Research Organization for Next Generation Vehicles

https://www.waseda.jp/inst/nextgv/

Research on deNOx Catalysts for H_2 Internal Combustion Engines

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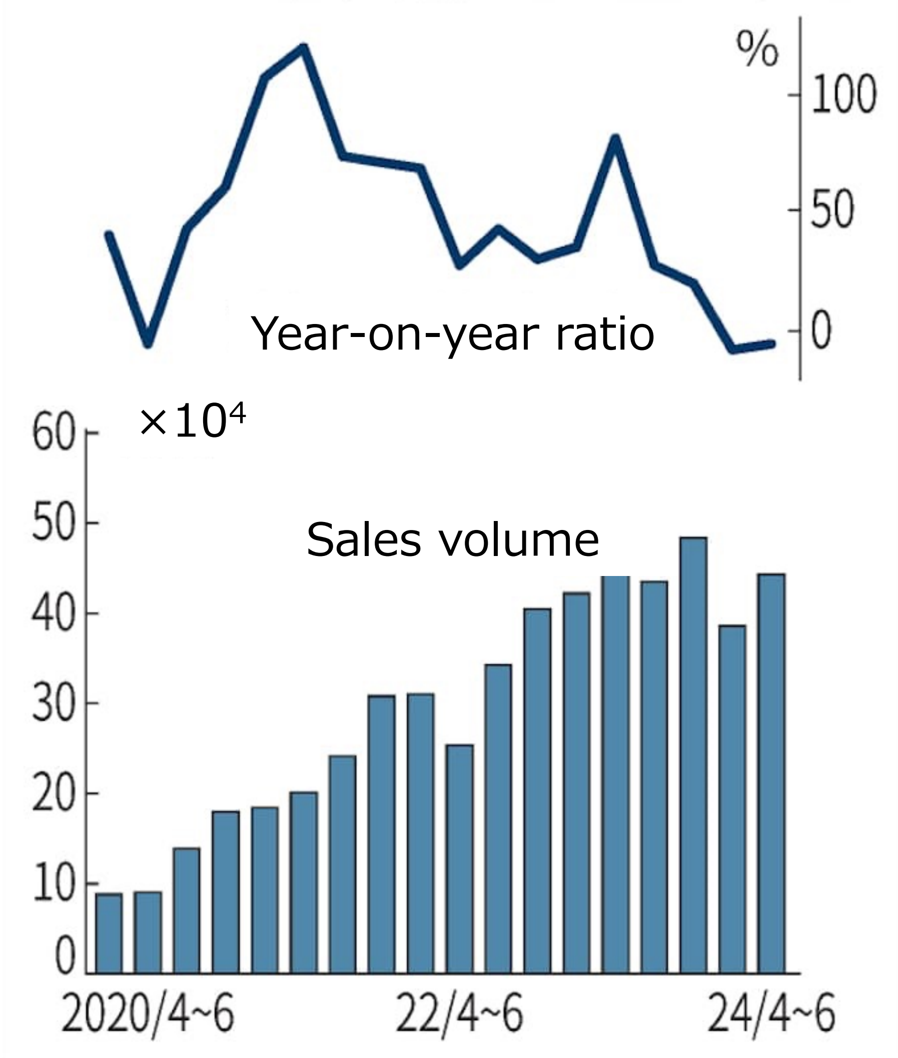
Waseda University

HEV is reversing to BEV in US

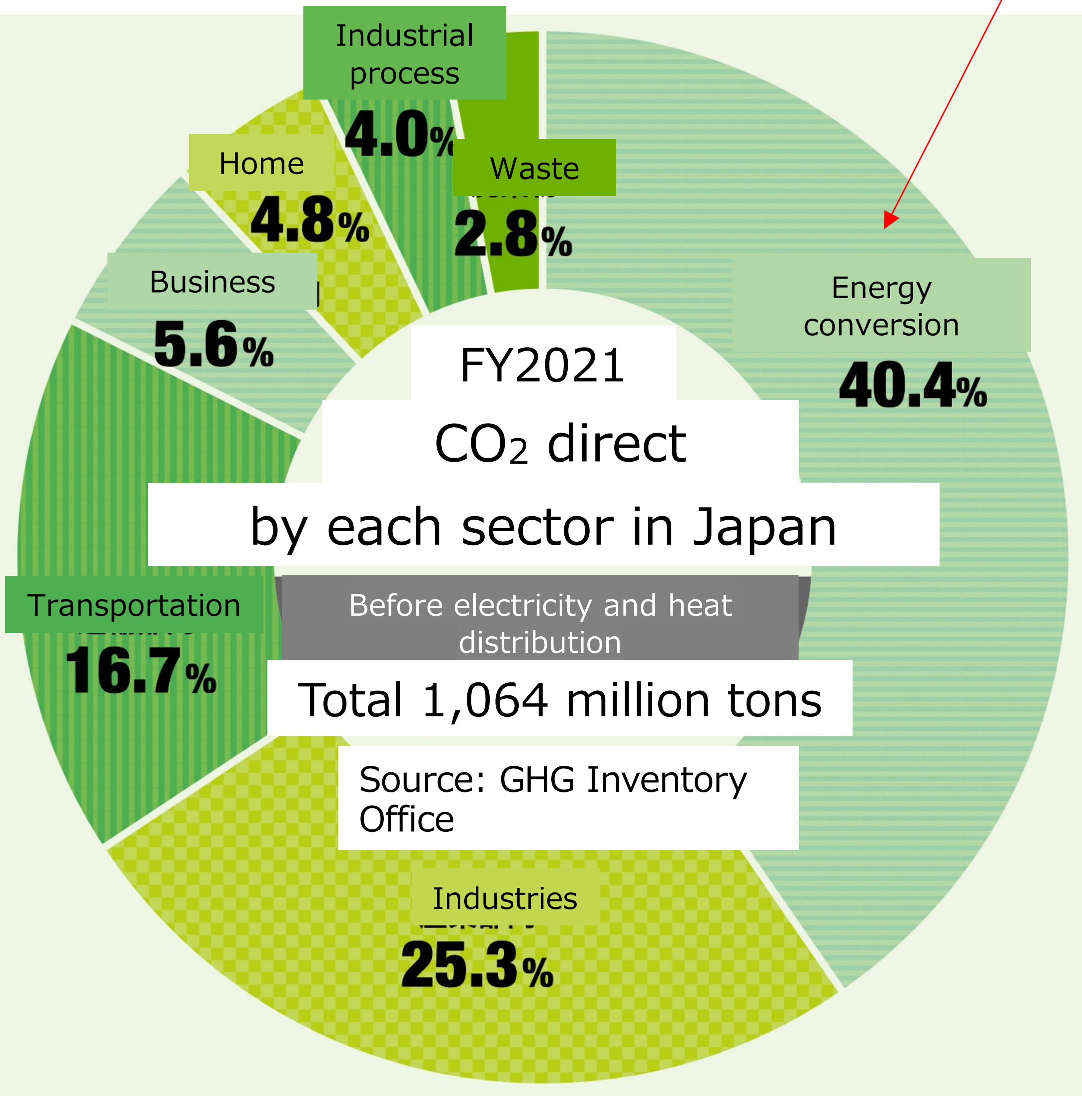
- BEV specialized model is at a crossroads
- World major market is HEV and PHEV
- GM is reviewing its EV strategy, which was based on the expansion of the EV market
- In-house development of Ford pickup EV truck once again is postponed
- The European Union (EU) initially had a policy of completely banning the sale of new engine vehicles in 2035, but sales continued as long as synthetic fuels were used

Tesla global sales slow down clearly

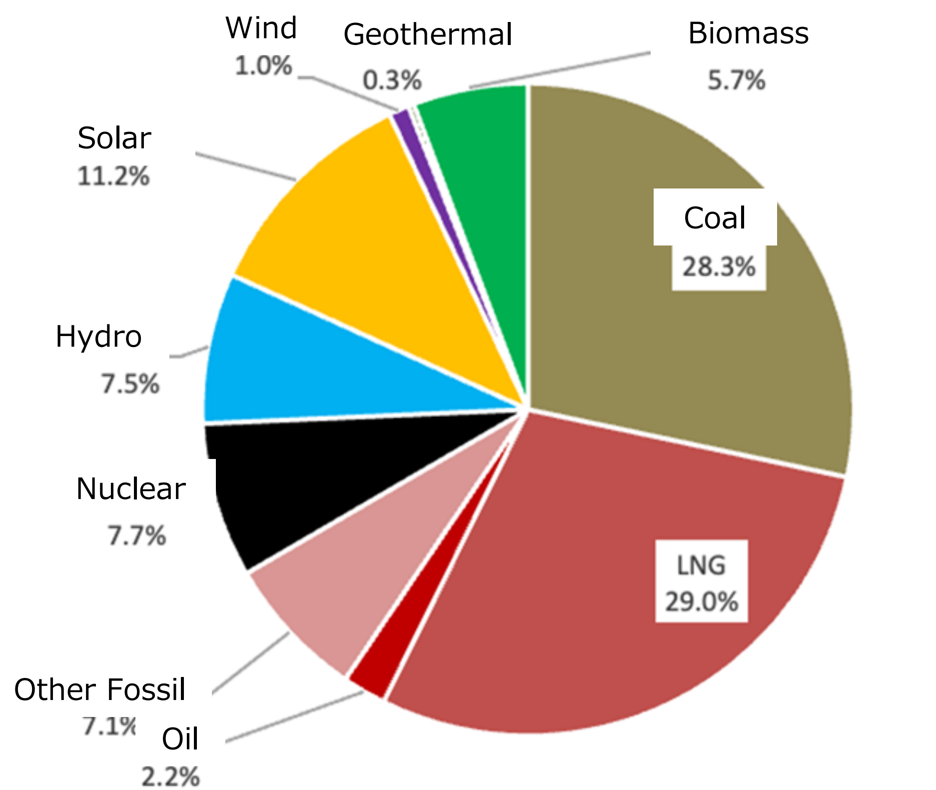


CO_2 emissions in Japan in FY2021 (direct emissions)

In Japan, CO_2 emissions will not decrease no matter how many electric vehicles are used.

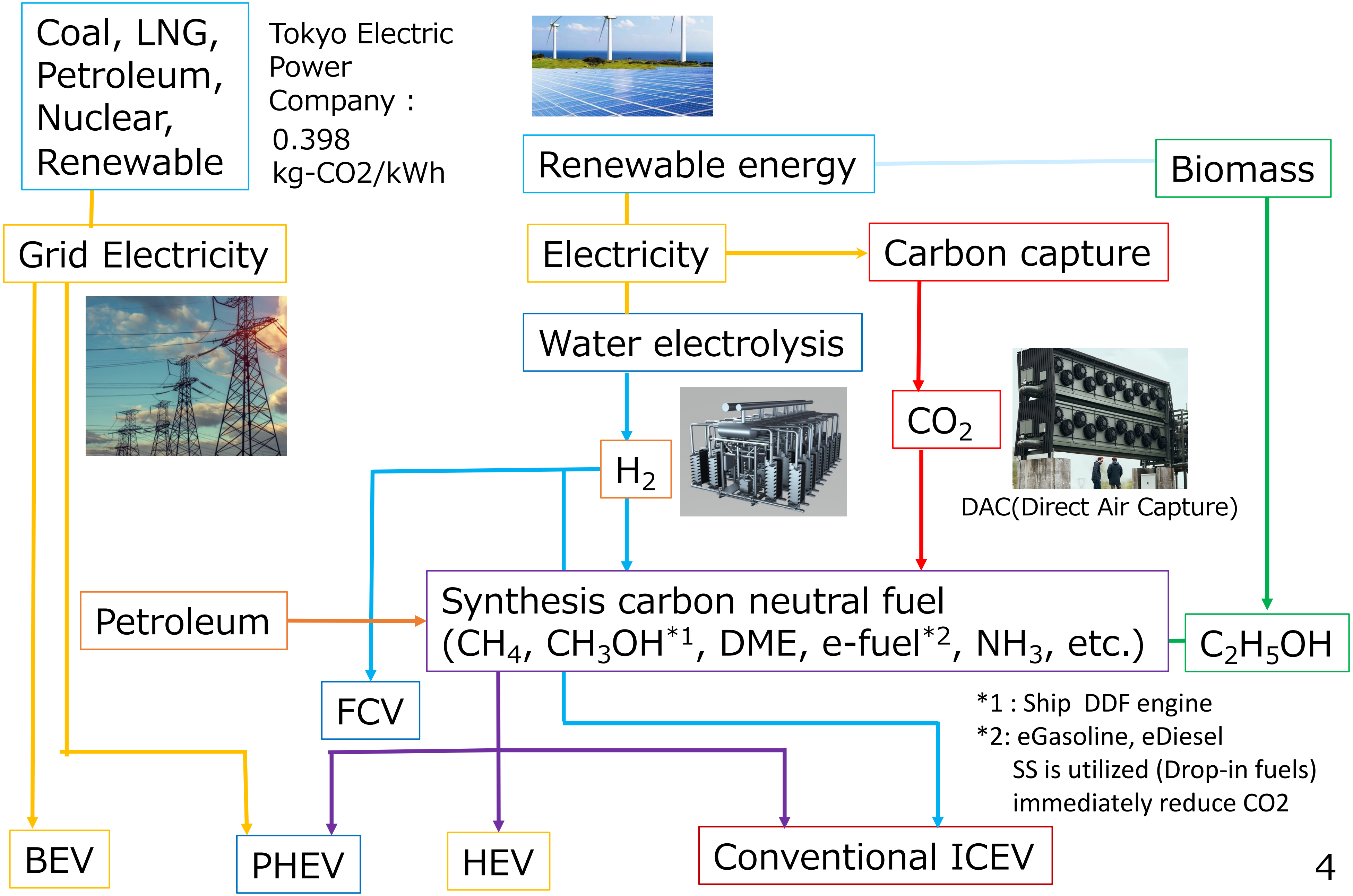


Renewable: 25.7%
Nuclear: 7.7%



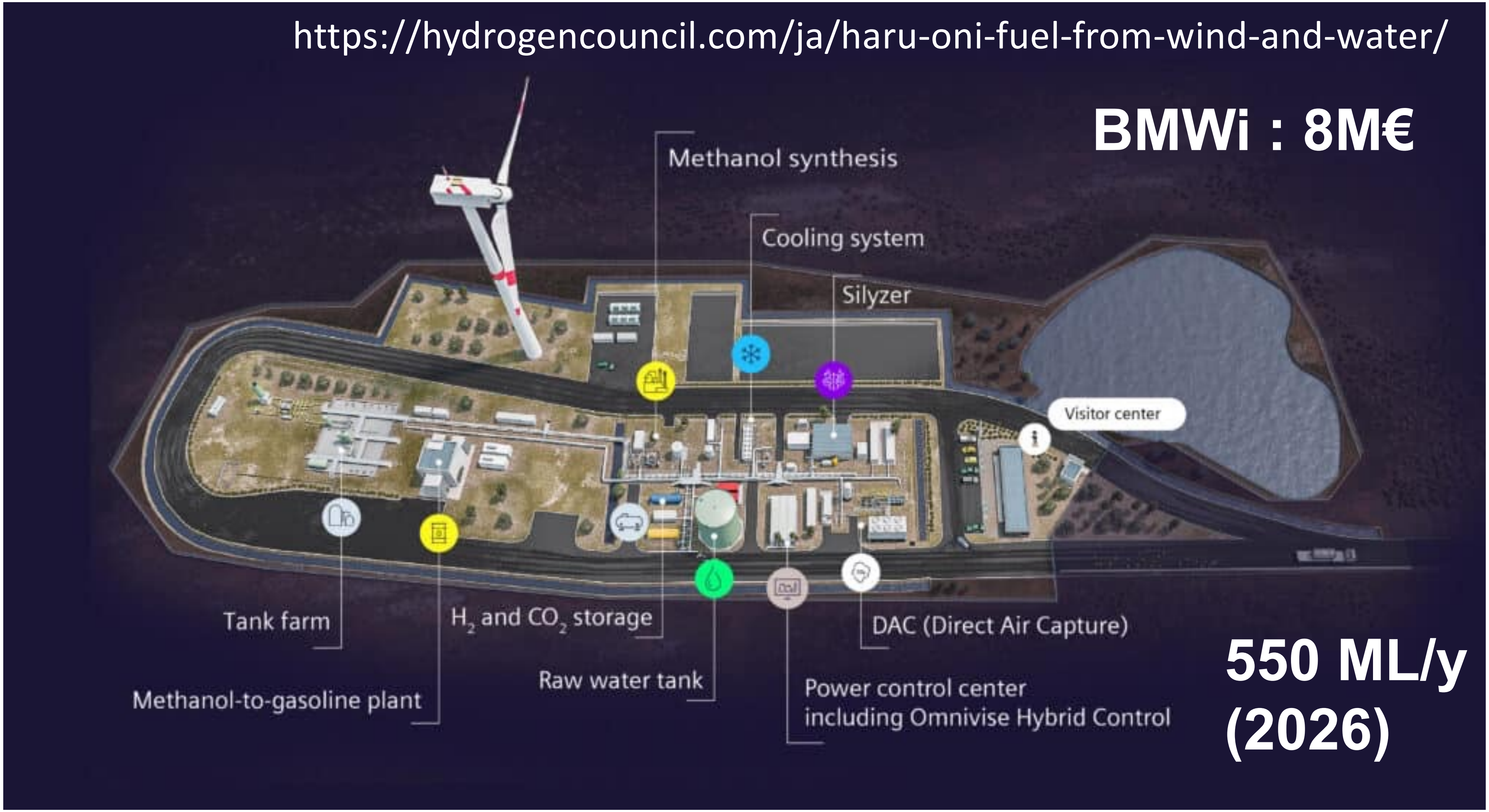
Source of power generation in Japan as preliminary data for 2023

Carbon neutral energy and synthetic fuels for mobility



Haru-Oni efuel(eGasoline) plant

Chilean power company AMF, HIF, Chilean national oil company ENAP, Italian Enel, German Siemens, Porsche, BMWi (German Ministry of Economy and Industry), US Exon Mobile



MAN will introduce "hydrogen engine HD trucks in 2025

- Introduce heavy-duty truck hTGX with hydrogen combustion engine in 2025
- First 200 units manufactured
- Slight CO_2 emissions, but classified as zero-emission in Europe
- NOx increases in hydrogen combustion due to high temperature and lean mixture ($2<\lambda<3$)
- PN10 support
- Hydrogen infrastructure (number of SS and future pipeline) is also important

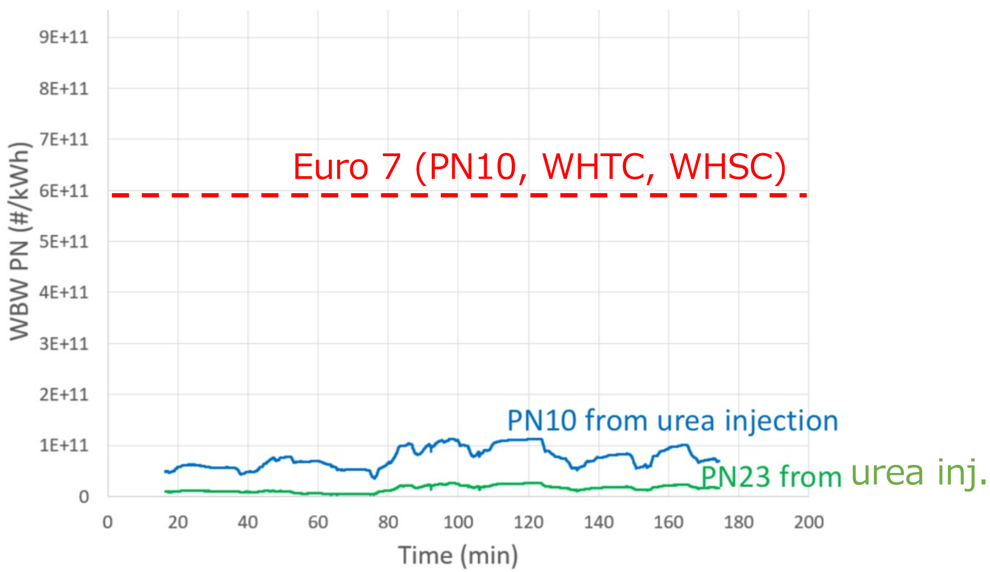
https://bestcarweb.jp/fullload/839421, 2024.4.13

Pyrolysis reactions at high temp.

$$O_2 \rightleftarrows 2O$$

Extended Zeldovich reactions

$$O + N_2 \rightleftarrows NO + N$$
$$N + O_2 \rightleftarrows NO + O$$
$$N + OH \rightleftarrows NO + H$$



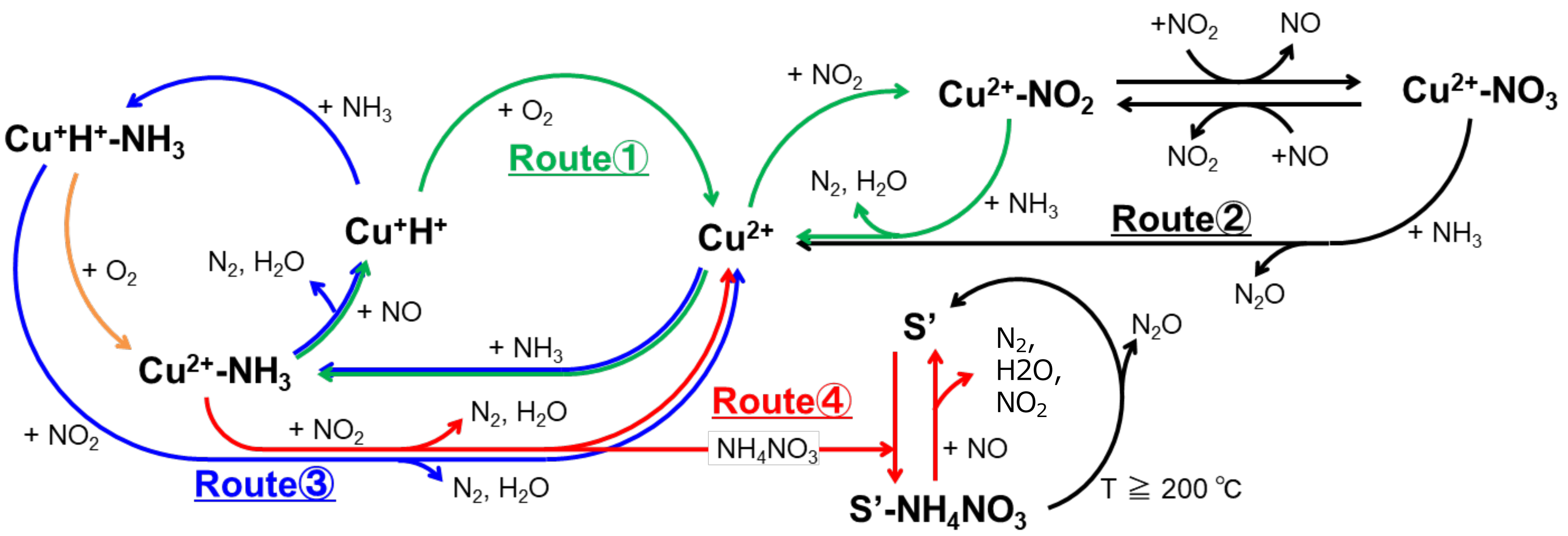
Euro 7 and 6 limitations for NOx, PN_{10} (PN_{23}), PM, NH_3, CH_4, N_2O, CH_4, CO and NMOG for HDD[2]

Pollutant emissions	Euro 7 limits		Euro 6 limits	
	WHTC (CI/PI) and WHSC (CI) kWh	REAL Driving Emissions (RDE) kWh	WHTC (CI/PI) / WHSC(CI) kWh	PEMS (including. (CF)) kWh
NOx mg	200	260	460/400	690
PN10 Particles	6.00×10^{11}	9.00×10^{11}	PN_{23} 6.00×10^{11} / 6.00×10^{11}	PN_{23} 9.78×10^{11}
PM mg	8	-	10/10	-
NH_3 mg	60	(85)	10/10 (ppm)	-
N_2O* mg	200	260	-	-
CH_4 ** mg	500	650	500 (PI only)	750 (PI only)
CO mg	1.50×10^3	1.95×10^3	4.00×10^3 / 1.50×10^3	6.00×10^3
NMOG mg	80	105	160 / 130 (CI: THC, PI: NMHC)	240 (CI: THC, PI: NMHC)

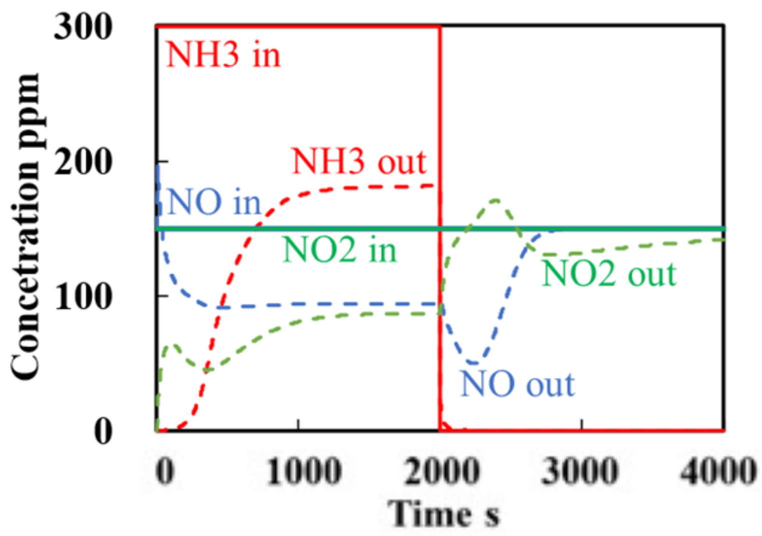
* Global warming potential : 310

** Global warming potential : 25

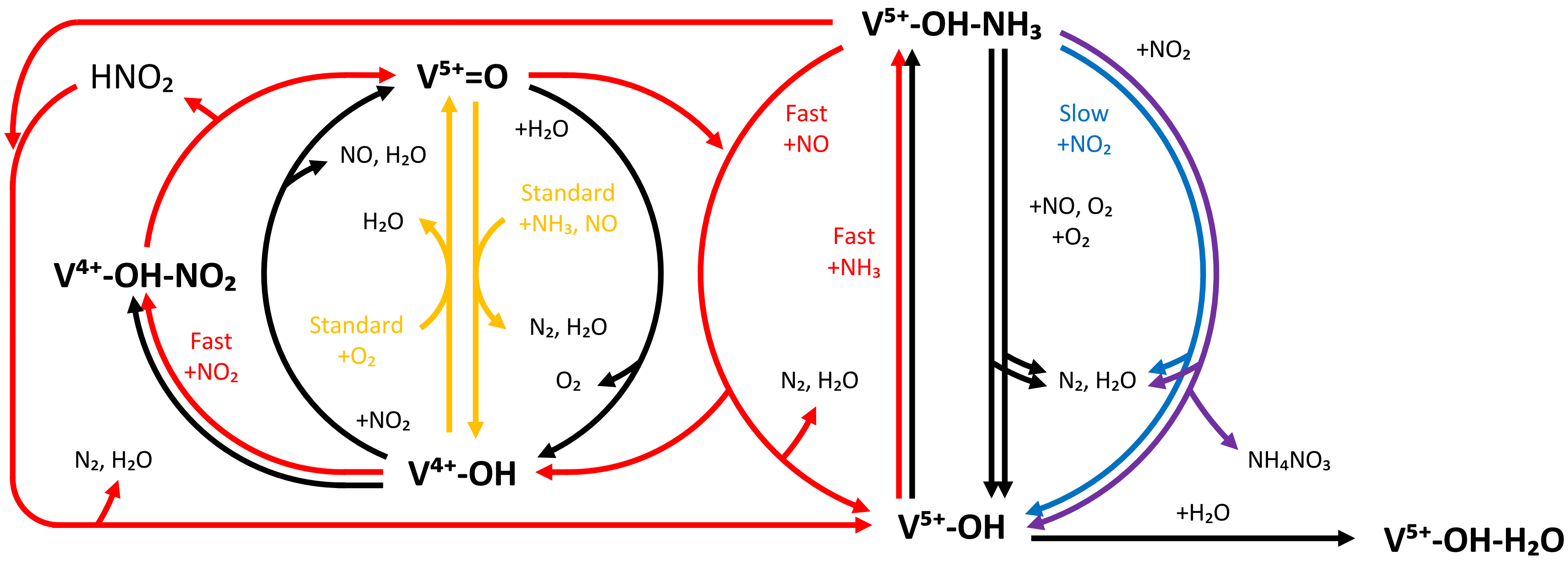
Reaction mechanism of Cu-Chabazite SCR [1], [3], [4]



- High NOx conversion rate
- Much NH_3 storage
- NH_3 slip
- Formation for S′-NH_4NO_3
- N_2O desorption



Reaction mechanism of vanadium SCR[5]



[6] Xiangmin Wang, Xuesen Du, Guangpeng Yang, Jingyu Xue, Yanrong Chen and Li Zhang, Chemisorption of NO2 on V-Based SCR Catalysts: A Fundamental Study toward the Mechanism of "Fast SCR" Reaction, 2019

[7] Topsoe, N. Y. Mechanism of the selective catalytic reduction of nitric oxide by ammonia elucidated by in situ on-line fourier transform infrared spectroscopy. Science 1994,265, 1217−1219

[8] Nova, Ciardelli, Tronconi, Chatterjee, BandlKonrad, NH_3-NO/NO_2 chemistry over V-based catalysts and its role in the mechanism of the Fast SCR reaction, 2006, 112, 3-12

Cu-zeolite vs Vanadium

	Cu-zeolite	Vanadium
Conversion(purification) rate	○	
NH_3 storage	○	
N_2O formation		○
Sulfur poisoning		○
Thermal resistance	○	
Price		○

Carry over Diesel EATS for EU7

Urea SCR catalyst

① $4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$ Standard SCR reaction

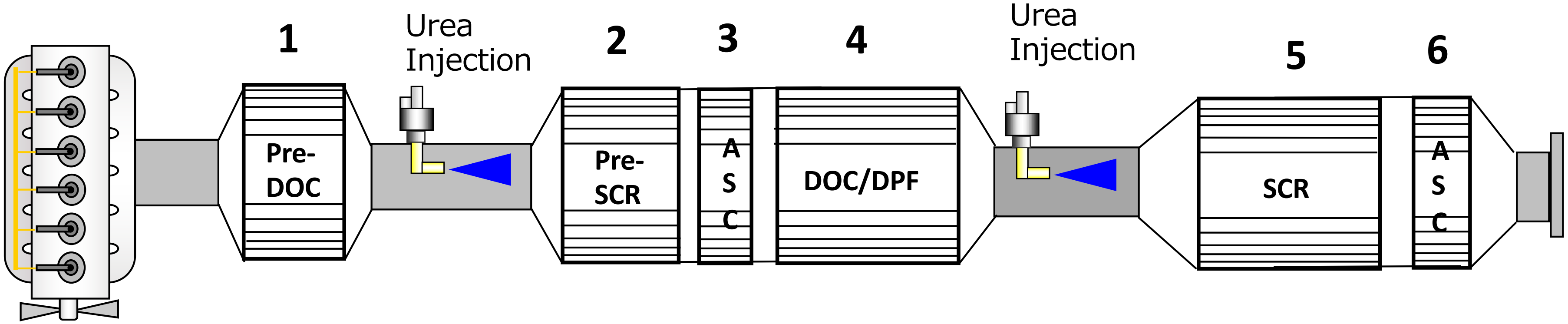
② $NO + NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O$ Fast SCR reaction

③ $6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O$ NO_2 SCR reaction

Urea Pyrolysis, hydrolysis reactions

$(NH_2)_2CO \rightarrow HNCO + NH_3$

$HNCO + H_2O \rightarrow CO_2 + NH_3$



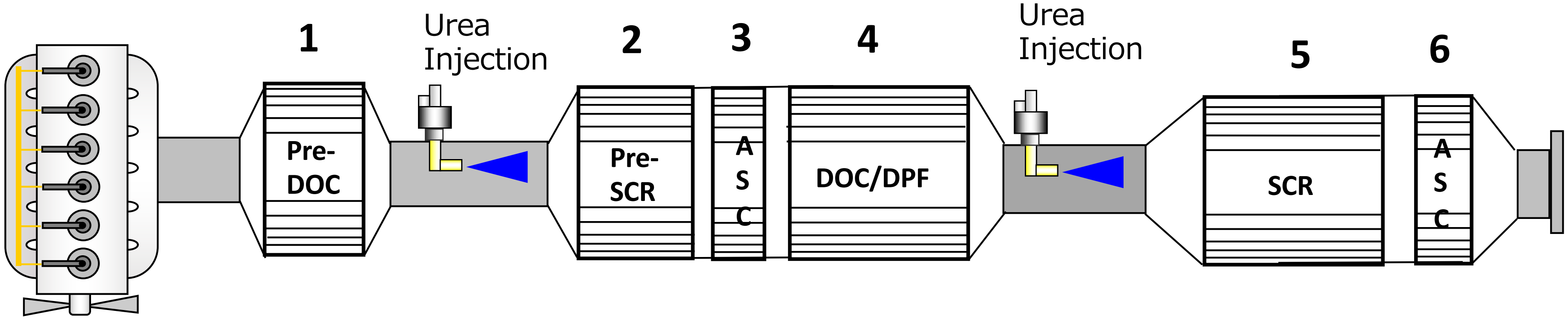
1 Pre-DOC : Exothermic reaction by H_2 supply
NO_2/NOx ratio(NO oxidation)

2 Pre-SCR + ASC: NOx conversion and NH_3 slip removal
ASC: Ammonia Slip Catalyst

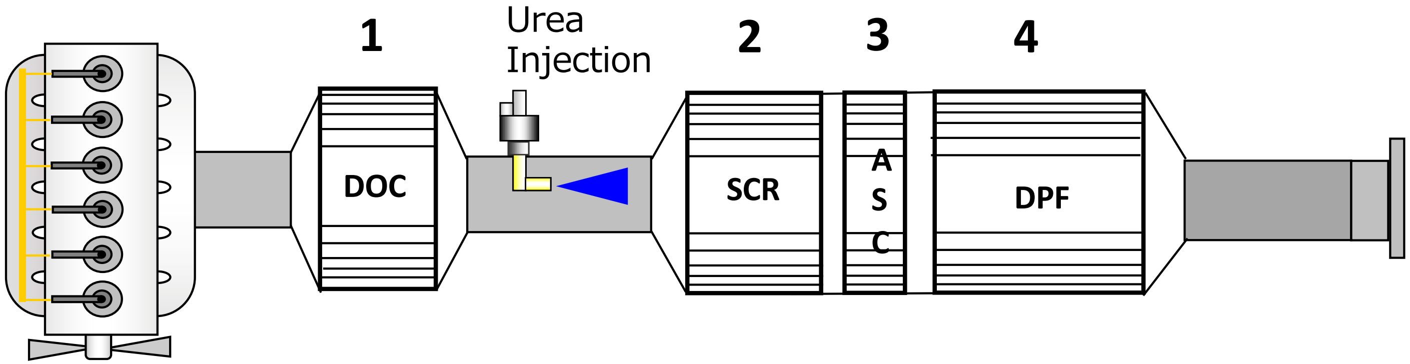
3 DOC/DPF: Filtration for PN (urea born, lubricant)
NO oxidation

4 SCR : NOx conversion

5 ASC : Ammonia removal



Dedicated H_2 engine SCR



1 DOC : NO_2/NOx ratio (NO oxidation)

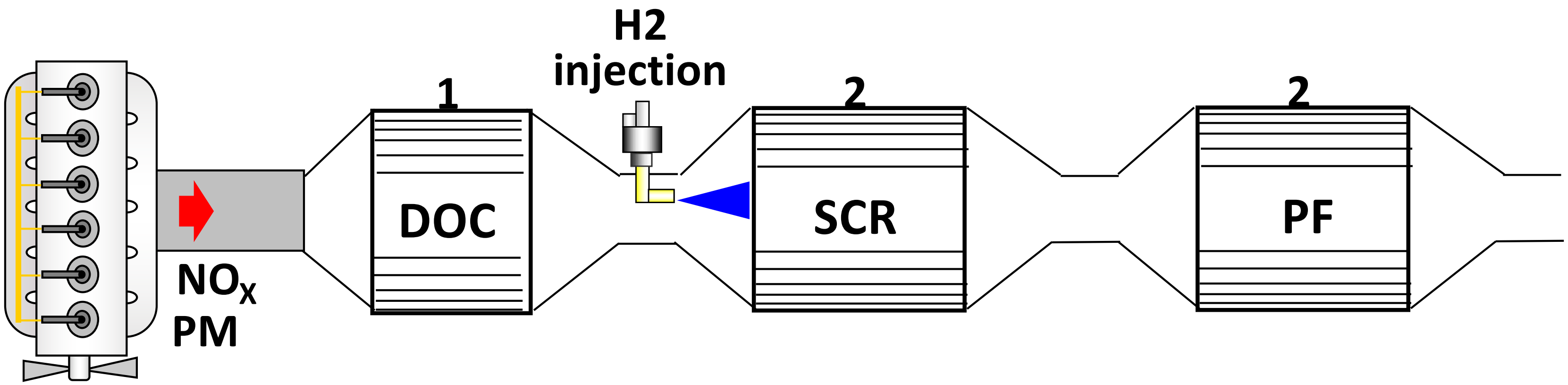
2 SCR: Cu-zeolite or Vanadium

3 ASC: Ammonia removal

4 DPF: PN10(Urea born, lubricant) removal

SCR catalyst using hydrogen as reductant

It is preferable not to have a urea water tank.
If zeolite or vanadium is used, nonpolar H_2 is most likely not adsorbed. Therefore, We will explore new active metals. The H_2 injection control is expected to be more important.



SCR: Catalytic active metals are newly explored

H_2 engine exhaust (WHTC)

- High H_2O concentration (～30%)
- Exhaust temp. (room temp. ～400 deg.C)
- Excess air ratio ($1.5 < \lambda < 3.0$)
- NO/NO_2 ratio (2～40)

Key points of R&D

- Ensuring purification performance of Cu zeolite and vanadium catalysts under conditions of H_2O mole fraction up to 30% and high temperature
- Development for dosing strategies of reducing agent
- Unravel the hydrothermal degradation mechanism under high-temperature exhaust gas equivalent to that of a spark ignition engine and its countermeasures
- Development of a new catalyst that uses H_2 as a reducing agent
- Construction of a numerical calculation model

Next-generation heavy duty vehicle development promotion project by industry-academia collaboration for decarbonization (6th phase)

脱炭素に向けた産学官連携による次世代大型車両開発促進事業　（第６期）

MLIT
Ministry of Land, Infrastructure, Transport and Tourism

早稲田大学 研究院 Research Council

- A mini-reactor experiments
- Modeling
- Dosing strategies
- Performance and mechanism feedback

Waseda University

Catalyst company

- Reactor experiments
- Durability analysis
- Test piece
- Full-size catalyst

Automobile company

- Actual engine test
- Catalyst evaluation

Thank you for your attention

Reference

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5. Yuya Kotani, Mai Shinkawa, Research progress report for the 4th Research and Development Meeting, 2024, August

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