Topics on Emission Measurement for Ethanol-Gasoline Blended Fuel Vehicles “Flex-Fuel Vehicles”

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Confidential

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Professional outline

2003 Graduated from Doshisha University in Kyoto / Master of Engineering
- Joined HORIBA at Automotive analytical R&D Dept.

2007 Visiting researcher at University of California, Irvine, USA
- Well-to-Wheel assessment on hydrogen automotive society
- Plug-in Hybrid vehicle emission testing

2011 Product master at HORIBA Europe in Germany
- Supporting sales activities of FTIR exhaust gas analyzer

2014 Manager at Automotive analytical R&D Dept. in HORIBA, Japan
- Project leader of new FTIR exhaust gas analyzer development

2022 Senior Meister at Sales Promotion Dept.
- Supporting sales activities as technical sales

Academic activities

2018-2020 Chairperson of a committee in JSAE (Society of Automotive Engineers of Japan, Inc.)
2020- Member of editorial board of JSAE Engine technical Review magazine
2020- Executive Members of 2023 JSAE/SAE Powertrains, Energy & Lubricants International Meeting

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Agenda

1	**Current Regulations on Alcohol Fuel Emission Testing**
2	**Outlines of Flex-Fuel Vehicle**
3	**Emission Measurement of Flex-Fuel Vehicle**
4	**Measurement Needs for Flex-Fuel Vehicle Emission Control**
5	**Summary**

1.

Current Regulations on Alcohol Fuel Emission Testing

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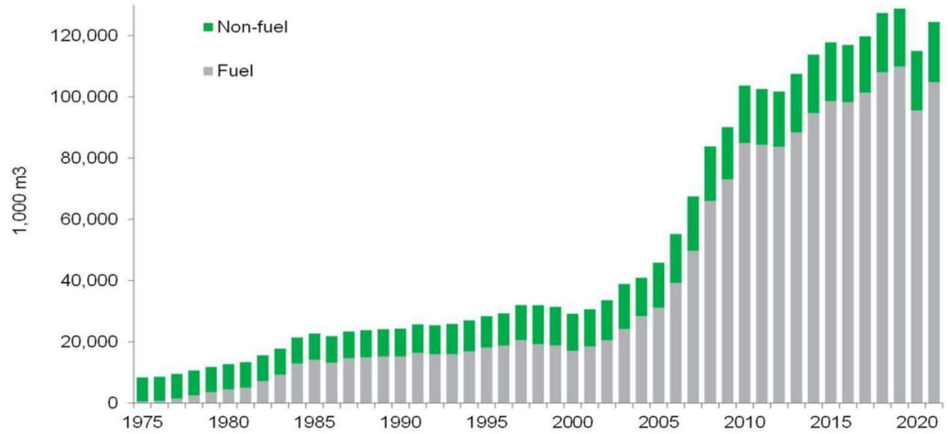
Background of the widespread use of Ethanol fuel

- With the first oil shock in the 1970s, oil prices soared, and ethanol fuel came to attract attention.

- In the 1980s, ethanol production expanded by utilizing the world's surplus sugar cane and corn.

- **India is phasing in the introduction of ethanol fuel and currently has set a target to introduce E20 fuel by April 2023.**

World Ethanol production



Source: https://informaconnect.com/world-ethanol-production-to-rebound-in-2021/

Current regulations on Alcohol fuel vehicles

Item	Carbonyl measurement (Aldehyde, Ketone)	Alcohol / NMOG measurement (Ethanol)
Current regulation	HCHO (U.S. Tier3, CARB LEV III) Aldehydes (Brazil Proconve L6)	NMOG (U.S. Tier3, CARB LEV III)
Regulations under consideration	*HCHO (EU Euro7 2025?~(LDV))* HCHO (Brazil PROMOT M5 2023~(Motorcycle)) HCHO (China 7)	*NMOG (Euro7 2025?~(LDV))* NMOG (Brazil Proconve L7 2022~)
Measurement Technologies	DNPH cartridge or Impinger (DNPH liquid solution) (US CARB)	Alcohol Impinger (US CARB)
	DNPH cartridge or Impinger (DNPH liquid solution) (US EPA)	Alcohol Impinger or Photoacoustic (US EPA)
	Impinger (DNPH liquid solution) (Brazil)	Alcohol Impinger (Brazil)
	DNPH cartridge FTIR by measuring diluted exhaust gas from CVS PTR-MS (GTR No. 15>> Future consideration)	Impinger DNPH cartridge FTIR by measuring diluted exhaust gas from CVS PTR-MS (GTR No. 15>> Future consideration)

EU NMHC vs US NMOG Regulations

Why should NMHC/NMOG be regulated?

- **NMHC/NMOG + NOx + Sunlight -> Photochemical oxidizers (Ozone)**
- **Ozone can harm human or animal health and damage plants**

NMHC （India・Japan・EU・China）

(FID)

NMHC : **N**on-**M**ethane **Hydrocarbons**

Hydrocarbons

CH_4

+

HCs with Oxygen

Alcohol

Carbonyl

Formaldehyde

Subtract CH_4

FID sensitivity of Alcohols and Carbonyls are small.

THC FID relative sensitivity to Propane (=1.0)

acetaldehyde	0.50
ethanol	0.75
formaldehyde	0.00
methanol	0.63
propanol	0.85

NMOG （US）

(FID)

NMOG : **N**on-**M**ethane **O**rganic **G**ases

Hydrocarbons

CH_4

+

HCs with Oxygen

Alcohol

Carbonyl

Formaldehyde

\+

Alcohol

Carbonyl

Formaldehyde

Subtraction of CH_4

Subtract oxygenated hydrocarbons with response factor

(Impinger+GC, DNPH+HPLC)

$$m_{NMOG} = m_{NMHC} - \rho_{NMHC} \cdot \sum_{i=1}^{N} \frac{m_{OHCi}}{\rho_{OHCi}} \cdot RF_{OHCi[THC\text{-}FID]} + \sum_{i=1}^{N} m_{OHCi}$$

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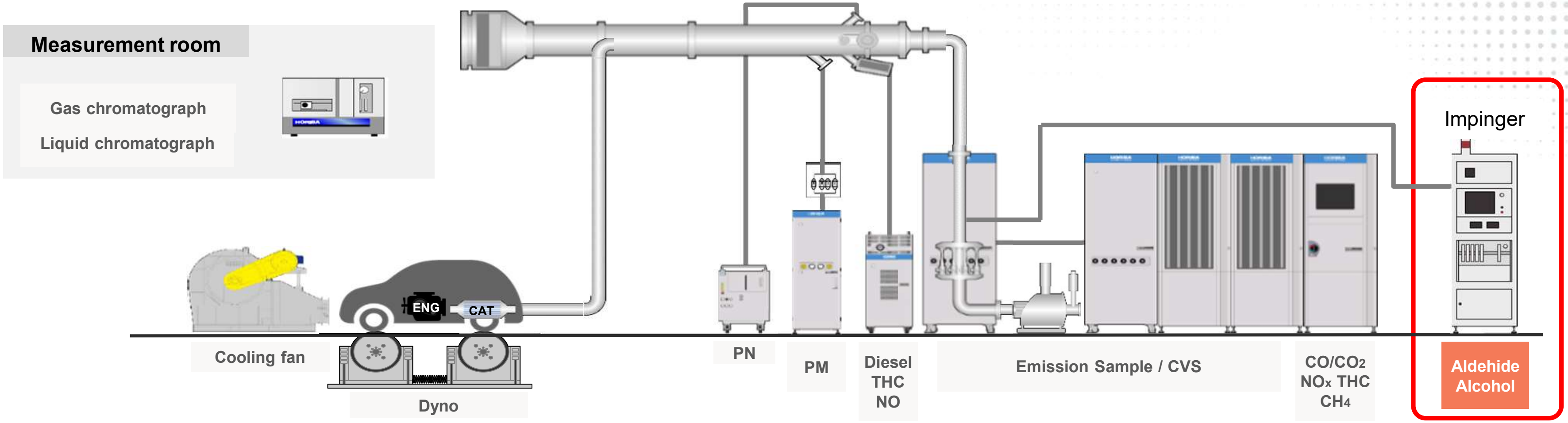
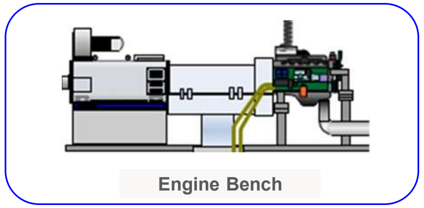
Alcohol fuel emission measurement systems in the Americas
(Current regulations)

Image for emission measurement system (NMOG) with alcohol fuel exhaust gas



or



Example for emission measurement system with alcohol fueled exhaust gas in CFR

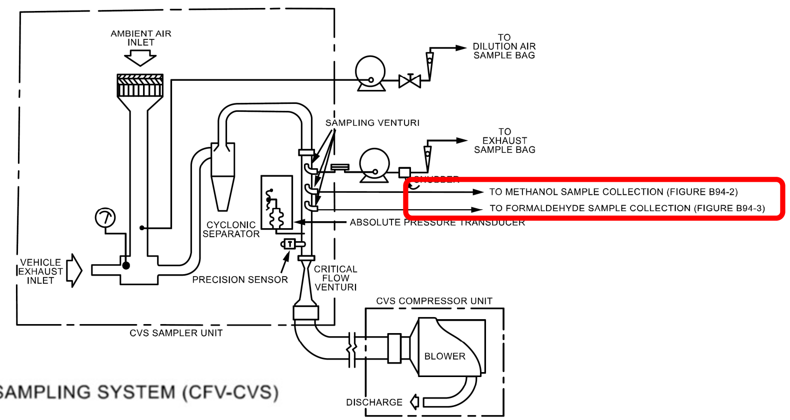


FIGURE B94-4 EXHAUST GAS SAMPLING SYSTEM (CFV-CVS)

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Proposed Species and Measurement Methods of Euro7

Proposed species to be included in Euro 7

Species	Groups	PEMS available Traditional/New	Technologies in-laboratory /on-board
Nitrogen Oxides, NO_x	AQ (1,2,3,4,5,8)	Yes/Yes	Dual CLD, NDUV, QCL, FTIR / on-board PEMS could be by QCL or FTIR.
Carbon Monoxide, CO	AQ (1)	Yes/Yes	NDIR, FTIR /PEMS currently poor. Improvement needed by using e.g. FTIR.
Solid particles, SPN	AQ (1)	- /Yes	PN23 available. PN10 at the market-ready stage. PMP work
Particulate matter, PM	AQ (1,7,8)	Yes (not for cars)	PM-PEMS used for HDVs is not practical for cars.
New species			
Ammonia, NH_3	AQ (1,3,4,8)	- /Yes	LDS, QCL, FTIR / on-board PEMS could be by QCL or FTIR.
Nitrous Oxide, N_2O	GHG & AQ (1, 6)	Yes/Yes	GC-ECD, QCL, NDIR, FTIR / on-board could be FTIR or QLC.
Methane, CH_4	GHG & AQ (1, 5)	Yes (not for cars)/Yes	FID with cutter, GC-FID, FTIR / on-board could be FTIR.
Formaldehyde, HCHO	AQ (1,2,5)	- /Yes	DNPH&HPLC, PTR-MS, FTIR / on-board could be FTIR.
Non-Methane Organic Gases, NMOG	AQ (1,2,5,8)	- /Calculated	NMOG could be FID (THC) minus CH_4 plus HCHO. If other than FID (THC), oxygenates to be analysed by FTIR, GC.

(1) health (2) vegetation (3) acidification (4) eutrophication (5) tropospheric ozone (6) stratospheric ozone (7) GWP black carbon (8) sec. aerosols

Source: AGVES 8th April 2021 https://circabc.europa.eu/d/d/workspace/SpacesStore/83a09cc8-7f8f-4ca6-9764-0b77da57d4cc/AGVES-2021-04-08-LDV_Exhaust.pdf

Impinger system

FTIR gas analyzer

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Proposed Species and Proposed limits of Euro7

Lower impact scenario

Evaluated emission limits Lower Option	Cars	Small vans	Large vans
NO_x	60	75	82
PM	4.5	4.5	4.5
PN (#/km)	6×10^{11}	6×10^{11}	6×10^{11}
CO	500	630	740
THC	100	130	160
NMHC	68	90	108
NH_3	20	20	20
Evaporative	2 g/test	2 g/test	2 g/test

These three regulation value scenarios have been proposed.
With the tentative agreement to reach zero emissions in 2035 (Oct.28), the regulation are expected to be lower impact scenario.

Medium impact scenario

Evaluated emission limits Medium Option	Cars and vans	Large vans if underpowered
NO_x	30	45
PM	2	2
$PN_{>10nm}$ (#/km)	1×10^{11}	1×10^{11}
CO	400	600
NMOG	45	45
NH_3	10	10
N_2O+CH4	45	55
HCHO	5	10
Evaporative	0,5 g/test+ORVR	0,7 g/test+ORVR
Brake emissions	7	7
Battery Durability in 5/8 years	80/70%	80/70%

Stricter impact scenario

Evaluated emission limits Stricter Option	Cars and vans	Large vans if underpowered
NO_x	20	30
PM	2	2
$PN_{>10nm}$ (#/km)	1×10^{11}	1×10^{11}
CO	400	600
NMOG	25	25
NH_3	10	10
N_2O+CH4	20	25
HCHO	5	10
Evaporative	0.3 g/worst diurnal test + ORVR	0.5 g/worst diurnal test + ORVR
Brake emissions	5	5
Battery Durability in 5/8 years	90/80%	90/80%

2.

Outlines of Flex-Fuel Vehicle

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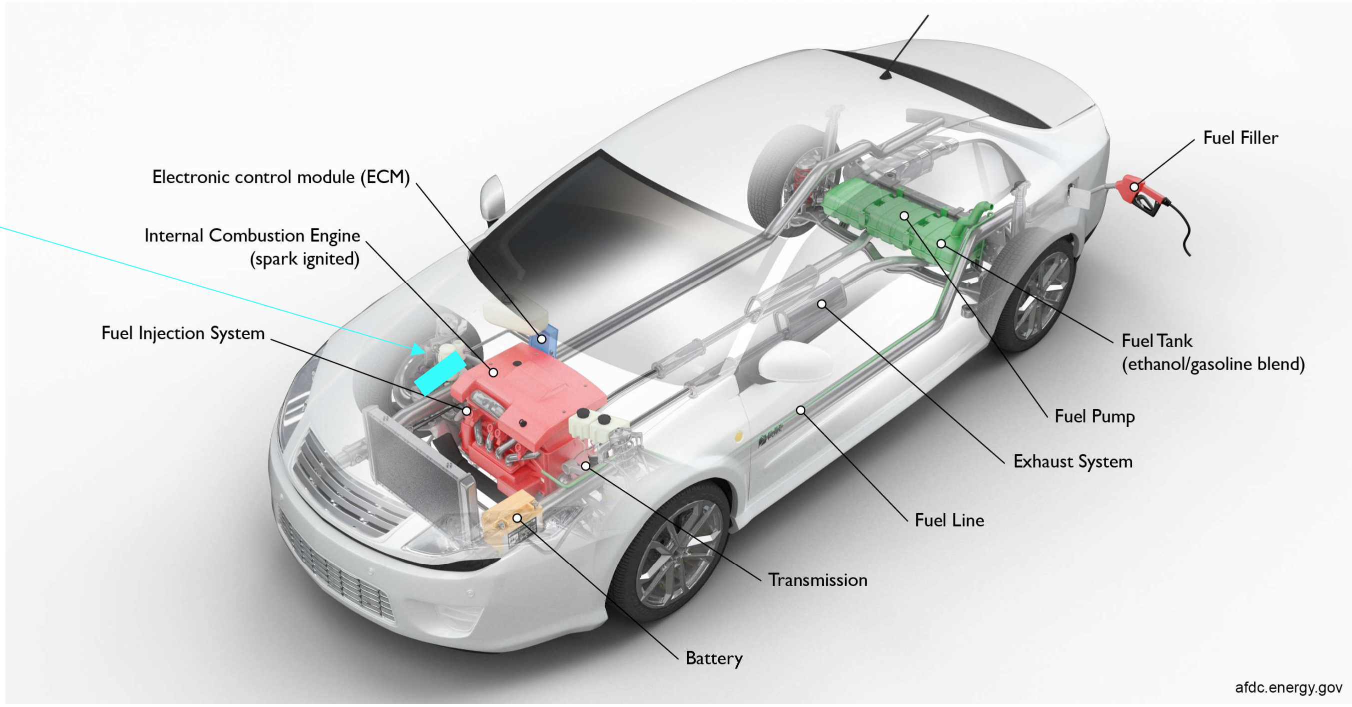
Flex / Flexible-Fuel Vehicle (FFV)

It can operate by Gasoline-Alcohol blended fuel (E0 – E100) with single fuel tank and fuel line

Flex Fuel Sensor
Measures the ethanol content in the car's fuel system. The sensor is installed between the fuel pressure regulator and the fuel tank.

Source: https://www.z1motorsports.com/haltech-accessories/haltech/haltech-flex-fuel-composition-sensor-p-9122.html



Source: https://afdc.energy.gov/vehicles/how-do-flexible-fuel-cars-work

Key Components of a Flex Fuel Vehicle

Electronic control module (ECM): The ECM controls the fuel mixture, ignition timing, and emissions system; monitors the operation of the vehicle; safeguards the engine from abuse; and detects and troubleshoots problems.
Exhaust system: The exhaust system channels the exhaust gases from the engine out through the tailpipe. A three-way catalyst is designed to reduce engine-out emissions within the exhaust system.
Fuel line: A metal tube or flexible hose (or a combination of these) transfers fuel from the tank to the engine's fuel injection system.
Fuel tank (ethanol/gasoline blend): Stores fuel on board the vehicle to power the engine.

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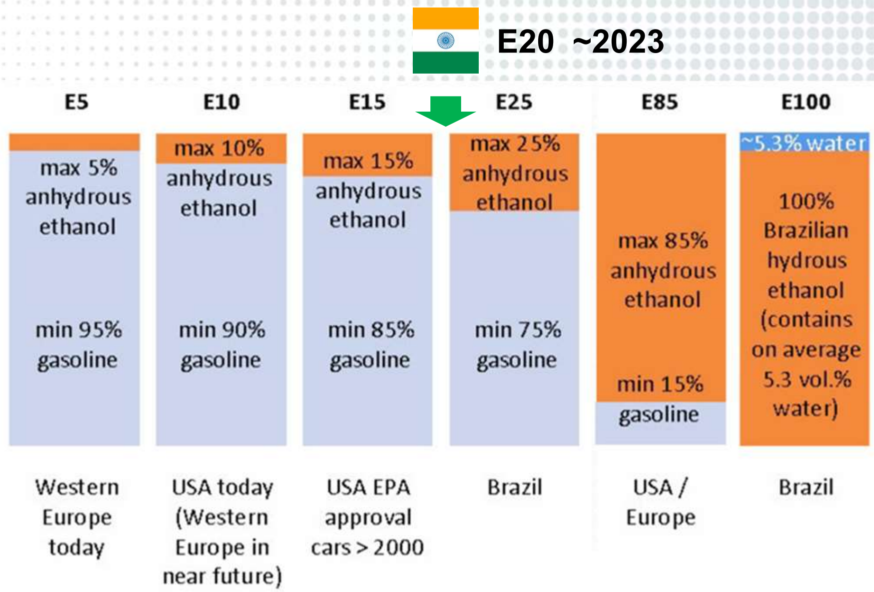
Flex-Fuels



Source: https://www.wikiwand.com/en/Common_ethanol_fuel_mixtures

E5 – E85: Gasoline + Anhydrous ethanol

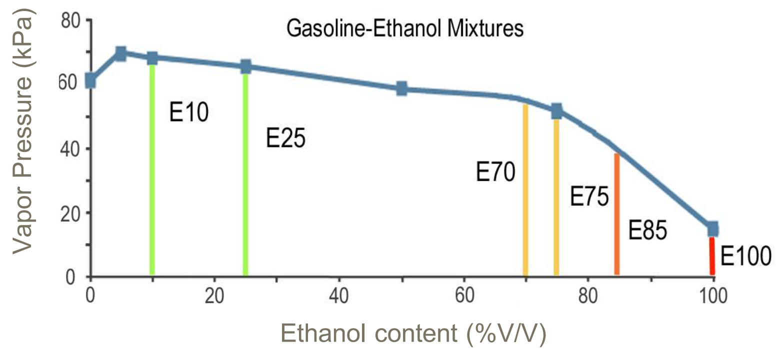
(100% alcohol obtained by removing water from hydrous ethanol)

E100: Hydrous ethanol

(about 5% of the water content obtained when it is distilled at the manufacturing stage)

Characteristics

- Low carbon monoxide (CO) and soot (black smoke) emissions
- A lot of water in exhaust gas than gasoline fuel
- Prone to aldehyde production
- Poor cold starting due to low vapor pressure, and high unburnt fuel emissions
- Depending on the combination of alcohol species and materials, there is a tendency for corrosion of metals, swelling of rubber, and degradation of resins



Source: https://www.wikiwand.com/en/Common_ethanol_fuel_mixtures

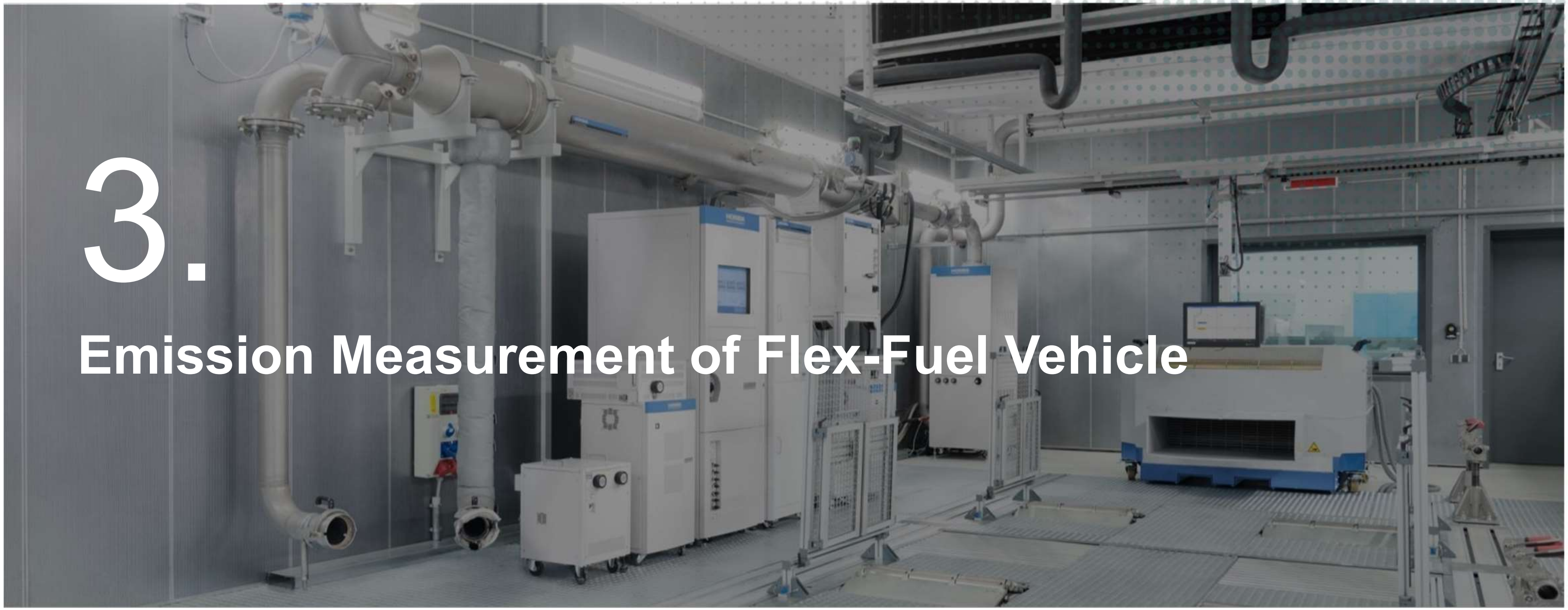
Required modifications/R&D for different blends of ethanol fuel

Ethanol blend	Carburetor	Fuel Injection	Fuel pump	Fuel pressure device	Fuel filter	Ignition system	Evaporative system	Fuel tank	Catalytic converter	Basic engine	Motor oil	Intake manifold	Exhaust system	Cold start system
≤ 5%	Modifications not necessary for any vehicle													
E5 to E10		Modifications not necessary for vehicles since about 1987-92												
E10 to E25	Specially designed vehicles													
E25 to E85	Specially designed vehicles													
E85 to E100	Specially designed vehicles													
			Modifications not necessary						Modifications probably necessary					

https://en.wikipedia.org/wiki/Common_ethanol_fuel_mixtures#cite_note-TRS08-117

3.

Emission Measurement of Flex-Fuel Vehicle



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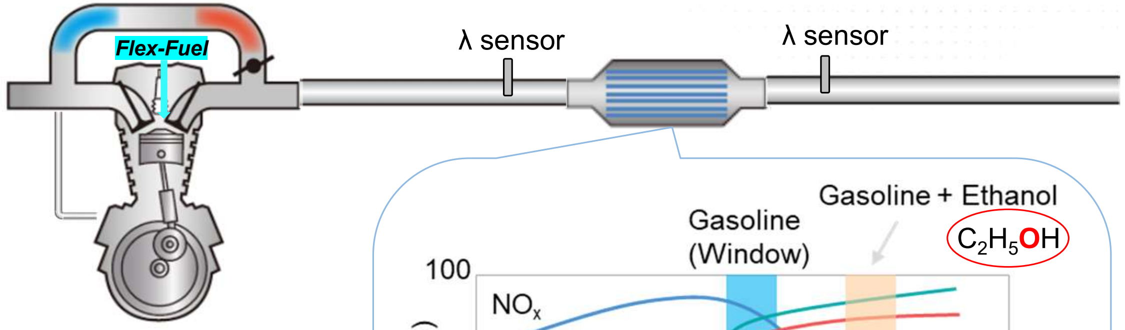
In the case of using Flex-Fuel (>E10) in a normal Gasoline Engine

Gasoline Engine

TWC
(Three-way Catalyst)

Air
N_2: 78 vol%
O_2: 21 vol%
H_2O: 0.8 vol%

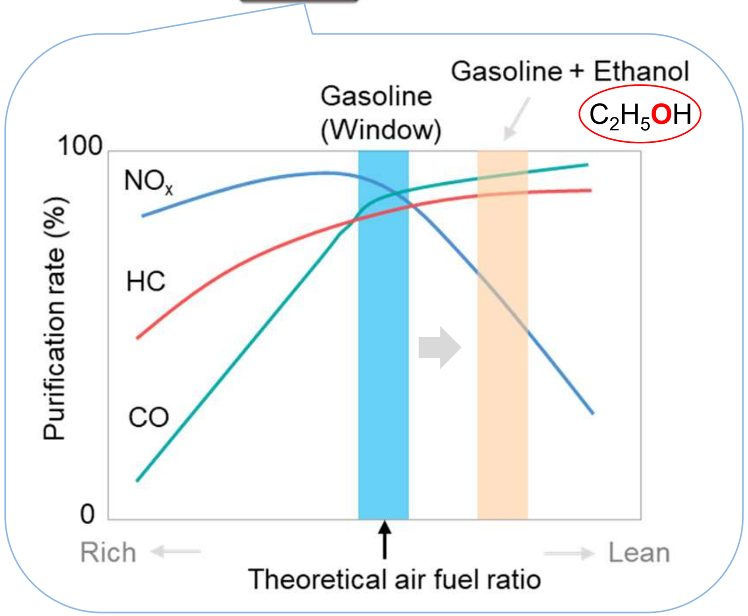


Flex-Fuel

Gasoline (0 – 100%):
$C_8H_{15}+11.75O_2+44.19N_2 = 8CO_2+7.5H_2O+44.19N_2$
[max H_2O: 12.6vol%]

+

Ethanol (0 – 100%):
$C_2H_5OH+3O_2+11.322N_2 = 8CO_2+3H_2O+11.322N_2$
[max H_2O: 18.4vol%]



The actual air fuel ration becomes lean due to the Ethanol fuel contains oxygen

Ethanol ↑
CO ↓
HC ↓
NOx ↑

Specific Engine calibration for Ethanol fuel (>E10) is required

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Emission measurement for calibrating Flex-Fuel Engine (for R&D)

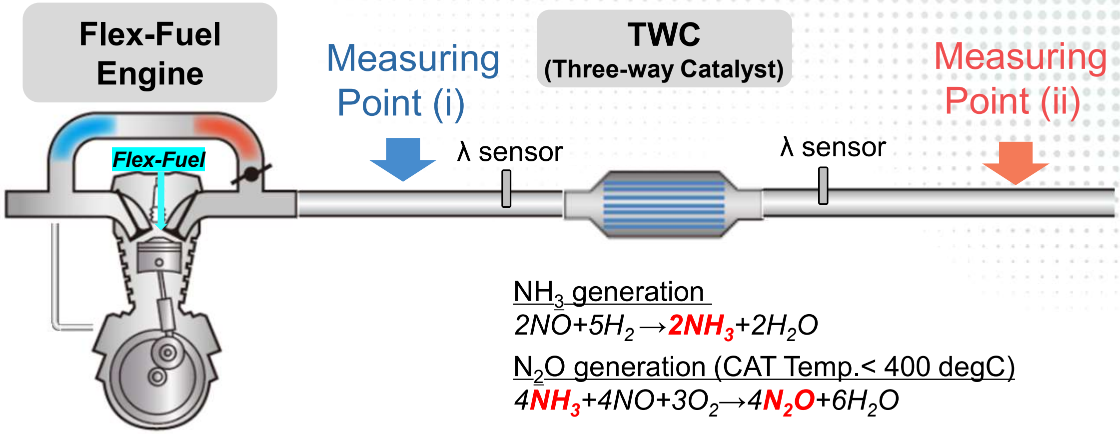
Concept for Light duty vehicle

Flex-Fuel

Gasoline (0 – 100%):
$C_8H_{15}+11.75O_2+44.19N_2 = 8CO_2+7.5H_2O+44.19N_2$
[max H_2O: 12.6vol%]

+

Ethanol (0 – 100%):
$C_2H_5OH+3O_2+11.322N_2 = 8CO_2+3H_2O+11.322N_2$
[max H_2O: 18.4vol%]



NH$_3$ generation
$2NO+5H_2 \rightarrow \mathbf{2NH_3}+2H_2O$

N$_2$O generation (CAT Temp.< 400 degC)
$4\mathbf{NH_3}+4NO+3O_2 \rightarrow 4\mathbf{N_2O}+6H_2O$

	Measuring Point (i) Engine-out	Measuring Point (ii) Tailpipe
E0- E10	Normal Gasoline emission measurement	Normal Gasoline emission measurement
E10-E100	For combustion control and TWC control ・**Unburned C_2H_5OH (FTIR)** ・Generated H_2O (FTIR) ・**Generated NO_x (CLA/FTIR/QCL-IR)** ・**Generated H_2 (※) (Mass spectroscopy) ~3vol%** ・Residual O_2 (MPA) for A/F (for λ sensor correction)	For reducing harmful emissions ・**Unburned C_2H_5OH (FTIR)** ・**Generated CH_3CHO (FTIR) at low temp.** ・**Generated HCHO (FTIR/QCL-IR) at low temp.** ・**Generated NH_3 (FTIR/QCL-IR)** ・**Generated N_2O (FTIR/QCL-IR)** ・Generated THC (FIA) ・Generated PN (Particle counter) ・**Residual NO_x (CLA/FTIR/QCL-IR)**

(※) Heat decomposition of C_2H_5OH around 650K in combustion chamber

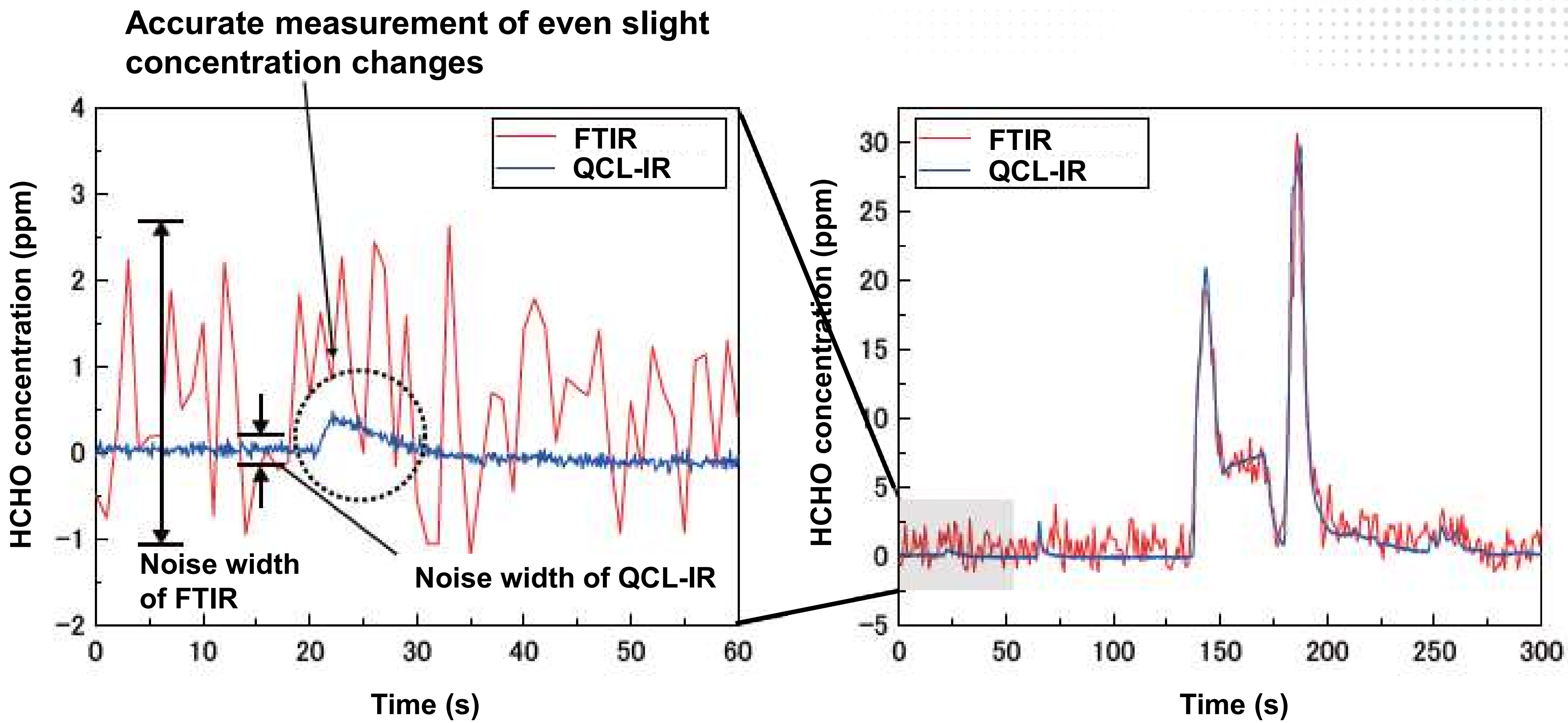
MPA: Magneto-Pneumatic Analyzer
CLA: Chemiluminescence Analyzer
FIA: Flame Ionization Analyzer

Examples of Exhaust Gas Analyzers for Flex-Fuel Engine (for R&D)

	Multi Gas Analyzer	High Sensitivity Gas Analyzer		Hydrogen Gas Analyzer
Measurement Principle	**FTIR** (28 components)	**QCL-IR** (4 components)	**QCL-IR** (single component)	**Sector Mass Spectrometer** (single component)
Measurement components	C_2H_5OH, HCHO, CH_3CHO, NO, NO_2, N_2O, NH_3,etc. (max. 28)	NO, NO_2, N_2O, NH_3	HCHO	H_2
Sampling condition	Direct (Wet)	Direct (Wet)	Direct (Wet)	Direct (Wet)
Sampling temperature	113 degC or 191 degC	113 degC	113 degC	113 degC
Sampling rate	5 Hz	10 Hz	10 Hz	5 Hz
Ranges	200 ppm (N_2O) 100/1000 ppm (NH_3)	200/6000 ppm (NO) 100/3000 ppm (NO_2) 200/6000 ppm (N_2O) 100/3000 ppm (NH_3)	100/3000ppm	5 vol%
Response time (T_{10-90})	≤ 2.0 sec (CO) ≤ 4.0 sec (NH_3 100ppm)	≤ 2.5 sec (N_2O) ≤ 5.0 sec (NH_3)	≤ 3.0 sec	≤ 1.0 sec
Flow rate	3.5 L/min	8.0 L/min	4.0 L/min	3.5 L/min
LOD (Limit of detection)	3.0 ppm (C_2H_5OH) 5.0 ppm (HCHO) 5.0 ppm (CH_3CHO) 4.0 ppm (NO) 1.0 ppm (NO_2) 1.0 ppm (N_2O) 2.0 ppm (NH_3)	0.4 ppm (NO) 0.2 ppm (NO_2) 0.4 ppm (N_2O) 0.2 ppm (NH_3)	0.2 ppm	50 ppm

Detection sensitivity (FTIR vs. QCL-IR)

HCHO (formaldehyde) measurement result

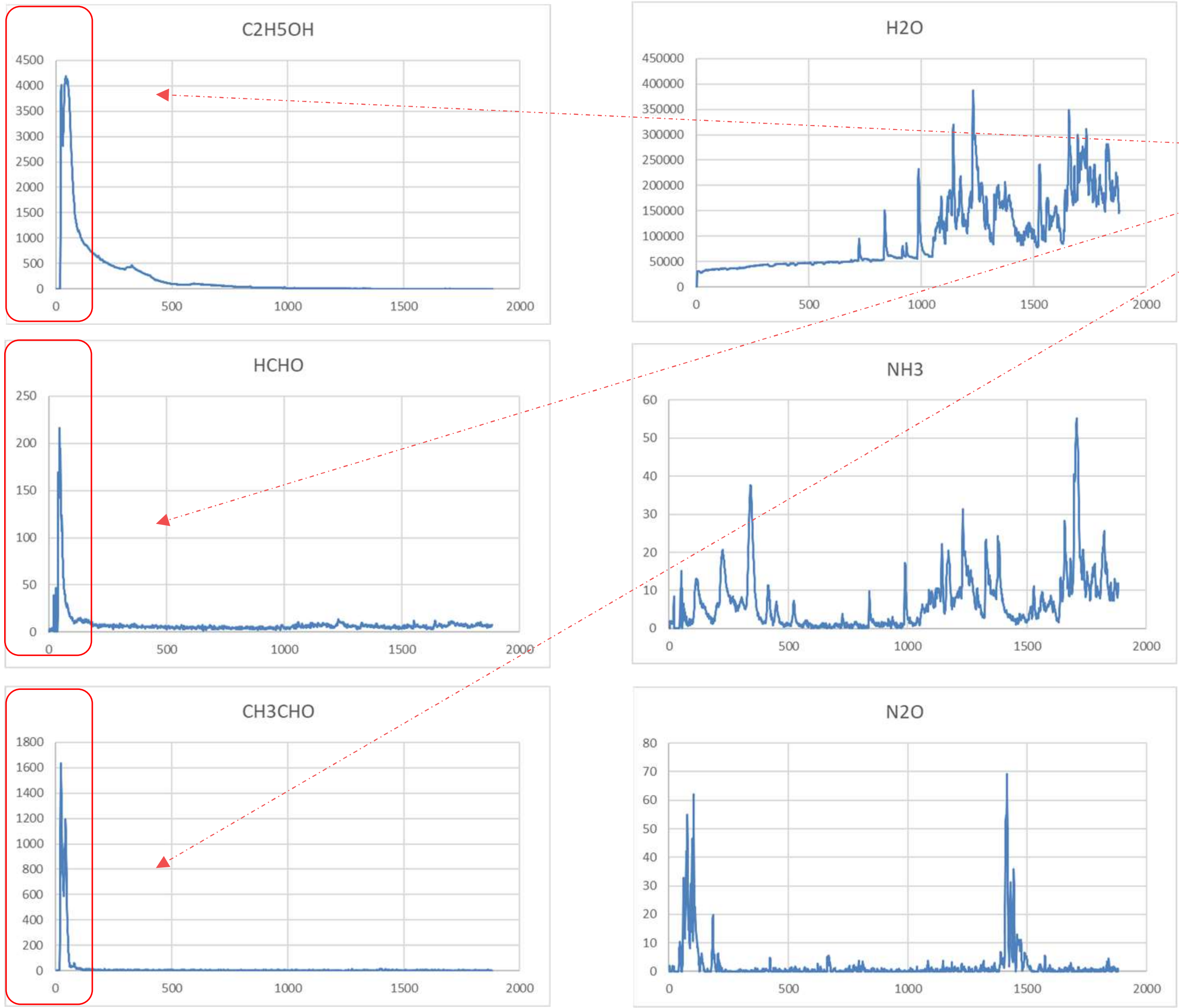


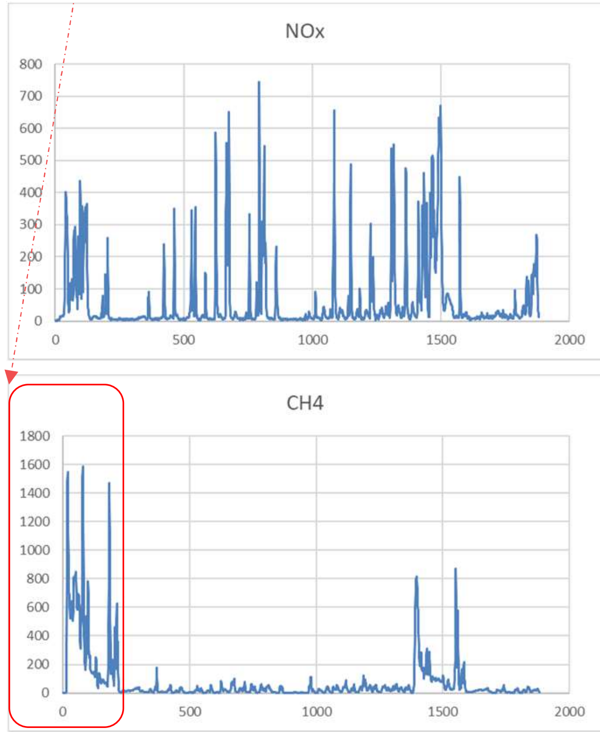
Examples of Direct Measurement (E100, FTIR at Tailpipe)

FTP75 measurement mode

x axis: Time, y axis: ppm

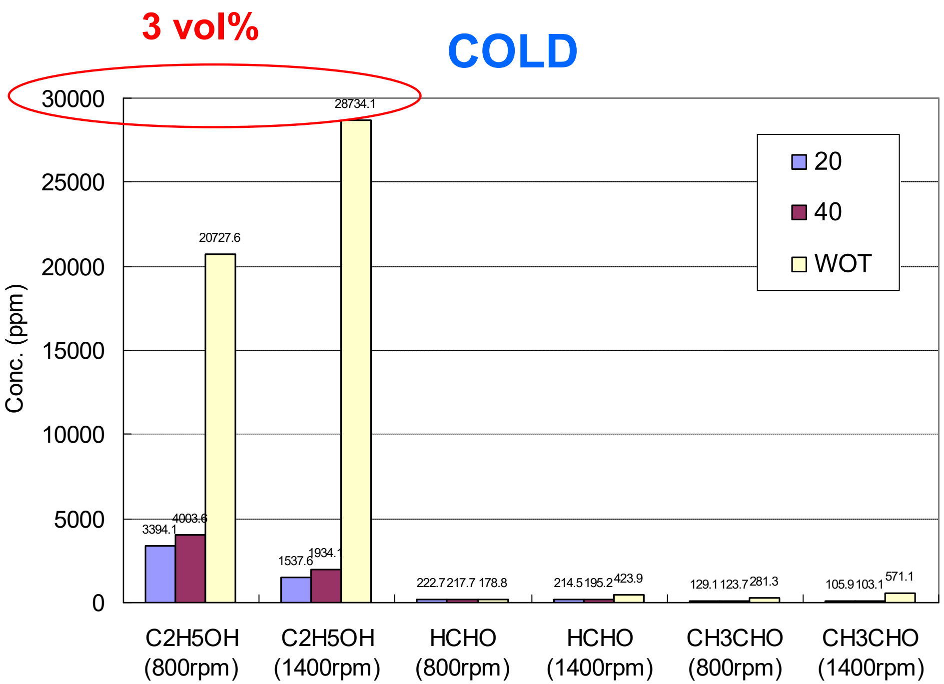
Higher emission before catalyst warms up

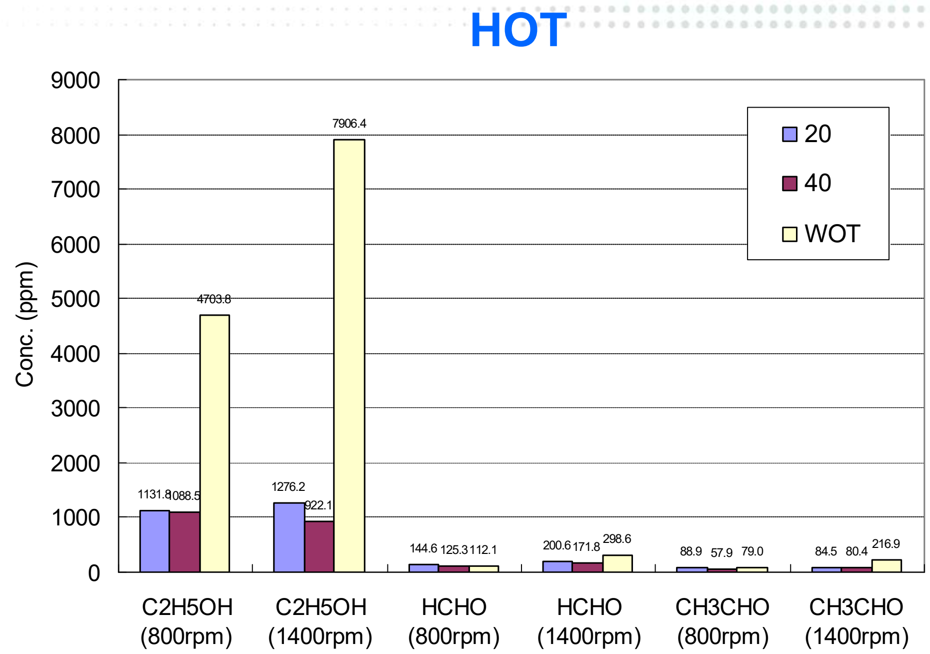




Examples of R&D Measurement (E100, FTIR at Engine-out)

Engine bench testing, with uncalibrated engine





For measurement in R&D, maximum of 3vol% Ethanol was detected with E100 fuel, needs to consider corrosion countermeasures for the sampling system

4.

Measurement Needs for Flex-Fuel Vehicle Emission Control

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Measurement Needs for Flex-Fuel Vehicle Emission Control

- **Unburned ethanol and aldehyde measurement to reduce emissions before catalyst warms up**

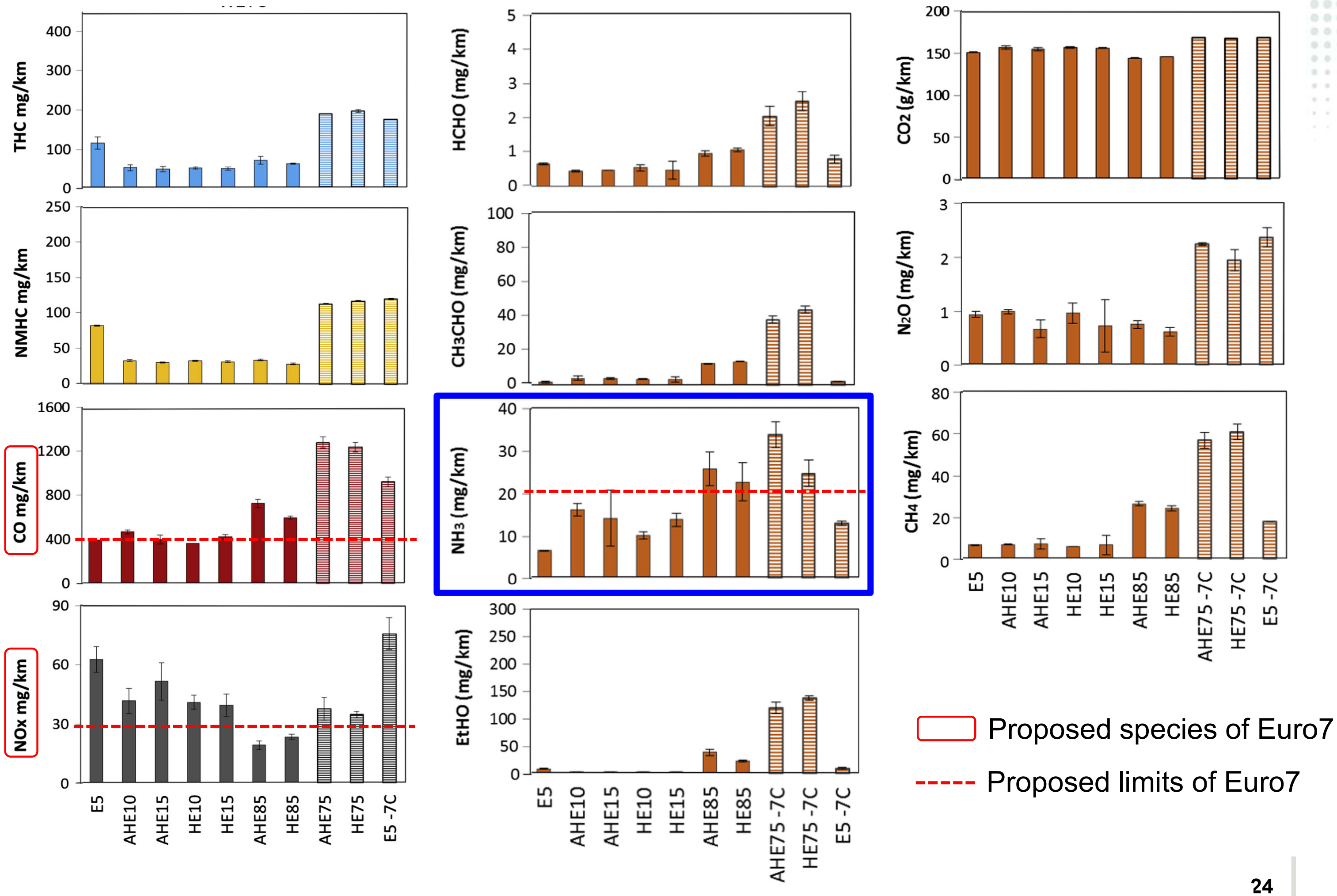
- **O_2 measurement at engine out for more accurate A/F control**
  ⇒ λ sensor (A/F sensor) might be affected by higher concentration of ethanol fuel emission

- **H_2 and NO_x measurement at the engine out to control the amount of NH_3**
  ⇒ Ethanol is thermally decomposed in the combustion chamber and H_2 will be generated. This H_2 and NO_x react with a three-way catalyst, causing to the generation of NH_3.

Flex-Fuel Emission evaluation results from JRC report

Driving cycle	Ambient Temp.	Test fuels
WLTC	23 degC	E5 AHE 10 AHE15 HE10 AHE85 HE85 AHE75 HE75
	-7 degC	AHE75-7C HE75-7C E5-7C

AHE : Anhydrous Ethanol
HE: Hydrous Ethanol



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Source: Suarez-Bertoa, R.; Zardini, A. A.; Keuken, H.; Astorga, C. Impact of ethanol containing gasoline blends on emissions from a flex-fuel vehicle tested over the Worldwide Harmonized Light duty Test Cycle (WLTC). Fuel 2015, 143, 173– 182,

5. Summary

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Summary

1. Regulations concerning alcohol fuel emission testing

- Currently, only the U.S. has regulation values for alcohol and aldehydes.
  (Brazil has only aldehydes)
- Measurements allowed by regulation include using Impingers and chromatography.
- In the near future, Europe is also going to establish regulations for alcohol and aldehydes.

2. Emission Measurement of Flex-Fuel Vehicle

- FTIR can be used to measure unburned ethanol and aldehyde at cold start, and for R&D use, it may require a high concentration measurement range of 3 vol% ethanol.
- QCL-IR is preferable for HCHO measurement for NMOG calculation.

3. Measurement Needs for Flex-Fuel Vehicle Emission Control

- At cold start, ethanol and aldehyde measurement to reduce emissions and O_2 measurement for A/F control accurately
- H_2 and NO_x measurement at the engine out to control the amount of NH_3, and NH_3 at tailpipe.

Omoshiro-okashiku
Joy and Fun

Thank you

Cảm ơn

감사합니다

ありがとうございました

Dziękuję

धन्यवाद

Grazie

Merci

谢谢

ขอบคุณครับ

நன்றி

Gracias

Obrigado

Σας ευχαριστούμε

Děkuji

Teşekkürler

شكرا

Tack ska ni ha

Danke

Большое спасибо