A Low Temperature Catalyst to Enable Fuel-Efficient Vehicle Commercialization

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Oak Ridge National Laboratory
National Transportation Research Center

2017 Technology Innovation Program (TIP) Showcase

October 3, 2017

ORNL's Sustainable Transportation Program operates DOE's only transportation user facility: the National Transportation Research Center

Partnering with industry to shape America's mobility future

Thousands of visitors and hundreds of collaborators

$80M R&D volume

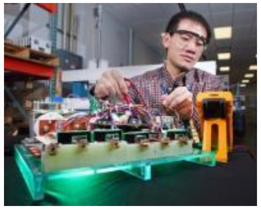
19 R&D 100 Awards of ORNL's 200

16 University Partners

DOE National User Facility

20 CRADAs
Cooperative Research & Development Agreement

86 SPP
Strategic Partnership Projects



ORNL Sustainable Transportation Program… "all of the above" needed for national goals

Electrification

- Advanced power electronics and traction motors.
- Wireless power transfer
- Modeling, manufacturing, and materials for improved batteries
- Fuel Cells

Efficiency

- Advanced combustion engines and emission controls
- Integrated powertrain solutions
- Light-weight materials

Alternative fuels

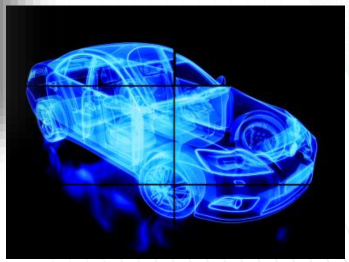
- Drop-in biofuels for legacy cars
- Renewable fuels for fuel diversification
- Natural gas

Intelligent systems

- Cyber security, data science, and vehicle controls for ITS.
- Efficient operations in commercial vehicles
- Predictive data for decision-making

New technologies and processes for:

- Efficient, safe, and affordable vehicles for passengers and freight
- Relies on domestically-produced transportation fuel
- Reducing environmental impacts of transportation
- Predictable, reliable transport schedules



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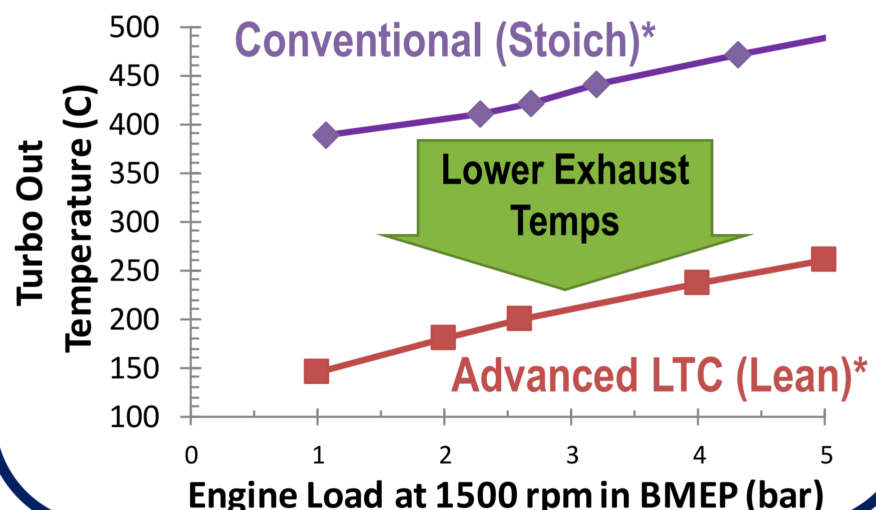
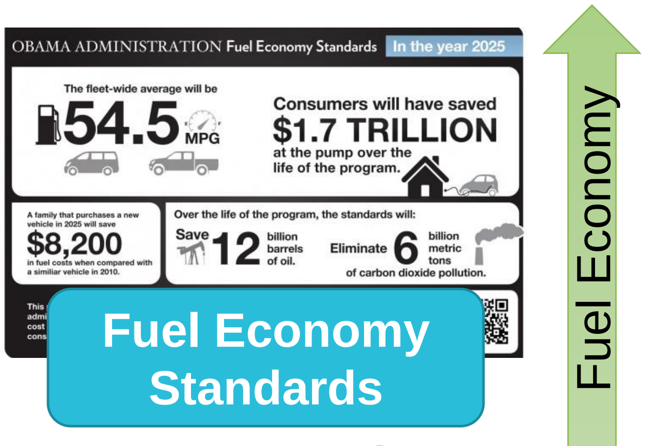
Regulations driving fuel efficiency and emissions, and the each regulations affects the other

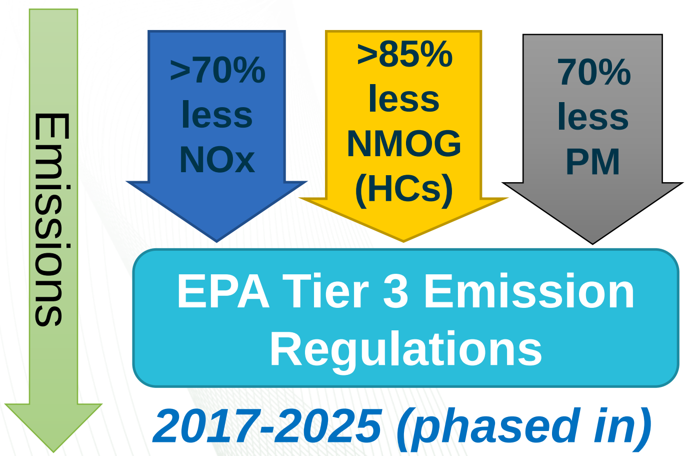
- Greater combustion efficiency lowers exhaust temperature
- Catalysis is challenging at low temperatures
- Emissions standards getting more stringent

Higher efficiency engines have lower exhaust temperatures





54.5 mpg CAFE by 2025



2017-2025 (phased in)

*"**Conventional**": modern state-of-the-art Gasoline Direct Injection Turbocharged stoichiometric-burn engine vs.
"**Advanced LTC**": Reactivity Controlled Compression Ignition (RCCI) [an advanced lean-burn Low Temperature Combustion (LTC) engine]

more efficient engines = lower exhaust temps = catalyst challenges

Industry Catalyst R&D Needs Defined by Government-Industry Partnerships

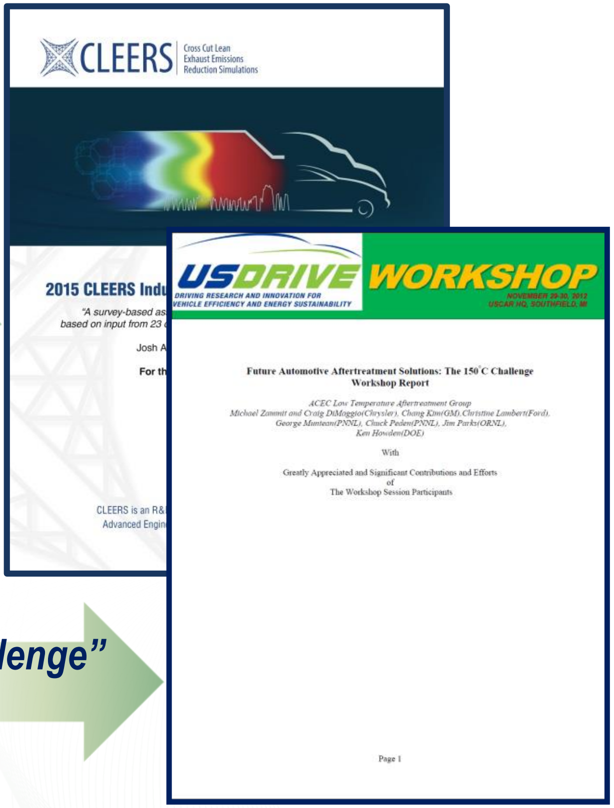
CLEERS Cross Cut Lean Exhaust Emissions Reduction Simulations

21st CENTURY TRUCK PARTNERSHIP

USDRIVE DRIVING RESEARCH AND INNOVATION FOR VEHICLE EFFICIENCY AND ENERGY SUSTAINABILITY

2015 CLEERS Industry Priorities Survey*

USDRIVE "The 150ºC Challenge" Workshop Report*



*available at www.cleers.org

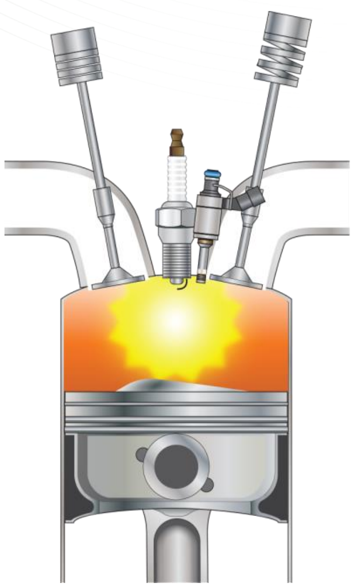
Vehicle Technologies Office:

Objective: Develop new emission control technologies to enable fuel-efficient engines with low exhaust temperatures (<150ºC) to meet emission regulations cost-effectively with low energy penalty

DOE Goal: >90% Conversion of CO, HCs, and NOx at 150ºC

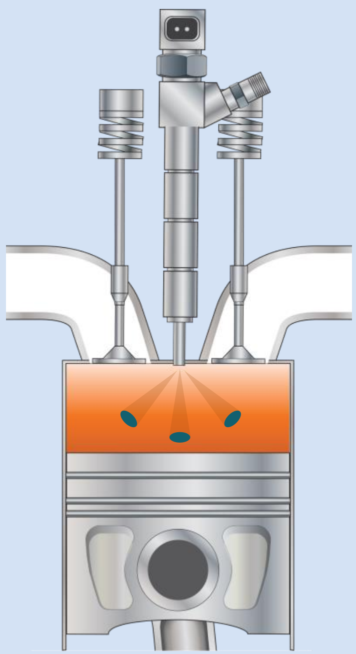
New Low Temperature Combustion approaches are enabling high fuel efficiency and low emissions

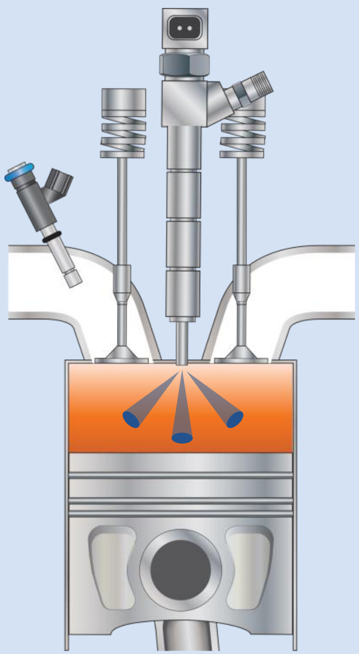
Spark Ignition Gasoline



Low Reactivity Fuel

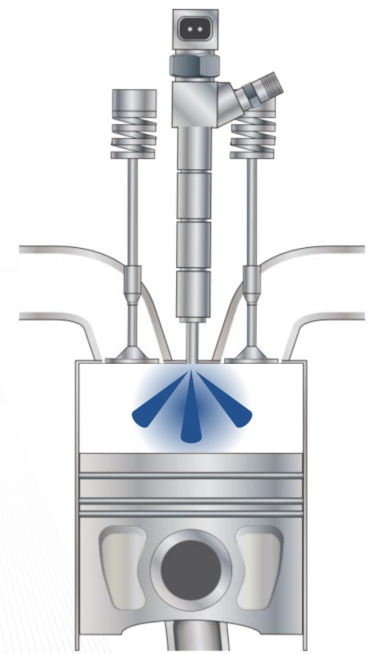
Low Temperature Combustion





Range of Fuel Properties TBD
(depends on combustion mode)

Compression Ignition Diesel



High Reactivity Fuel

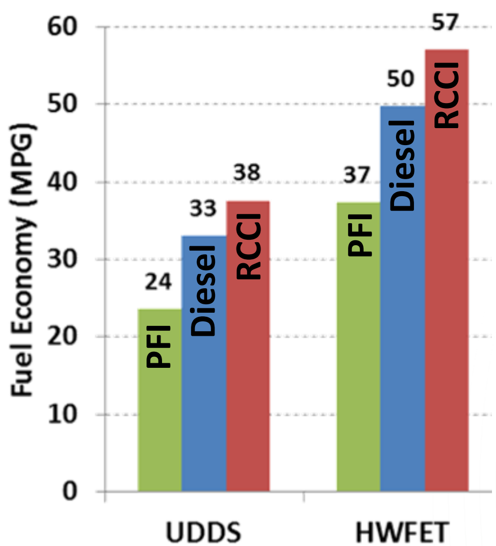
"RCCI" is a Low Temperature Combustion technique that has been demonstrated on multi-cylinder engines

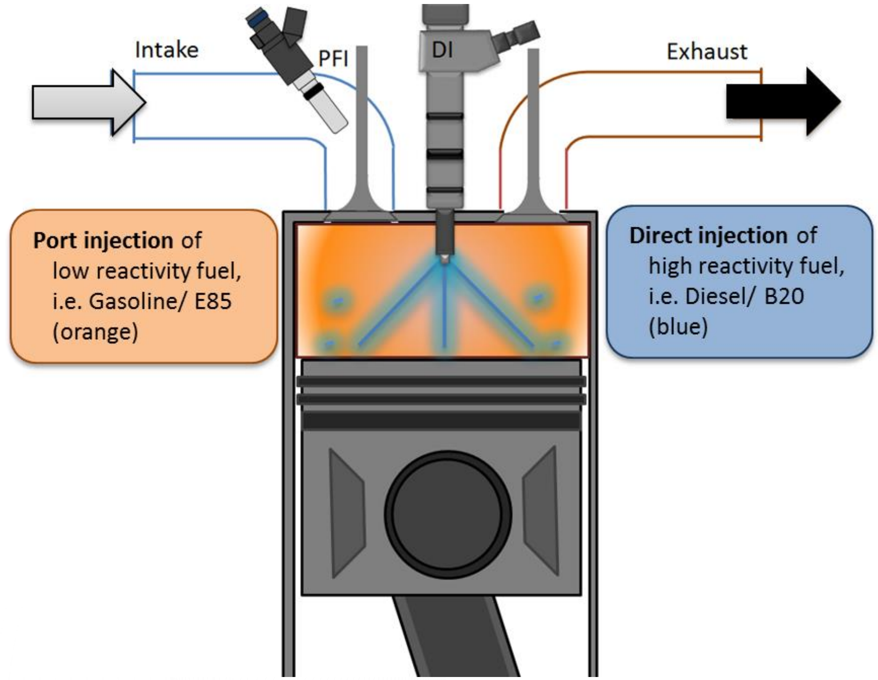
Reactivity controlled compression ignition (RCCI) allows precise reaction and heat-release control

– **A <u>low-reactivity</u> fuel is introduced early and premixed with air, and a <u>high-reactivity</u> fuel is injected into the premixed charge before ignition.**

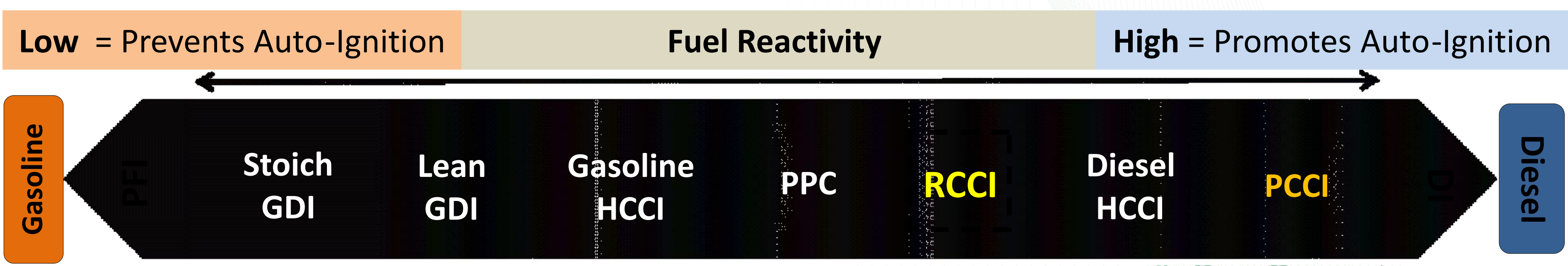
- **RCCI can achieve greater fuel economy than diesels**
- **Low NOx and soot achieved, but CO and HCs increase**
- **Exhaust temperatures are significantly lower (causing issues for oxidation at low loads)**

<u>Modeled</u> Fuel Economy



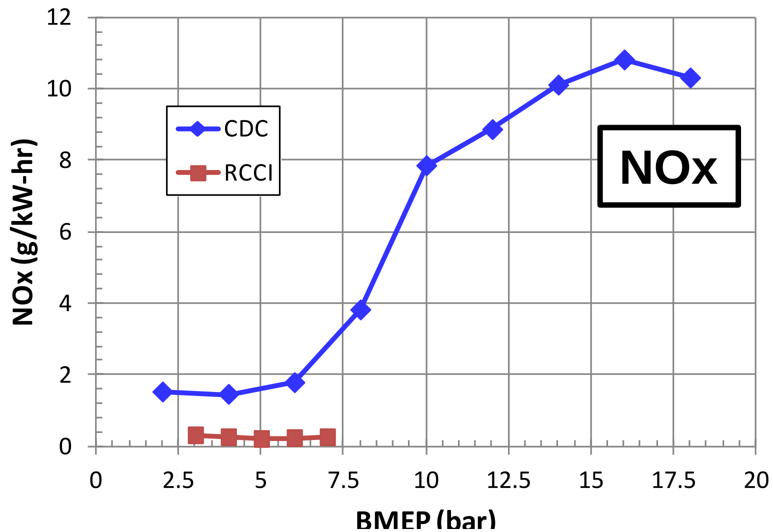


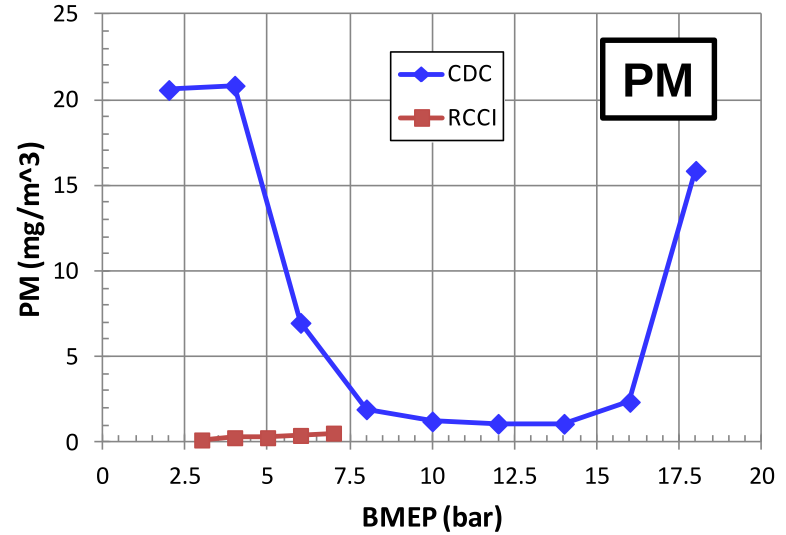
Adapted from Hanson, UW-M Engine Research Center

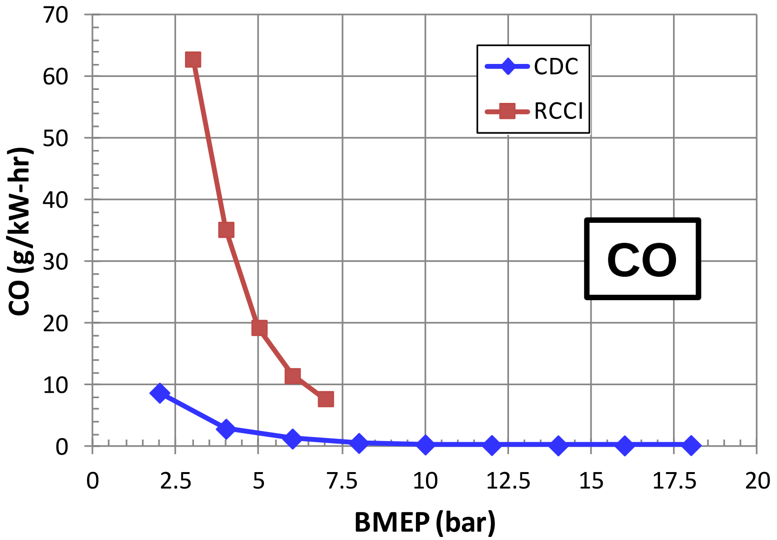


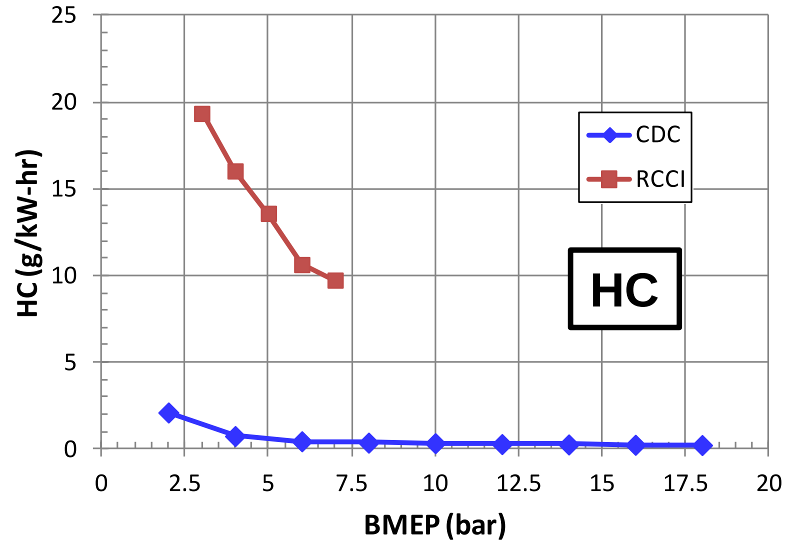
Emission Comparison: RCCI vs. Conventional Diesel Combustion (CDC)

- RCCI reduces NOx and PM greatly, but CO and HC increase (2500 rpm data)









Experimental data on RCCI from studies at ORNL on a modified 1.9-liter, 4-cylinder, turbocharged GM diesel engine

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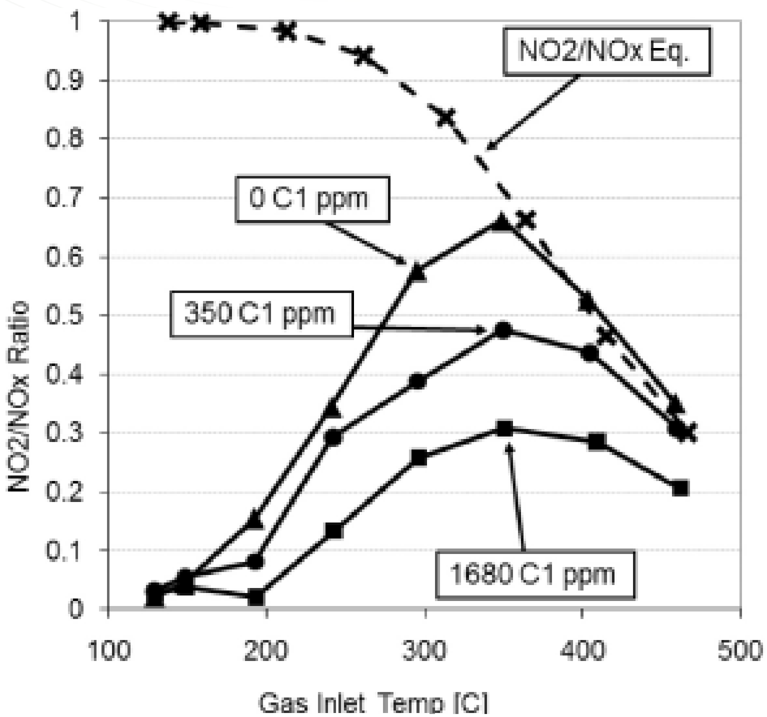
Competition for catalyst sites between pollutants ("inhibition") is problematic – even more for RCCI exhaust

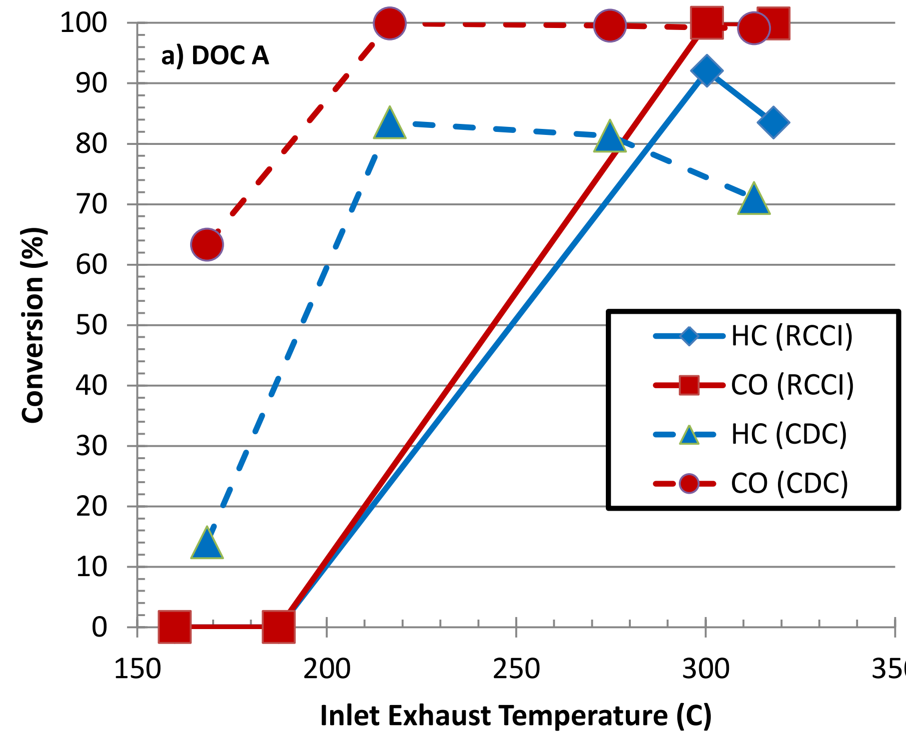
- Adsorption of one species on catalyst sites can inhibit/foul the oxidation/reduction of other exhaust species

HCs limit NO to NO_2 oxidation for DOC catalyst



C. Henry, et al., SAE 2011-01-1137

Higher HC and CO emissions from advanced combustion shift light-off curves higher due to inhibition



V. Prikhodko, et al., SAE 2013-01-0515

Also: Al-Harbi, Hayes, Votsmeier, Epling, *The Canadian Journal of Chem.Eng.* **90**, 1527-38 (2012)

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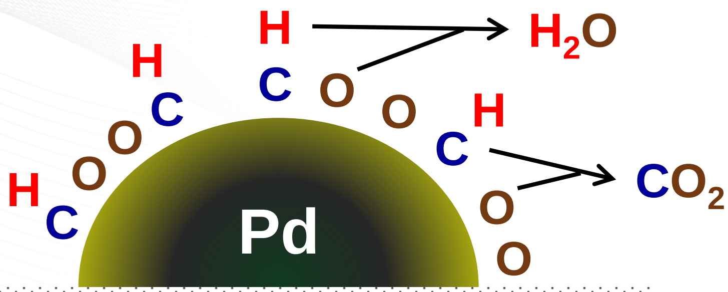
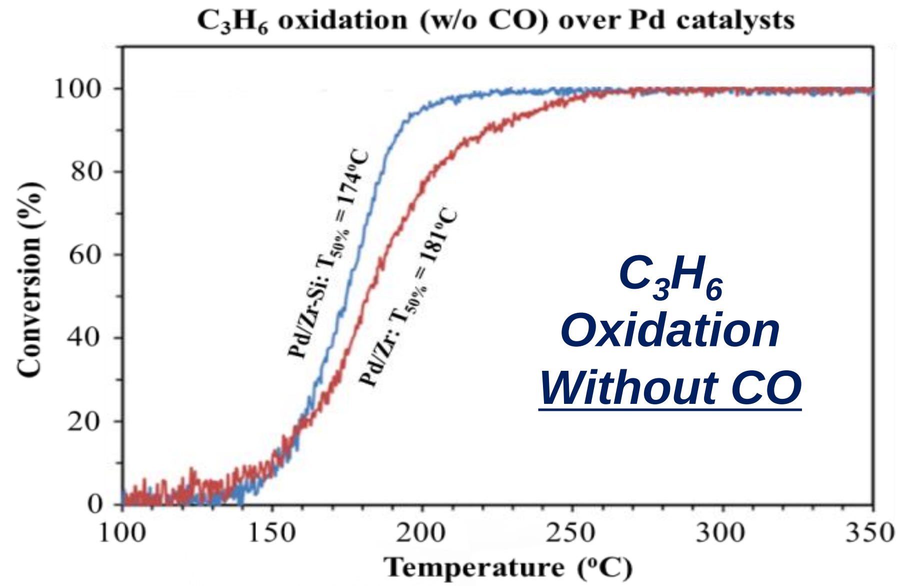
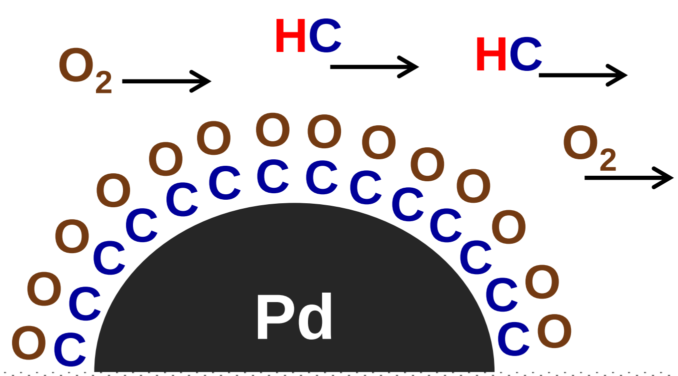
Inhibition of HC light-off by CO is common for Platinum Group Metal (PGM) based catalysts

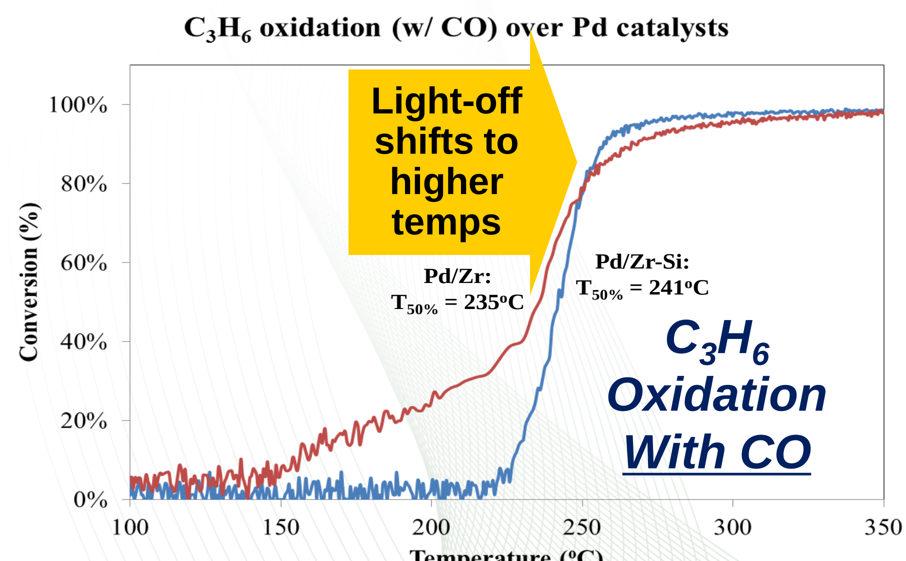


Without CO, HCs and O_2 chemisorb on Pd unimpeded and oxidation occurs





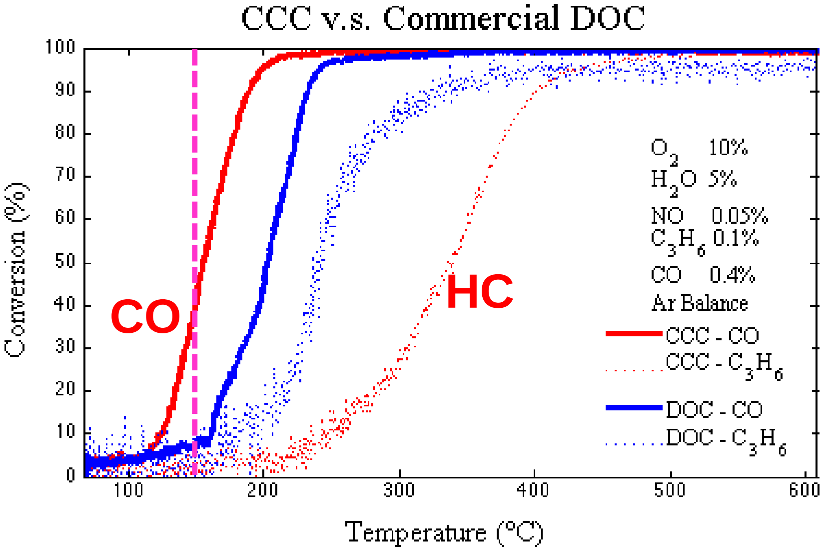
With CO, the presence of CO inhibits HCs from chemisorbing to the Pd and oxidizing



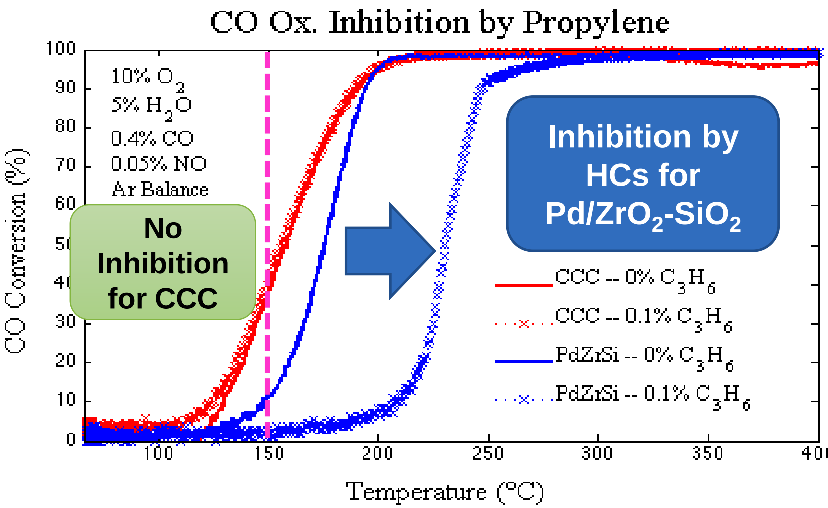
New CuO_x-CoO_y-CeO_2 catalyst oxidizes CO without HC inhibition (a major breakthrough)

Co-precipitated CuO_x, CoO_y, and CeO_2 (dubbed CCC catalyst) has shown to have both ***high CO oxidation activity*** *and* ***exceptional tolerance for propylene.***

- PGM-Free CCC (red) **outperforms commercial catalysts** currently used in DOC (blue) washcoats for oxidation of CO
  - However, hydrocarbon oxidation temperature higher
- **Projected cost to be very low.**



- CO oxidation inhibition by propylene is readily seen on platinum group metal (PGM) catalysts such as the Pd/ZrO_2-SiO_2 catalyst shown here (blue).
- **But…No inhibition found for CCC catalyst** (red).



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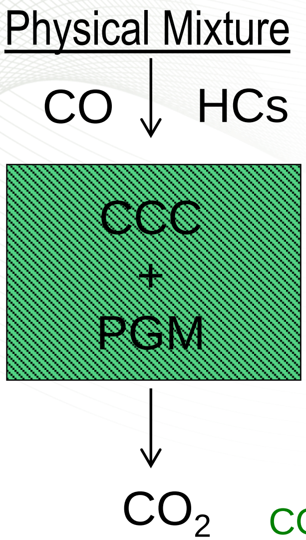
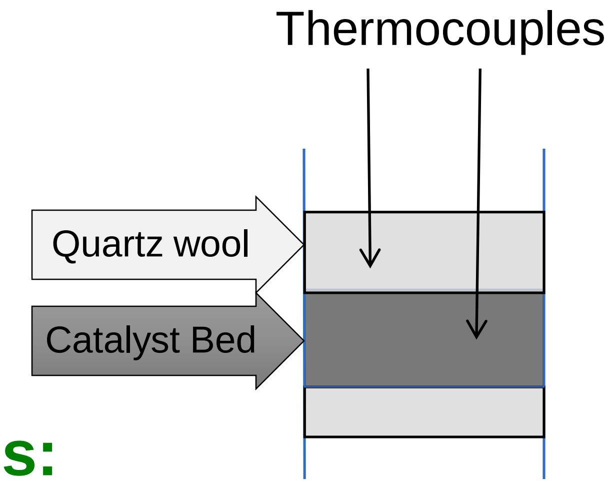
CCC + Pt/Al_2O_3 combination demonstrates the lowest combined CO and HC light-off temps

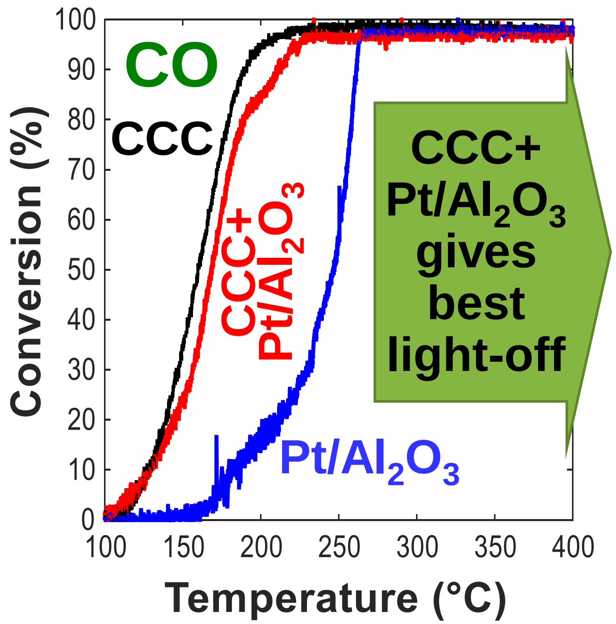


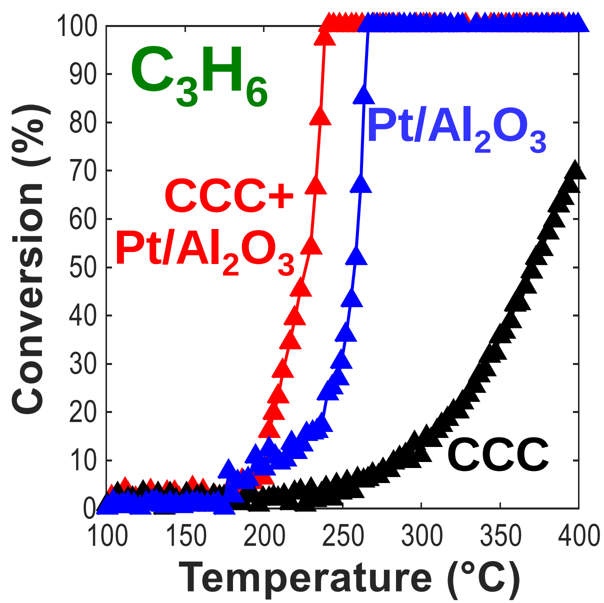
- Physical mixture of 50% CCC and 50% Pt(1% wt.)/Al_2O_3 allows for high CO and propene oxidation with half as much total Pt content vs. Pt/Al_2O_3
- C_3H_6 light-off greatly improved with CCC + Pt physical mixture

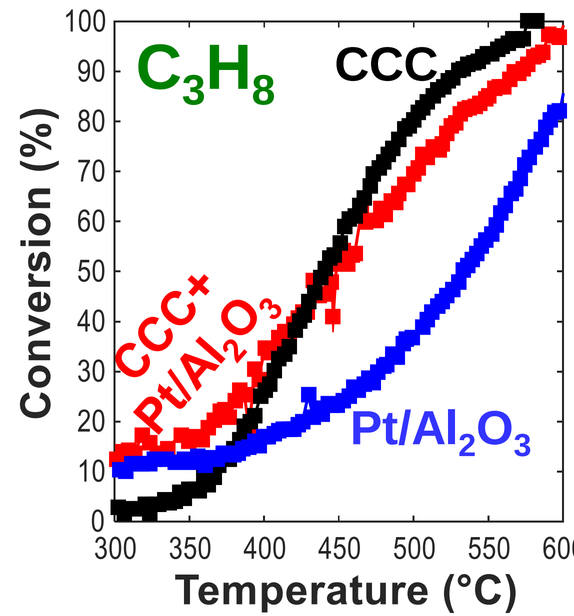


CO+HC+NOx Conditions:

CO (1%), C_3H_6 (500ppm), C_3H_8 (500ppm), NO (500ppm), O_2 (10%), H_2O (5%)



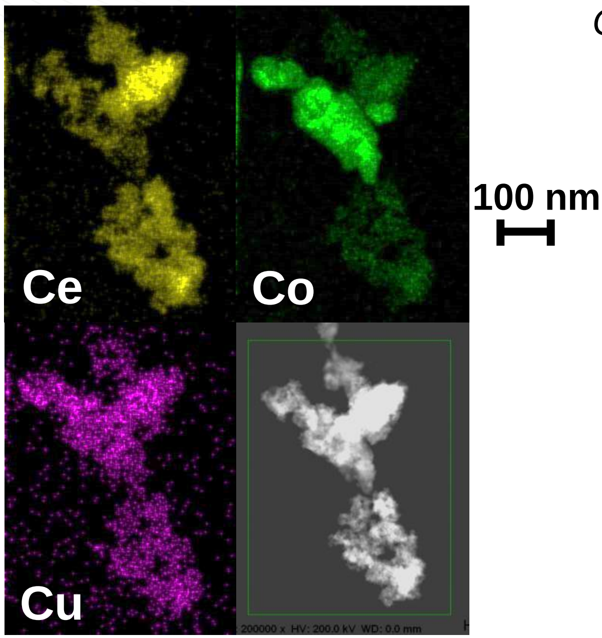




SV ~150k/hr

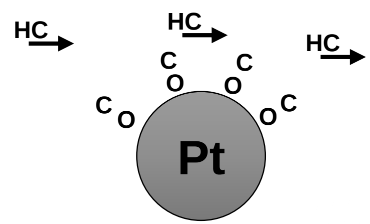
Unique "CCC" Catalyst Addresses Long-Standing Inhibition Problem for CO and HC Control at Low Temperatures

1. BES research on Co-Cu-Ce catalyst
2. EERE applied research under automotive conditions shows Co-Cu-Ce overcomes inhibition
3. Co-Cu-Ce catalyst improves low temperature oxidation at lower Pt loading



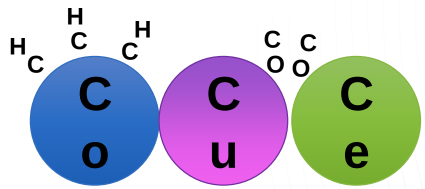
Conventional Pt Catalyst:

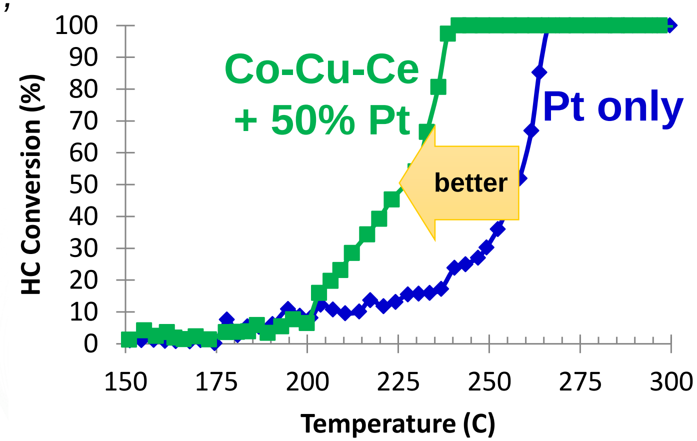
CO and HCs compete for active site; CO inhibition limits HC oxidation



New Co-Cu-Ce Catalyst:

Separate active sites for CO and HCs prevent inhibition





Note: the Co-Cu-Ce+Pt catalyst has 50% less Pt than the Pt only catalyst

Z.-G. Liu, S.-H. Chai, A. Binder, Y.-Y. Li, L.-T. Ji, S. Dai, *Appl. Catal. A-Gen.* **2013**, *451*, 282–288.

A. J. Binder, T. J. Toops, R. R. Unocic, J. E. Parks II, S. Dai, *Angewandte Chemie Intl. Ed.* **54**, 13263 –13267 (2015).

Co-Cu-Ce catalyst gives lower temperature CO & HC control at 50% less cost

Commercial Requirements for Emission Control Catalysts

1. Needs to have fundamental understanding of function
   – Chief engineers must be assured of minimal warranty exposure
2. Must meet the emission regulation cost-effectively
3. Must meet the durability requirement
   – Light-duty (U.S. EPA Tier 3) requires 150,000 mile full useful life
   – Heavy-duty requires 435,000 mile full useful life
4. Needs to be manufactured with scalable processes

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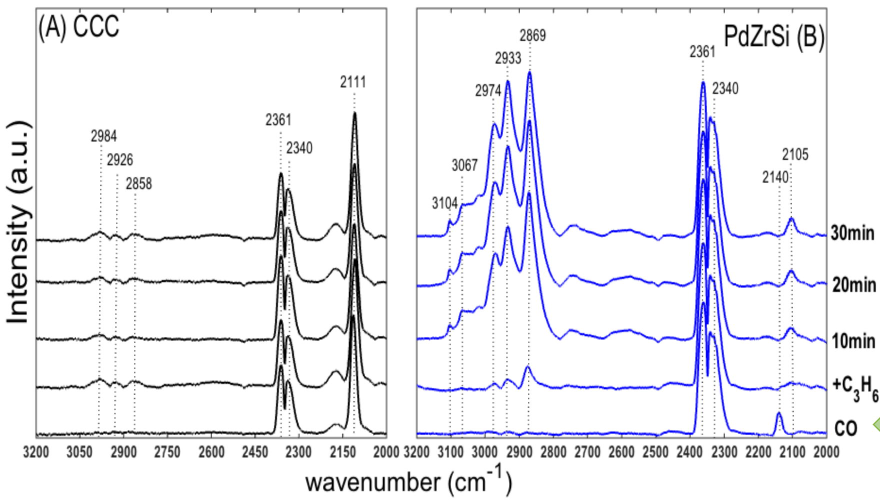
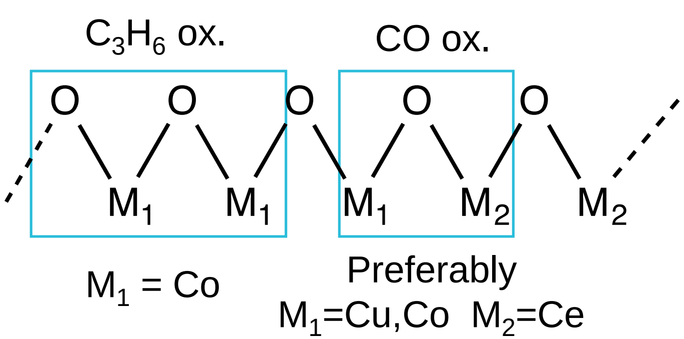
DRIFTS provides insights into CCC hydrocarbon inhibition resistance; initial aging results obtained

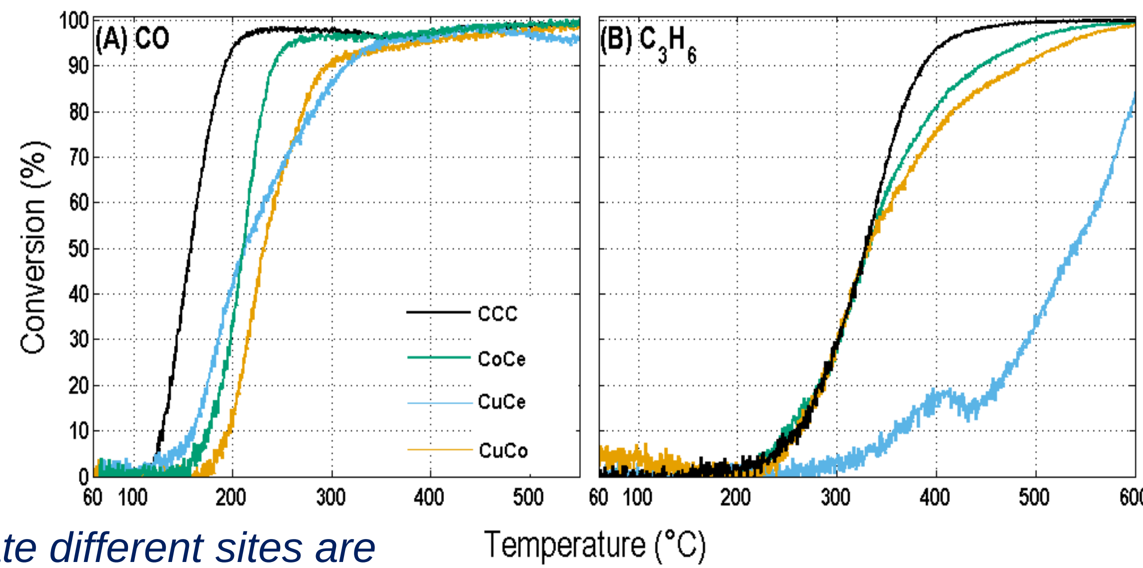


Wavenumber	Assignment
2105	Pd^{+}-CO
2140	Pd^{2+}-CO
2111	Cu^{+}-CO
2340,2361	CO_2 gas
2800-3200	C-H stretch

DRIFTS data indicates a lower adsorption of C_3H_6 on CCC (compared to Pd/ZrO_2-SiO_2) and almost no effect on the Cu-carbonyl binding site due to introduction of propene

CO coverage to start; HC added





Binary catalyst comparisons indicate different sites are important for CO or C_3H_6 activity under simulated exhaust

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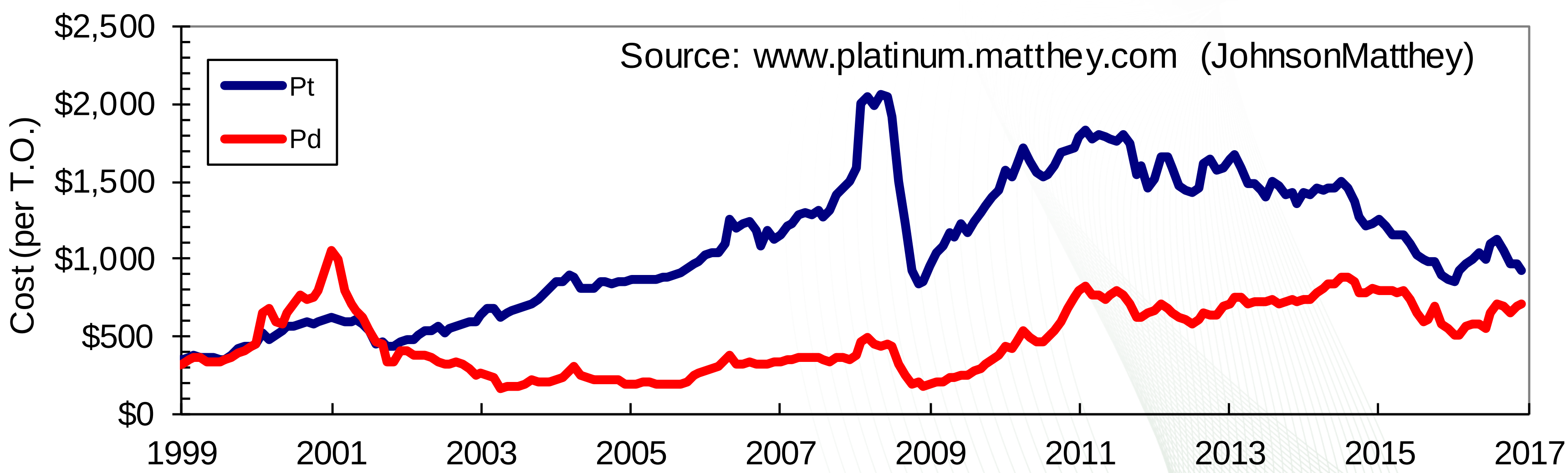
CCC enables better performance with 50% less PGM loading

- The CCC has two separate sites for CO and hydrocarbon (HC) oxidation → a fundamental advantage of Platinum Group Metals (PGMs) that suffer from inhibition between CO and HCs
- Performance indicators:
  - Lower “light-off” temperature **= lower certification emissions**
  - Lower PGM loading **= lower cost and lower cost volatility**



Avg. PGM Cost in Automotive Catalyst=$145.45 (per Foresight)

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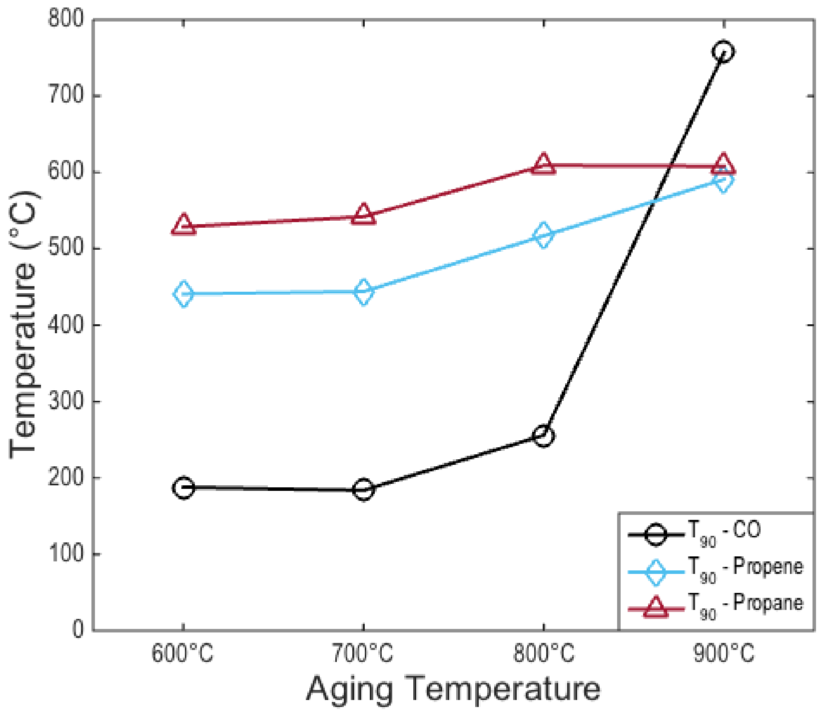
Initial hydrothermal aging results promising for most applications

- Hydrothermal aging shows CCC to be very stable up to 800°C with major deactivation at 900°C
- Maintains low temperature CO oxidation even in the presence of multiple hydrocarbon species (propene + propane shown)



Hydrothermal durability suitable for:

- Low Temperature Combustion (Advanced Combustion)
- Clean Diesel Combustion
- Lean Gasoline Engines

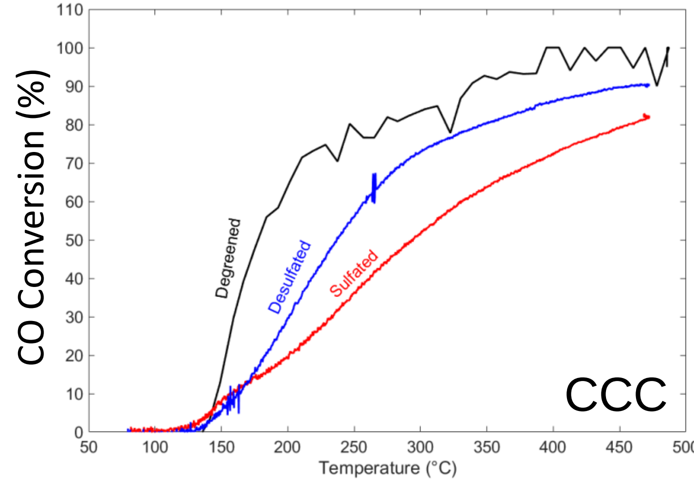
Needs further stabilization for:

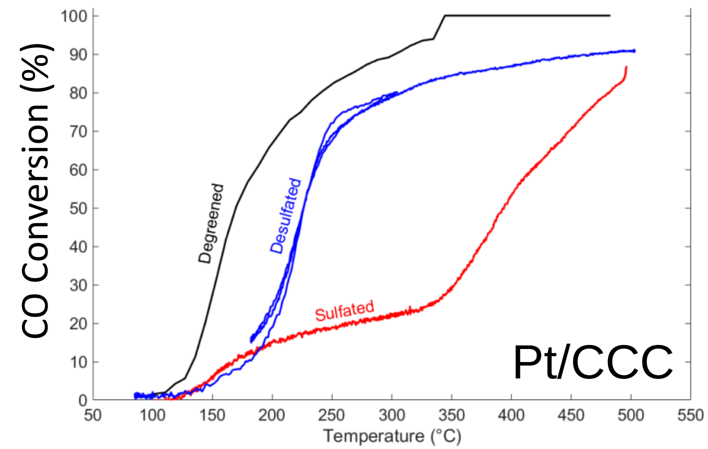
- Stoichiometric Gasoline Engines

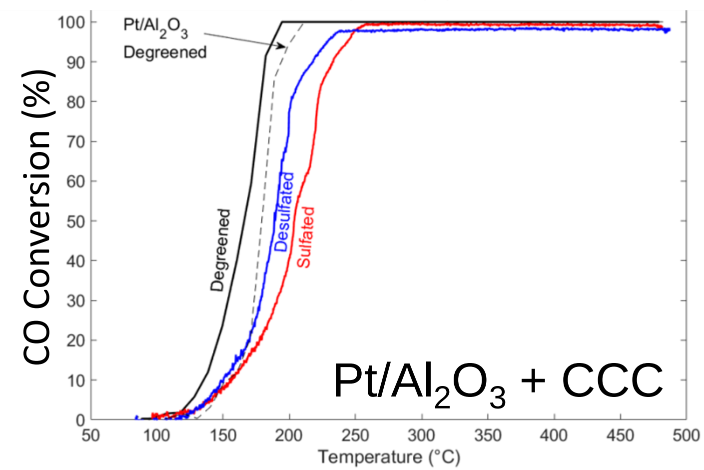
Initial results from Sulfur aging (poison) promising: PGM role important

Inclusion of PGM improves sulfur tolerance and sulfur removal (desulfation) of CCC

- Employed USDRIVE protocol for sulfur poisoning
  - Flow 5 ppm SO_2 at 300°C for 5 hours
  - 200 L/g-hr (GHSV ~300,000 h^{-1})
    - Dense catalyst results in small volume
- After sulfation, ramp under LTC-D conditions to investigate full reactivity
- Desulfation attempted at 600°C under cycling lean and rich conditions
  - 10% O_2 and 1% H_2
  - 30 seconds each, 30 minutes total
- Results show the presence of Pt help protect/recover activity of the catalysts
  - Unclear if CCC has role as desulfated evaluation behaves similar to Pt/Al_2O_3







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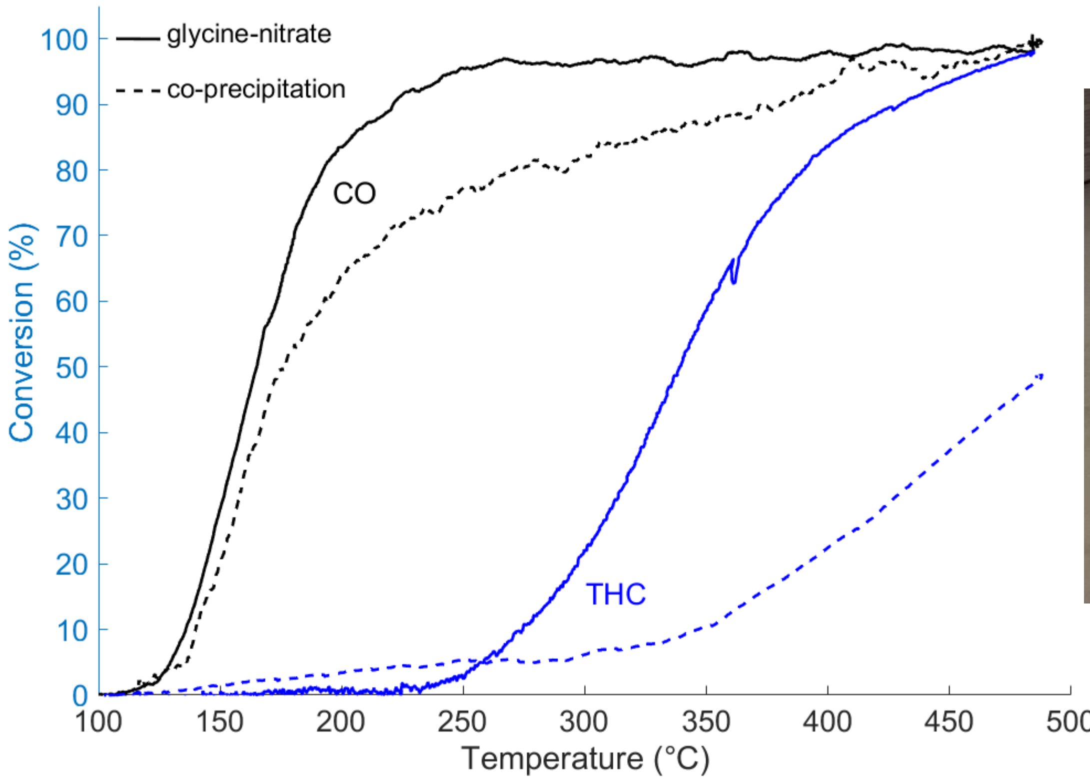
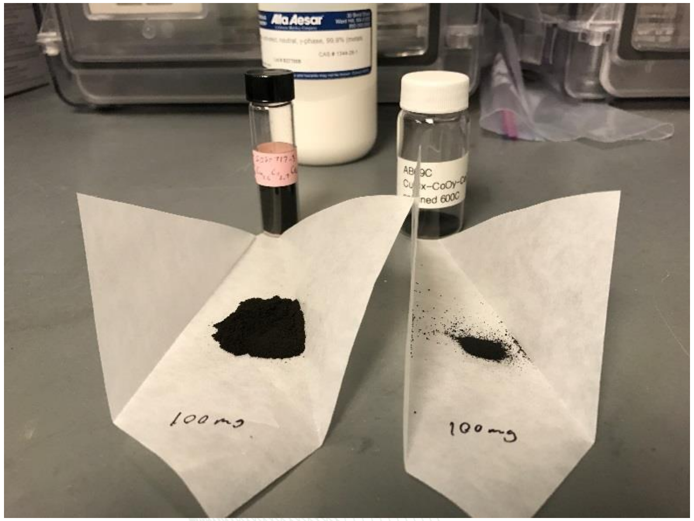
Scalability of CCC production demonstrated with Glycine Nitrate Production Process

- Production scale method demonstrated to produce CCC catalyst via glycine nitrate process
- Better performance achieved with the scalable process (higher surface area likely)



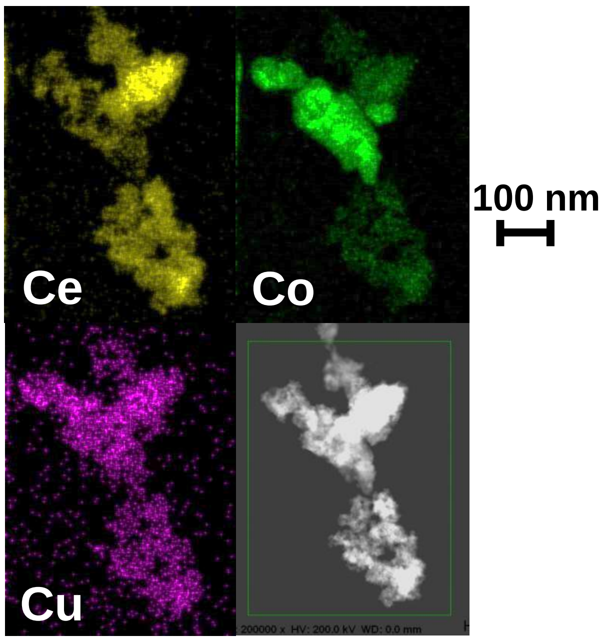


TIP Project Funded by ORNL Partnerships

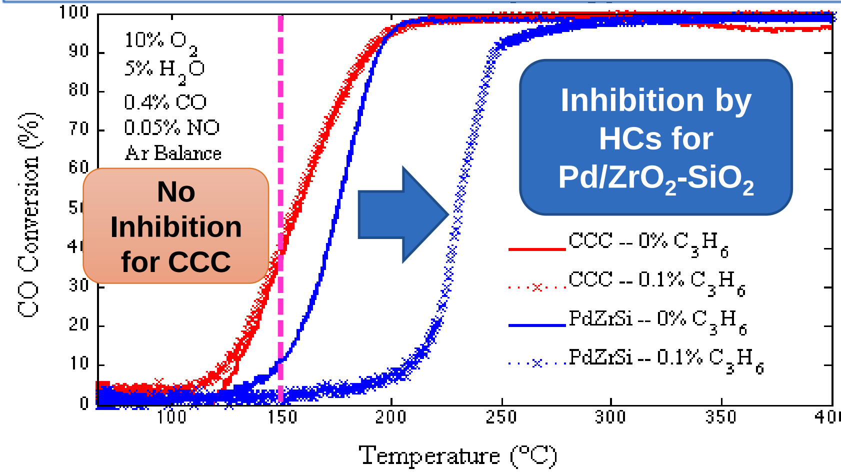
- **Research Objective:** Scale up catalyst from current powder form to a coated monolith form and demonstrate monolith-based catalyst in real engine exhaust (simulated exhaust used to date)
  - **Task 1:** Scale up production of CCC material to >1 kg batch size
  - **Task 2:** Develop capability to coat ceramic monolith with CCC catalyst and produce catalyst suitable for engine studies
  - **Task 3:** Compare CCC performance to state-of-the-art oxidation catalyst on diesel engine at representative load and speeds of interest to customers
- **Ultimate Goal:** Demonstrate performance advantage of CCC catalyst over baseline state-of-the-art PGM-based catalyst on engine and license technology to commercial partner

Low Temperature Oxidation Catalyst "CCC"

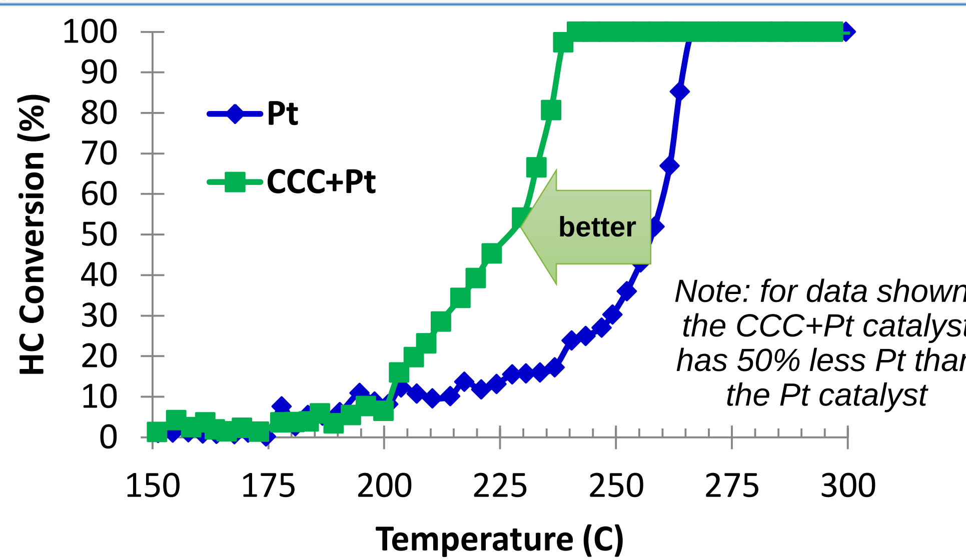
The Invention:
A ternary catalyst called "CCC" composed of oxides of Ce, Co, and Cu that enables:
(1) lower temperature oxidation of CO and hydrocarbons and
(2) lower costs (via Platinum Group Metal or "PGM" reduction)



The Science: ORNL discovered that, for the CCC catalyst, CO oxidation is not inhibited by hydrocarbons; thus, the CCC has a unique and unexpected advantage over PGM catalysts



The Utility: When combined with PGMs, the CCC catalyst outperforms PGM-based catalysts at low temperatures with lower overall cost for hydrocarbon and CO oxidation in combustion exhaust streams



Reference:

A. J. Binder, T. J. Toops, R. R. Unocic, J. E. Parks II, S. Dai, "Low Temperature CO Oxidation over Ternary Oxide with High Resistance to Hydrocarbon Inhibition", *Angewandte Chemie International Edition* **54**, pp. 13263 –13267 (2015).

Intellectual Property:
Patent Pending. Patent Application submitted April 20, 2016. ORNL Invention Disclosure #201403345.