# Three-way Catalyst Reactivity of Novel High-performance Fuels for SI/ACI Engine Emissions Control

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- **Assistance and data from current and former ORNL coworkers**
  - Todd Toops, John Thomas, Brian West, Shean Huff

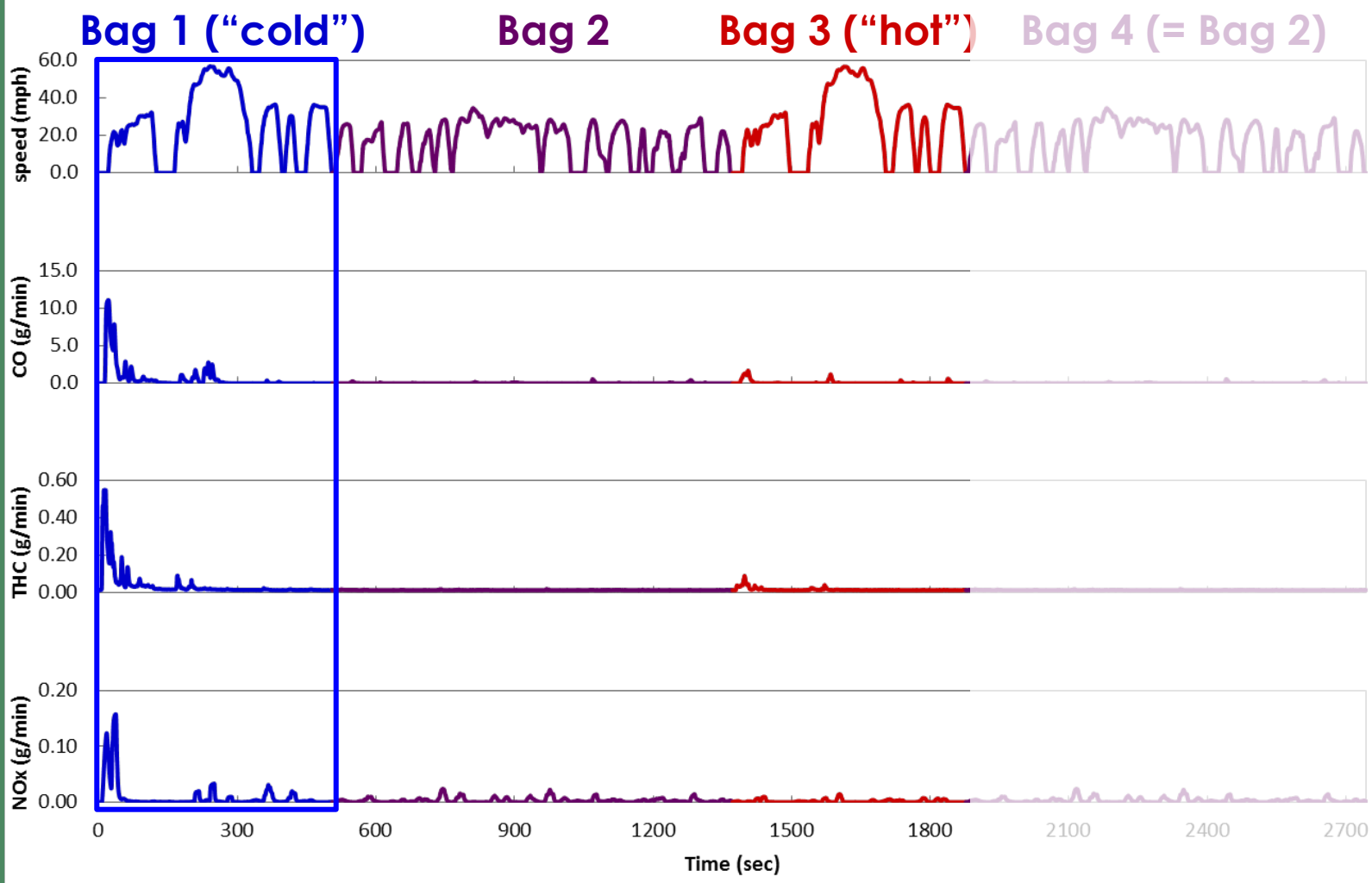
# This work is a part of the U.S. DOE Co-Optimization of Fuels and Engines Initiative

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.

**Better Fuels.**
**Better Engines.**
**Sooner.**

Advanced engines running on high performance fuels still must meet emissions regulations. Our role in Co-Optima is to identify emissions control challenges and opportunities created by changes in fuel chemistry.

# Cold start is the critical emissions control challenge for LD gasoline vehicles; changes to fuel chemistry may impact cold start performance




**FTP-75 emissions data from a 2013 Ford Focus ST (SAE-2018-01-1264)**

- U.S. EPA regulates emissions of:
  - Carbon monoxide (CO)
  - Non-methane organic gases (NMOG)
  - Nitrogen oxides (NOx)
  - Particulate Matter (PM)
- Modern gasoline engines run stoichiometric air/fuel ratios to enable use of three-way catalysts (TWCs) for CO/NMOG/NOx
- TWCs are very effective when hot
- Most emissions occur during cold start before TWC "light-off"
- Changes to fuel chemistry may impact TWC light-off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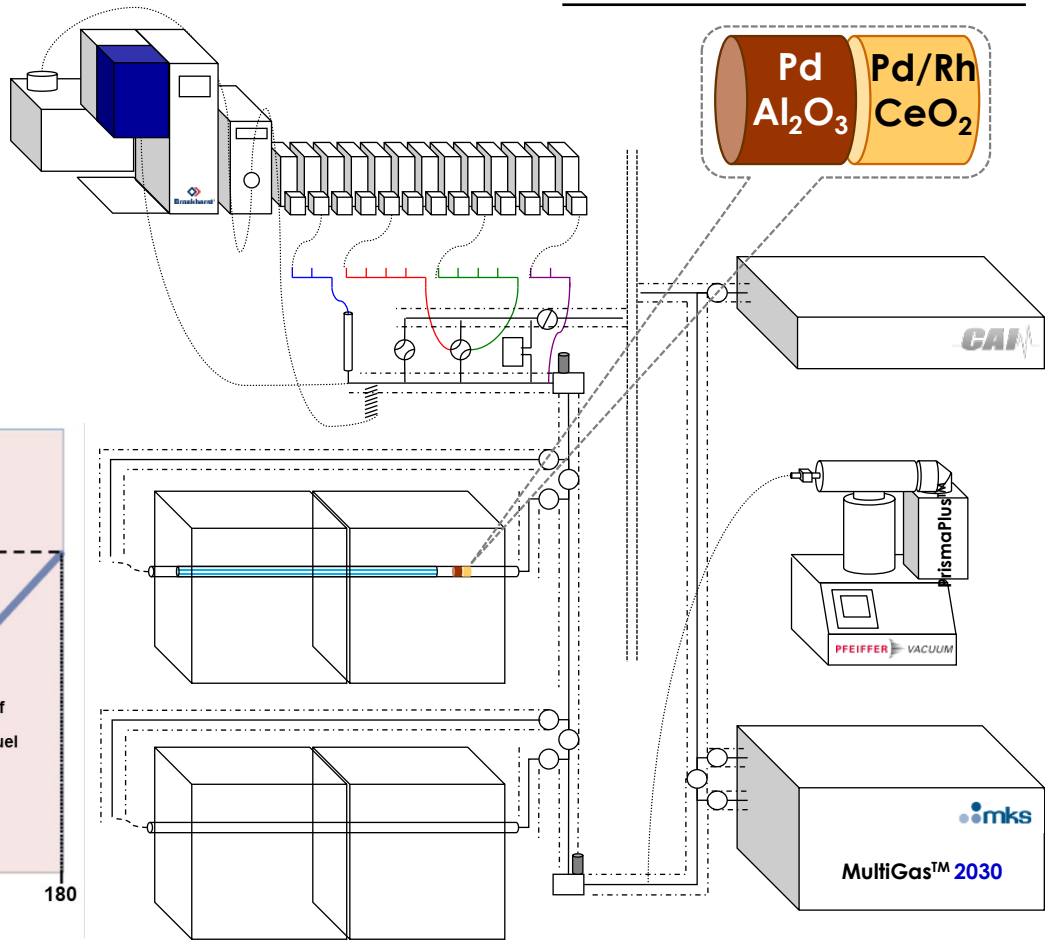
# Synthetic exhaust flow reactor experiments conducted according to U.S. DRIVE protocols were used to quantify effects of fuel chemistry on TWC light-off

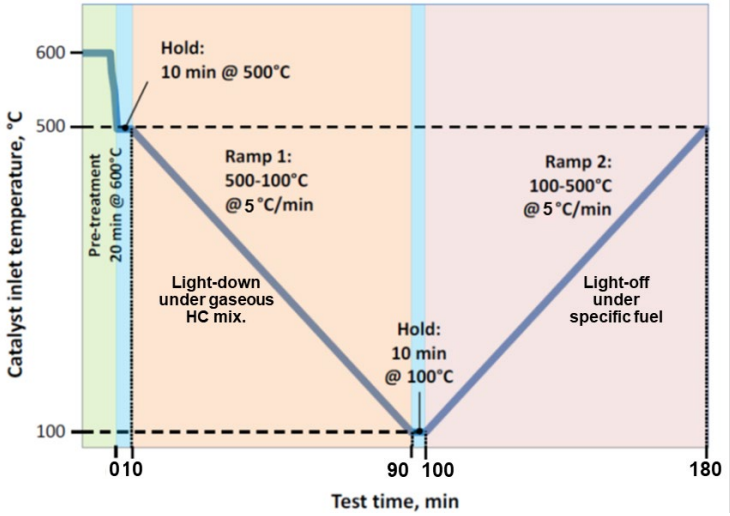
- Experiments conducted on an automated synthetic exhaust flow reactor
  - vapor delivery system for liquid fuel components
  - FID, FTIR, and MS for gas analysis
- Commercial dual-zone Pd-based TWC sample aged according to U.S. DRIVE ACEC Low Temperature Aftertreatment protocol*
  - 50 h @ 800 °C catalyst inlet temperature
  - Cycled between neutral/rich/lean conditions

**2009 Chevy Malibu PZEV TWC**

| | | |
|---|---|---|
| Pd (g/l) | 7.3 | 1.1 |
| Rh (g/l) | 0 | 0.3 |




- TWC light-off experiments based on U.S. DRIVE ACEC protocol*
  - Repeated ≥ 3 times for each fuel




*http://cleers.org/wp-content/uploads/2015_LTAT-Oxidation-Catalyst-Characterization-Protocol.pdf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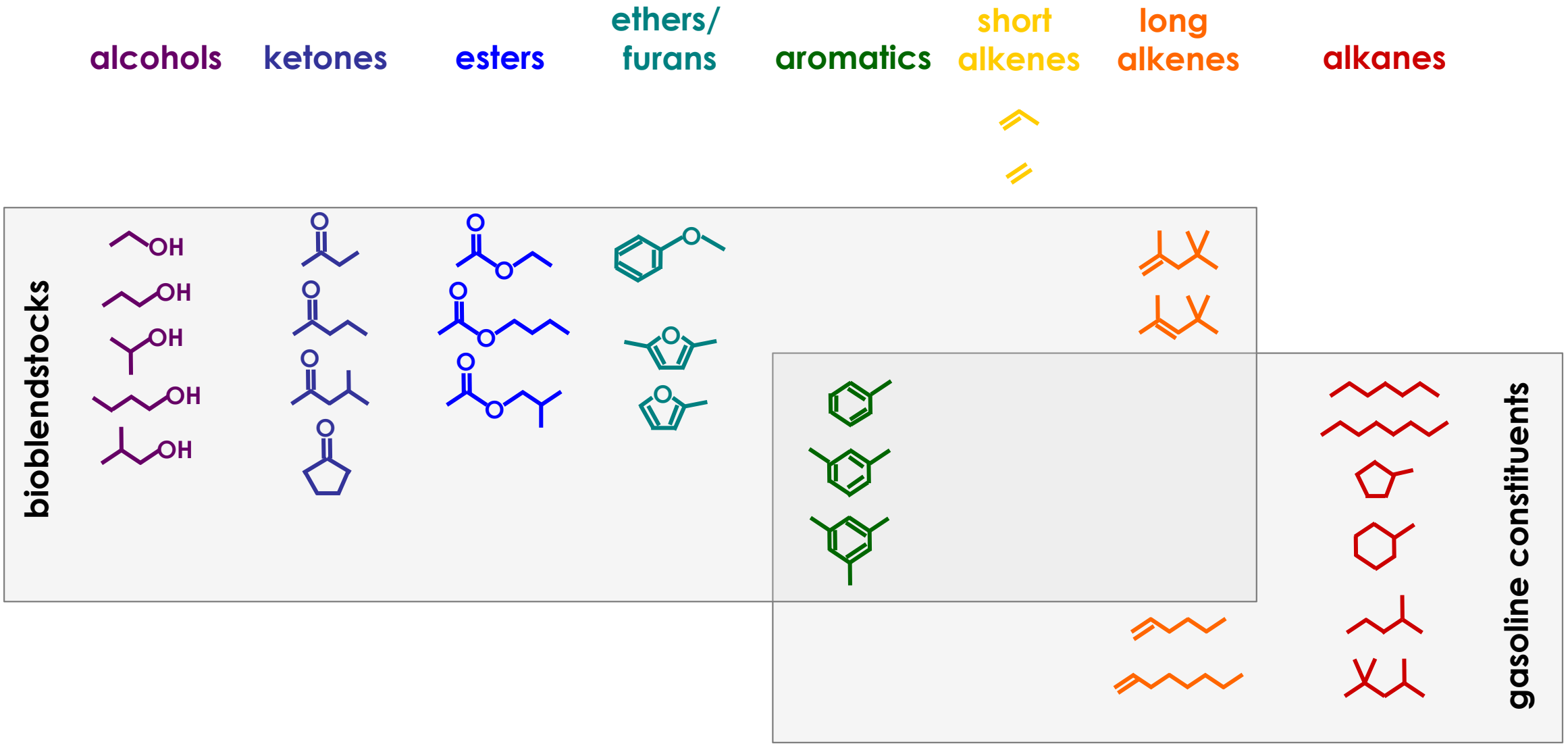
# Experiments included a wide range of chemical structures from both biomass and petroleum sources





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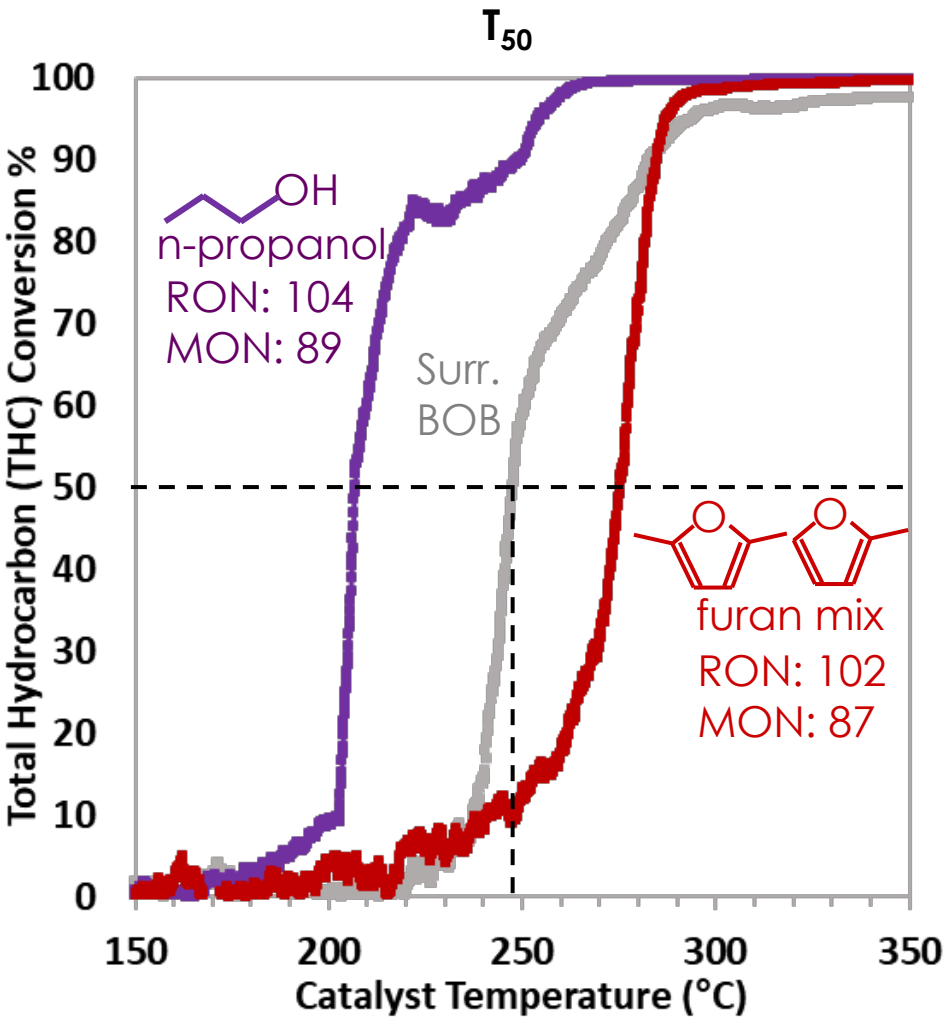
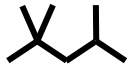
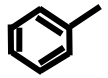
# Fuel chemistry impacts TWC light-off

- Surrogate Blendstock for Oxygenate Blending (BOB) formulated by Co-Optima researchers for blend fuel property measurements
- TWC light-off with Surrogate BOB very similar to gasoline
- Sample light-off curves show fuel chemistry significantly shifts TWC light-off curves
- Catalytic reactivity does NOT correlate with gas phase reactivity (RON, MON) or other standard fuel properties
- $T_{50}$ = temperature at which 50% conversion is achieved




**Surrogate BOB:**

| | |
|---|---|
| 55% |  |
| 25% |  |
| 15% | |
| 5% | |

**Synthetic Exhaust:**

| | |
|---|---|
| $CO_2$ | 13% |
| $H_2O$ | 13% |
| CO | 0.5% |
| $H_2$ | 0.17% |
| NO | 0.1% |
| HC (as $C_1$) | 0.3% |
| $O_2$ | Varies |
| $\lambda$ | 0.999 |
| SV | 30000 $h^{-1}$ |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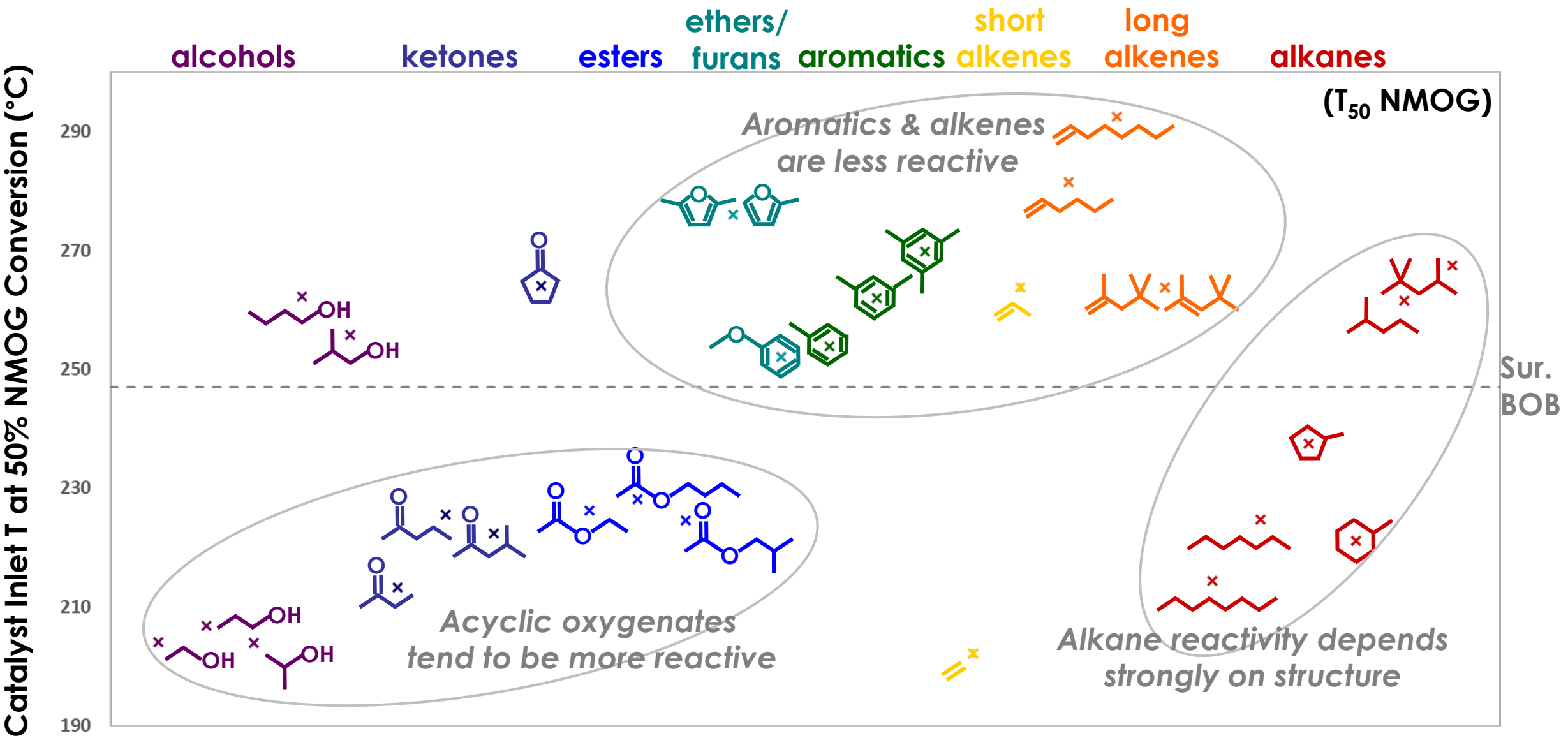
# TWC reactivity depends on chemical structure



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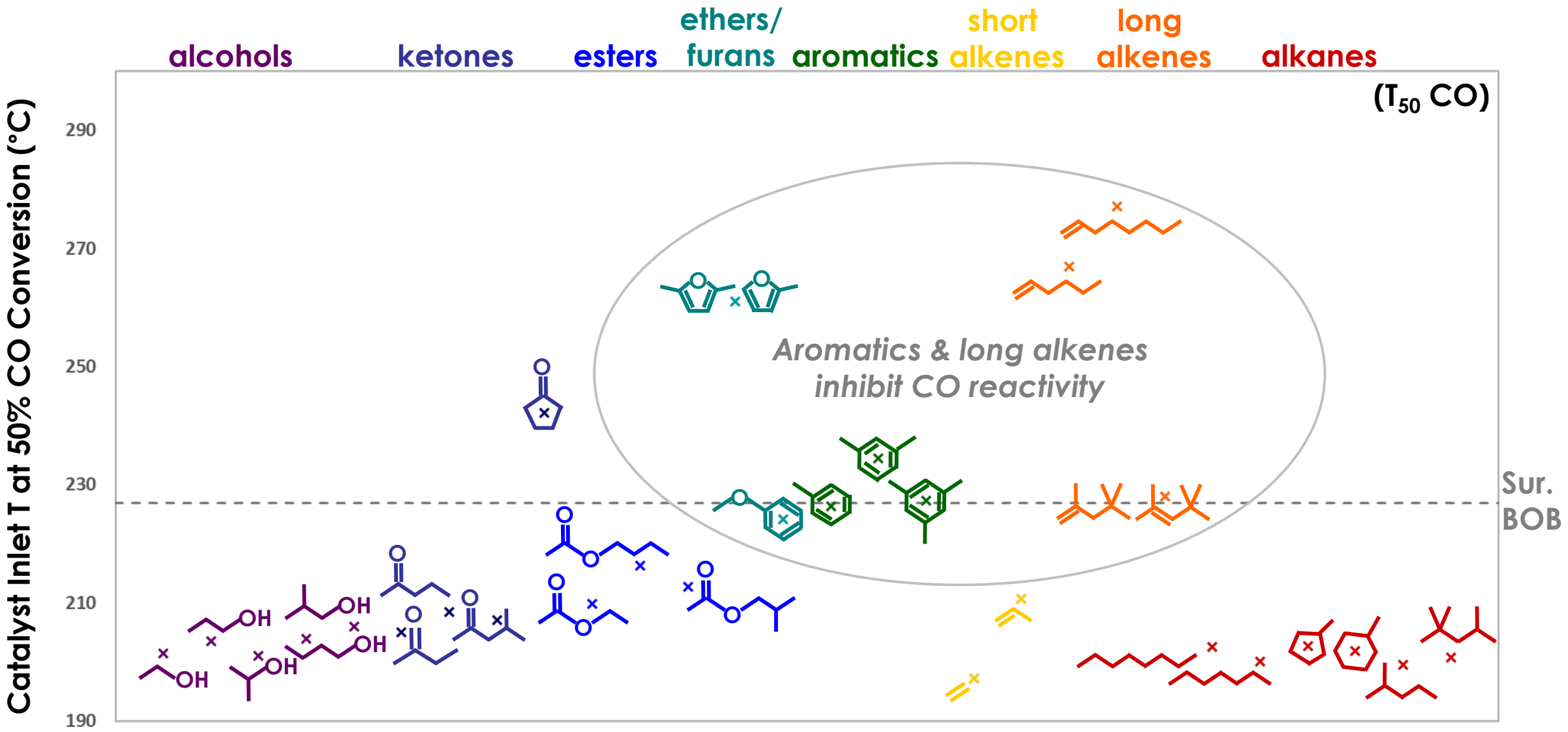
S. Sinha Majumdar, J. A. Pihl, and T. J. Toops, Applied Energy, 255, 113640, 2019.

# CO light-off temperatures show that aromatics and alkenes inhibit CO reactivity




S. Sinha Majumdar, J. A. Pihl, and T. J. Toops, Applied Energy, 255, 113640, 2019.



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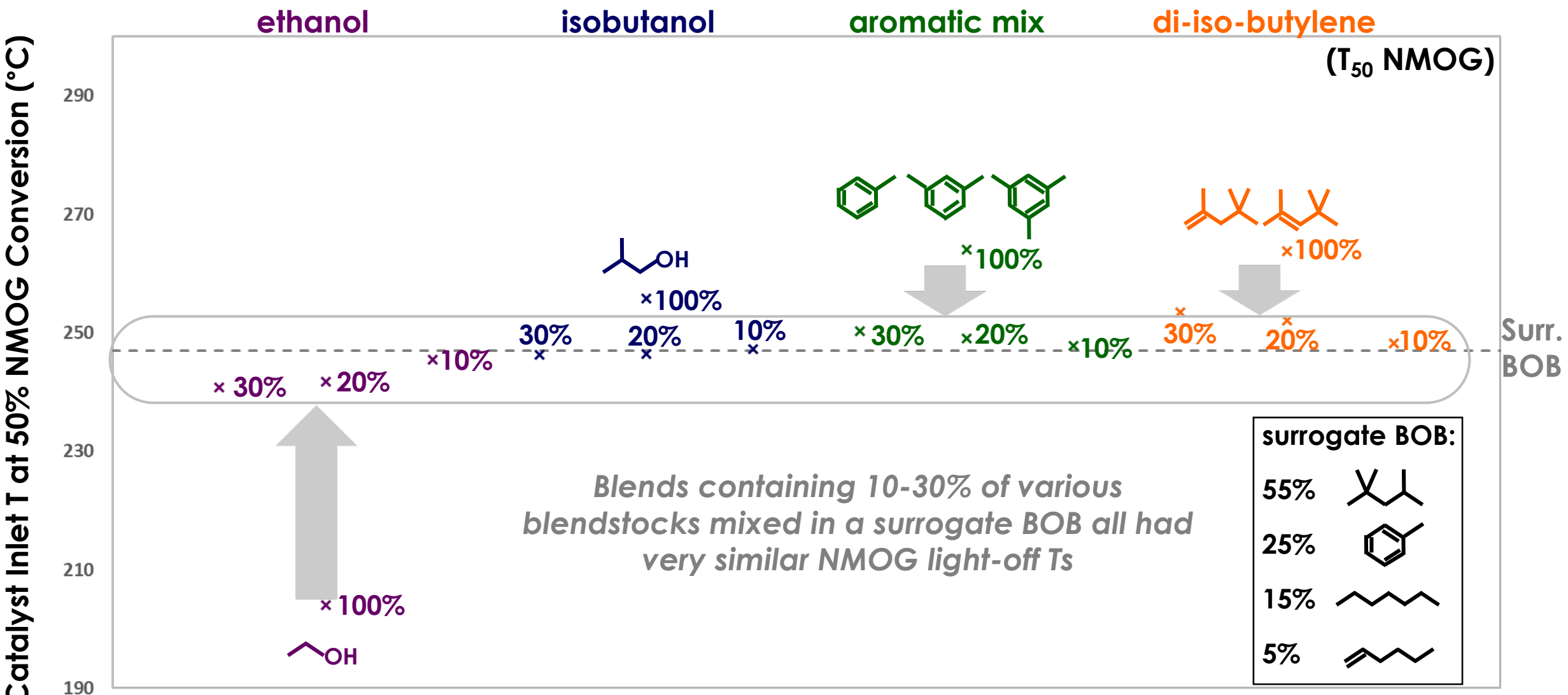
# Bioblendstocks have minimal impact on NMOG light-off temperature when blended up to 30 vol% into a surrogate BOB

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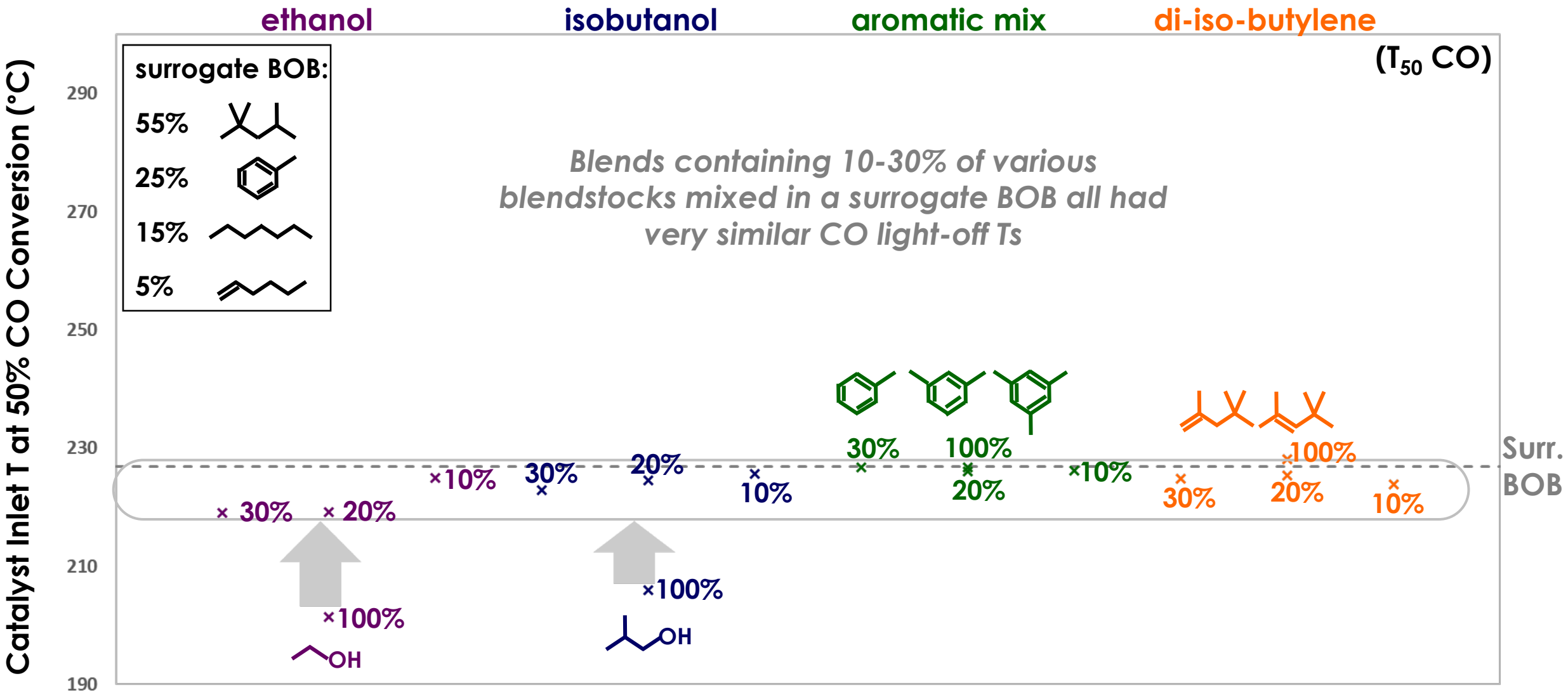




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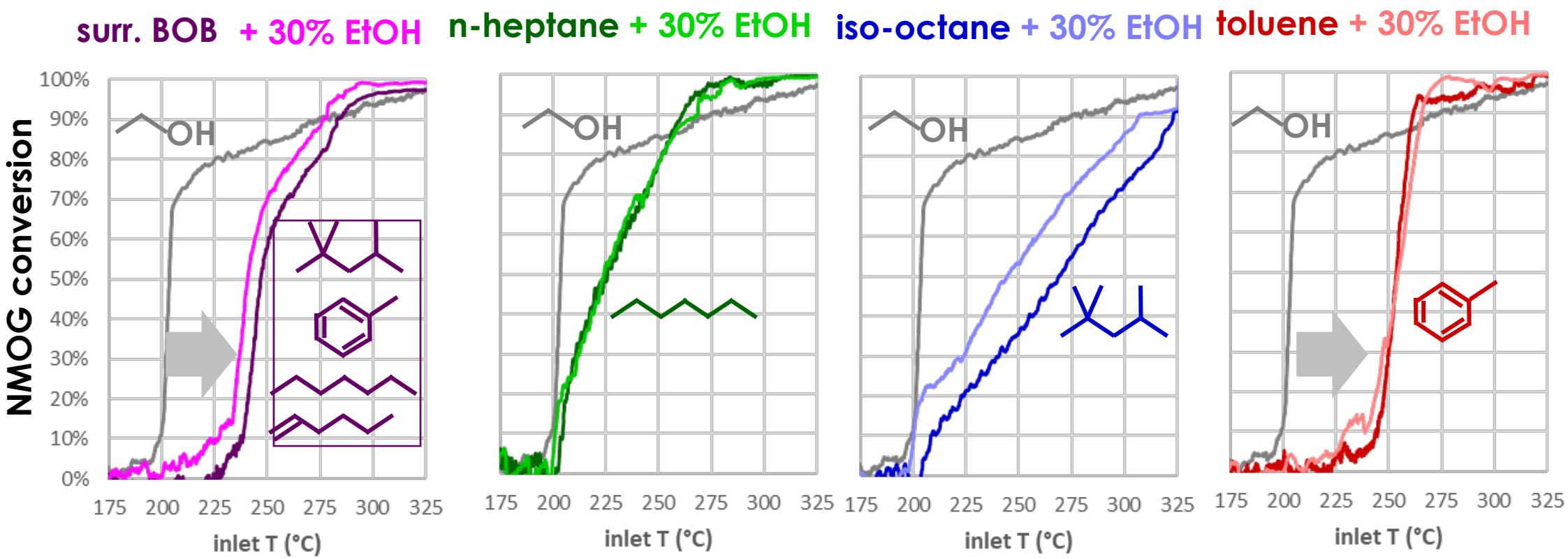
# Do one or more components of the surrogate BOB control the light-off of the blends?




- Observed low T ethanol reactivity over catalyst in mixtures with alkanes
- Observed minimal low T catalytic conversion in mixtures containing toluene
- Aromatic species are likely blocking catalytic active sites, preventing adsorption of reactive species
- ***Light-off temperature of blends is primarily controlled by aromatic content of the surrogate BOB***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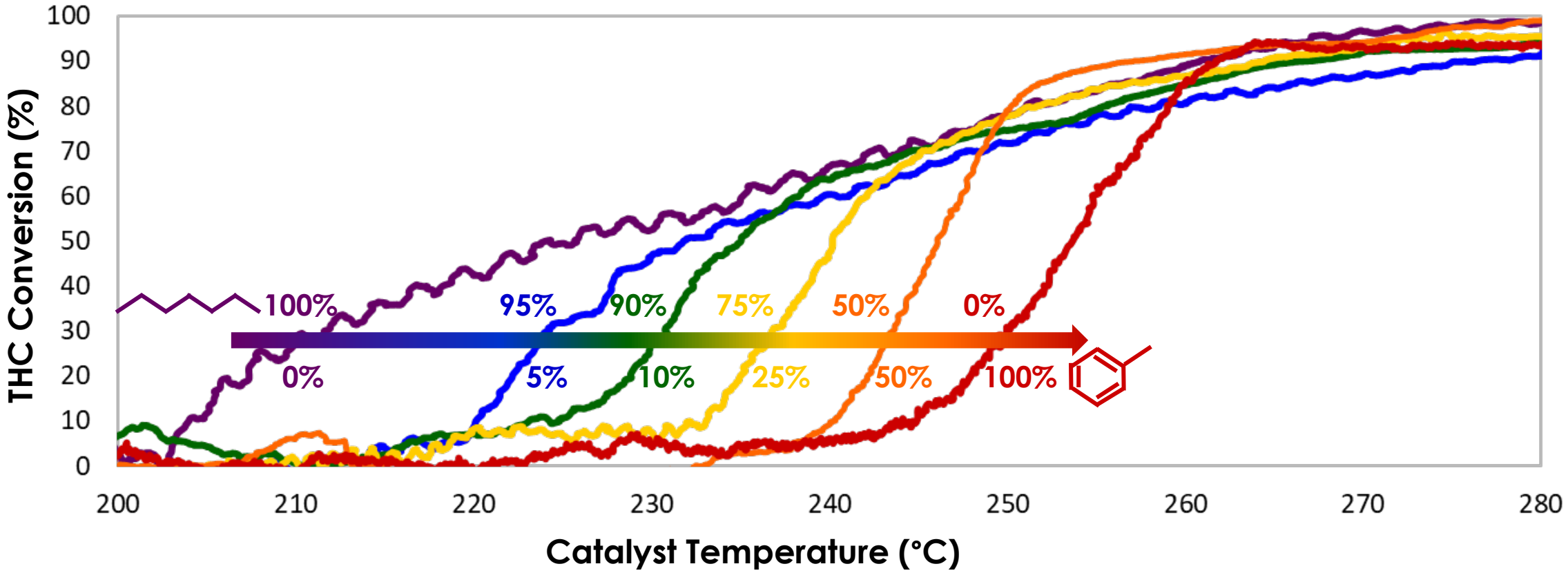
# At what blend level do aromatics start dominating the light-off behavior of the overall fuel blend?



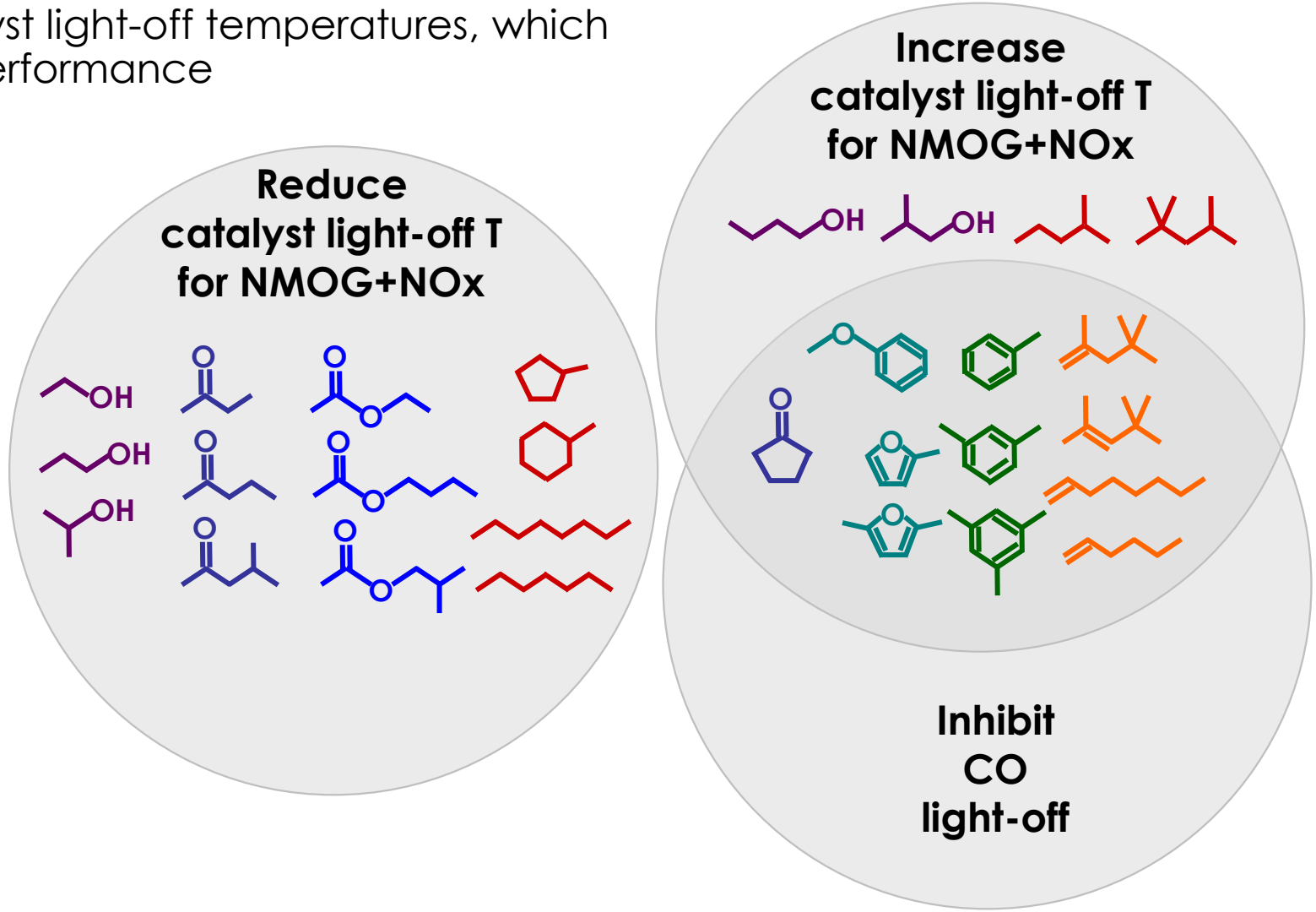

- Catalyst light-off is a nonlinear function of toluene blend level – reducing toluene content by half results in a ~8 °C drop in light-off temperature
- ***Taking advantage of fuel constituents with higher catalytic reactivities to improve catalyst light-off will require reducing the aromatic content of the fuel***




S. Sinha Majumdar and J. A. Pihl, Energy & Fuels, *Accepted*, 2020.

# Summary of fuel chemistry effects on stoichiometric TWC light-off

- Fuel composition impacts catalyst light-off temperatures, which will affect cold start emissions performance
- NOx performance generally tracks NMOG conversion since NMOG reduces NOx over the TWC
- Aromatics & alkenes inhibit TWC activity for other species
- For blends containing ≤ 30% bioblendstocks in a conventional petroleum-based BOB, the light-off behavior is controlled by the aromatic content of the BOB
- Taking advantage of the higher catalytic reactivity of some bioblendstocks would require reducing the aromatic content of the fuel





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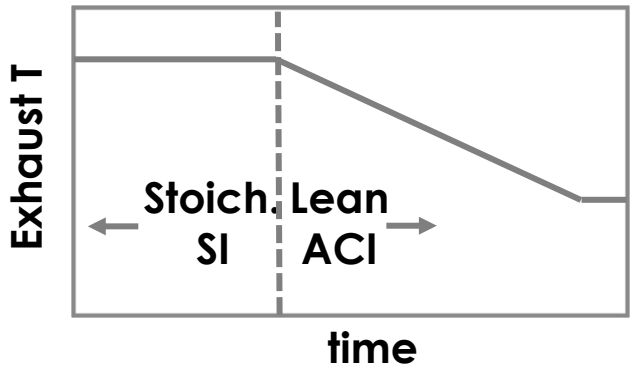
# Multimode combustion strategies may introduce additional emissions control challenges due to low temperature lean exhaust

- Multimode gasoline engines could reduce drive cycle fuel consumption
  - use stoichiometric SI combustion at high loads for power density
  - use lean spark ignition (SI) or advanced compression ignition (ACI) combustion strategies at low loads to increase efficiency
- Multimode engines would create a new set of emissions challenges
  - High load SI operation: emissions handled by TWC
  - Cold start: use stoich. combustion for catalyst heating, so all prior conclusions regarding TWCs would still be relevant
  - Mode switch from high load stoichiometric SI operation to low load lean SI or ACI operation:
    - Exhaust composition abruptly changes from stoich. to lean
    - Exhaust temperature rapidly drops, perhaps below typical TWC operating temperatures resulting in catalyst "light-down"
- Additional synthetic exhaust flow reactor experiments were conducted to quantify the effects of fuel chemistry on TWC performance under lean light-down conditions

| Synthetic Exhaust | | |
|---|---|---|
| | Stoich. | 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% |
| $O_2$ | ~0.7% | 12% |

**Light-down (stoich. SI to ACI)**





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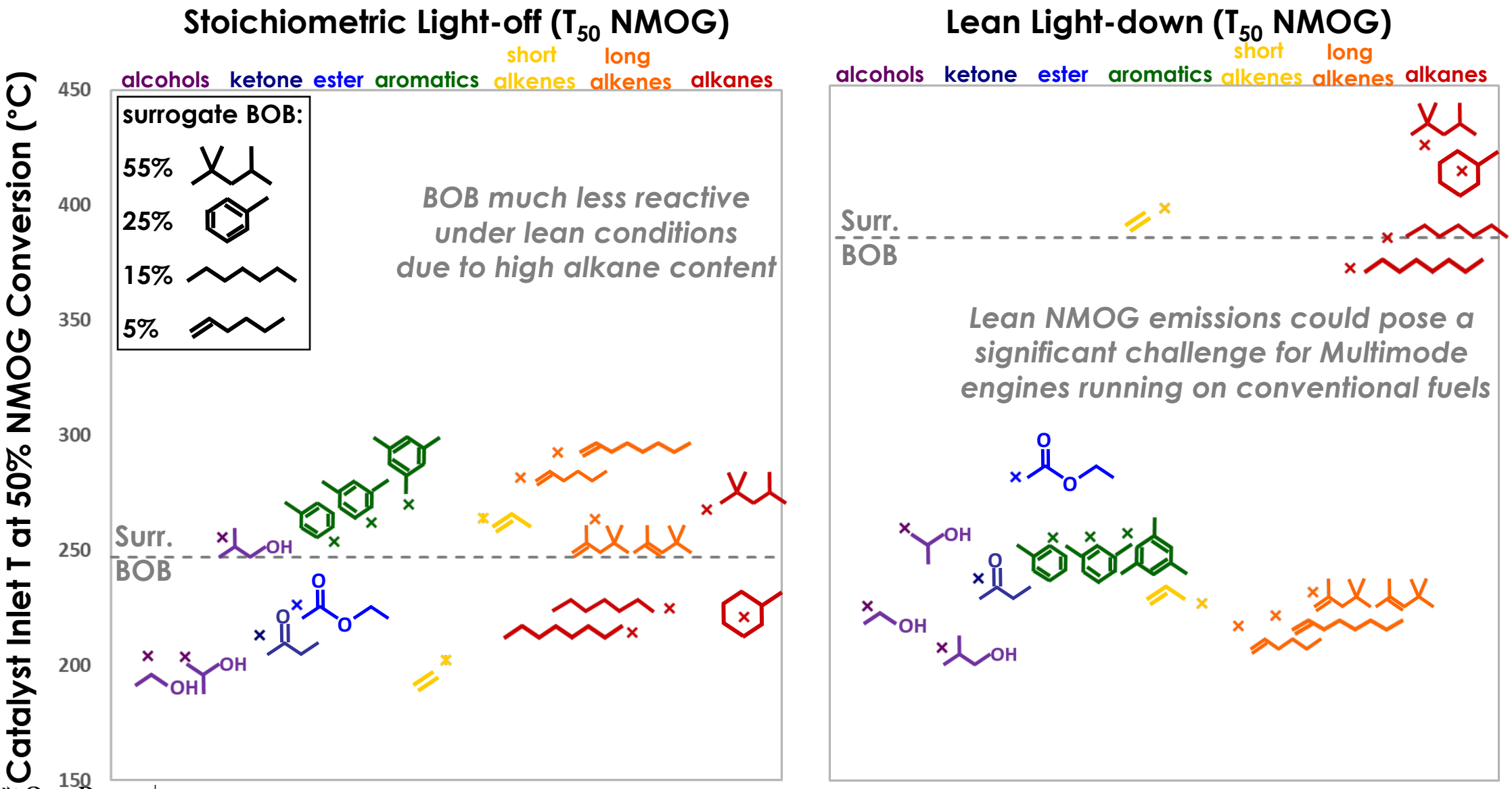
# Lean exhaust alters the relationships between chemical structure and reactivity





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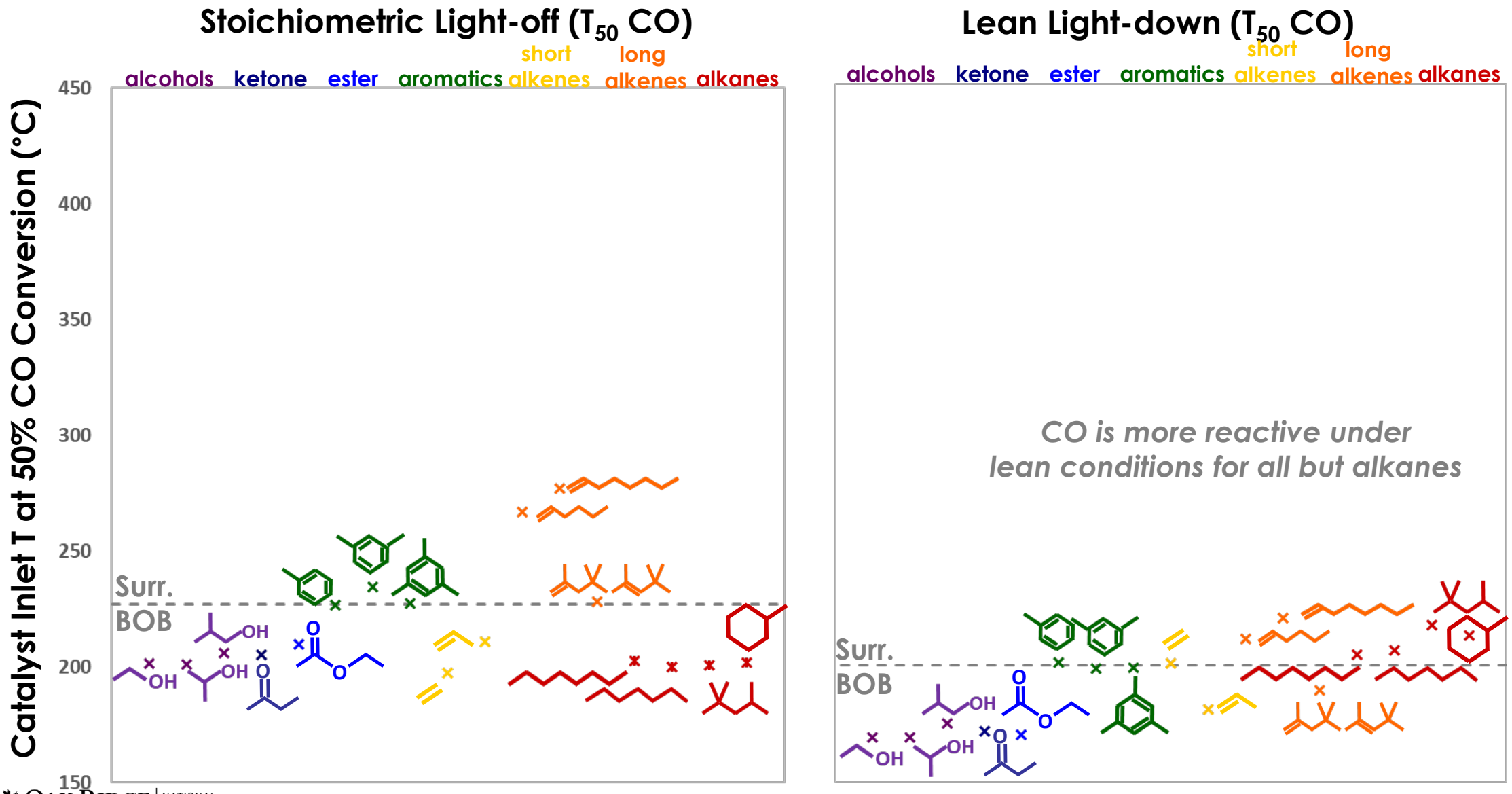
# Minimal differences in CO reactivity with fuel chemical structure under lean conditions





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# Exhaust composition impacts on reactivity trends are likely due to changes in the surface chemistry of the Pd active sites

- Shifting from stoichiometric to lean exhaust conditions changes TWC reactivity trends
- ***Hypothesis: Pd active site chemistry is altered by $O_2$ concentration, changing the impact of adsorption properties of organic species in the exhaust mixture.***
  - **Stoichiometric conditions:**
    - Aromatics and alkenes form strongly adsorbed intermediates that do not react further at low temperatures
    - Strongly adsorbed intermediates prevent CO and other organics from accessing active sites, thereby inhibiting light-off
    - In the absence of strongly adsorbed intermediates, other organic species can effectively adsorb and react at low temperatures
  - **Lean conditions:**
    - Aromatics and alkenes adsorb strongly to the catalyst surface and undergo complete oxidation, leaving active sites free to adsorb other species
    - Species that do not strongly adsorb, such as alkanes, have much lower reactivity
- ***Impacts on emissions control devices should be considered when developing novel fuels for higher efficiency and reduced $CO_2$ emissions***


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# Thank You!

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