Co-Optimization of
Fuels & Engines

Co-Optima Emissions and Emissions Control for Spark Ignition and Advanced Compression Ignition Multi-Mode Combustion

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VTO Program Managers: Kevin Stork, Gurpreet Singh, Michael Weismiller

June 3rd, 2020

Project # FT073

Acknowledgements

U.S. DEPARTMENT OF ENERGY

- **Funding and guidance from the Department of Energy Vehicle Technologies Office**
  - *Kevin Stork, Gurpreet Singh, Mike Weismiller*

- **Discussions & guidance from the Co-Optima team:**
  - *Bob McCormick, Dan Gaspar, Jim Szybist, Magnus Sjöberg*

Overview

Timeline

- Project start date: 10/1/2018
- Project end date: 9/30/2021*
- Percent complete: 58%

*Start and end dates refer to three-year life cycle of DOE lab-call projects, Co-Optima is expected to extend past the end of FY20

Budget

	FY19	FY20 (expected)
E.1.3.1 (ORNL)	$250k	$338K
Fuel impacts on emissions control catalyst light-off/light-down. ***Sinha Majumdar***		
E.2.2.7 (ORNL)	$220k	$300K
Fuel Impacts on PM and Gaseous Emissions during MM operation. ***DeBusk***		
E.1.3.2 (PNNL)	--	$250k
PNNL Low Temperature Oxidation of Unburned Fuels. ***Wang***		

Barriers from US DRIVE ACEC Roadmap

- U.S. EPA Tier 3 Bin 30 emissions
- Reduced cold start emissions
- "…greater understanding of how new fuels impact advanced combustion strategies and aftertreatment systems"

Partners/ Collaborations

- Co-Optima partners
  - 9 National Labs, 20+ Universities, 80+ Stakeholder organizations
- Direct communications with OEMs and catalyst suppliers
- CLEERS community (emissions control)
  - OEMS, Universities, and National Labs

Co-Optima Overarching Relevance

Delivering Foundational Science

- The U.S. DOE Co-Optima initiative is **delivering foundational science** to develop fuel and engine technologies that will work in tandem to achieve efficiency, environmental and economic goals

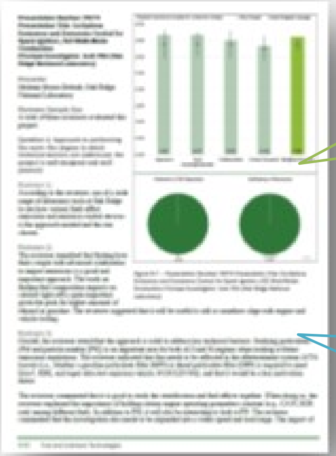
General Relevance

- Internal combustion engines and the use of liquid fuels projected to dominate transportation for many years
- Significant opportunities exist to further improve engine efficiency and corresponding vehicle fuel economy
- Research into better integration of fuels and engines is critical to accelerating progress towards achieving efficiency, environmental and economic goals
- Research addresses engine fuel barriers and opportunities for light-duty boosted SI, medium-duty and heavy-duty MCCI, and ACI combustion approaches

LD = light duty; MD = medium duty; HD = heavy duty; SI = spark ignition; ACI = advanced compression ignition; MCCI = Mixing-controlled compression ignition

Relevance of Emissions Control tasks to overall Co-Optima program

2019 Merit Review



Reviewer 1: "…this is a critical area that not only helps guide the catalyst development at OEMs and suppliers, but also provides insight and influences engine operating strategy. It supports the DOE objectives very well."

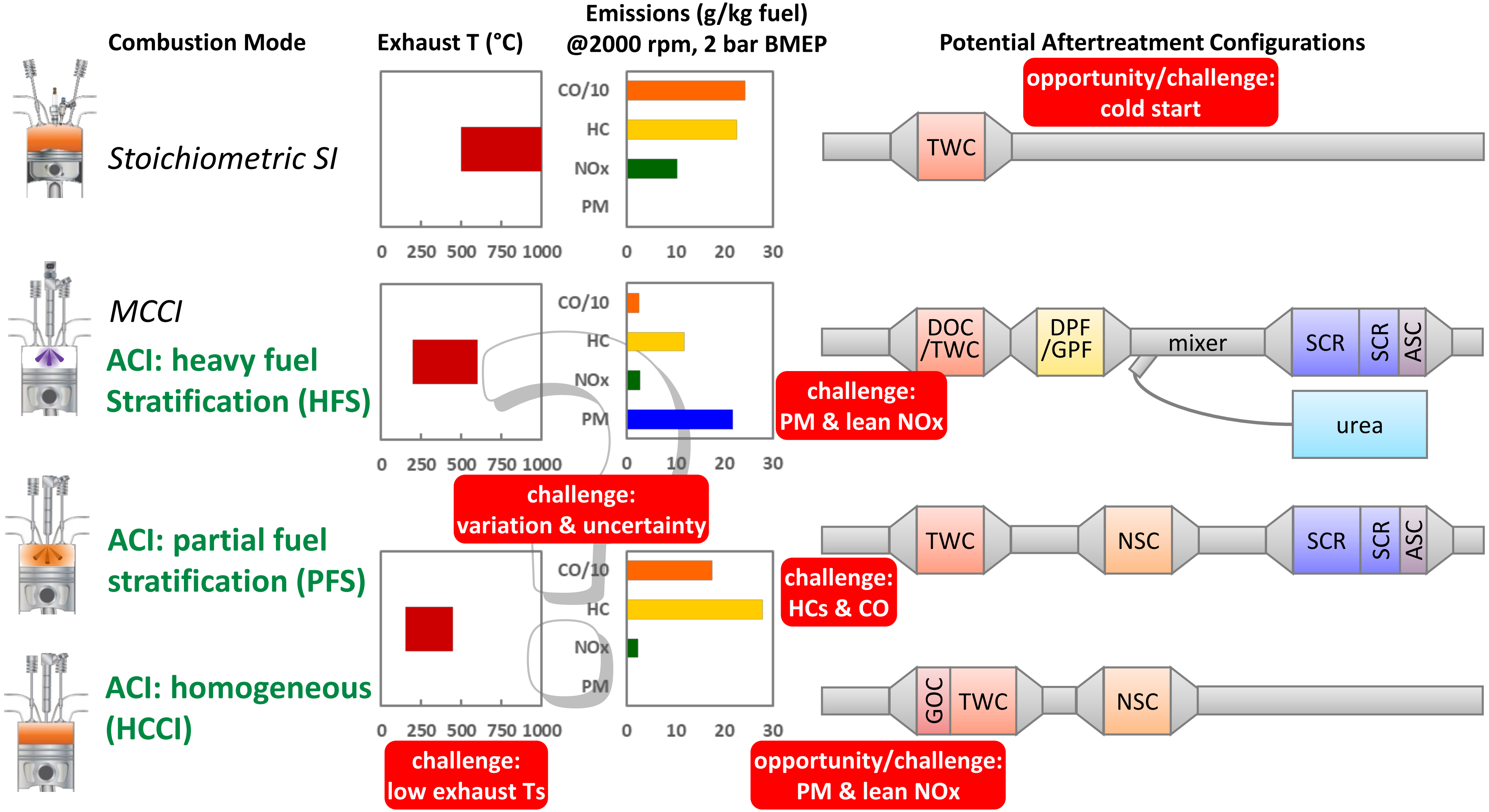
Reviewer 3: "…A coupled study of fuels and emissions is quite important to the overall DOE goal of improving fuel efficiency and meeting strict tailpipe criteria pollutant targets.."

- Advanced engines running on high performance fuels must still meet emissions regulations
- Advanced Compression Ignition (ACI) presents a new set of emission challenges that are as yet not completely understood
- Changes in fuel chemistry and combustion strategy impact engine emissions (NOx, CO, PM formation, THC and NMOG speciation)
  - Introducing new challenges & opportunities in emissions and emissions control

We need to understand how fuel chemistry impacts exhaust composition and performance of emission control devices to predict the effects of Co-Optima blendstocks on regulated emissions

NOx = oxides of nitrogen; PM = particulate matter; THC = total hydrocarbons; NMOG = non-methane organic gases

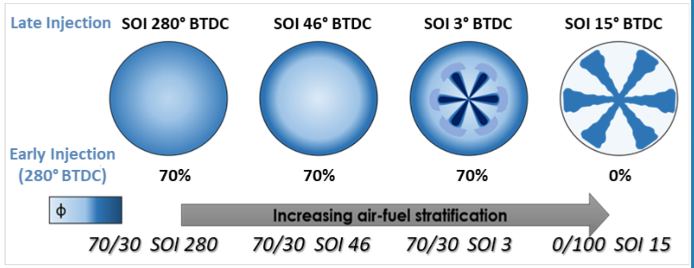
SI/ACI and ACI engine aftertreatment configurations will be more complex than SI only

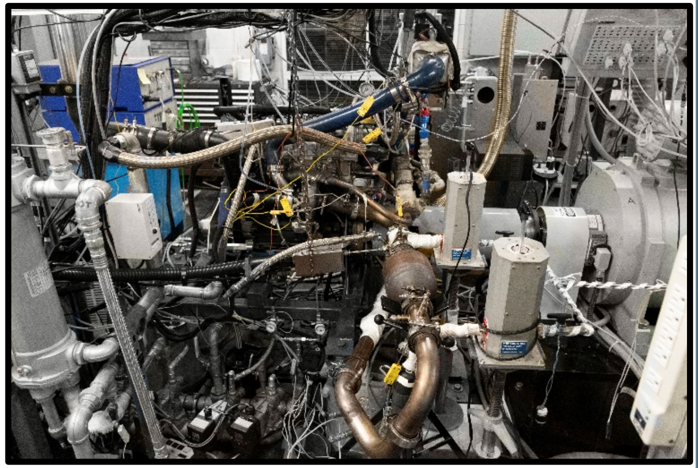


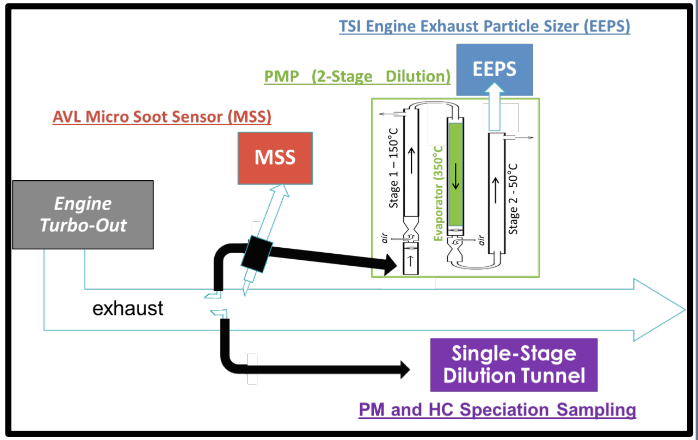
TWC= 3-way catalyst; DOC/GOC = oxidation catalyst; DPF/GPF = particulate filter; SCR = selective catalytic reduction; ASC = ammonia slip catalyst; NSC = NOx storage catalyst

Milestones

Task	Lab	Timing	Description of Milestone or Go/No-Go Decision	Status
E.1.3.1	ORNL	FY19 Q4	Measure TWC light-off of five or more Co-Optima blendstocks under lean conditions to evaluate behavior under ACI operation for SI/ACI multimode engines	Complete
E.1.3.1	ORNL	FY20 Q1	Submit a manuscript on three-way catalyst light-off measurements with surrogate fuel blends containing promising Co-Optima blendstocks	Complete
E.1.3.2	PNNL	FY20 Q1	Evaluate oxidation and adsorption characteristics of pure components of the BOB	Complete
E.1.3.2	PNNL	FY20 Q2	Investigate impact of unburned fuel functionality on HC oxidation	On Track
E.1.3.1	ORNL	FY20 Q4	Complete flow reactor measurements of light-down temperatures for fuel blends containing 3 Co-Optima blendstocks at 3 blend levels over a TWC under ACI conditions.	On track
E.1.3.5	ORNL	FY20 Q4	Complete a PM and gaseous emission sampling study on the GM multimode Engine	On Track







Melanie Moses-DeBusk, John Storey, Sam Lewis, R. Maggie Connatser, Scott Curran and Flavio Dal Forno Chuahy (ORNL)

Relevance:

- Advanced engines & fuels must meet emissions standards
- Ideal fuel and specific ACI combustion modes undefined for SI/ACI MM
- To develop an effective MM emissions control solution, a more complete understanding of ACI emissions over a range of fuel properties and ACI modes is needed
  - History has shown that emissions are sensitive to changes in fuel properties and to combustion mode

Objectives:

- Understand impact of chemical and physical fuel properties on emissions
  - aromatic content (chemical) and distillation range (physical)
- How changes to ACI mode influence the fuel property impacts on emissions
  - Specific impacts of fuel injection strategy/timing
- How are the emissions impacts influenced by engine hardware (FY20)

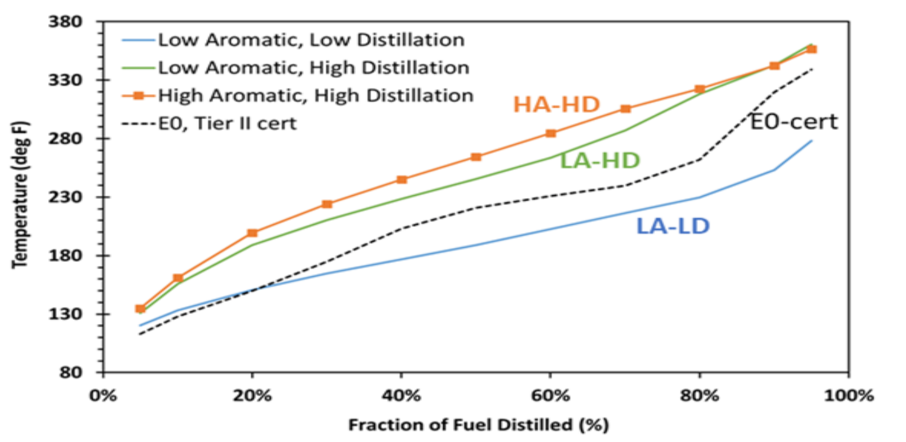
ACI: advanced compression ignition; PM: particulate matter; SI: spark ignited; MM: multimode SI/ACI

Studied impact of fuel aromatic content and distillation range over series of ACI modes

Relevance | Approach | Technical | Collaboration | Future Work

3 Fuels Studied (FY19)

	LA-LD	LA-HD	HA-HD
RON	89.7	90	89.6
MON	85.1	85.4	83.5
sensitivity	4.6	4.6	6.1
Aromatic	6.9%	8.10%	26.3%
Olefin	6.0%	5.2%	5.9%
Saturate	87.1%	86.7%	67.8%
T50 (F)	189.2 F	245.7 F	264.5 F
T90 (F)	253.3 F	342.8 F	342.4 F
RVP @100F	8.5 psi	7.6 Psi	7.1 psi



Hardware: modified 1.9L GM light-duty, diesel engine (multi-cylinder)
Speed/Load: 2000rpm 4-5 bar
CA50: 8° ATDC

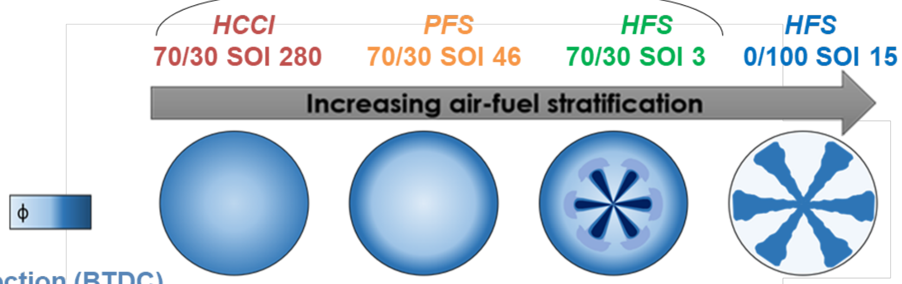
- Isolated fuel property impact by limiting changes in fuel sensitivity and RON while varying aromatic content and distillation range of the fuel

Physical Property

Chemical Property	Low Distillation	High Distillation
Low Aromatic	LA-LD	LA-HD
High Aromatic		HA-HD

Property changes relative to Tier II – E0 certification fuel

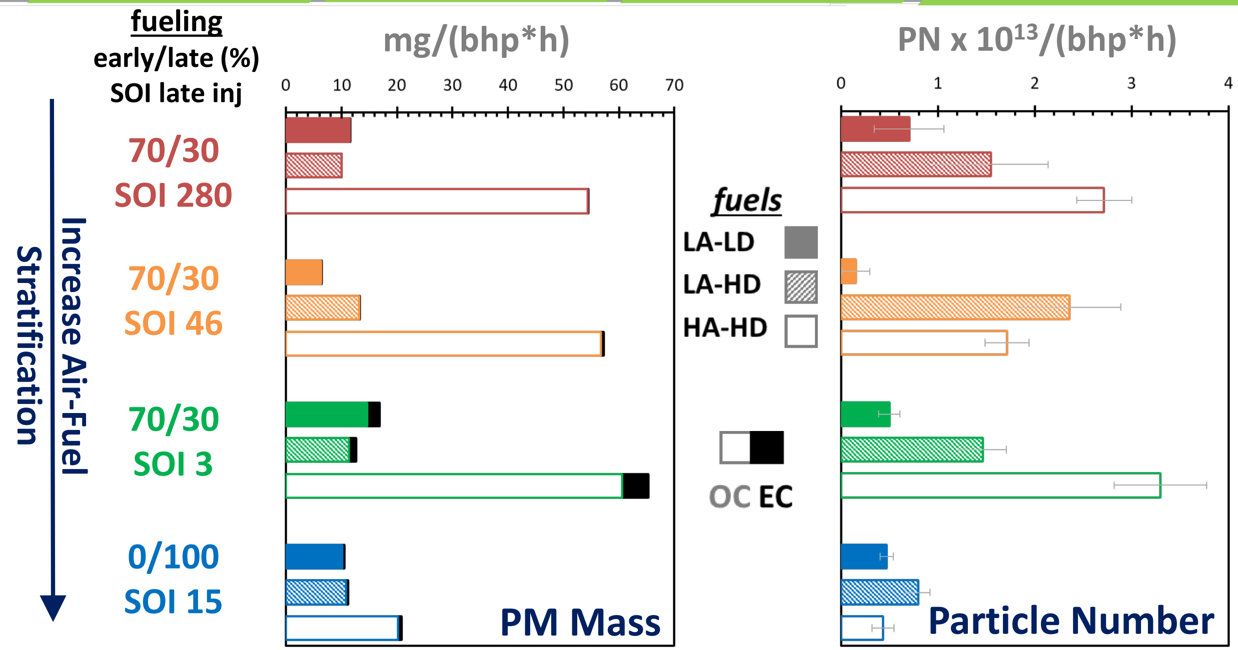
- Evaluated each fuel at 4 different ACI modes (constant CA50)



Fuel Injection (BTDC)				
Early Injection	SOI 280°	SOI 280°	SOI 280°	n/a
fuel fraction	*70%*	*70%*	*70%*	*0%*
Late Injection	**SOI 280°**	**SOI 46°**	**SOI 3°**	**SOI 15°**

HCCI: homogeneous charge compression ignition; PFS: partial fuel stratification; HFS: high fuel stratification

Fuel chemical property impacts PM mass; ACI mode impacts PN and size

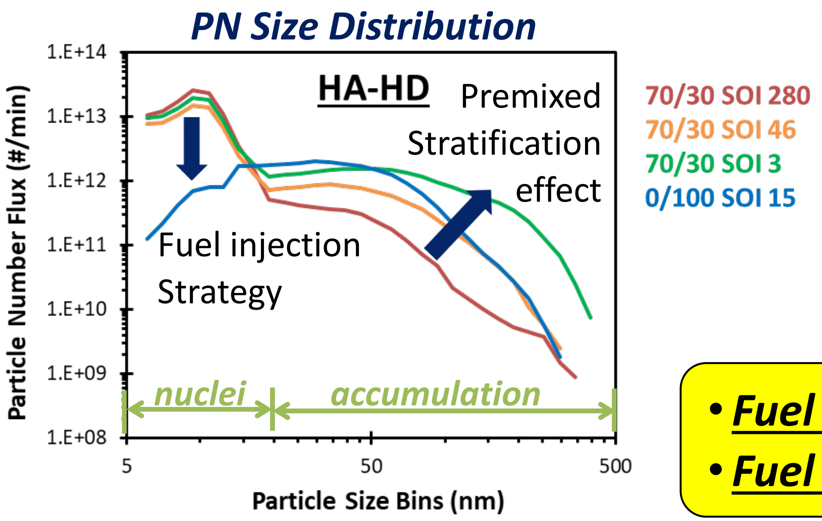


Impacts on PM Mass Emissions

- **High aromatic** (LA-HD vs. HA-HD) ↑ **PM mass**
  - more significant at the partially premixed modes
  - PM mass from ACI mode was almost all OC
  - fuel aromatics known to increase EC PM in SI and CDC

Impacts on Particle Number (PN)

- **High distillation (HD)** range (LA-LD vs. LA-HD) ↑ **PN**
  - regardless of stratification or premixing
- **HD + no premixing** (LA-HD & HA-HD) Significant ↓ **PN**

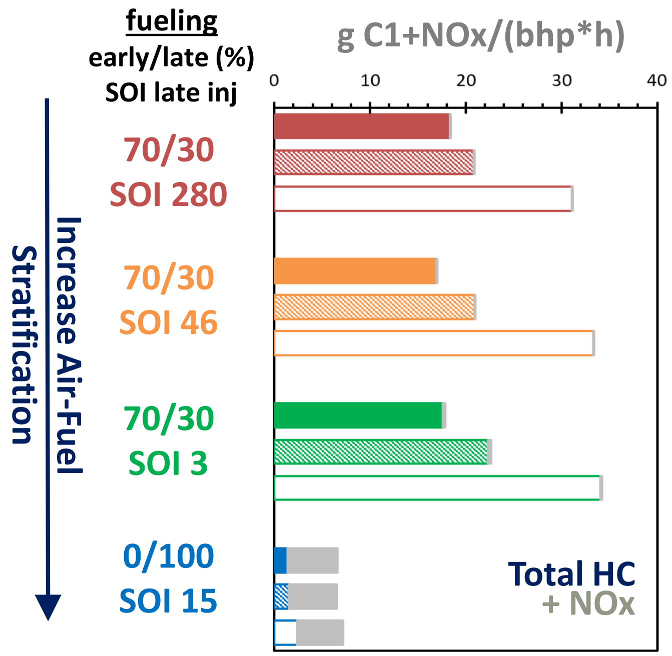


PM Mass correlation to Particle Number (PN) size range

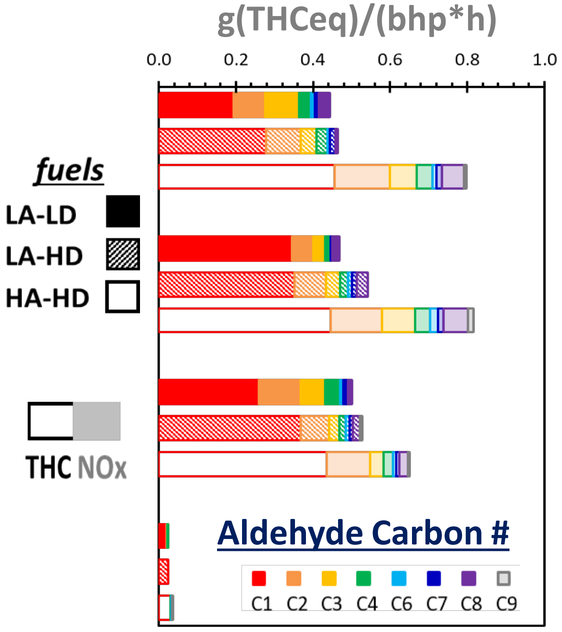
- **HA-HD +** no premixing **(0/100 SOI 15)**:
  - ↓ **PM** mass and ↓ **PN** correlates to a ↓ nuclei mode particles
- **HA-HD ↑ stratification + partial premixing** (70/30) ↑**large particles**
  - **HA-HD** + **70/30 SOI 3** had greatest ↑ **PM mass and ↑ PN**
    - correlates to high nuclei mode and increase in large particles

- ***<u>Fuel chemical properties have a significant impact on PM mass</u>***
- ***<u>Fuel mixing and stratification impact size and number of PM particles</u>***

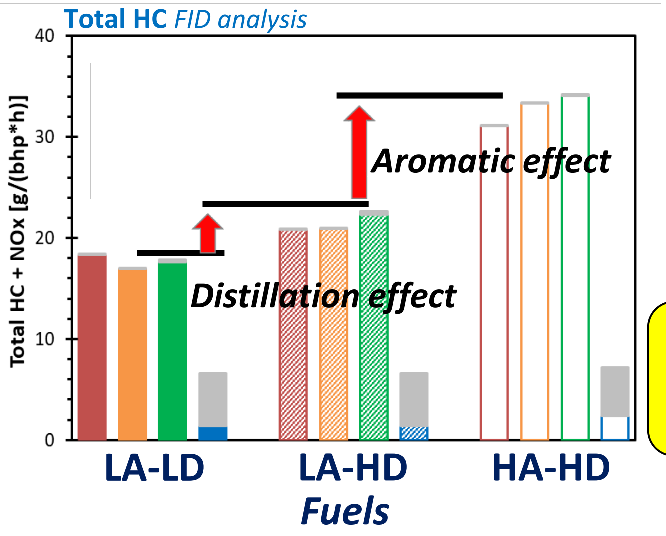
Fuel chemical property impacted gaseous HC emission more than physical; ACI partial fuel premixing required to drop NOx



Total HC *FID analysis*



Aldehydes DNPH *analysis*



Impacts on Gaseous HC Mass Emissions

- **↑ OC PM mass = ↑ gaseous HC**
- **High Aromatic** (HA) fuel **↑ HC** mass (~5000-6000ppm)
  - More significant than ↑ HC mass from high distillation (HD)
- Stratification of partially premixed modes had little impact
- **No premixing**, regardless of fuel, **↓ HC** mass

Impacts on NOx Mass Emissions

- **↑ NOx** only impacted by **no premixing**
  - **0/100 SOI 15**: NOx = ~500-600ppm
- **NOx/HC trade-off**: NOx control difficult at ACI
  - Low temperature exhaust of ACI increases complexity of MM aftertreatment solution

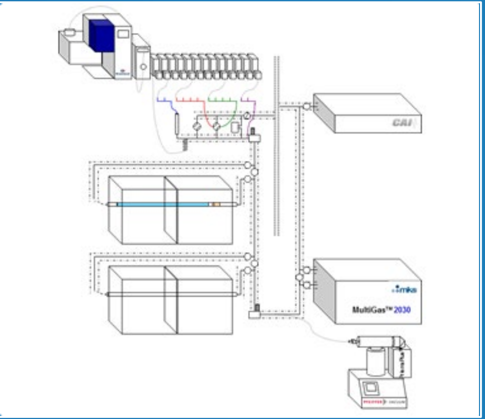
Impacts on Aldehyde Mass Emissions

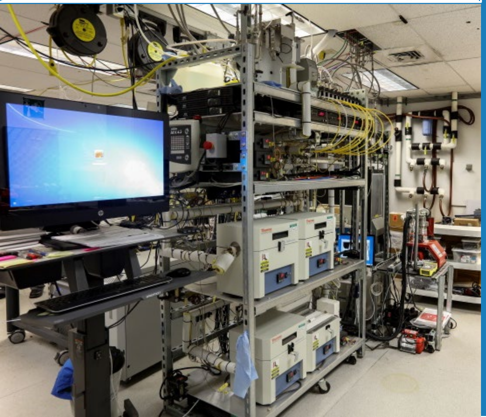
- Aldehydes follow same trend as HC emissions
- **Partial Premixing ↑** contribution of **larger aldehydes** (C3-C9)
  - including aromatic aldehydes (C7-C9)

- ***<u>Partially premixed ACI modes required to drop NOx</u>*** *but increase HC emissions.*
- ***<u>HC emission impacted more by fuel chemical properties</u>*** *than the physical properties*

DNPH: 2,4-Dintrophenylhyrdazine; NOx: nitric oxides

E.1.3.1: Fuel Impacts on Emissions Control Performance & Durability





Sreshtha Sinha Majumdar and Josh Pihl (ORNL)

Relevance:

- Co-Optimized engines + fuels still must meet emissions regulations
- Changes in fuel chemistry may affect catalyst performance, potentially impacting emissions control system compliance, fuel penalty, or cost

Objectives:

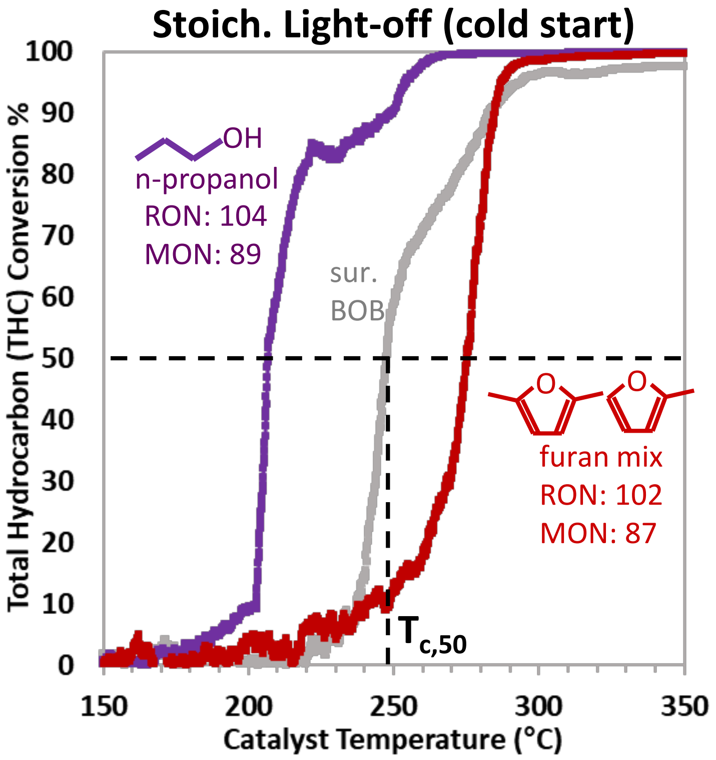
- Identify challenges & opportunities from new fuels
  - catalyst light-off performance during cold start
  - catalyst light-down performance during lean operation

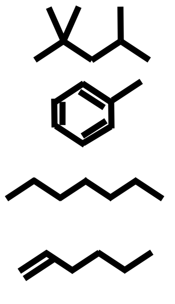
Approach:

- Use synthetic exhaust flow reactors to measure the impacts of fuel chemistry changes on commercially relevant catalyst materials
- Measure three-way catalyst (TWC) reactivity under both stoichiometric (SI) and lean (ACI) exhaust conditions for LD SI/ACI multimode

Measured TWC light-off temperatures on a synthetic exhaust flow reactor to capture changes in cold start catalytic activity

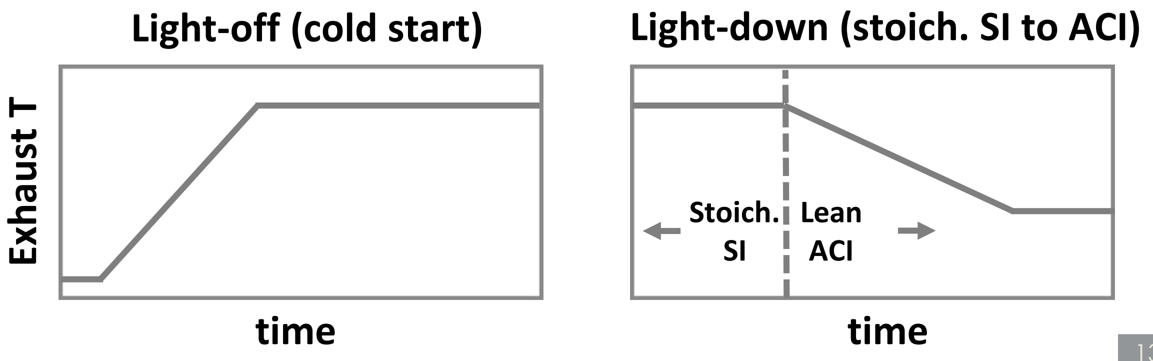
- LD multimode SI/ACI engines will still rely on TWCs for stoichiometric SI operation (high loads, cold start)
- Fuel chemistry impacts the temperatures at which TWCs are effective at controlling emissions
- Prior work measured fuel chemistry effects on TWC reactivity under increasing temperatures and stoichiometric exhaust ("light-off" conditions)
- Current efforts measuring fuel chemistry effects on TWC reactivity under decreasing temperatures and lean exhaust ("light-down" conditions)
  - Occurs during switch from SI to ACI operation
- Synthetic exhaust flow reactor experiments provide a means to measure light-off for a wide range of fuels
  - aged commercial TWC core sample
  - protocols developed by industry**
- TWC reactivity does not correlate with gaseous fuel reactivity (RON, MON)





Synthetic exhaust:

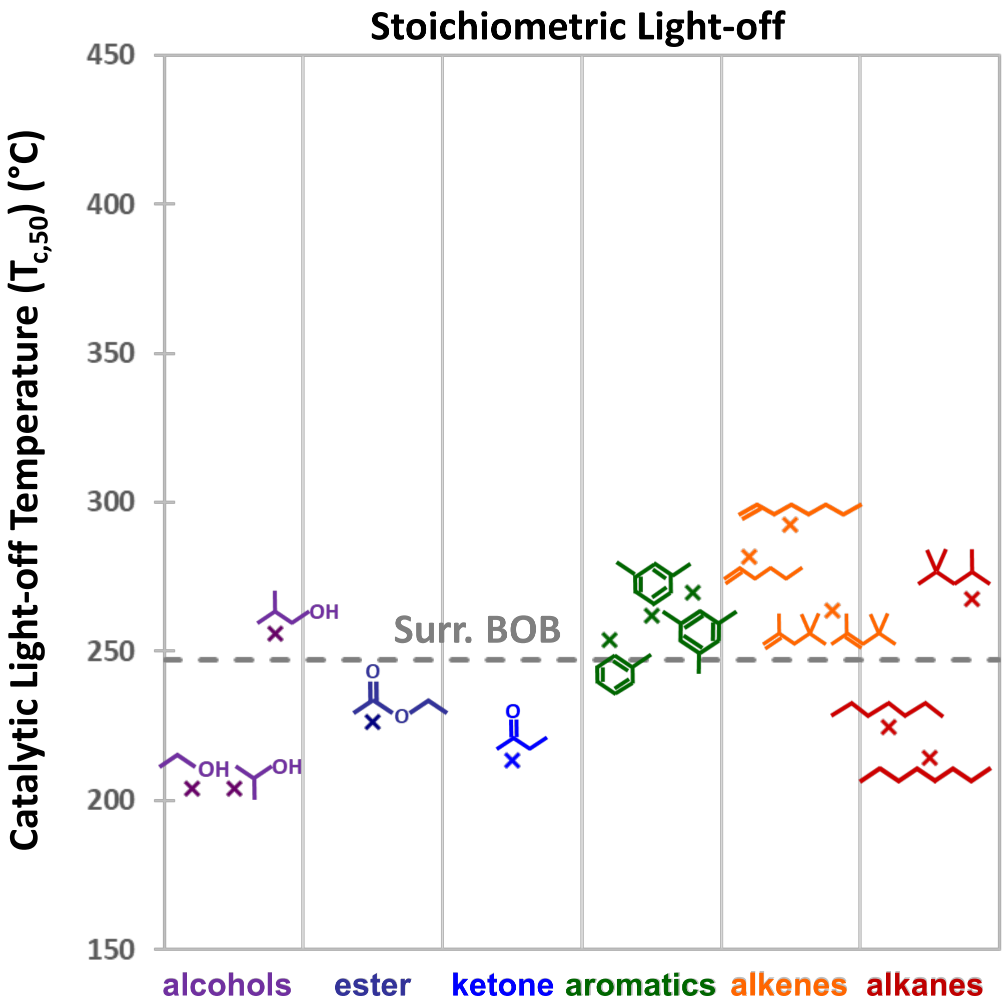
CO_2	13%
H_2O	13%
CO	0.5%
H_2	0.17%
NO	0.1%
HC (as C_1)	0.3%

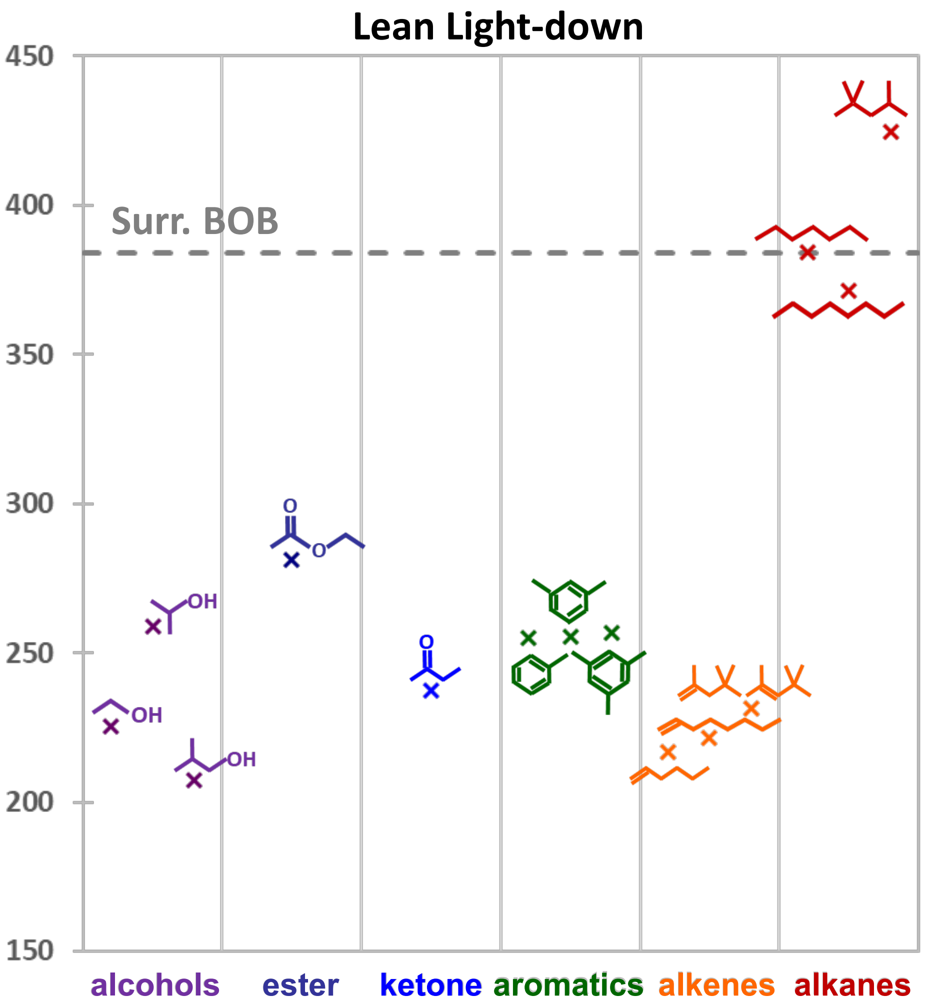


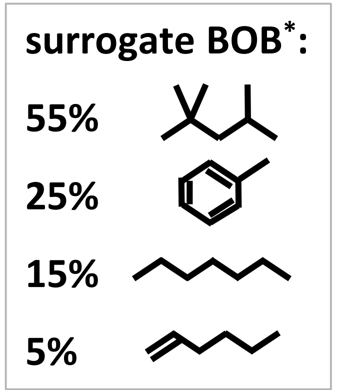
** U.S.DRIVE Low Temperature Oxidation Catalyst Test Protocol

* chemical names in back-up slides

Catalytic reactivity changes significantly between stoichiometric and lean exhaust conditions







Synthetic Exhaust

Reactants	Stoic.	Lean
CO_2	13%	6%
H_2O	13%	6%
CO	0.5%	0.2%
H_2	0.17%	0.07%
NO	0.1%	0.01%
HC (as C_1)	0.3%	0.3%

HC emissions control will be more challenging under ACI operating strategies with traditional petroleum-based fuel blends; will addition of Co-Optima blendstocks improve catalyst performance?

* chemical names in back-up slides

E.1.3.2-PNNL Low Temperature Oxidation of Unburned Fuels

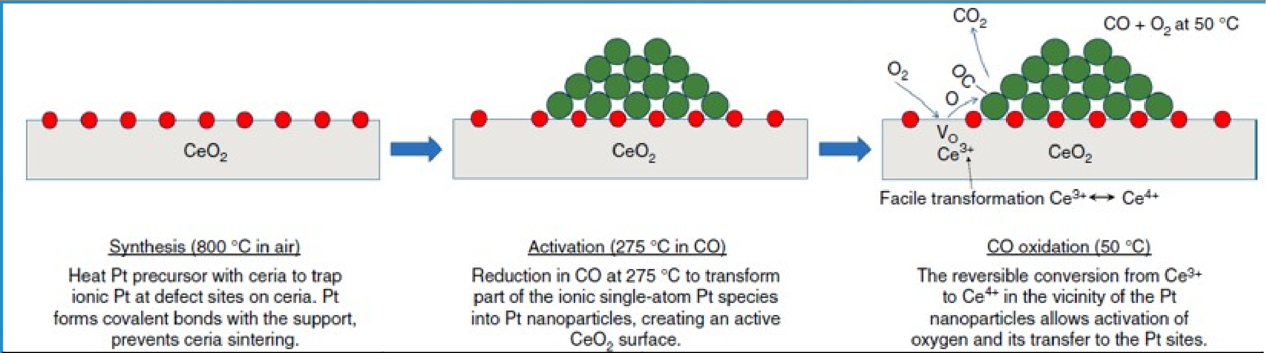
Yong Wang and Fan Lin (PNNL)

Relevance:

- Co-Optimized fuels and engines must still meet emissions regulations
- New fuels bring new challenges and opportunities for emission control

Objectives:

- Evaluate advanced catalysts in the context of fuels relevant to Co-Optima high-performance fuel blendstocks



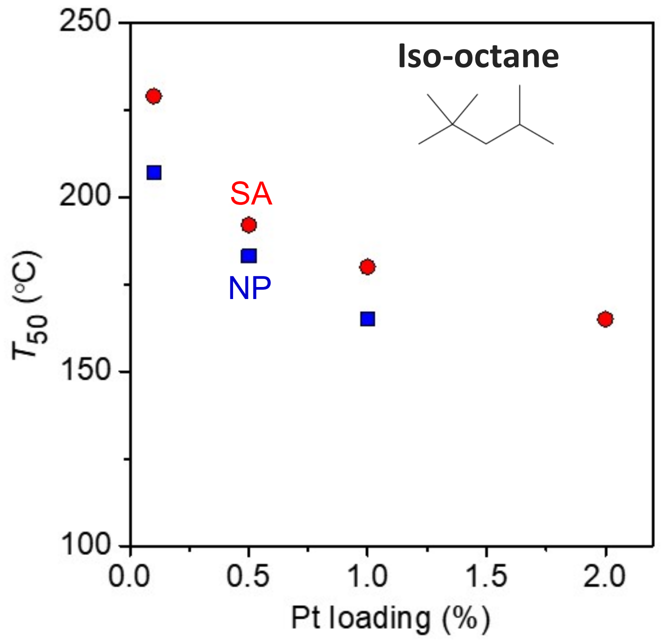
0.5% Pt/CeO_2	Heat treatment	After calcination, all catalysts were reduced by 10% CO at 150ºC
Nanoparticles (NP)	500 ºC, 4 h	
Single atoms (SA)	800 ºC, 12 h	

Pereira-Hernández et al., *Nature Commun.* **2019,** *10*, 1358.

Approach:

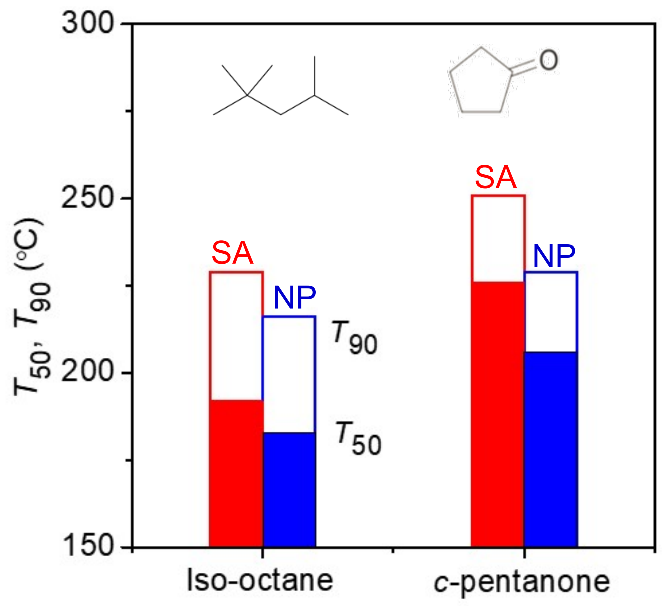
- Use micro-reactors to measure the impacts of fuel chemistry changes on advanced catalytic materials*

*Developed under other DOE funded projects



Reaction Conditions

0.75% O_2
3000 ppm C_1
200 L h^{-1} g_{cat}^{-1}



Increasing Pt loading on Pt/CeO$_2$ lowers the iso-octane T_{50} for both nanoparticle (NP) and single (SA) catalysts.

The T_{50} and T_{90} of iso-octane and cyclopentanone (c-pentanone) on 0.5%Pt/CeO$_2$ NP are lower than the SA catalyst.

Single-atom Pt/CeO$_2$ does not show advantages over nanoparticle Pt/CeO$_2$.

Collaboration and Coordination with Other Institutions

Collaborative approach:

- Catalyst experiments use protocols developed by the U.S.DRIVE ACEC Tech Team Low Temperature Aftertreatment Working Group
- Catalyst experiments use a surrogate BOB developed by the Co-Optima Fuel Properties team to screen blendstocks
- Fuel blendstock choices are based on Co-Optima High Performance Fuel team recommendations

Dissemination of results:

- Results shared with larger Co-Optima team through presentations to Stakeholder teleconferences and All-Hands meetings
- Emissions and catalysis results are shared with the aftertreatment community though the CLEERS organization, which includes dozens of OEMs and suppliers
- Catalyst light-off results have been presented directly to U.S. OEMs and catalyst suppliers

USDRIVE DRIVING RESEARCH AND INNOVATION FOR VEHICLE EFFICIENCY AND ENERGY SUSTAINABILITY

Co-Optimization of Fuels & Engines

CLEERS Cross-Cut Lean Exhaust Emissions Reduction Simulations

Remaining Challenges	Future Work* *(subject to change with funding levels)*

• ACI operation creates new emissions challenges (relative to boosted SI):
  • low exhaust temperatures
  • high HC emissions
  • lean NOx
  • potential for increased PM and increased OC content in PM
• Potential mitigating or exacerbating effects of fuel chemistry on those challenges is not well understood
• Emission trends across different ACI engine hardware has not been thoroughly investigated
• Fuel chemistry effects on the reactivity of advanced catalyst formulations have not been studied
	Emissions:
	• Conduct FY20 experiments on a GM engine designed for SI/ACI multimode, but keep same gasoline-range fuels from FY19 investigation
	• Measure fuel property impacts on ACI emission in a MD/HD engine using diesel range fuels
	Catalysts:
	• Quantify Co-Optima blendstock effects on oxidation catalyst (DOC) light-off and light-down performance under MD/HD ACI conditions
	• Identify potential emissions control architectures for LD SI/ACI multimode engines
	• Investigate bimetallic-catalyst systems under exhaust relevant conditions

**Any proposed future work is subject to change based on funding levels*

Responses to FY 19 Reviewers' Comments

Reviewer Comments	Response
• "…good to study the stratification and fuel effects together. When doing so, the reviewer explained the importance of holding certain engine operating parameters constant (e.g., CA50..."	• The CA50 was held constant among the different fuels for which gaseous emissions and PM were investigated (FY19)
• "In addition to PM, it will also be interesting to look at PN."	• The impact of fuel property, fuel injection strategy and air-fuel stratification on PM and PN (FY19) have been included in FY20 AMR slides
• "…generating a clear list of speciation, especially under cold start, will be useful to guide HC trap development."	• Prior work looked at HC speciation under SI cold-start conditions (FY17), and there is ongoing work within the VTO emissions control portfolio on cold start emissions speciation (ACE153)
• "…catalyst light-off in the ACI mode is another key area that needs to be investigated"	• FY20 efforts have focused on catalytic reactivity under ACI operating conditions

Summary

Relevance:

- We need to understand how fuel chemical and physical properties, as well as different modes of ACI operation, impact exhaust composition and performance of emission control devices to predict the effects of ACI combustion and Co-Optima blendstocks on emissions compliance

Approach:

- Utilize unique lab capabilities to develop a fundamental understanding of how changes in fuel chemistry impact emissions and emission control devices

Accomplishments:

- Quantified changes in exhaust composition (particulate matter, hydrocarbon speciation) resulting from the effects of variations in air-fuel stratification of different ACI modes and further contributions caused by a change in fuel properties and fuel injection strategy
- Demonstrated that reactivity trends under stoichiometric light-off vs. lean light-down varied significantly with the chemical structure of the Co-Optima blendstocks, thus meriting further investigation of catalyst reactivity of fuel blends under lean conditions relevant to ACI
- Evaluated the efficacy of Pt/CeO_2 nanoparticle and single atom catalysts and established that the former is more active for oxidation of selected hydrocarbons/oxygenated fuels

Collaborations:

- CLEERS, Advanced Combustion and Emissions Control Tech Team members, 9 national labs, 20+ universities, 80+ stakeholder organizations

Future Work* (subject to change based on funding levels):

- Evaluate how fuel chemistry composition and physical properties, like aromatic content and distillation curve, change PM and gaseous emissions at different ACI modes with relevant multimode fuels
- Evaluate impact of Co-Optima blendstocks on performance of a DOC under lean exhaust environments relevant to MD/HD ACI conditions
- Evaluate the efficiency of bi-metallic catalyst systems under exhaust-relevant conditions for low temperature oxidation of unburned fuels

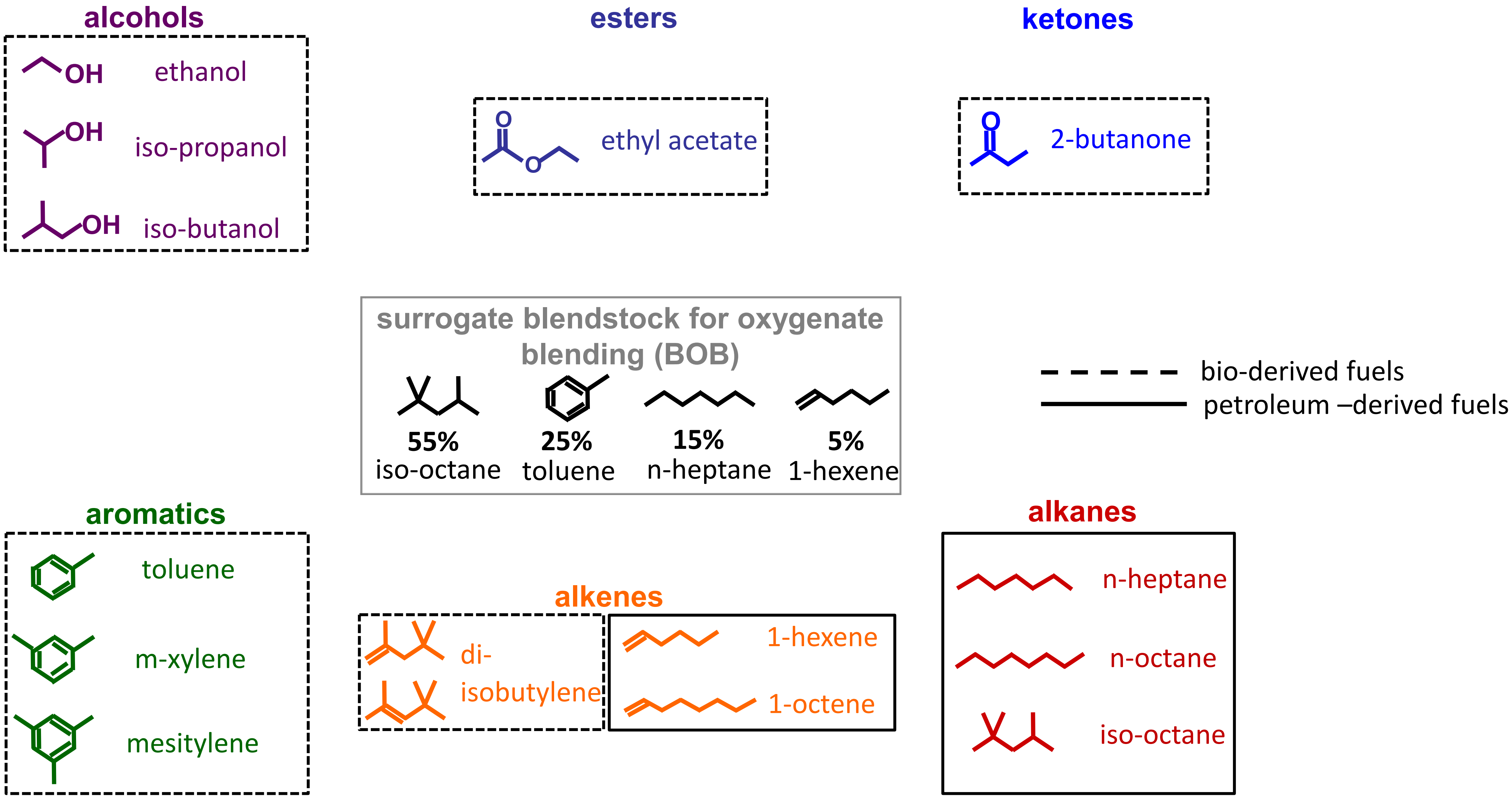
**Any proposed future work is subject to change based on funding levels*

Technical Back-Up Slides

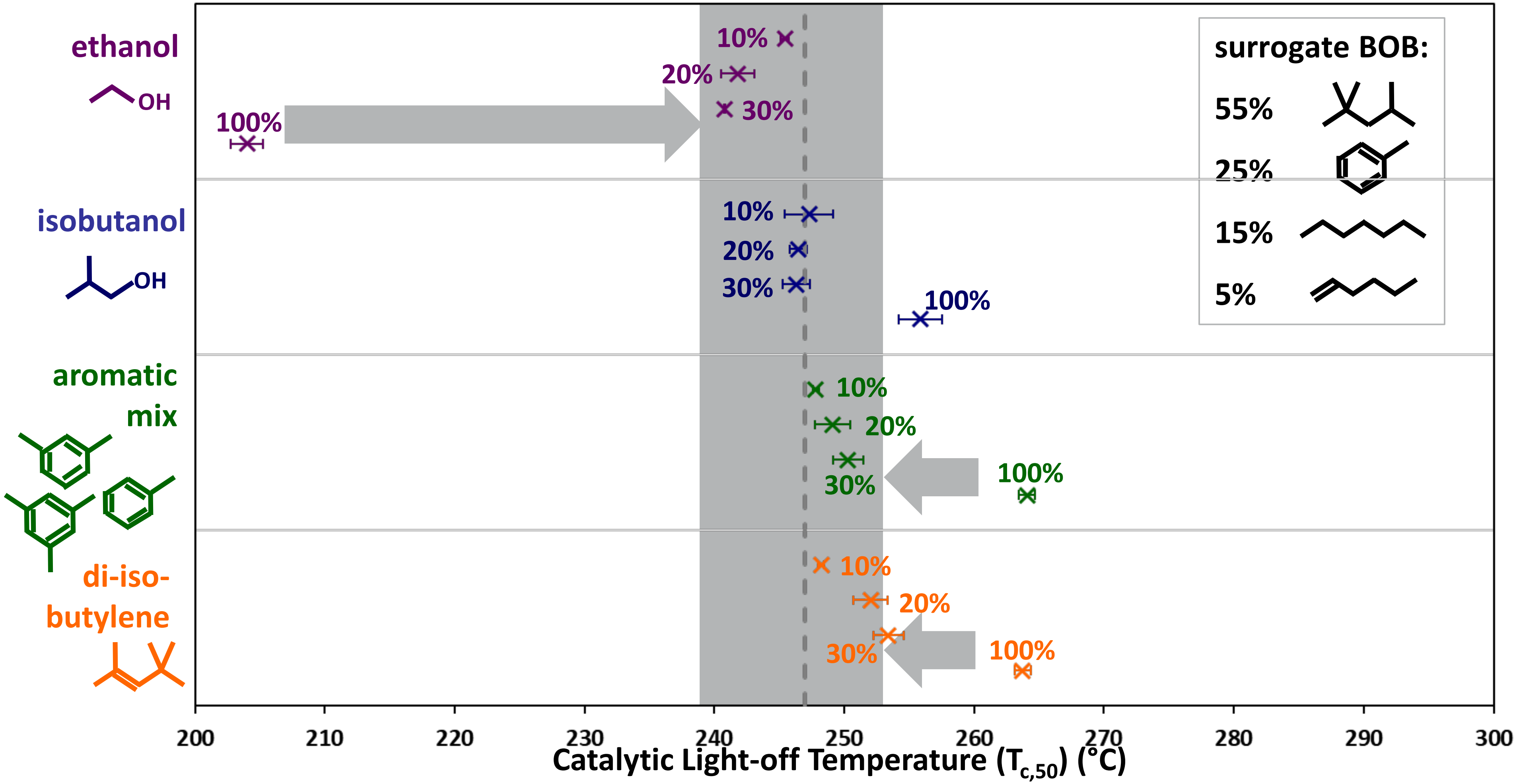
E 2.2.7. Engine operating conditions

	Increasing Air Fuel Stratification →			
Mode	70/30 SOI 280	70/30 SOI 46	70/30 SOI 3	0/3100 SOI 15
Engine Speed [rpm]	2000			
Fuel Energy [J/cyc]	2750			
Coolant Temperature [°C]	90			
Oil Temperature [°C]	90			
Rail Pressure [bar]	500			
Global ϕ [-]	0.38 ± 0.02			
Desired CA50 [°ATDC]	8 ± 1			
Background ϕ [-]	0.38	0.27	0.27	0
Start of 1st Injection [°BTDC]	280	280	280	N/A
Start of 2nd Injection [°BTDC]	N/A	46	3	15
Mass in 1st Injection [%]	100	70	70	0

E.1.3.1: Fuel Components used in the investigations include a wide range of functional groups

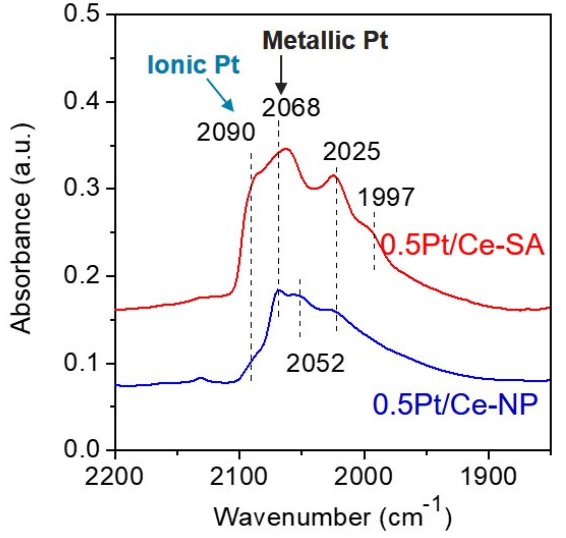


E.1.3.1: Blends containing up to 30% of Co-Optima blendstocks in a typical BOB will likely neither harm nor help control of gaseous emissions from boosted SI engines (FY19)

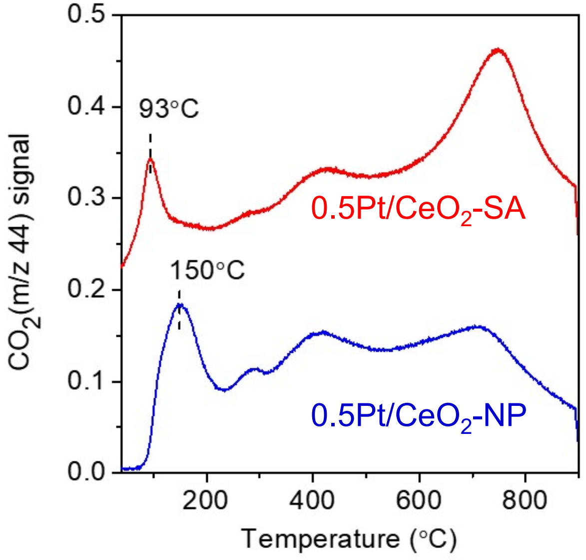


- Blend experiments show that aromatic species inhibit catalytic light-off of more reactive fuel constituents (FY19)
- Taking advantage of fuel constituents with higher catalytic reactivities to improve catalyst light-off will require reducing the aromatic content of the fuel

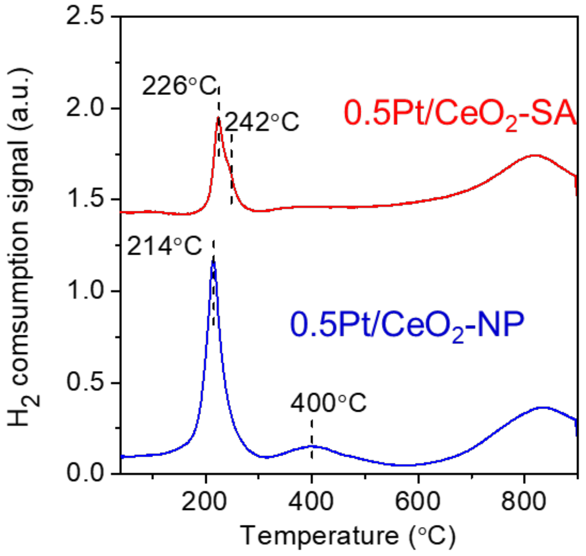
E.1.3.2- Characterization of single atom (SA) and nanoparticle (NP) Pt/CeO_2 catalysts



DRIFTS spectra of CO adsorption on CO-reduced SA and NP 0.5Pt/CeO_2 catalysts (100ºC).



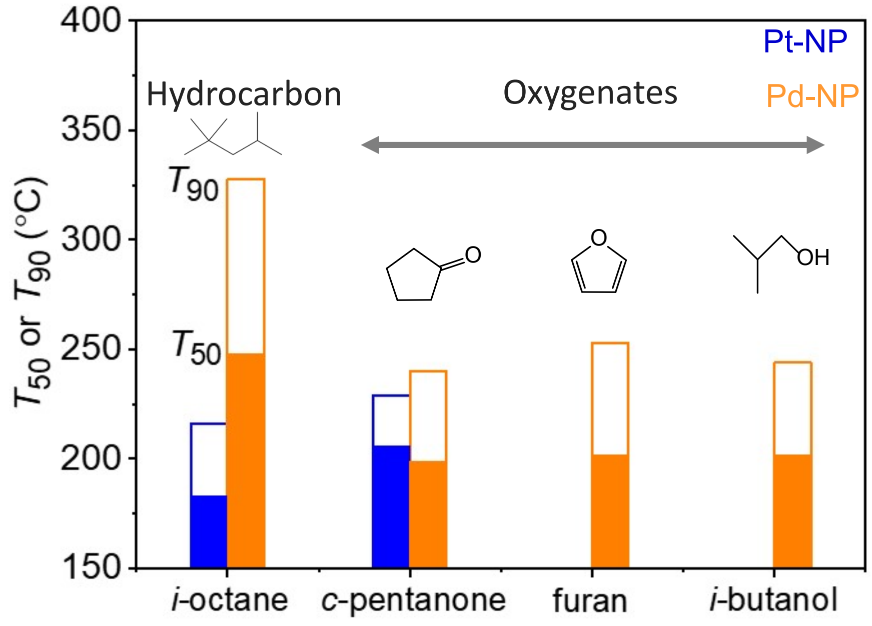
CO-TPR profiles of the as-synthesized SA and NP 0.5Pt/CeO_2 catalysts



H_2-TPR profiles of the as-synthesized 0.5Pt/CeO_2-SA and 0.5Pt/CeO_2-NP.

- Pt/CeO_2-SA has more ionic Pt after CO reduction, reducing the number of metallic Pt sites required for HC activation
- The surface oxygen of Pt/CeO_2-SA is more active, which, however, has limited contribution for HC oxidation
- H_2-TPR: the ionic Pt of 0.5Pt/CeO_2-SA is less reducible than 0.5Pt/CeO_2-NP.

E.1.3.2- Performance of Pt/ Ceria vs. Pd /Ceria nanoparticle catalysts (NP)



0.75% O_2, 3000 ppm C_1, 200 L h^{-1} g_{cat}^{-1}

Pt/CeO_2 NP is more active for selected hydrocarbon than for oxygenate whereas Pd/CeO_2 NP shows a reverse trend.