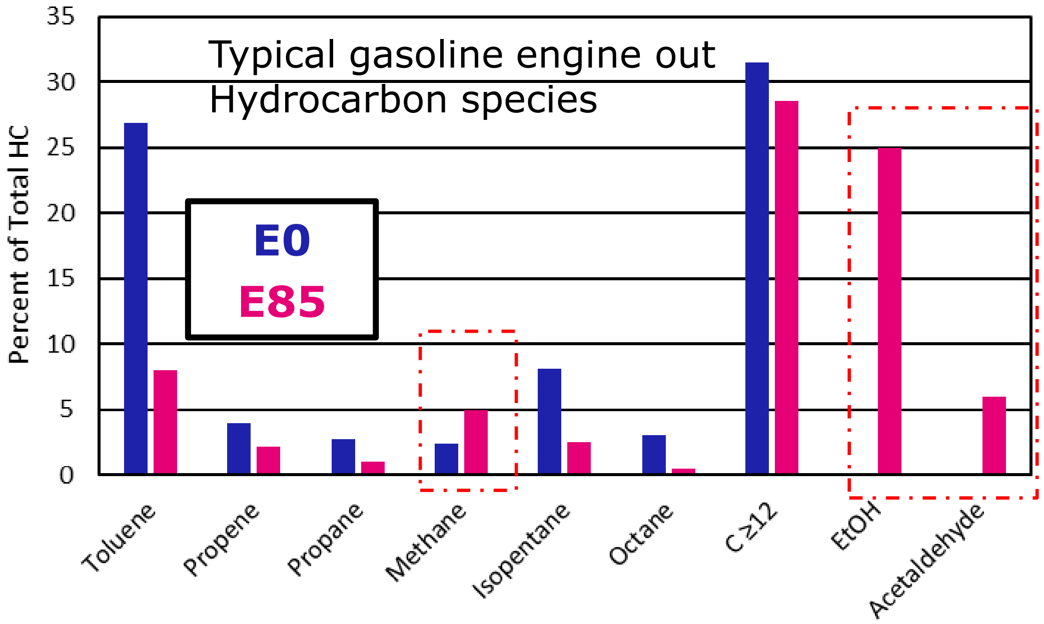
Johnson Matthey

Future Challenges of Alternative Fuel Applications on Gasoline Vehicles

ECMA Conference, 7 & 8th October 2025, New Delhi

Alternative Fuels and ethanol fuel facts

- Renewable fuel from biomass
  - **Corn starch ethanol** demonstrates positive energy balance
  - **Cellulosic ethanol** lower levels of life cycle GHS emissions
- Higher octane number than gasoline, lower-octane gasoline is blended with ethanol to attain the standard 87 octane
- Less energy density than gasoline
- E10 and E85 are typically used from blends of gasoline and ethanol



- EtOH remains un-combusted in a vehicle exhaust in significant quantities
- Increased methane emission due to EtOH decomposition

Ethanol Blending of Gasoline

Summary of Research 09/2025, Maria Vlachou

Results contained here:

- Lab reactor perturbed light off testing (λ=0.99) on 7 TWC powder components across 5 conditions: E0, E10, E20, E85 & E100

Conclusions

- Significant acetaldehyde and methane make is seen due to ethanol cracking on the TWC
  - Ethanol cracking begins at v. low temperature & before THC conversion (or other conversion)
  - Acetaldehyde-make correlates with ceria content
  - Pd produces more methane than Rh or Pt (easier for Pd to break the C=C bond)
  - No formaldehyde-make is seen
  - Significant ethylene-make is seen for Pt/alumina (some for Pd/alumina)
- Increasing ethanol content decreases CO conversions/shifts CO light-off to higher temperature
- Increasing ethanol content increases NH_3 selectivity (but NO_x conv. unchanged)

Perturbed Light-off Test Details

	E0	E10	E20	E85	E100
NO	1500 ppm	1500 ppm	1500 ppm	1500 ppm	1500 ppm
HC 1: Propylene	1800 ppm C1 (600 ppm C_3H_6)	1620 ppm C1 (540 ppm C_3H_6)	1440 ppm C1 (480 ppm C_3H_6)	270 ppm C1 (90 ppm C_3H_6)	-
HC 2: Propane	900 ppm C1 (300 ppm C_3H_8)	810 ppm C1 (270 ppm C_3H_8)	720 ppm C1 (240 ppm C_3H_8)	135 ppm C1 (45 ppm C_3H_8)	-
HC 3: Ethanol	-	100 ppm C1 (50 ppm CH_3CH_2OH)	200 ppm C1 (100 ppm CH_3CH_2OH)	850 ppm C1 (425 ppm CH_3CH_2OH)	1000 ppm C1 (500 ppm CH_3CH_2OH)
CO base	0.73%	0.73%	0.73%	0.73%	0.73%
H2 base	0.24%	0.24%	0.24%	0.24%	0.24%
O2 base	0.59%	0.56%	0.53%	0.34%	0.30%
CO pert	1.47% (2.2% total rich)	1.47% (2.2% total rich)	1.47% (2.2% total rich)	1.47% (2.2% total rich)	1.47% (2.2% total rich)
H2 pert	0.49% (0.73% total rich)	0.49% (0.73% total rich)	0.49% (0.73% total rich)	0.49% (0.73% total rich)	0.49% (0.73% total rich)
O2 pert	1% (1.59% total lean)	1% (1.56% total lean)	1% (1.61% total lean)	1% (1.34% total lean)	1% (1.30% total lean)
Total C from HCs	2700 ppm	2530 ppm	2360 ppm	1255 ppm	1000 ppm
Total H from HCs	6000 ppm	5700 ppm	5400 ppm	3450 ppm	3000 ppm
H:C Ratio of HCs	2.22	2.25	2.29	2.75	3
Total O from HCs	0 ppm	50 ppm	100 ppm	425 ppm	500 ppm

CO_2: 14%, H_2O: 5%, perturbation frequency: 0.167 Hz (3 s rich, 3 s lean), Perturbation Amplitude: 0.05, Average Lambda: 0.99, Ramp rate: 10°C/min
A lean pretreatment in 5% O_2/N_2 and held at 500°C for 15 mins was performed between tests.

TWCs were aged via redox ageing (λ=0.99±0.05 every 5 mins) at 950°C for 16 h.

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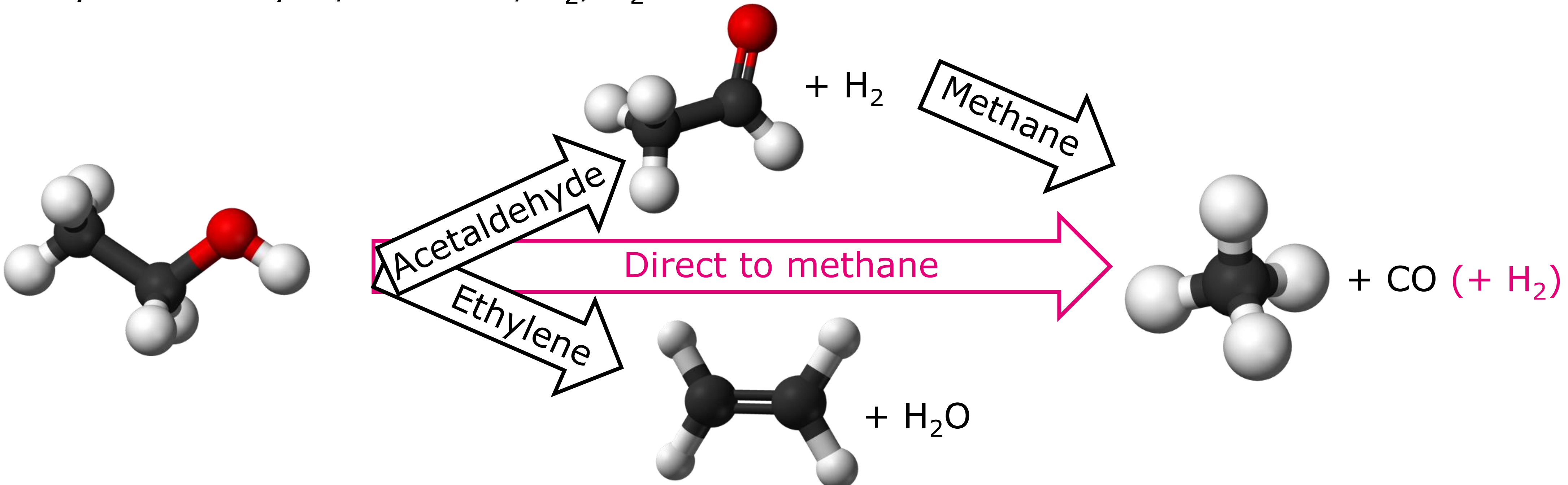
Important to know

Ethanol Cracking

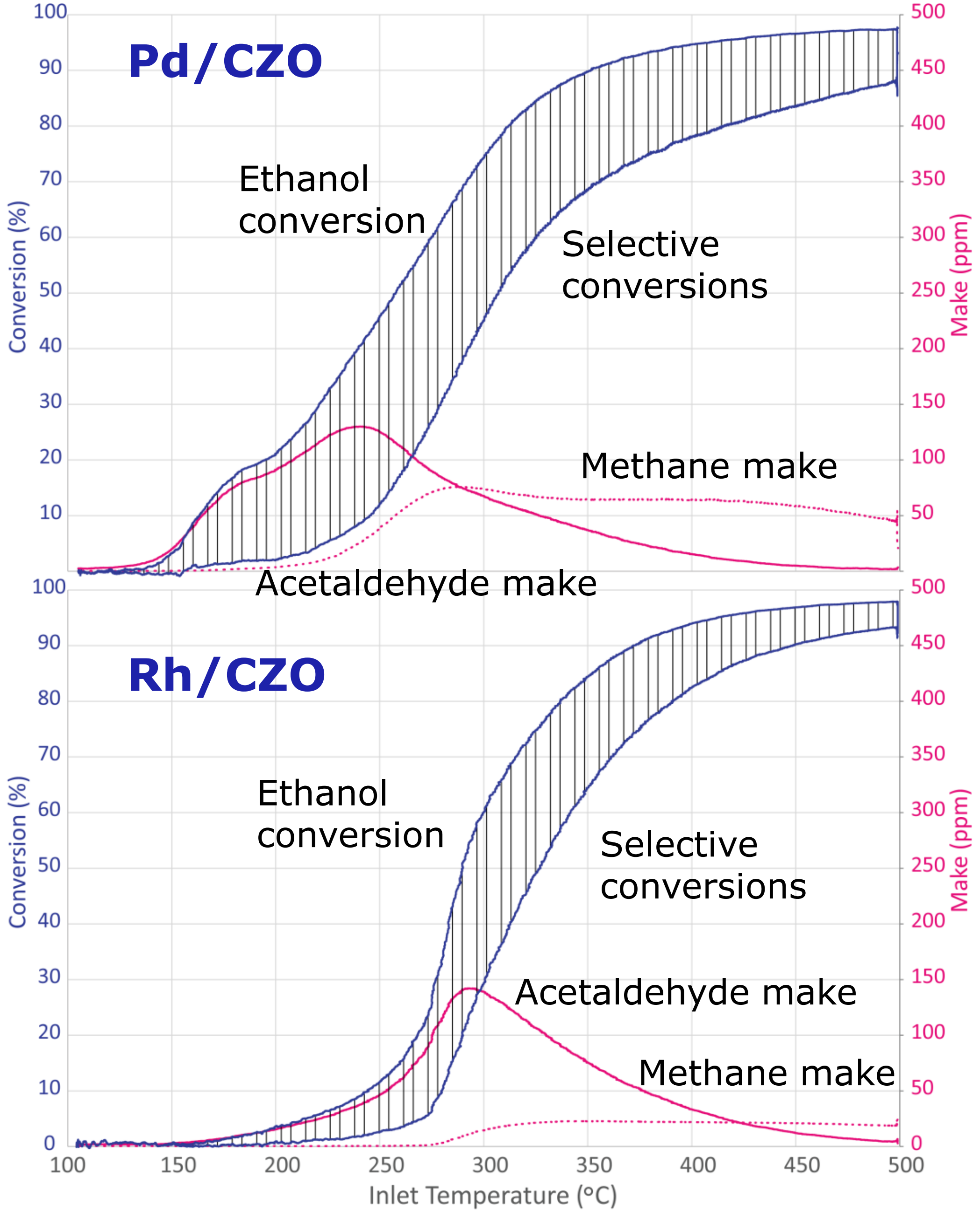
- Before "true" conversion, ethanol decomposes or "cracks" into other species via the TWC, primarily acetaldehyde, methane, H_2, H_2O and CO



- Smaller amounts of other HCs such as ethylene, ethane and propane are also produced (before conversion)
- Methane is still produced (and unconverted) by the end of the test at 500°C

Ethanol Conversion

- Ethanol conversion, through cracking, occurs relatively early; but this reaction not very selective
- Acetaldehyde is formed during EtOH light off, which is further converted into CH_4 at higher temperatures
- A "Gap" of undesired products is seen during the entire temperature window



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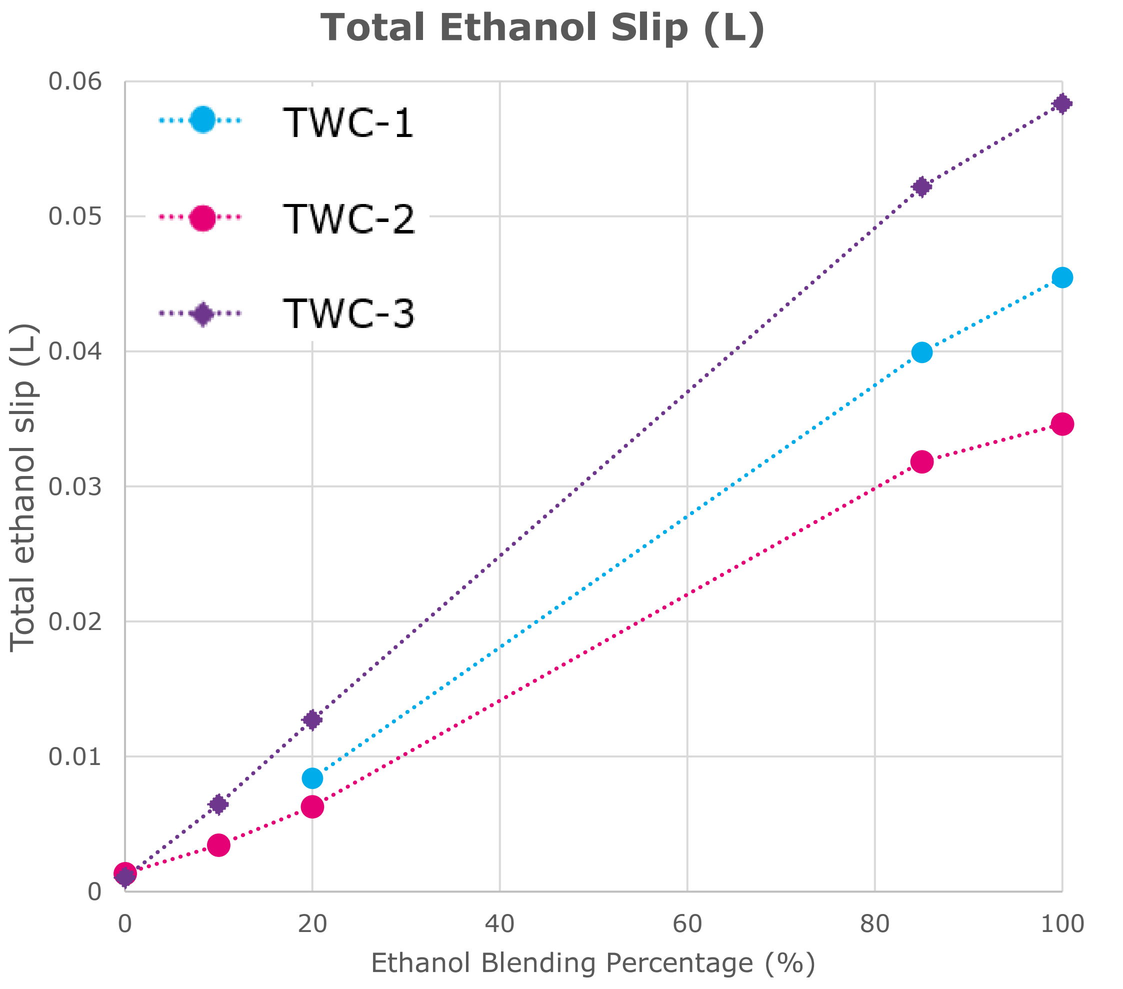
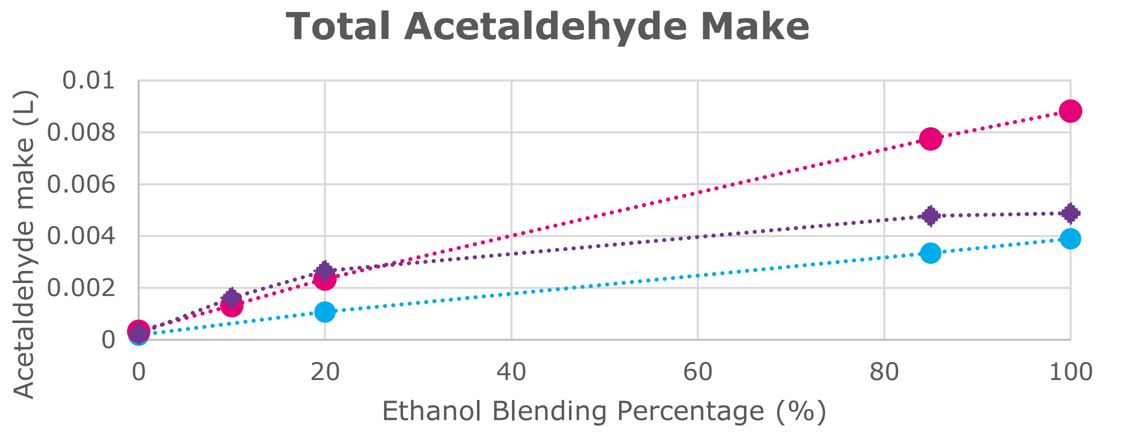
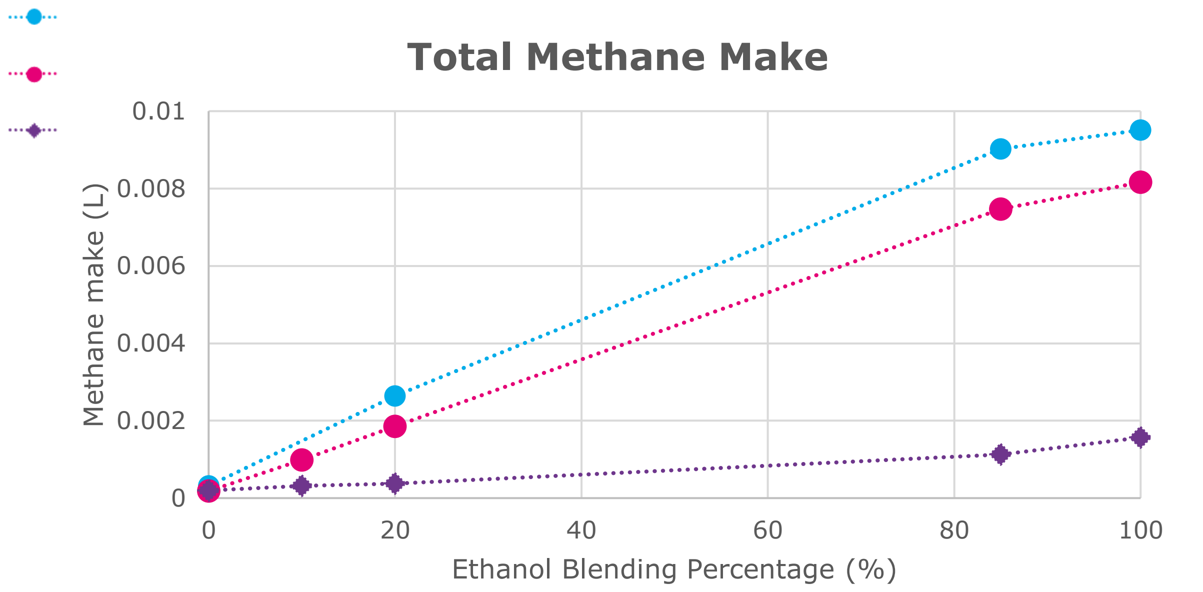
TWCs that reduce ethanol slip forms more intermediates due to cracking

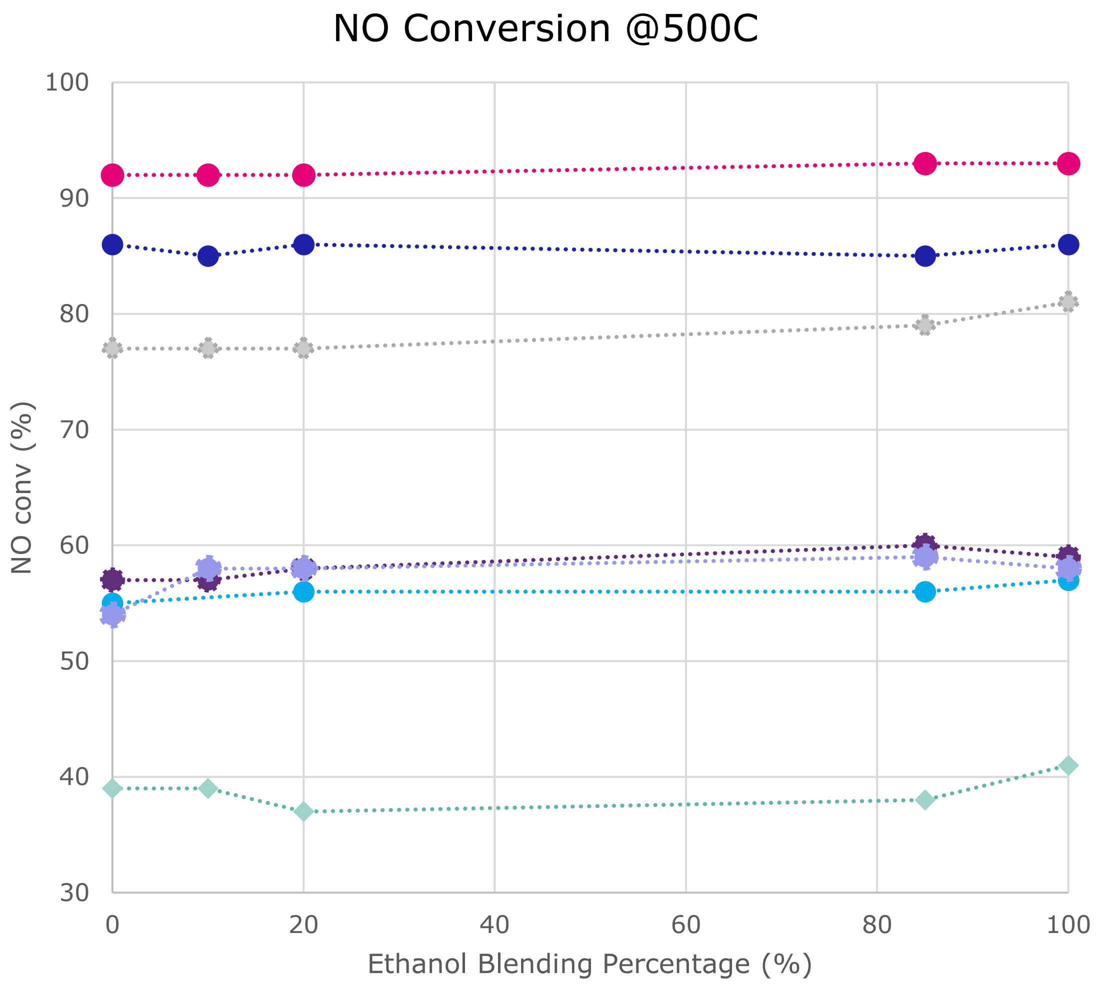


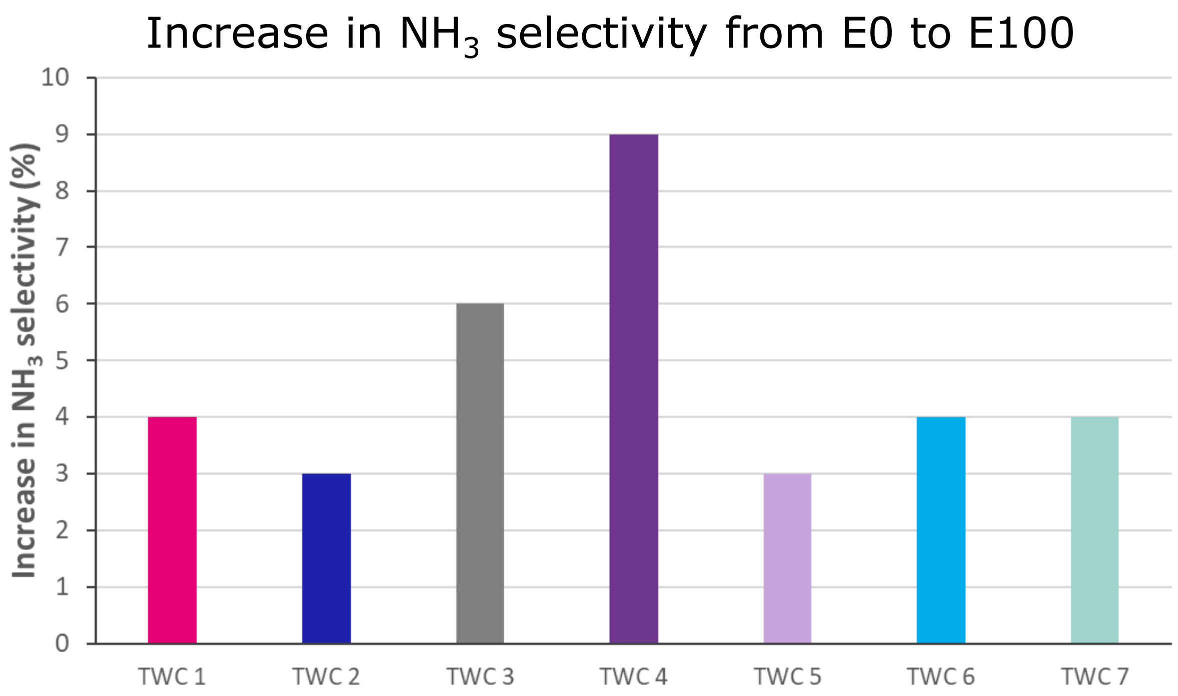




NO_x Activity Changes

No change to NO conversion, but NH_3 selectivity increases (N_2 selectivity decreases) with increasing ethanol content





Potentially due to increasing the H:C ratio with increasing ethanol content, i.e. 3 vs 2.22 for E100 vs E0

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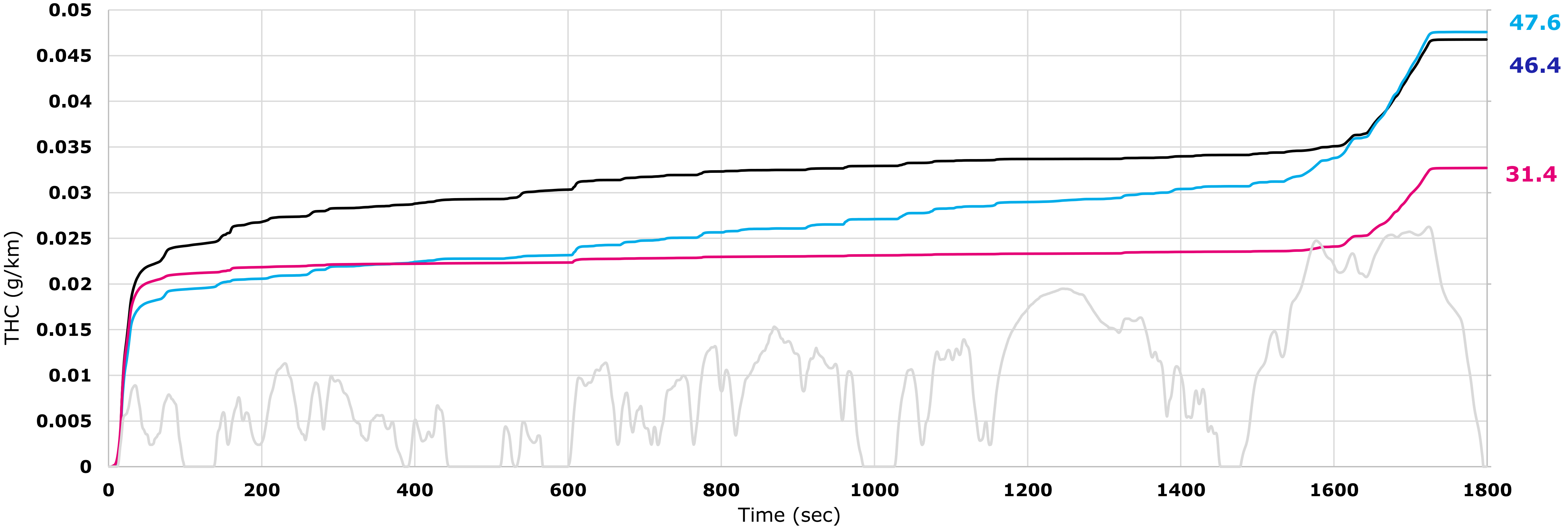
Bi-fuel CNG vehicle tests

WLTP cycle

Aging condition: 300hrs/950C+850C/redox

1	Market catalyst (Pd/Rh)
2	JM TWC design (Pt/Pd/Rh)
3	JM CNG design (Pt/Pd/Rh)



- **TWC design provide significantly improved LO, but lack of CH_4 conversion at high T**
- **CNG design significantly improves CH_4 conversion while still providing good light off**

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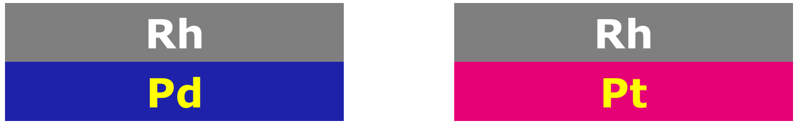
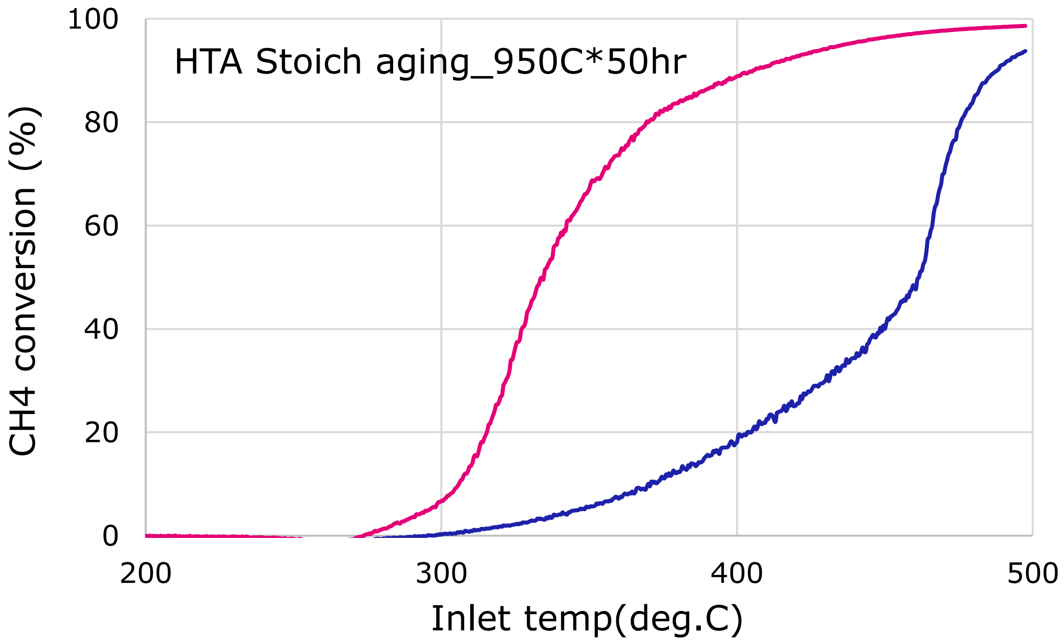
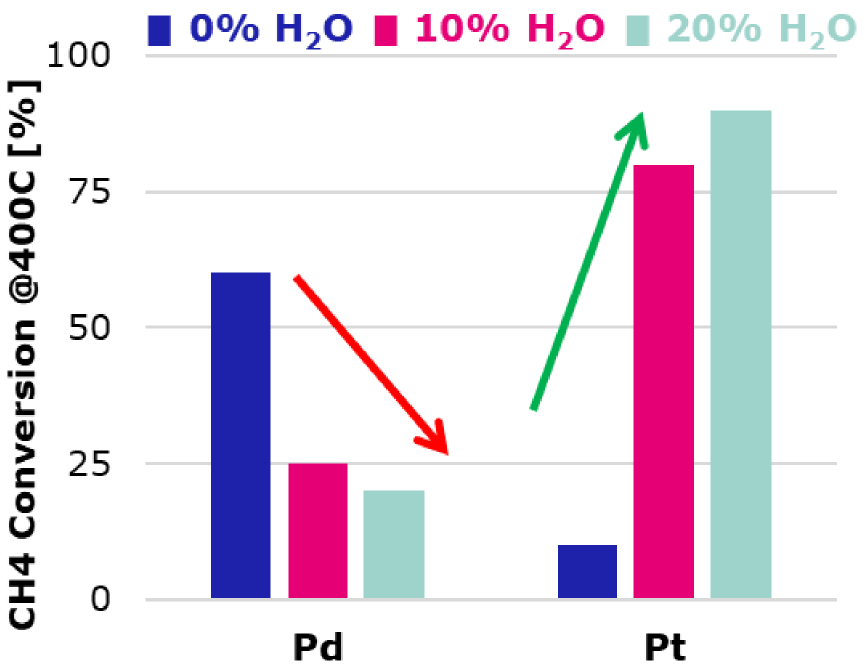
CH4 conversions on Pd and Pt catalysts





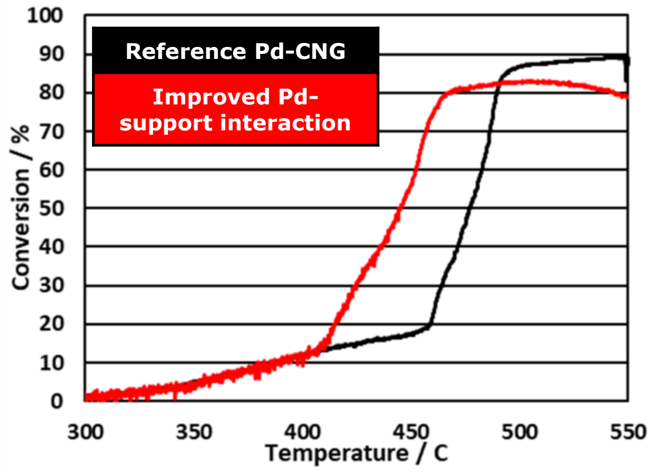
H_2O impact for CH_4 conversion from JMSH



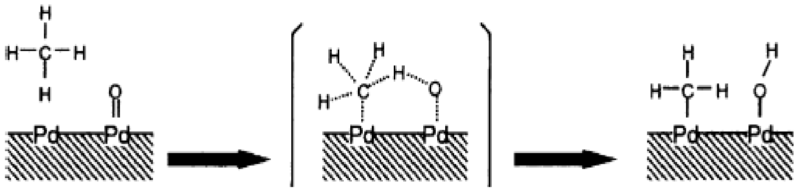
- Pt shows better activity than Pd under high H_2O
- The water content in EG EM is around 15-20%
- Pt would be beneficial in real application

Pt is more active for steam reforming which benefits by H_2O in the feed
Pd converts CH4 by oxidation which is inhibited by H_2O in the feed

CH_4 removal reaction mechanisms



K. Fujimoto, F.H. Ribeiro, M. Avalos-Borja, E. Iglesia, *J. Catal.* **1998**, *179*, 431.



It is believed both metallic and oxide PGM species are needed to activate CH_4 molecule

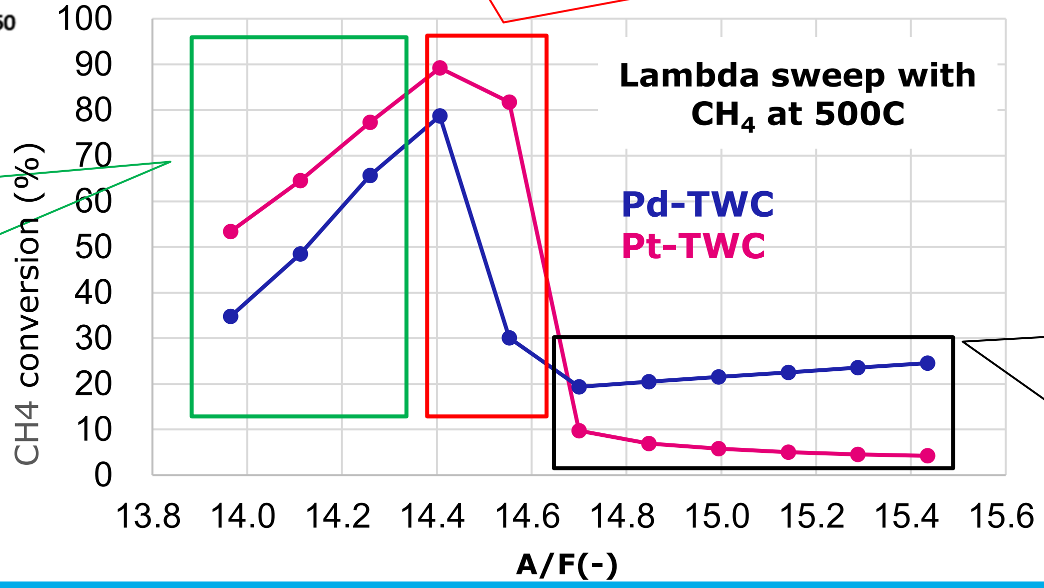
Adsorption of CH_4 on metallic PGM and oxygen activation on oxide PGM results in the initial hydrogen abstraction from CH_4

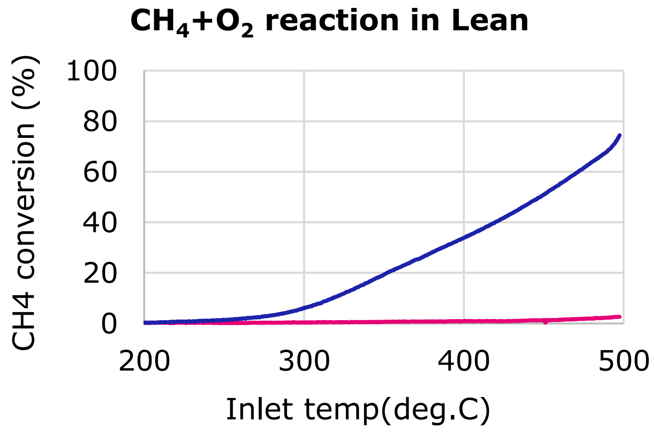
CH4 conversion under Stoich cond.
Reaction mechanism is complicated

CH_4 conversion under Rich cond.

$CH_4 + H_2O \leftrightarrows CO + 3H_2$
(Steam Reforming)

SR: Pt-metal > Pd-metal





CH_4 oxidation: PdO > PtO

- **Different CH_4 reaction mechanisms at different λ conditions (lean vs. rich vs. stoic)**
- **Reactions under stoic condition is most important but is also most complicated**

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Summary

Flex-fuel and Ethanol emission

- Conversion of Ethanol is not difficult; However, selectivity is the main challenge
  - High selectivity to CH_4 under certain conditions on a TWC catalyst
  - The CH4 selectivity can be reduced by optimizing catalyst formulation
    - PGM-support interactions and tandem/chain reactions between PGM species

CNG and CH_4 emission

- CH_4 emission control is important for both CNG and flex-fuel vehicles
- Both Pt and Pd are active for CH_4 under different conditions
- CH_4 conversion under stoic condition is most complicated, which requires careful tuning Pt and/or Pd by tuning the oxidation state and PGM-support interactions

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