhe; Final report, FVV-project No. 1134, FVV Spring Conference, Magdeburg ,27. March 2014

- Regeneration achieved if SO_2 was not present in operation

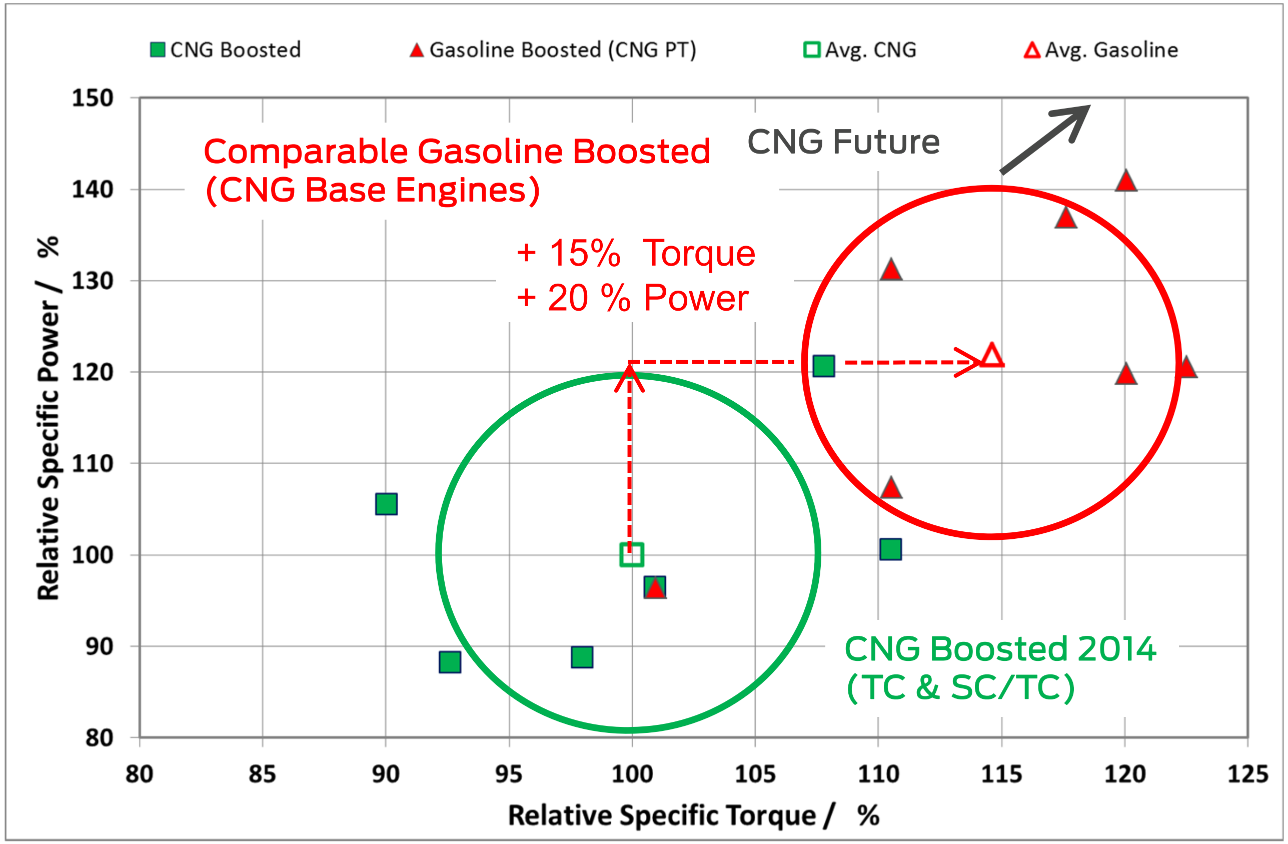
Regeneration of aged catalysts by reduction with H_2 at 400 degC for 1 h
→ No regeneration of SO_2 poisoned catalyst achieved.

NG / Methane Quality Requirements

Methane Number

Opportunity with <u>reliably</u> high Methane Number:

- **Design dedicated NG engine** (→ Content of EU Horizon 2020 Project "GasOn")
- **Increase downsizing factor by exploitation of high knock resistance of CH_4**
- **Increased efficiency of CNG engines, less CO_2**



2014 CNG vehicle market: CNG port fuel injection (CNG PFI) only

Torque & power penalty vs. gasoline DI (CNG displaces air → reduced vol. effy.)

- Low specific torque: ~15% below comparable average gasoline DI
- Low specific power: ~20% below comparable average gasoline DI