Low Life-cycle Carbon Fuel (LLCF) Effects on Emissions Control Catalyst Performance and Durability (Project ID: ACE170)

Oak Ridge National Laboratory
National Transportation Research Center

PI: Sreshtha Sinha Majumdar
Email: sinhamajumds@ornl.gov

2022 U.S. DOE Vehicle Technologies Office
Annual Merit Review

June 21st, 2022

ORNL is managed by UT-Battelle, LLC for the US Department of Energy

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Acknowledgements

- **Funding & guidance from DOE VTO Program Managers:**
  - Siddiq Khan, Kevin Stork, Gurpreet Singh, Mike Weismiller
- **Discussions & guidance from:**
  - Josh Pihl, Jim Szybist and Todd Toops
  - Dave Montgomery and Kenth Svensson
  - Yong Wang and Ken Rappe

Overview

Timeline

Project start date: FY 2022

Project end date: FY 2023

- builds on the Co-Optimization of Engines and Fuels project (2018-2021)
- evolves with DOE priorities and industry needs

Barriers

- Decarbonization of the hard-to-electrify rail, marine, and off-road sectors
- Maintaining compliance with emissions regulations for engines running on low life-cycle carbon fuels

Budget

	FY22
AOP TASK 1 3.5.2.503	$400k

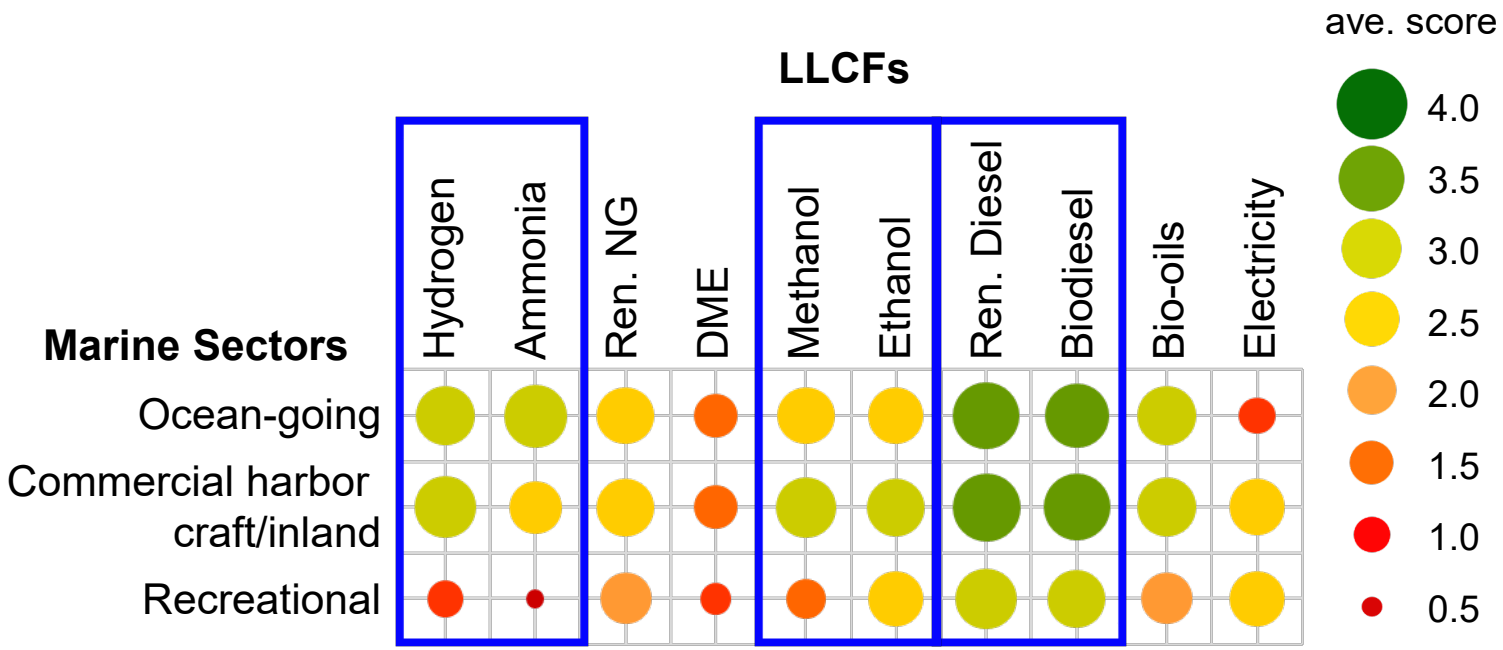
Partners

- Caterpillar Inc.
- Pacific Northwest National Laboratory (PNNL)

OAK RIDGE National Laboratory | NATIONAL TRANSPORTATION RESEARCH CENTER

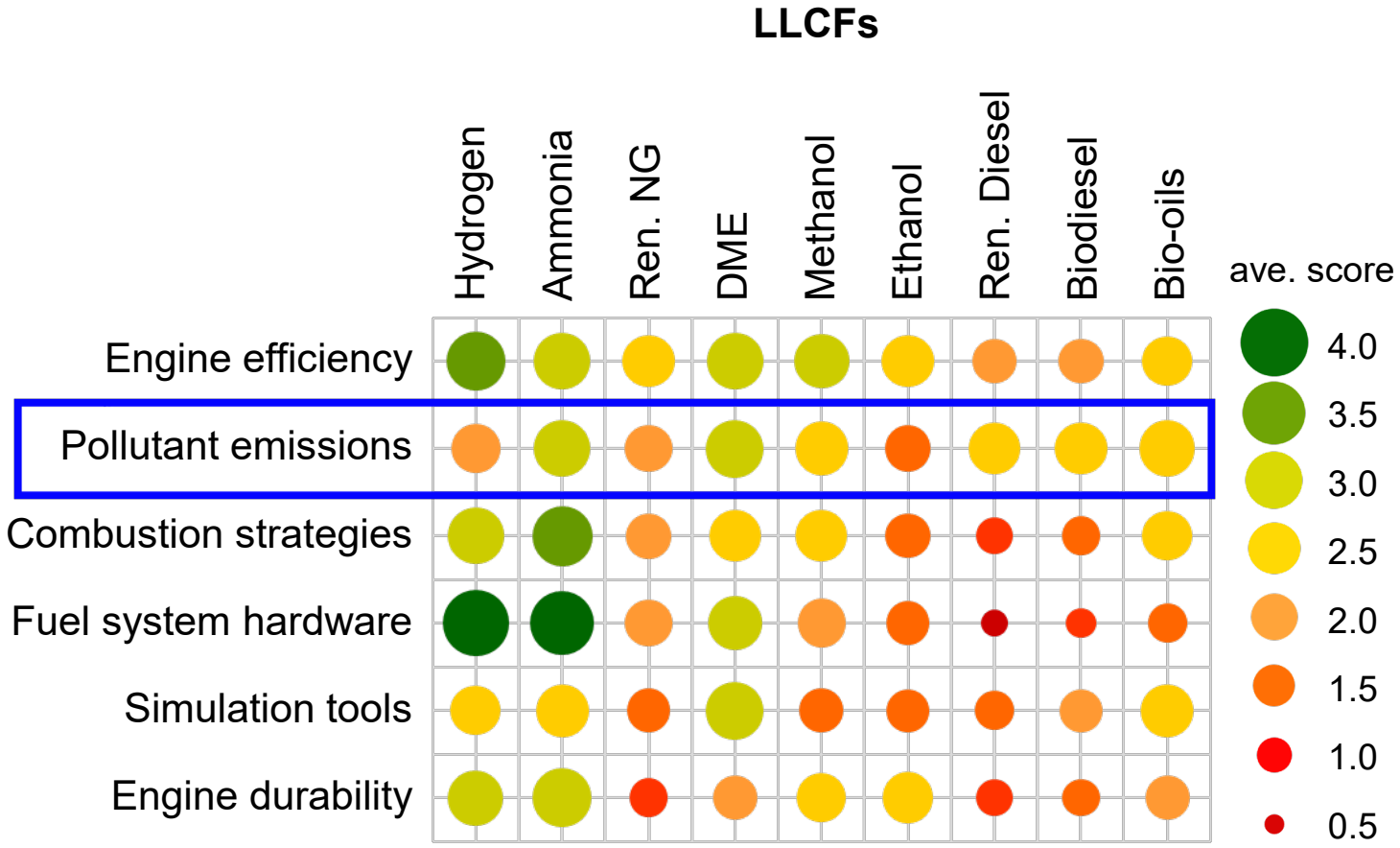
LLCFs will play a critical role in achieving decarbonization of hard-to-electrify off-road, rail, and marine sectors

- ORNL distributed questionnaires to industry stakeholders to identify likely decarbonization pathways and barriers to their implementation for the off-road, rail, and marine transportation sectors
- These sectors will be challenging to electrify due to application characteristics
  - distances traveled, loads, uptime requirements, remote locations…
- Low life-cycle carbon fuels (LLCFs) produced from renewable hydrogen, biomass, and/or captured CO_2 will be needed to achieve decarbonization of the hard-to-electrify sectors
- According to questionnaire responses:
  - renewable diesel & biodiesel will play a significant role in off-road, rail, and marine decarbonization
  - (but there will likely not be enough biomass to meet the needs of all hard-to-electrify transport sectors)
  - other LLCFs (hydrogen, ammonia, methanol, ethanol) are also expected to contribute significantly to decarbonization



Pollutant emissions are expected to be a key barrier for achieving decarbonization of hard-to-electrify sectors with LLCFs

- According to questionnaire responses:
  - Pollutant emissions ranked just behind engine efficiency as top barriers to achieving decarbonization with LLCFs
- LLCFs could create both benefits and challenges for emissions control
  - Prior Co-Optima results showed alcohols have low light-off temperatures over three-way catalysts
  - Caterpillar has expressed concern about aldehyde emissions from alcohols
- **Further understanding of LLCF reactivity over emissions control catalysts is needed**



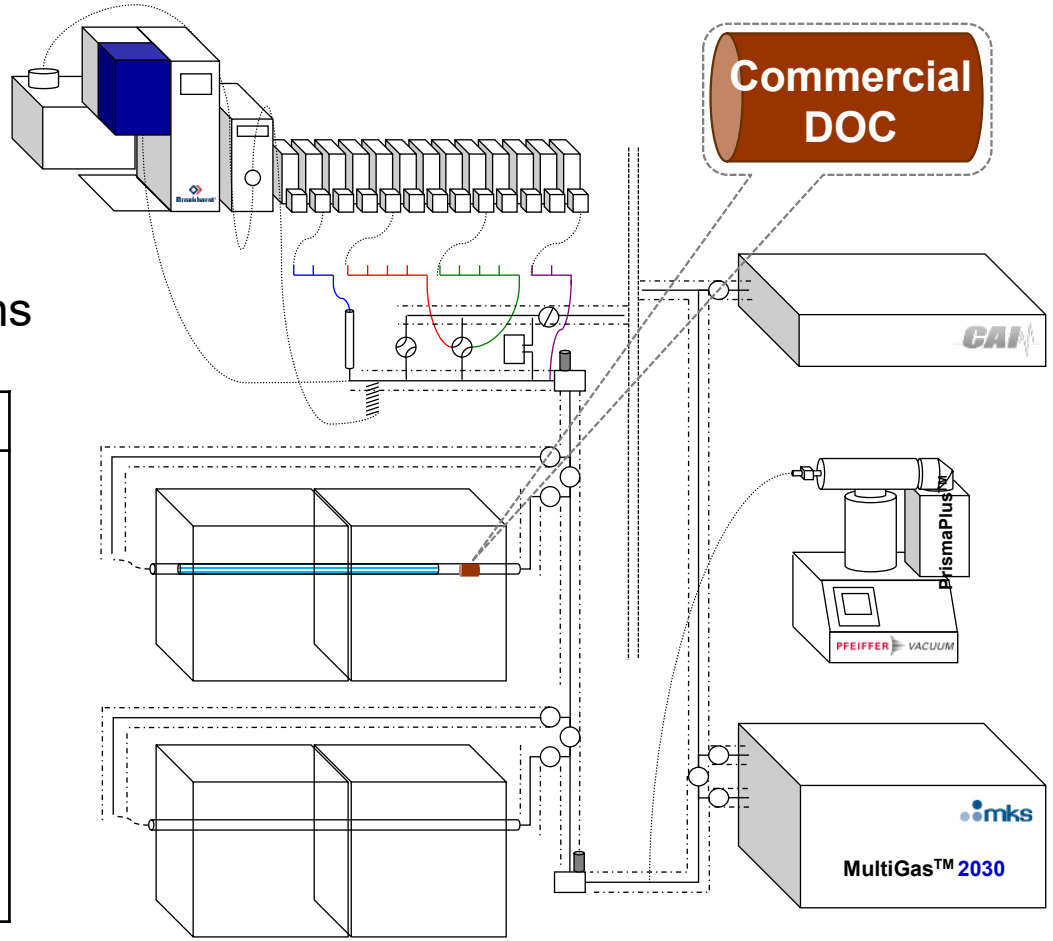
Milestones

FY	Qtr	Milestone	Status
2022	2	Measure DOC light-off for methanol, ethanol, and isobutanol	**Complete**
2022	4	Measure DOC light-off for formaldehyde, acetaldehyde, and isobutyraldehyde	**On-Track**

Synthetic exhaust flow reactor experiments conducted according to industry protocols* were used to quantify effects of fuel chemistry on DOC light-off

- Experiments conducted on an automated synthetic exhaust flow reactor
  - vapor delivery system for liquid fuel components
  - FID and FTIR for gas analysis
- Commercial diesel oxidation catalyst (DOC) sample aged for 50 h @ 800 °C catalyst inlet temperature under lean conditions
- DOC light-off/light-down experiments repeated ≥ 3 times for each fuel as per industry protocols*
  - Full synthetic exhaust mixture has been used for these experiments
  - Fuel concentration kept constant in the feed at 3000 ppm C_1

Synthetic Exhaust	
CO_2	6%
H_2O	6%
CO	0.2%
H_2	0.04%
NO	0.01%
HC (as C_1)	0.3%
O_2	12%
SV	30000 h^{-1}



*http://cleers.org/wp-content/uploads/2015_LTAT-Oxidation-Catalyst-Characterization-Protocol.pdf

Experiments included a range of LLCFs

alcohols

CH_3-OH
methanol

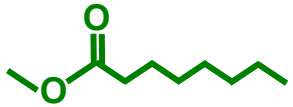
ethanol

isobutanol

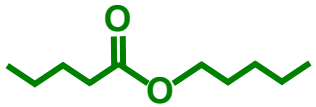
POME

dibutoxymethane

esters



methyloctanoate



pentylpentanoate

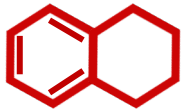
linear alkane *

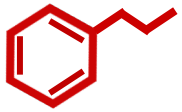
n-decane

cyclo-alkane *

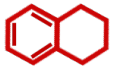
decalin

aromatics *


tetralin


n-propyl benzene

C10 Surrogate Diesel

49%		n-decane
24%		decalin
27%		tetralin

- *Some of the potential LLCFs are also currently found in diesel fuel
- C10 diesel surrogate consists of C_{10} (no. of C atoms =10) representative of each functional group (linear alkane, cyclic alkane, aromatic) contained in a surrogate diesel blend previously proposed in the literature**

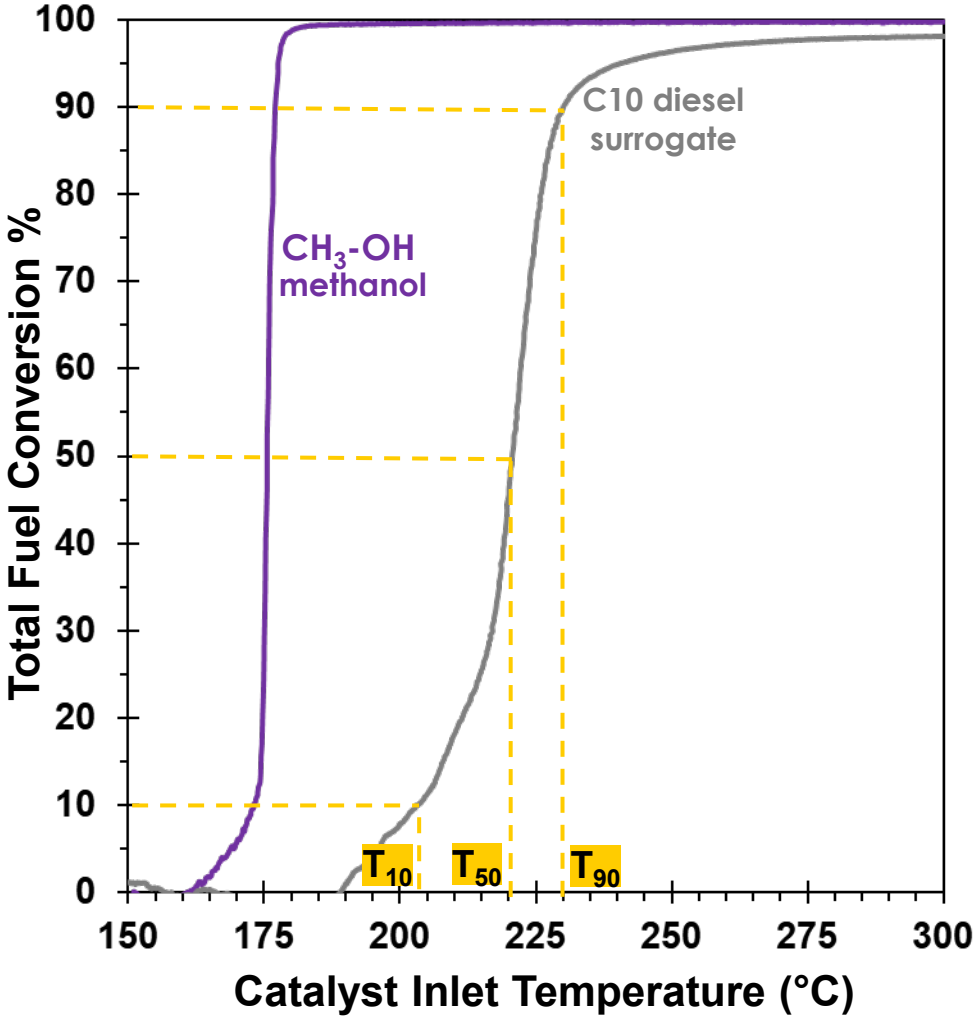
**G. Fioroni et al., SAE International, 2019-01-0570, 2019.

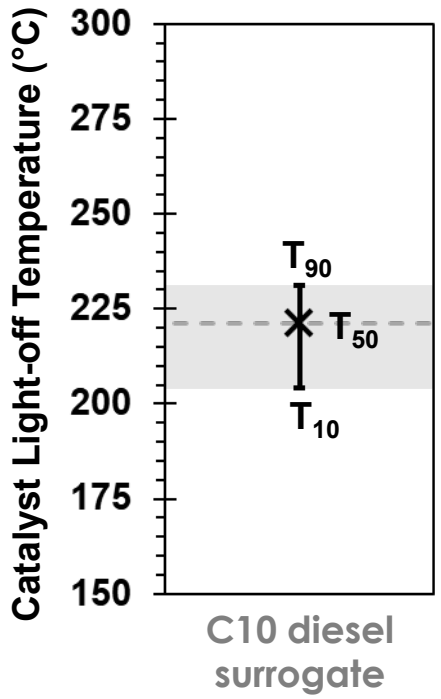
Fuel chemistry impacts DOC light-off behavior

- C10 diesel surrogate used as a baseline for comparison with LLCFs
- Sample light-off curves show fuel chemistry significantly shifts DOC light-off temperatures
- T_{50} = temperature at which 50% of a fuel is converted on the DOC indicated by 'X' symbol
- Temperature range from 10% to 90% conversion of fuel on DOC indicated by bar T_{10} to T_{90}

C10 Surrogate Diesel

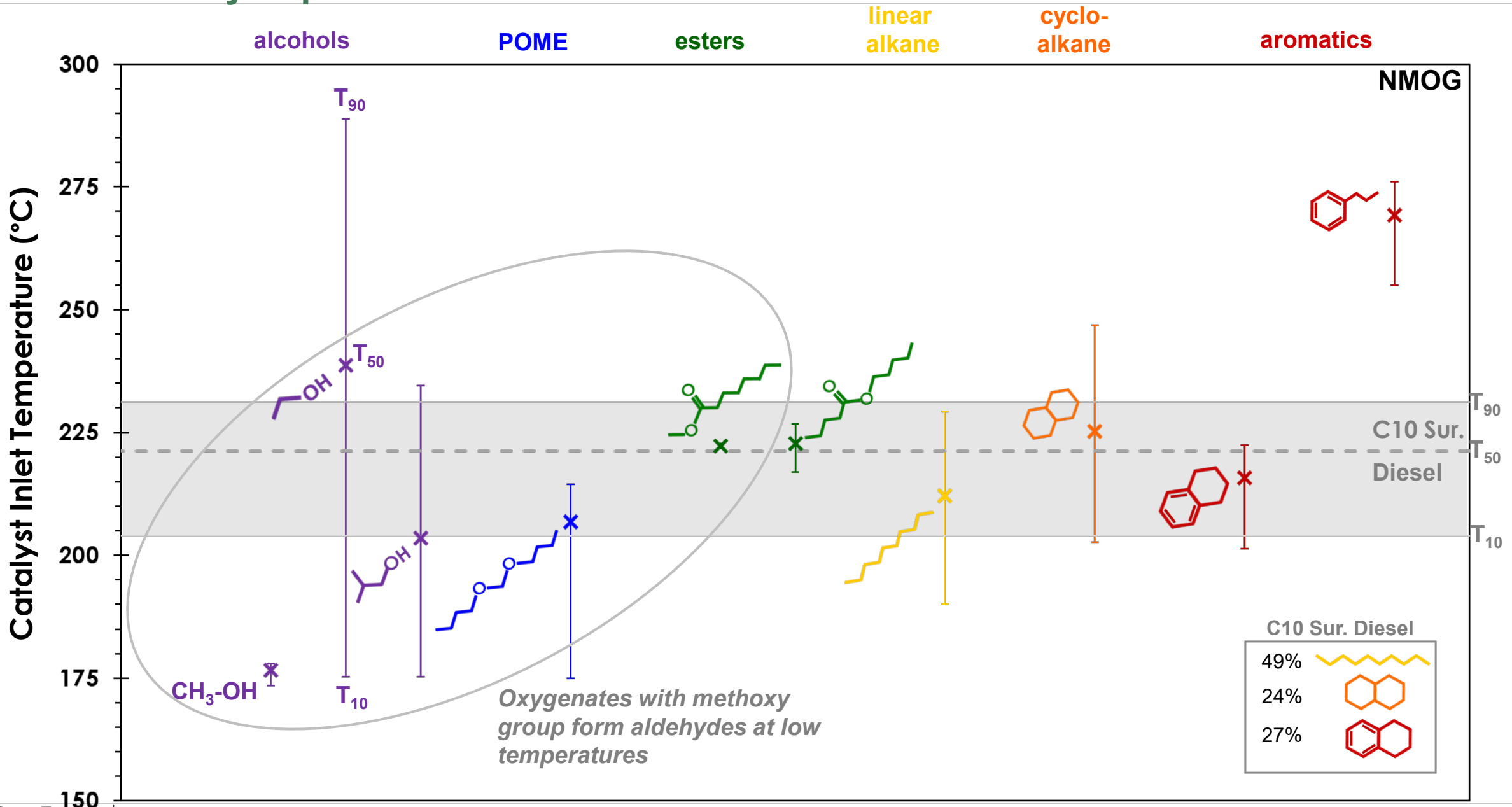
49%	n-decane
24%	decalin
27%	tetralin





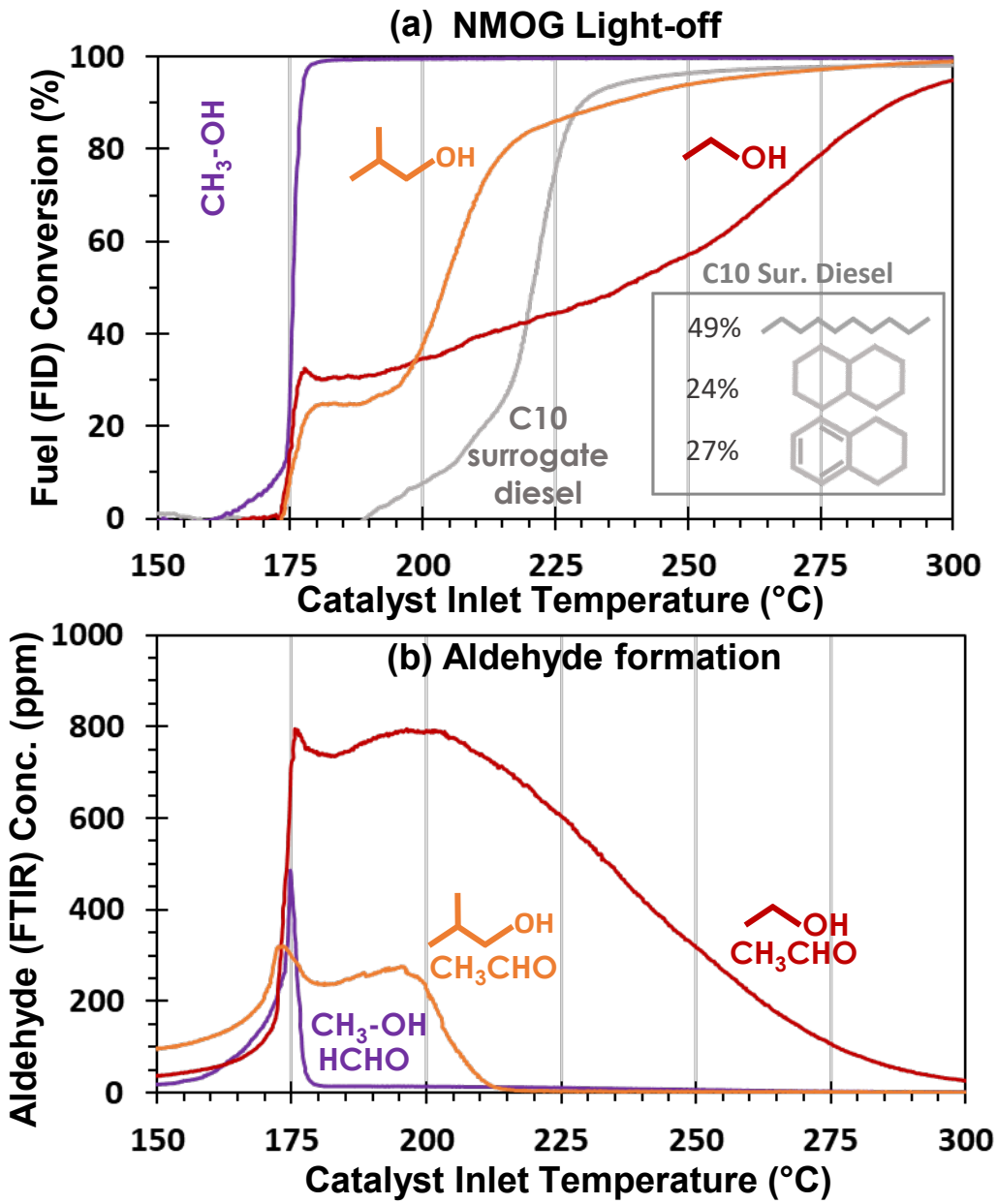
Synthetic Exhaust	
CO_2	6%
H_2O	6%
CO	0.2%
H_2	0.04%
NO	0.01%
HC (as C_1)	0.3%
O_2	12%
SV	30000 h^{-1}

DOC reactivity depends on the chemical structure of the LLCFs

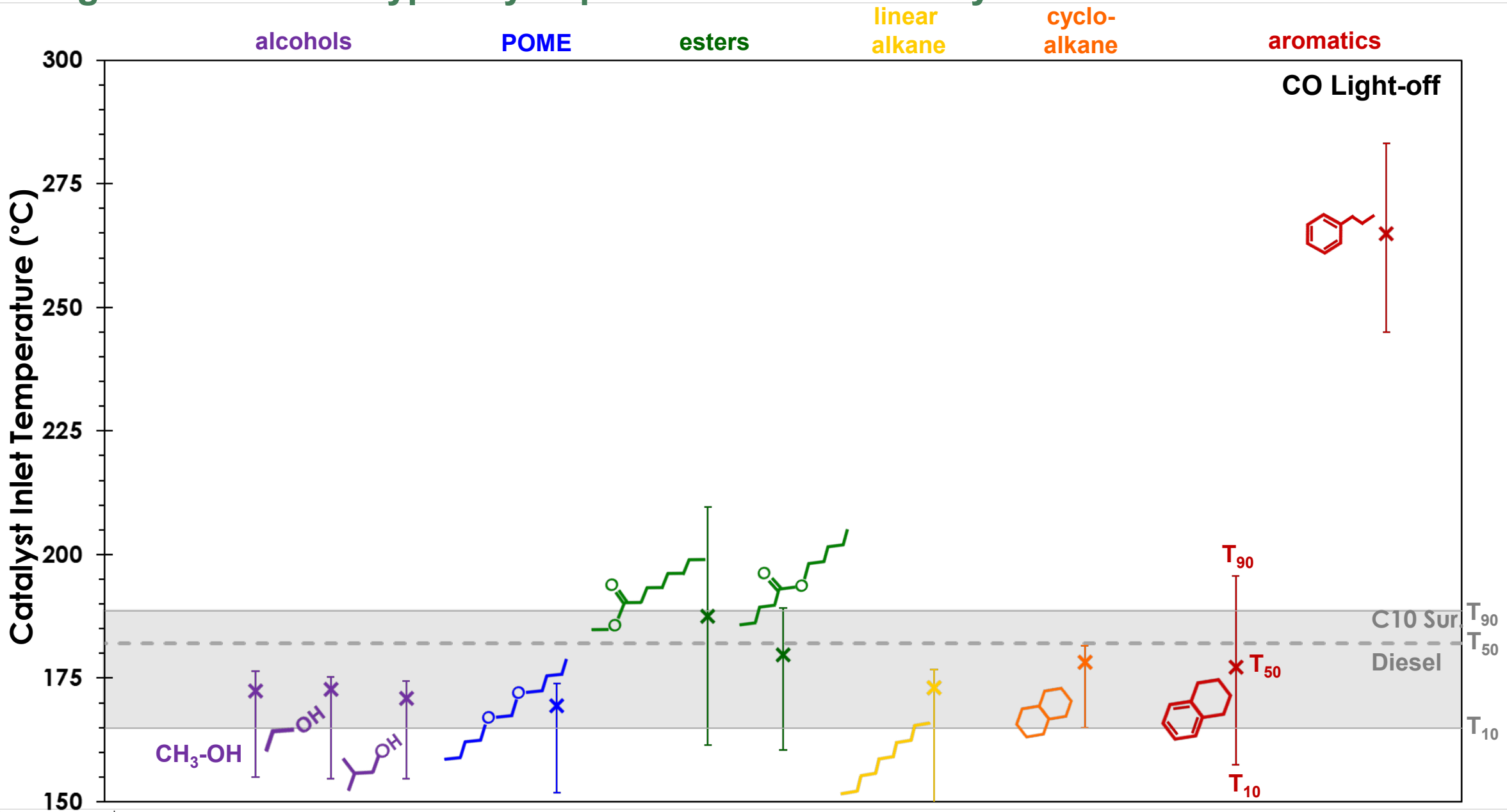


Alcohol LLCFs form aldehydes at low temperatures

- Alcohols start oxidizing on the DOC at lower temperatures compared to C10 diesel surrogate
- Oxidation of methanol, ethanol and isobutanol involves formation of aldehyde intermediates
- Ethanol forms significant levels of acetaldehyde which needs higher temperatures to oxidize completely over the DOC
- Aldehydes shown here are formed over the DOC during alcohol oxidation and does not account for aldehyde formation in the combustion chamber
  - Aldehydes formation can be an issue during idle condition or if the exhaust temperature is low

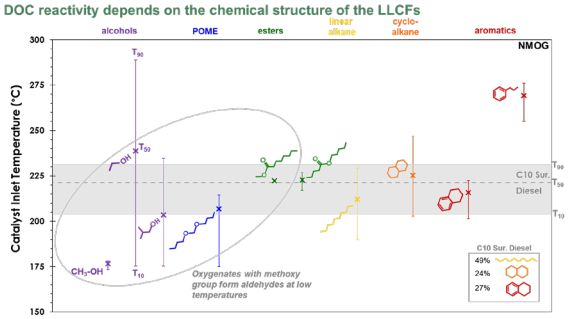


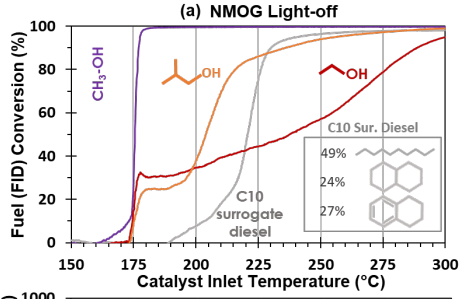
CO light-off does not typically depend on fuel chemistry

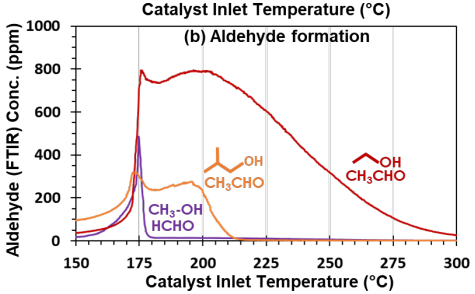


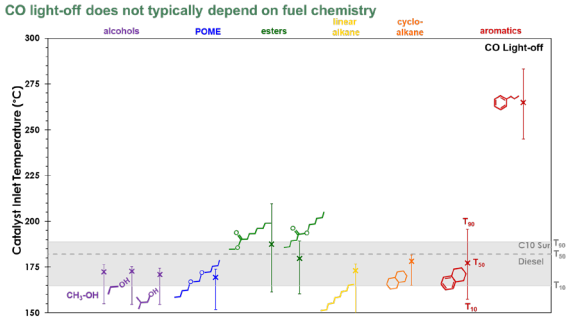
Summary of Technical Findings

- LLCFs could create both challenges and benefits for emissions control
- DOC reactivity depends on the chemical structure of the LLCFs
- Methanol is highly reactive on the DOC
- Ethanol starts oxidizing on the DOC at low temperature but forms significant levels of acetaldehyde
- Oxygenates with methoxy group form aldehydes at low temperatures
- CO light off does not typically depend on fuel chemistry









Collaborations

Caterpillar Inc.	Providing input on emissions challenges and operating conditions
Pacific Northwest National Laboratory	Sharing results and coordination of efforts

Responses to Comments from Reviewers

This is a new project, and it has not been reviewed before.

Remaining Challenges & Barriers/Future Work

Remaining Challenges:	**Future Work:** *(subject to change based on funding)*
• Low temperature oxidation of aldehydes from promising alcohol LLCFs	• Develop aldehyde delivery system • Evaluation of aldehyde reactivity on DOC • Identify and evaluate alternate oxidation catalyst formulations which may be more reactive for low temperature oxidation of aldehydes
• The reactivity of novel LLCFs identified by research partners on the emission control catalysts needs to be evaluated	• Quantify other LLCF effects on oxidation catalyst (DOC) light-off/light-down
• Non-road emissions control challenges identified by CRADA partnerships	• Develop emissions control solutions to overcome challenges identified by CRADA partners

Summary

- **Relevance**
  - LLCFs will play a critical role in achieving decarbonization of hard-to-electrify rail, marine, and off-road sectors
  - We need to identify emissions control opportunities and challenges created by running off-road diesel engines on low life-cycle carbon fuels to ensure emissions compliance
- **Approach**
  - Utilize unique lab capabilities to develop a fundamental understanding of how changes in fuel chemistry impact emissions and emission control devices
- **Technical Accomplishments**
  - Demonstrated that LLCF reactivity on a DOC depends on their chemical structure
  - Alcohols start oxidizing on the DOC at low temperatures, but form aldehyde intermediates
- **Collaborations**
  - Caterpillar Inc.
  - PNNL
- **Future Work** *(subject to change based on funding levels)*
  - Quantify novel LLCF effects on oxidation catalyst (DOC) light-off/light-down
  - Identify and evaluate alternate oxidation catalyst formulation which are more reactive for low temperature oxidation of aldehydes

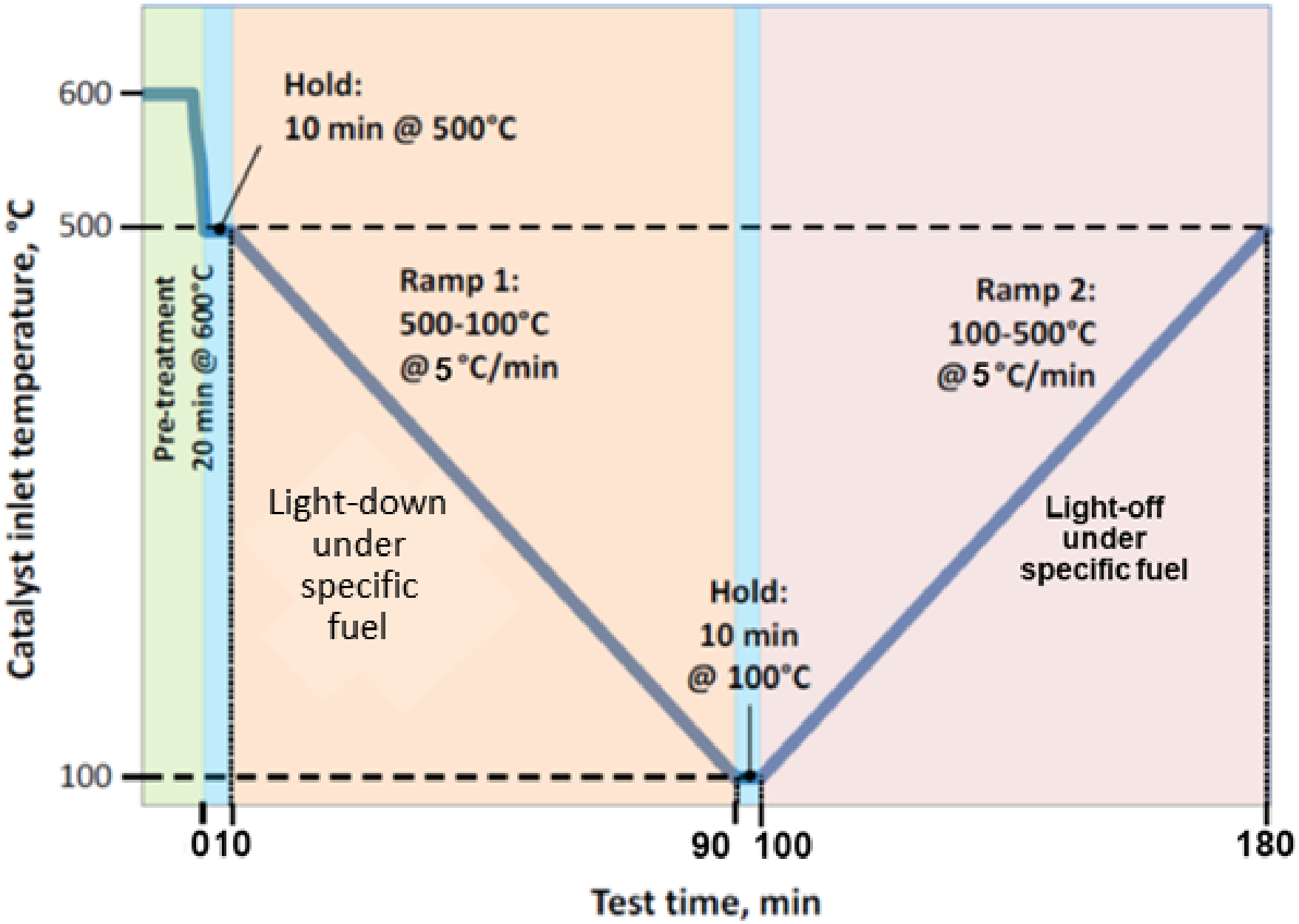
OAK RIDGE National Laboratory | NATIONAL TRANSPORTATION RESEARCH CENTER

Technical Backup Slides

Abbreviations

DOC	Diesel oxidation catalyst
LLCF	Low-lifecycle carbon fuel
NMOG	Non-methane organic gases
POME	Polyoxymethylene ether

Reaction profile used for quantifying LLCF reactivity on DOC



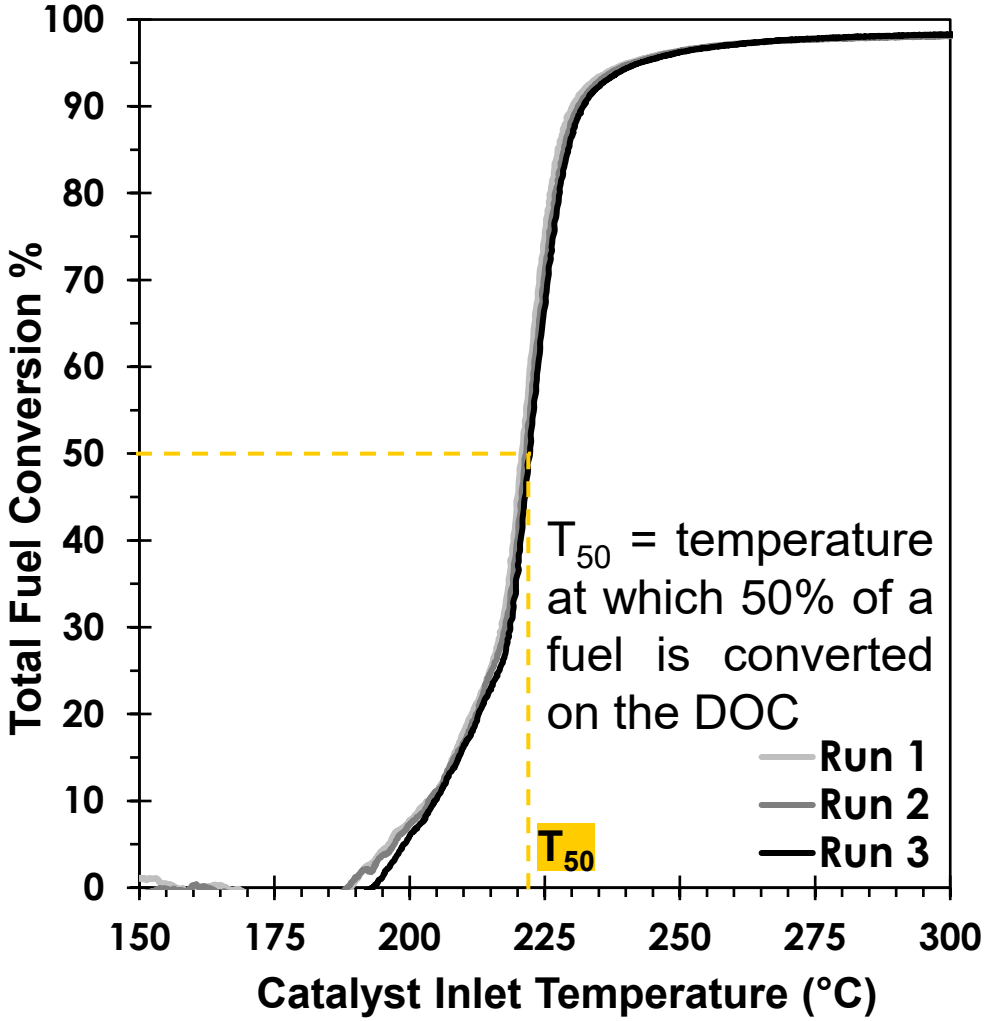
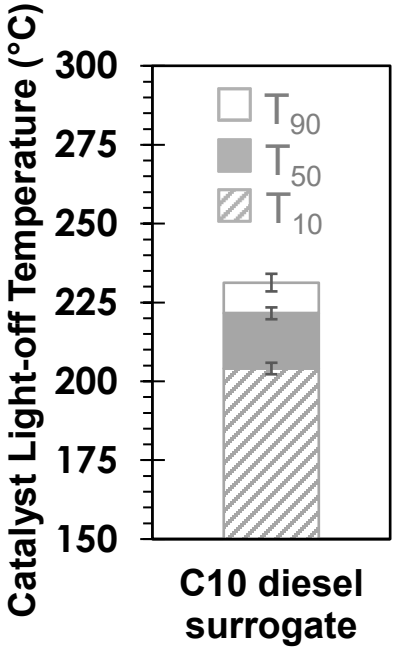
Pretreatment	
CO_2	6%
H_2O	6%
O_2	12%
SV	30000 h^{-1}

Synthetic Exhaust	
CO_2	6%
H_2O	6%
CO	0.2%
H_2	0.04%
NO	0.01%
HC (as C_1)	0.3%
O_2	12%
SV	30000 h^{-1}

Highly reproducible light-off behavior of fuels observed on the DOC

- Light-off experiment for each fuel repeated three times to ensure reproducibility of results
- Consistent results with small error bars achieved for each fuel under consideration

C10 Surrogate Diesel

49%	n-decane
24%	decalin
27%	tetralin

Synthetic Exhaust:	
CO_2	6%
H_2O	6%
CO	0.2%
H_2	0.04%
NO	0.01%
HC (as C_1)	0.3%
O_2	12%
SV	30000 h^{-1}