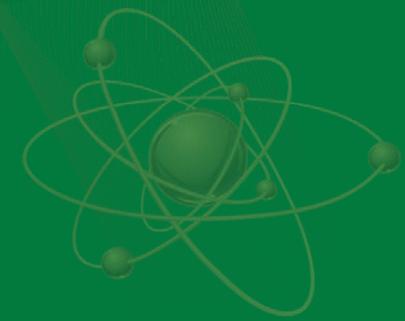


Reactivity of novel high-performance fuels on Three-Way Catalysts for Control of SI Engine Emissions

Sreshtha Sinha Majumdar, Josh Pihl,
Todd Toops

*Fuels, Engines, and Emissions Research
National Transportation Research Center
Oak Ridge National Laboratory*

September 18th, 2018



Acknowledgments



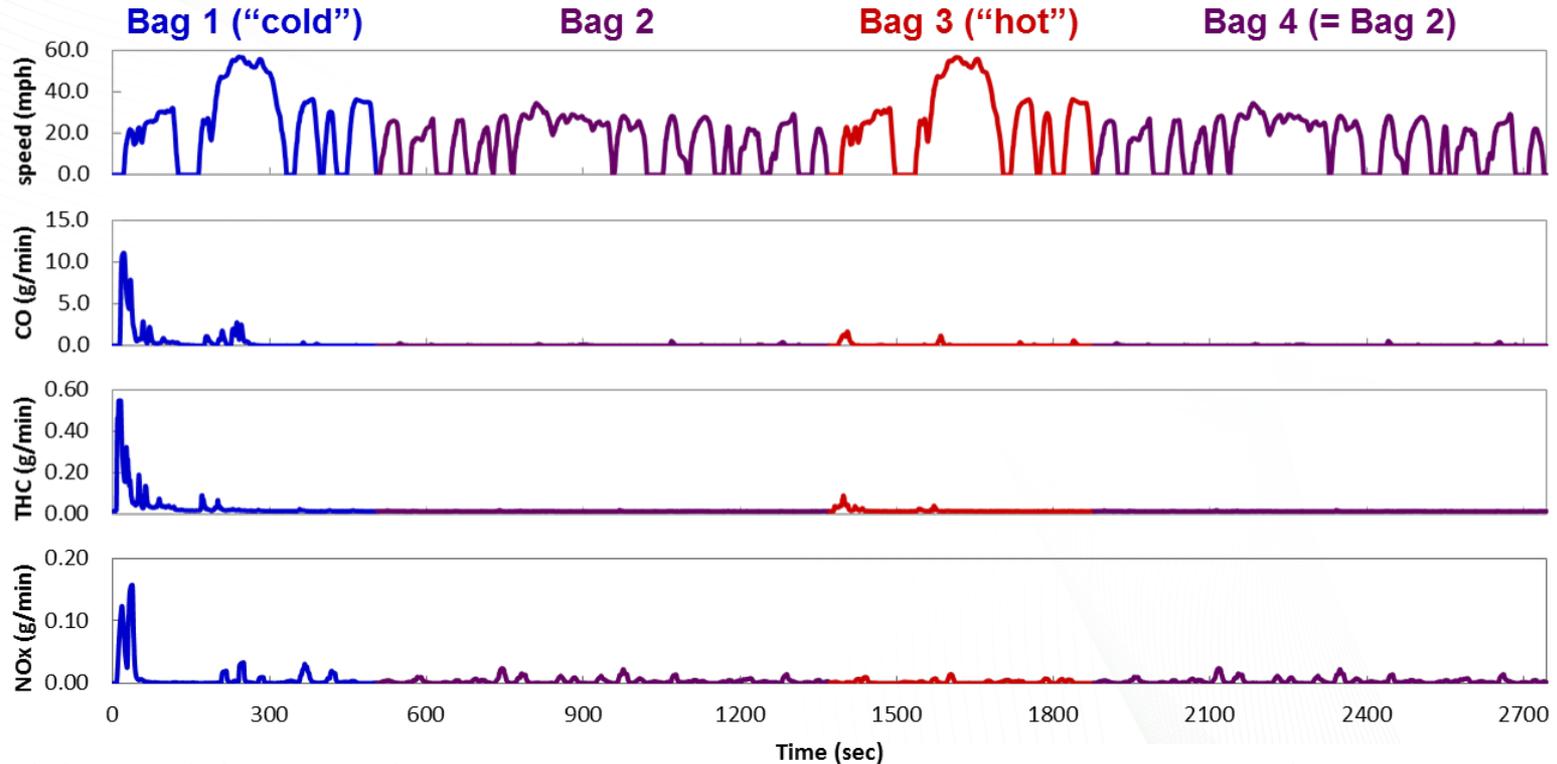
- **Funding from the Department of Energy Vehicle Technologies Office**
 - *Kevin Stork, Gurpreet Singh, Mike Weismiller*

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

- **Assistance, guidance, and data from coworkers in ORNL Fuels, Engines, and Emissions Research**
 - *Will Brookshear, John Thomas, Brian West, Shean Huff*

Introduction

- DOE-funded Co-Optimization of Fuels and Engines Initiative aims to simultaneously develop high performance fuels and advanced high efficiency engines to reduce petroleum consumption
- Three-way catalysts (TWCs) are extremely effective at controlling emissions from SI engines when hot

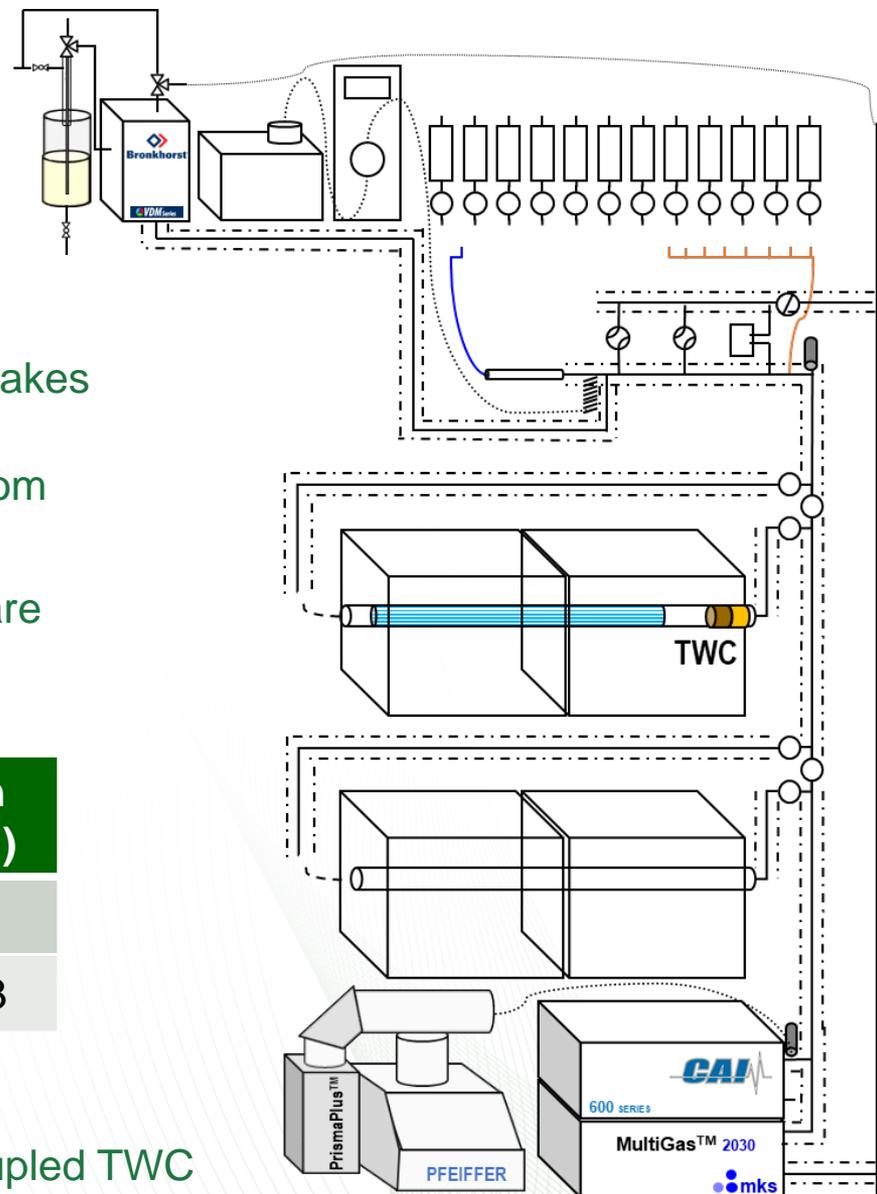


- Most CO, NMOG, and NO_x emissions occur during cold start before TWC achieves "light-off" temperature
- Cold start performance is critical for compliance with the U.S. EPA emissions regulations, and will depend on fuel composition
- To achieve commercialization, advanced engines running on novel fuels must still meet the stringent emissions regulations

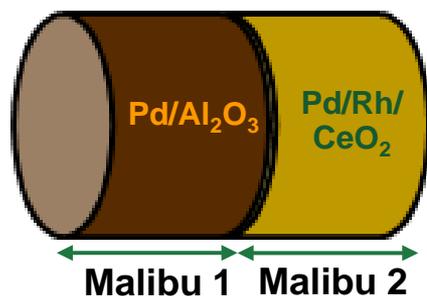
Approach

Synthetic Exhaust Flow Reactor Configuration

- Vapor delivery module used to introduce liquid hydrocarbons into the feed gas-stream:
 - most published emissions control work uses gaseous HC species for ease of operation
 - extensive range of liquid fuel components makes this study unique
- FID, FTIR and MS used to analyze exit stream from the reactor
- Automated reactor controlled by LabVIEW software



Catalyst Details

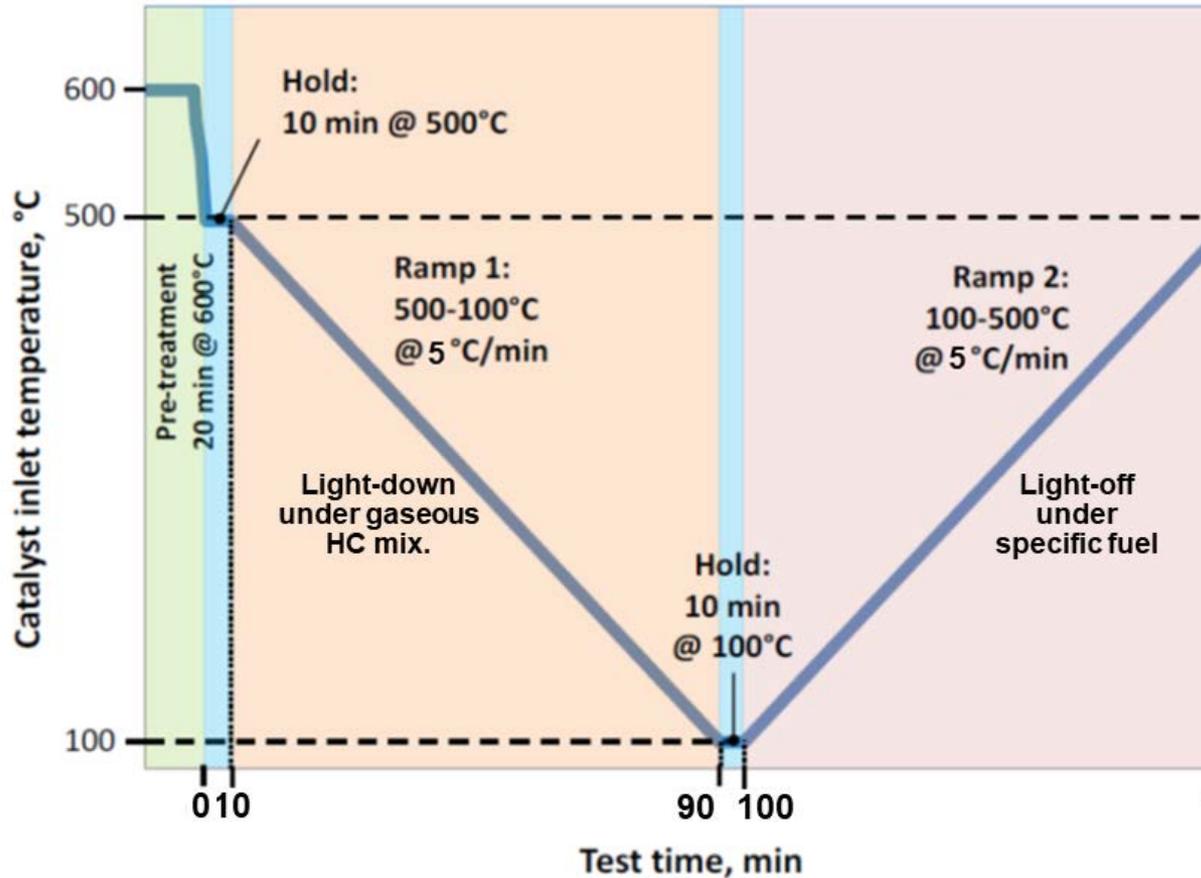


TWC	Pd (g/l)	Rh (g/l)
Malibu 1	7.3	0
Malibu 2	1.1	0.3

- Commercial three-way catalyst:
MY2009 Chevy Malibu SULEV/PZEV close-coupled TWC
- Dual-zone: Pd-rich front end and Pd/Rh/ ceria back end

Catalyst Aging and Performance Testing

Reaction Profile



Reaction Conditions:

Catalyst: Malibu 1+2
100 C-500 C
30000 hr⁻¹

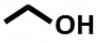
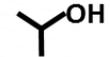
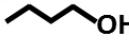
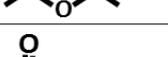
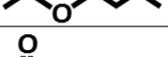
O₂ varies
13 % H₂O
13% CO₂
1670 ppm H₂

5000 ppm CO
1000 ppm NO
3000 ppm C₁ HC

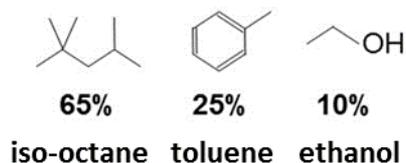
- Catalyst aging and evaluation experiments conducted according to the U.S. DRIVE Low-temperature aftertreatment test protocol (LTAT)*
- Aged 50 h @ 800 C
 - neutral/rich/lean cycles
- Light-down under gaseous hydrocarbon mix. (ethene, propene, propane) to ensure:
 - consistent initial state of the catalyst before fuel light-off
 - TWC is not aging over time
- Full synthetic exhaust mixture has been used for these experiments (not commonly found in literature)
- 3000 ppm HC (C₁ basis) constant between the runs
- The reaction profile is repeated thrice per fuel to ensure reproducibility of the results

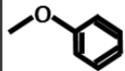
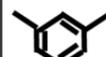
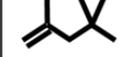
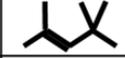
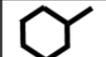
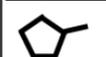
*http://cleers.org/wp-content/uploads/2015_LTAT-Oxidation-Catalyst-Characterization-Protocol.pdf

Fuel components used in investigations include a wide range of functional groups

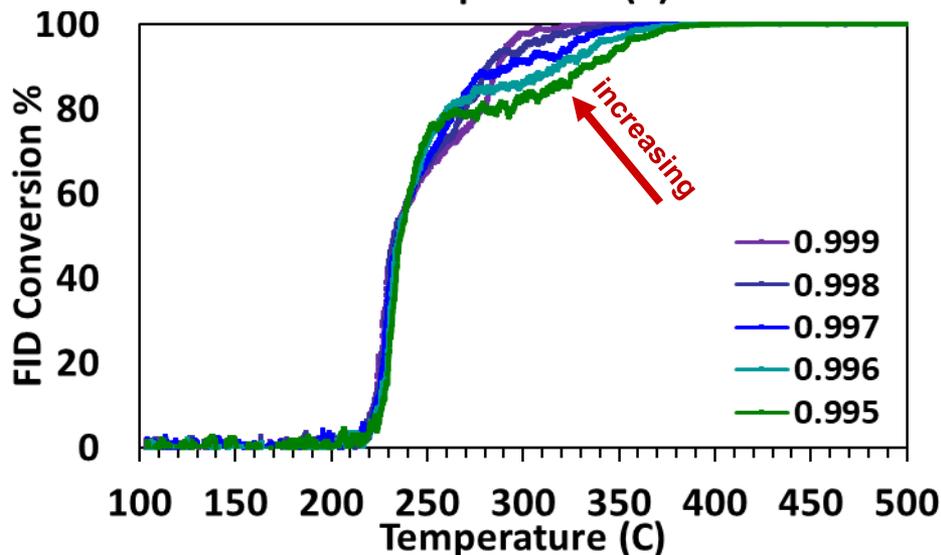
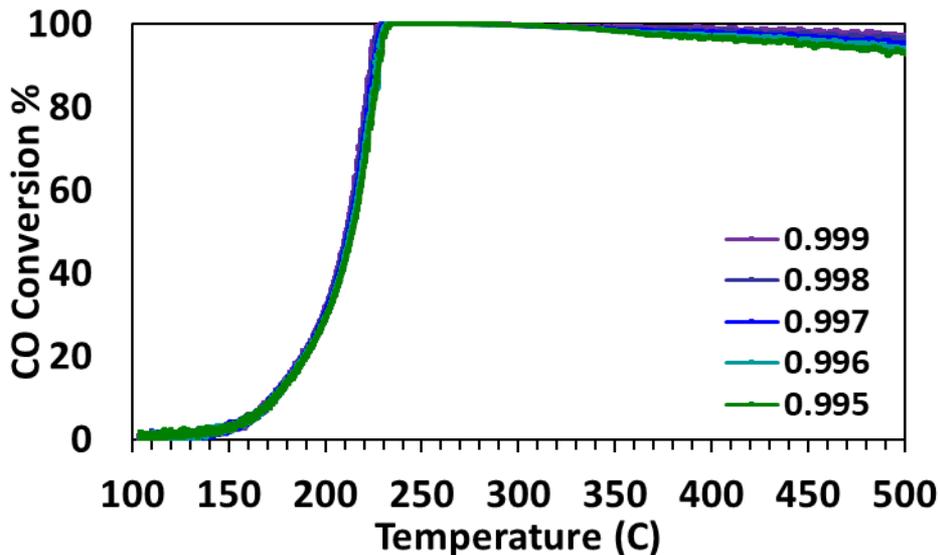
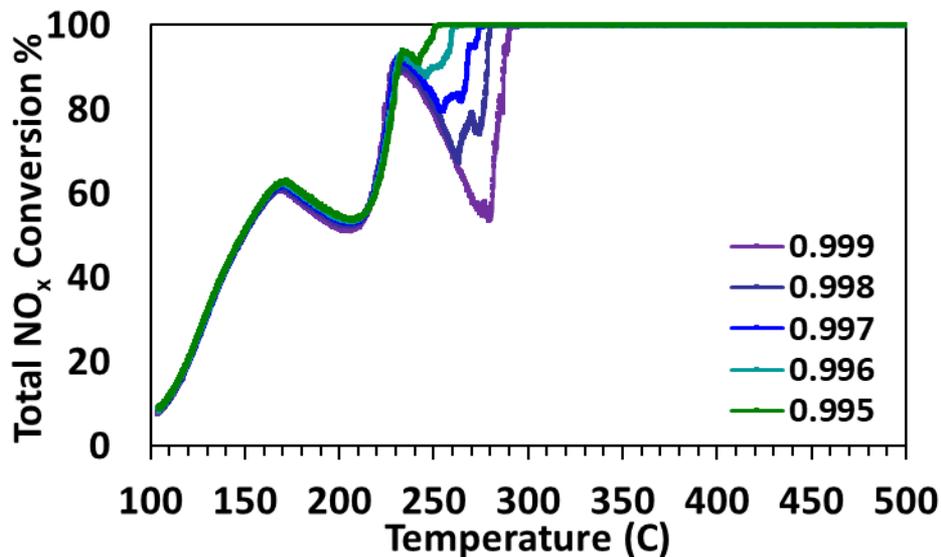
Functional Group	Structure
Alcohols	 ethanol
	 n-propanol
	 iso-propanol
	 n-butanol
	 iso-butanol
Ketones	 2-butanone
	 2-pentanone
	 cyclopentanone
	 methylisobutylketone
	Esters
 butyl acetate	
 Iso-butyl acetate	

E10 Surrogate



Functional Group	Structure
Aromatic Ethers	 anisole
	 2,5-dimethylfuran
	 2-methylfuran
Non-oxygenated aromatic hydrocarbons	 toluene
	 m-xylene
	 mesitylene
Alkenes	 ethene
	 propene
	 1-hexene
	 1-octene
	 diisobutylene
	 diisobutylene
Alkanes	 n-heptane
	 n-octane
	 2-methylpentane
	 iso-octane
	 methylcyclohexane
	 methylcyclopentane

Lambda sweep 0.999-0.995 with E10 surrogate fuel



E10 surrogate fuel composition

65% $i\text{-C}_8\text{H}_{18}$
 25% $\text{C}_6\text{H}_5\text{CH}_3$
 10% $\text{CH}_3\text{CH}_2\text{OH}$

Catalyst: Malibu 1+2
 100 C-500 C
 $\lambda = 0.999\text{-}0.995$

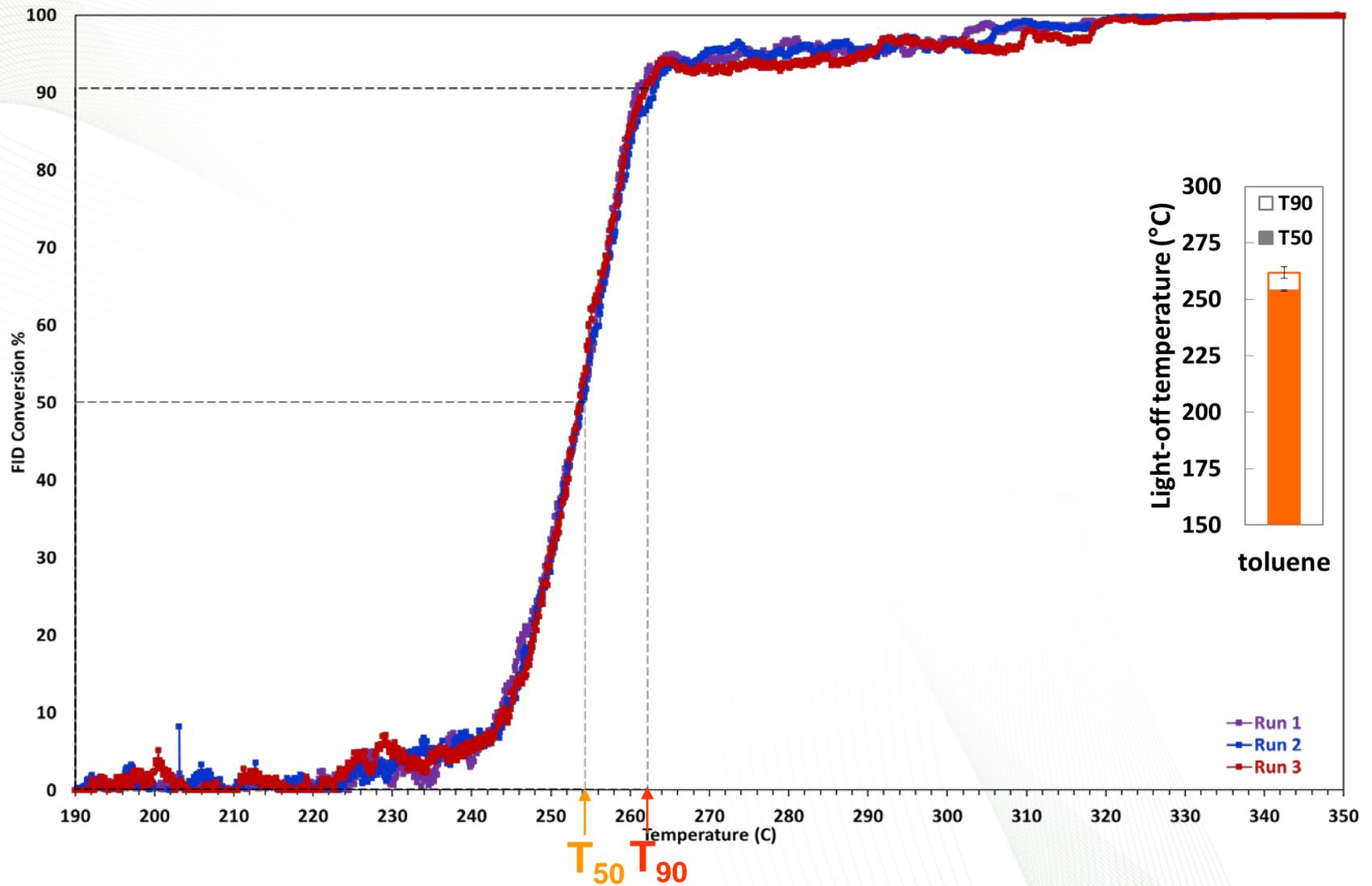
Reaction Conditions:

O_2 varies
 13% H_2O
 13% CO_2
 1670 ppm H_2
 5000 ppm CO
 1000 ppm NO
 3000 ppm C_1 HC

• λ was adjusted by varying the O_2 conc.

7 • $\lambda = 0.999$ was selected for further light-off experiments

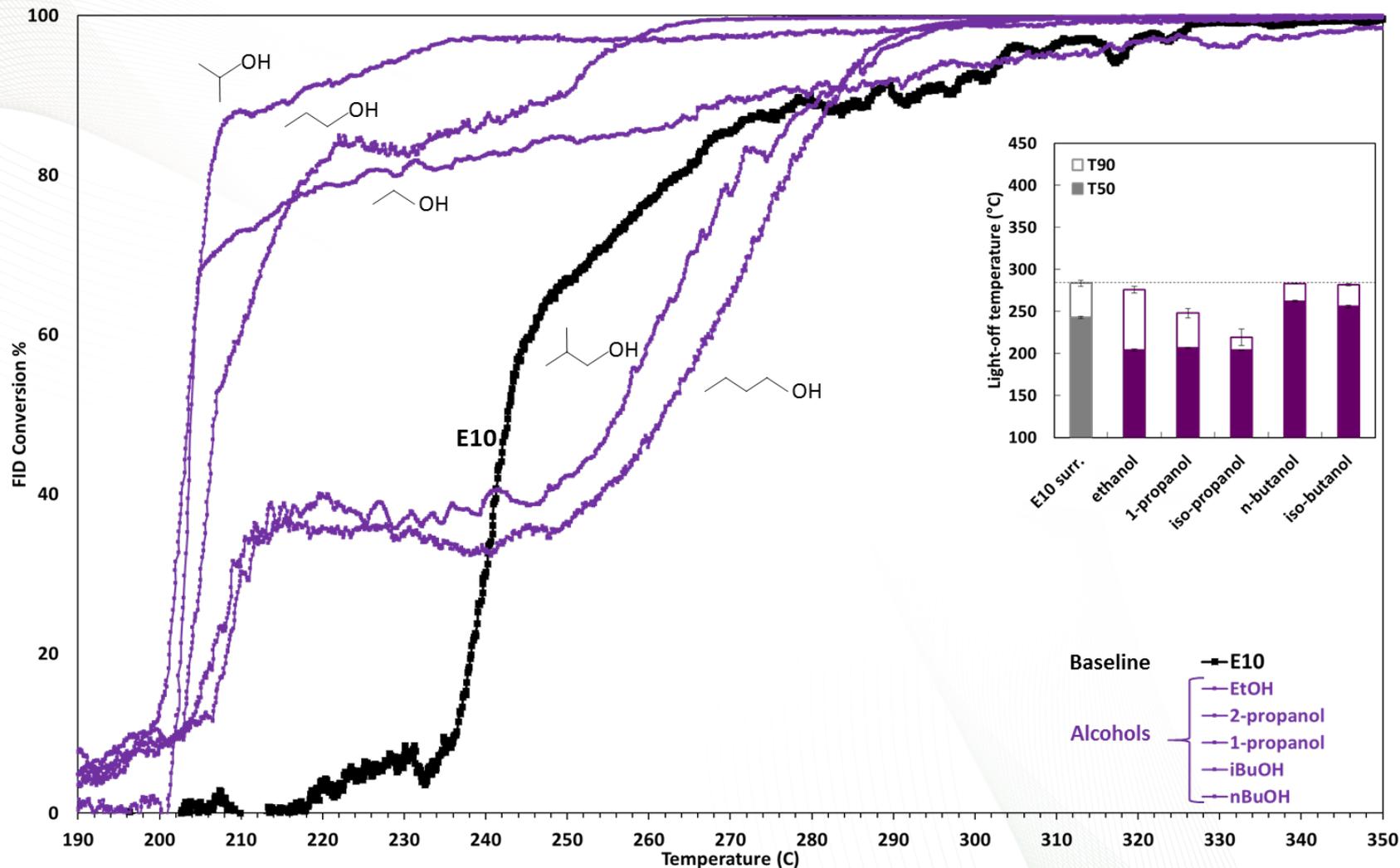
Reproducibility studies: Toluene



- Light-off experiment for each fuel was conducted three times to ensure reproducible results
- Consistent results with small error bars were achieved for each fuel under consideration

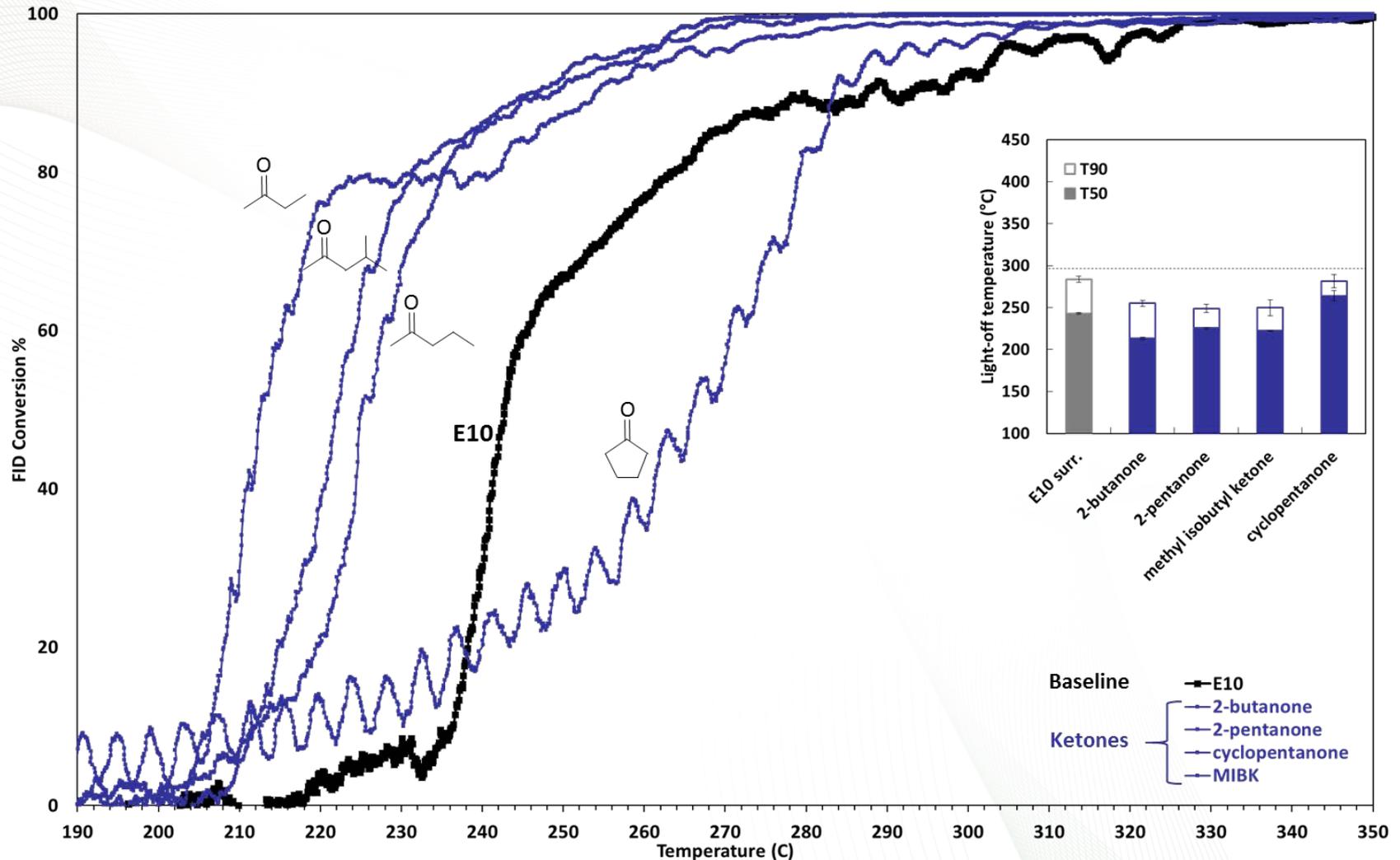
Total HC conversion comparisons based on functional groups

Alcohols



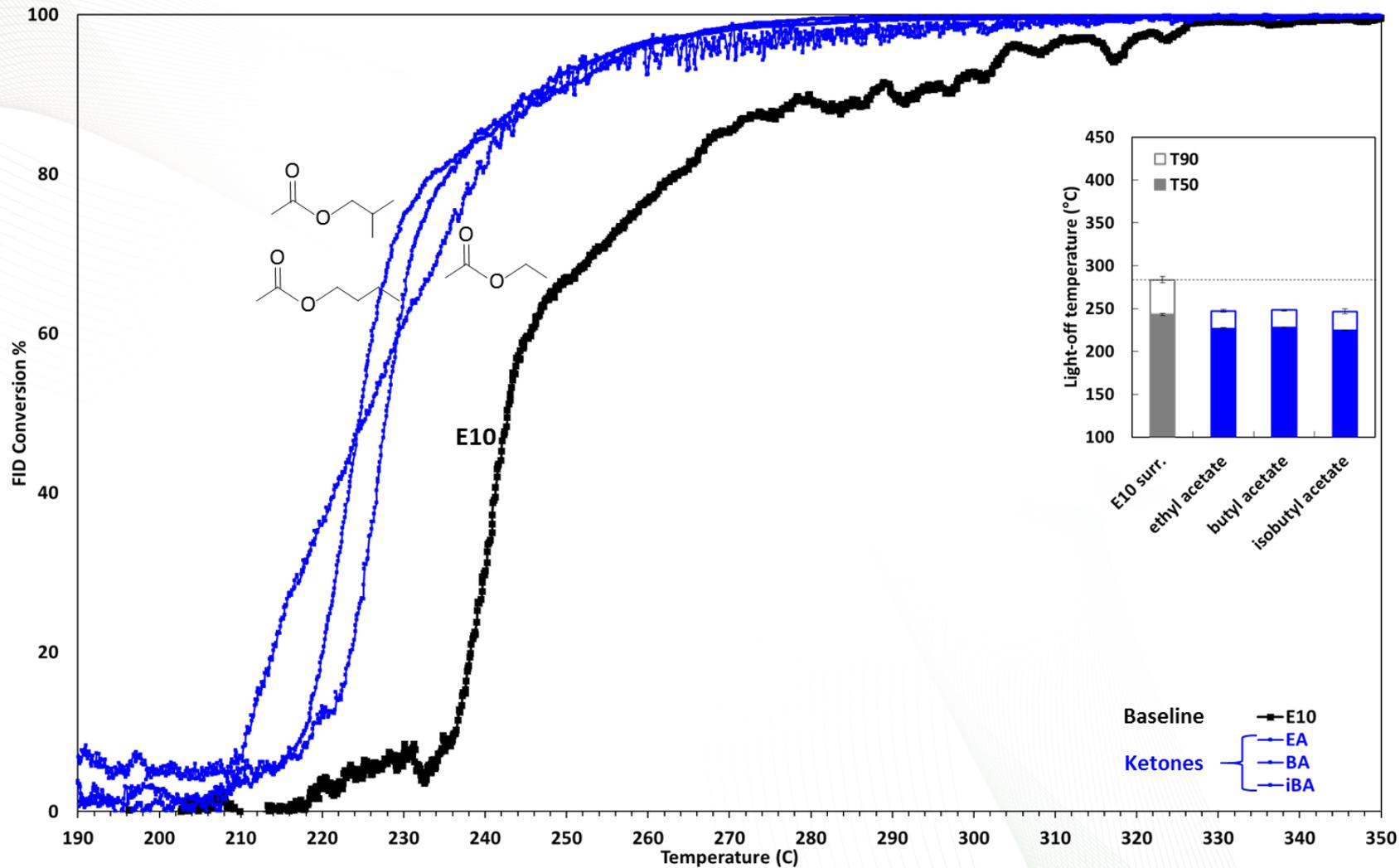
- Lowest LoT among all the fuels we have looked at
- For alcohols with 2 or 3 C atoms, T_{50} less than that of E10 surrogate
- No significant difference between primary versus secondary alcohols

Ketones



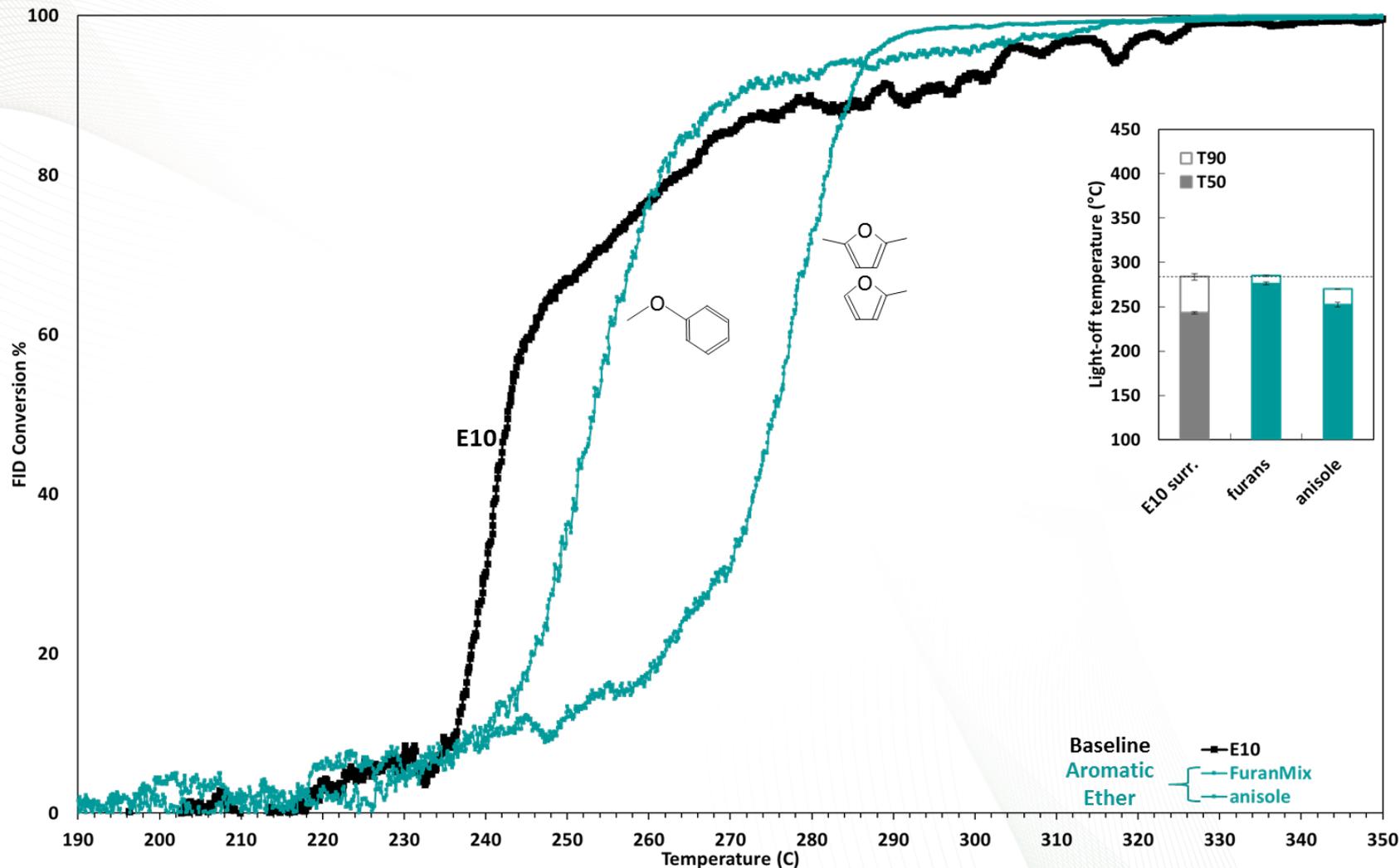
- Linear ketone T_{50} less than that of E10 surrogate: increase in no. of C atoms → higher LoT
- Ketone structure: cyclic vs. linear affects light-off curve

Esters



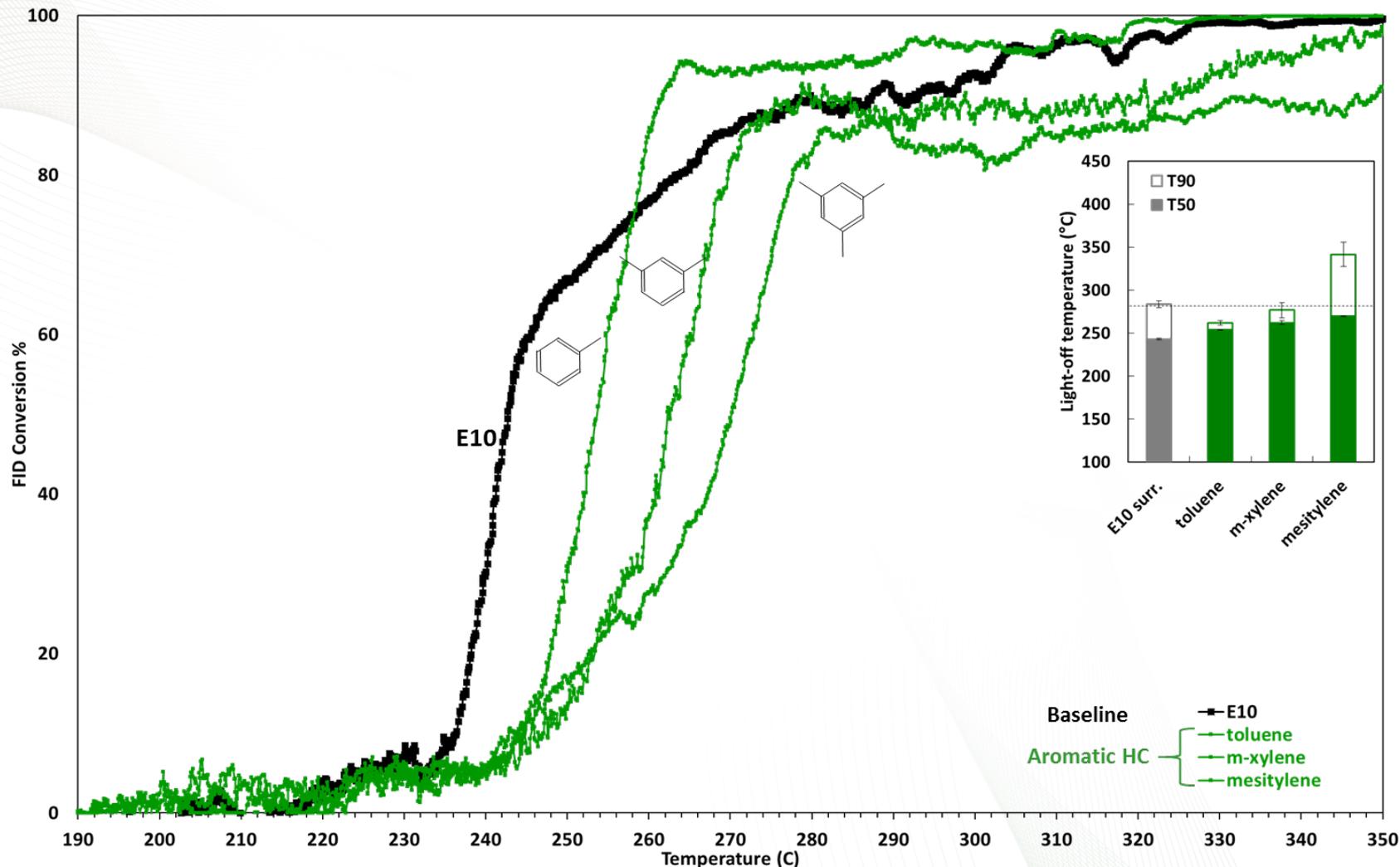
➤ Ester T_{50} less than that of E10 surrogate

Aromatic Ether



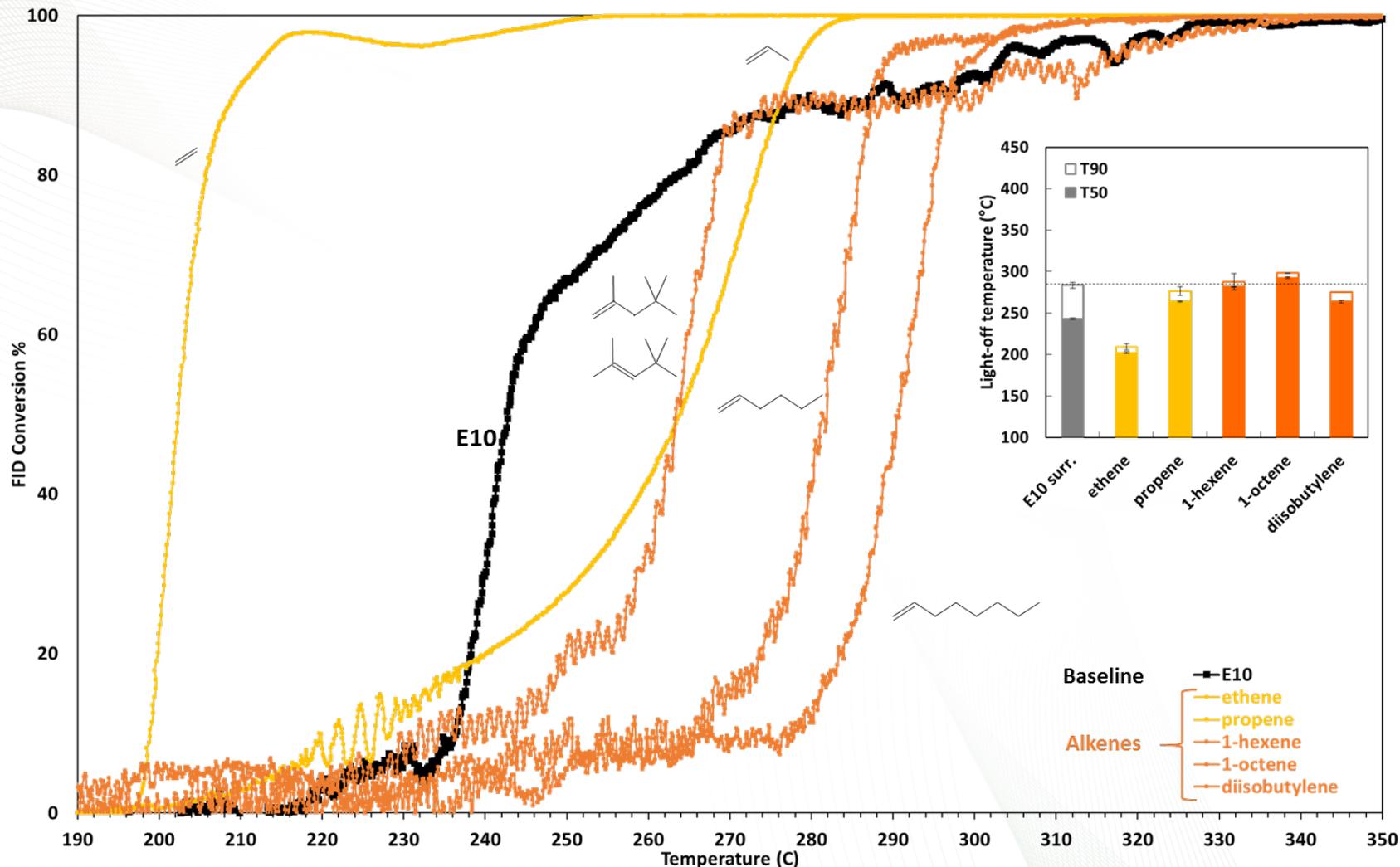
- Aromatic ethers light-off after E10 surrogate fuel
- Oxygenated fuels have a lower LoT than E10 except for aromatic ethers and cycloketone
- Aromatic ethers behave more like other non-oxygenated aromatic HCs than oxygenated fuels

Non-oxygenated aromatic HC



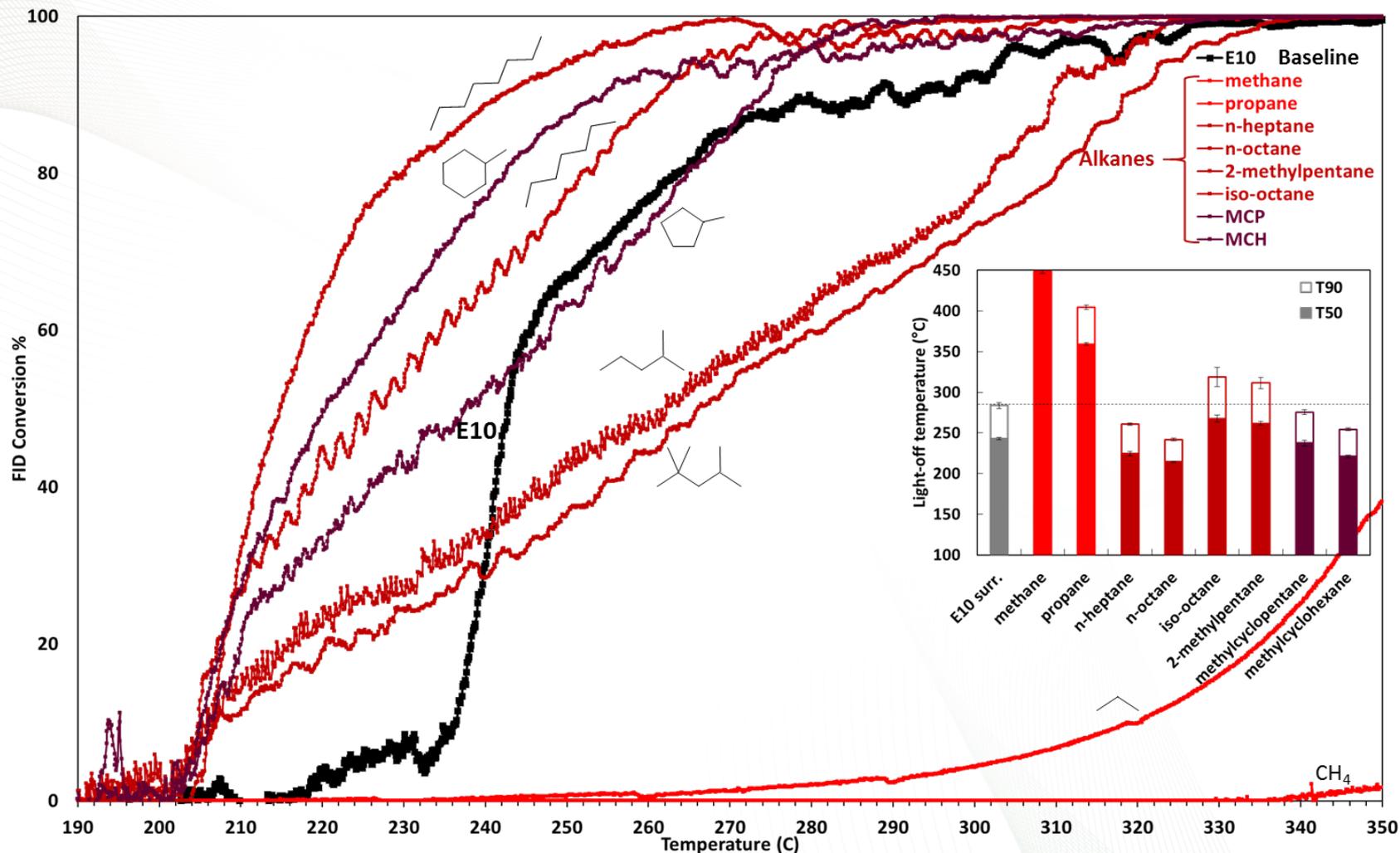
- Non-oxygenated aromatic HCs light-off after E10 surrogate fuel
- Higher degree of methyl substitution pushes T_{50} to higher temperatures
- Increase in methyl substitution lowers the ionization potential of the hydrocarbon → strongly-adsorbing stable intermediates → higher LoT

Alkenes



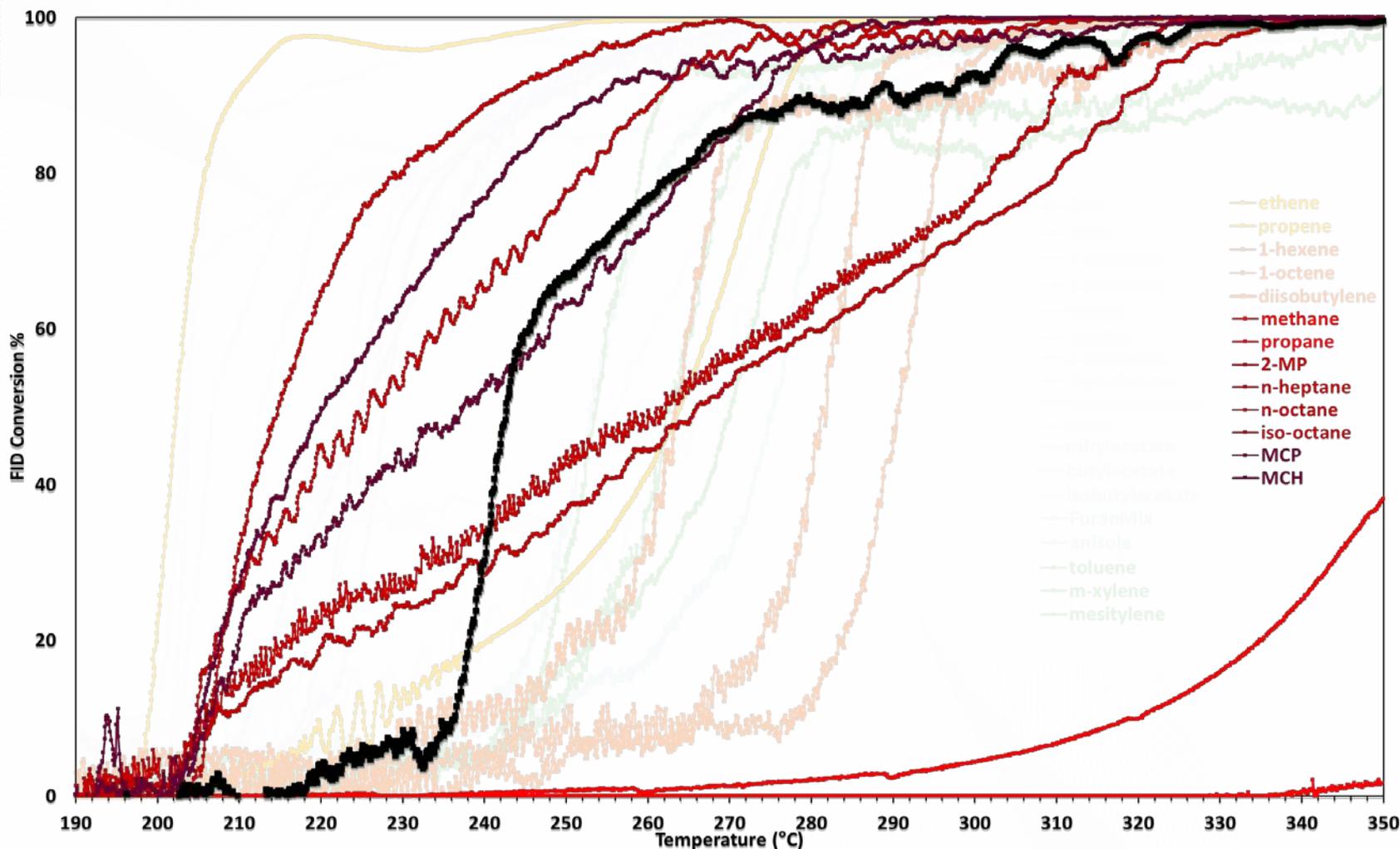
- Short-chain alkenes light off at lower temperature than long-chain alkenes
- On H-abstraction → resonance stabilized intermediates formed
- Increase in no. of C atoms in linear alkene → more stable intermediate complexes formed → higher LoT

Alkanes



- Short-chain alkane light-off at higher temperatures
- Long chain linear alkane lights off earlier than branched alkane with same no. of C atoms
- Cycloalkane lights off earlier although the difference is not much going from C₅ to C₆
- Linear alkane < cycloalkane < branched alkane < short-chain alkane

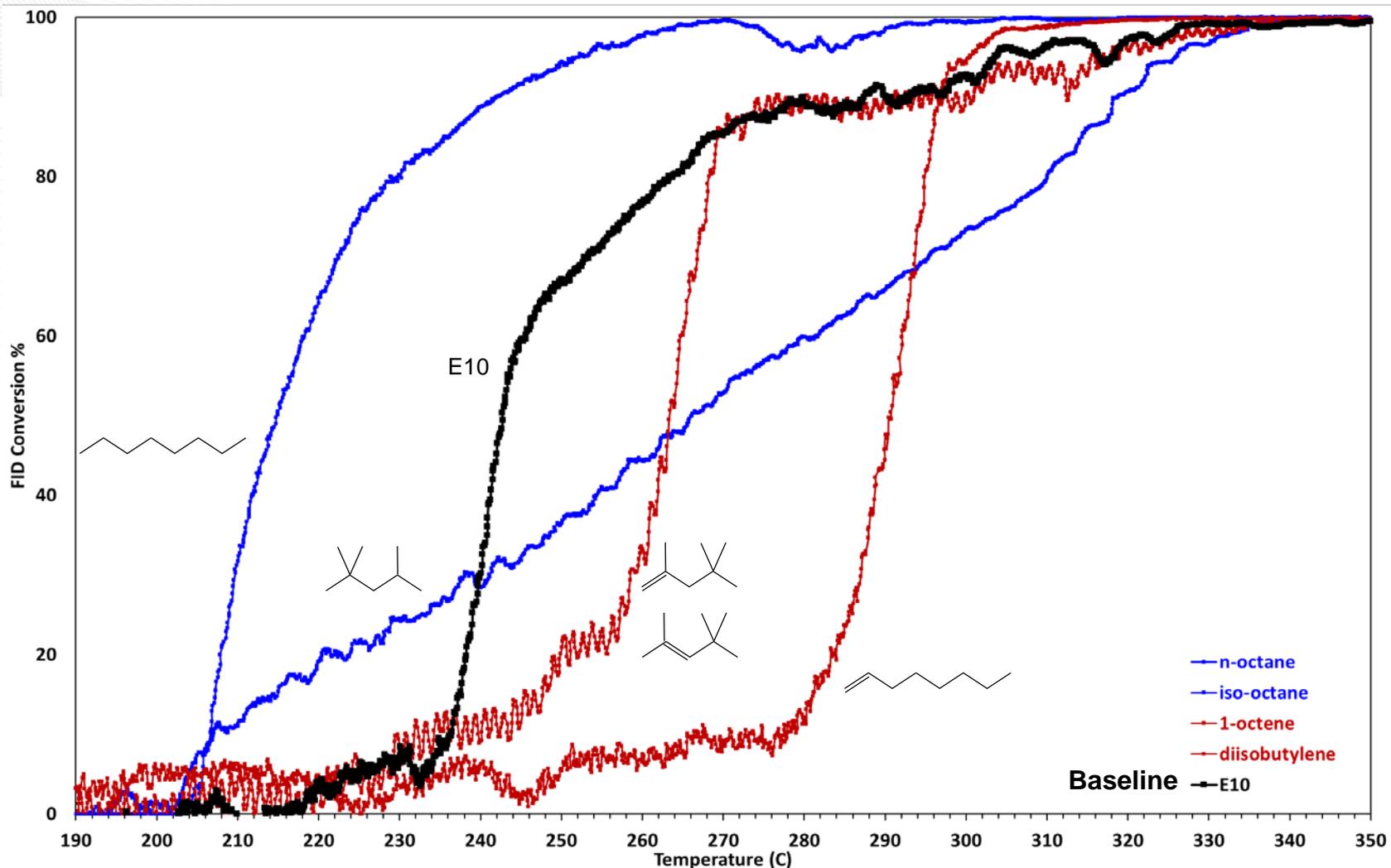
Comparison of light-off curves based on different functional groups



Overall, we observe the following trend in light-off temperatures:

C_2 , C_3 alcohols < linear, branched ketones < long-chain alkanes < esters, cycloalkanes < **E10 surrogate** < aromatic ethers, non-oxygenated aromatic hydrocarbons < C_{3+} alkenes < short-chain alkanes

Comparison between HC conversion of 8 C fuels



➤ Light-off temperature difference between 1-octane and 1-octene is large

➤ Opposite effect of branching:

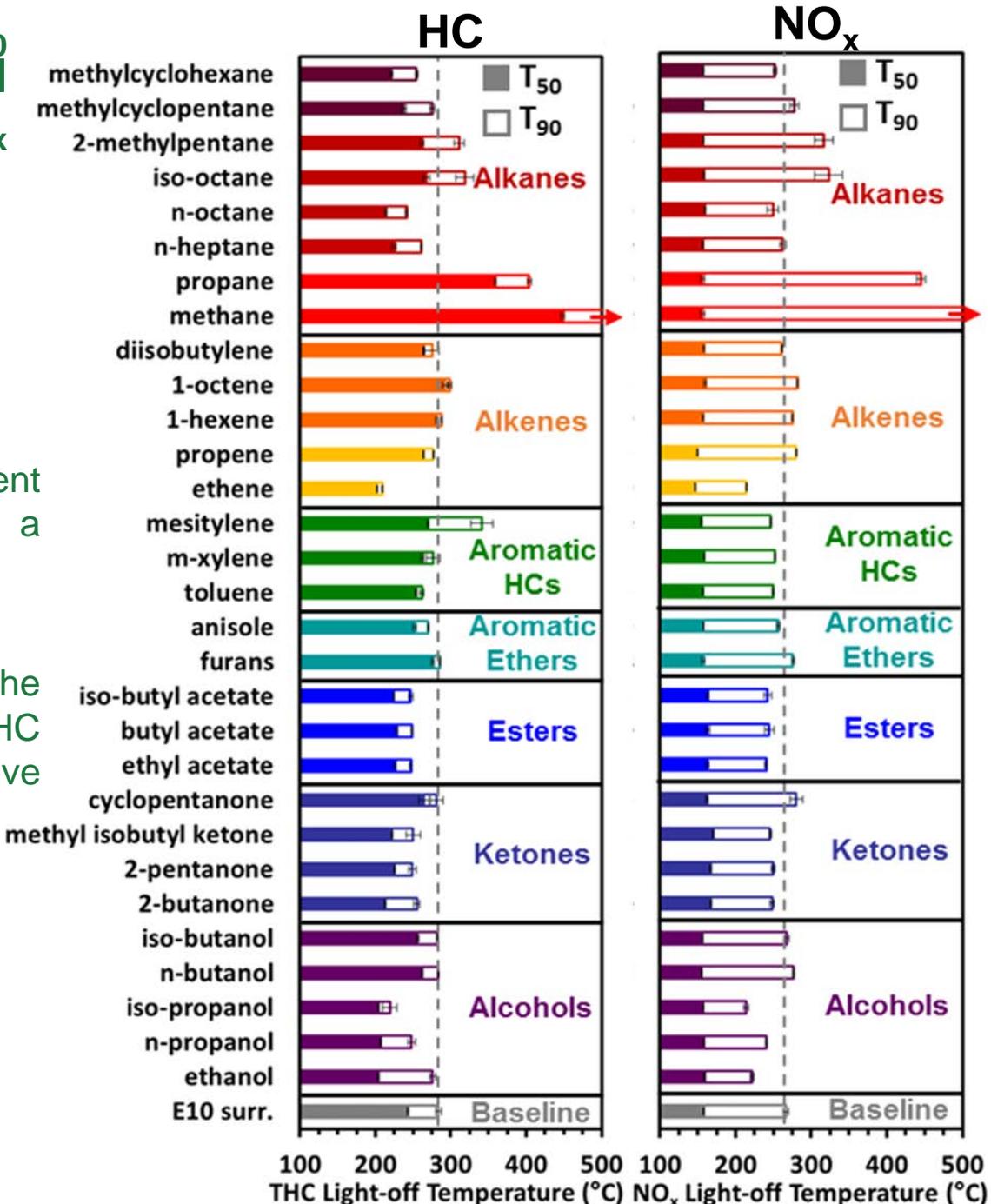
- Alkane: branching increases the light-off temperature
- Alkene: branching reduces the light-off temperature

Effect of HC fuel light-off on other regulated pollutants

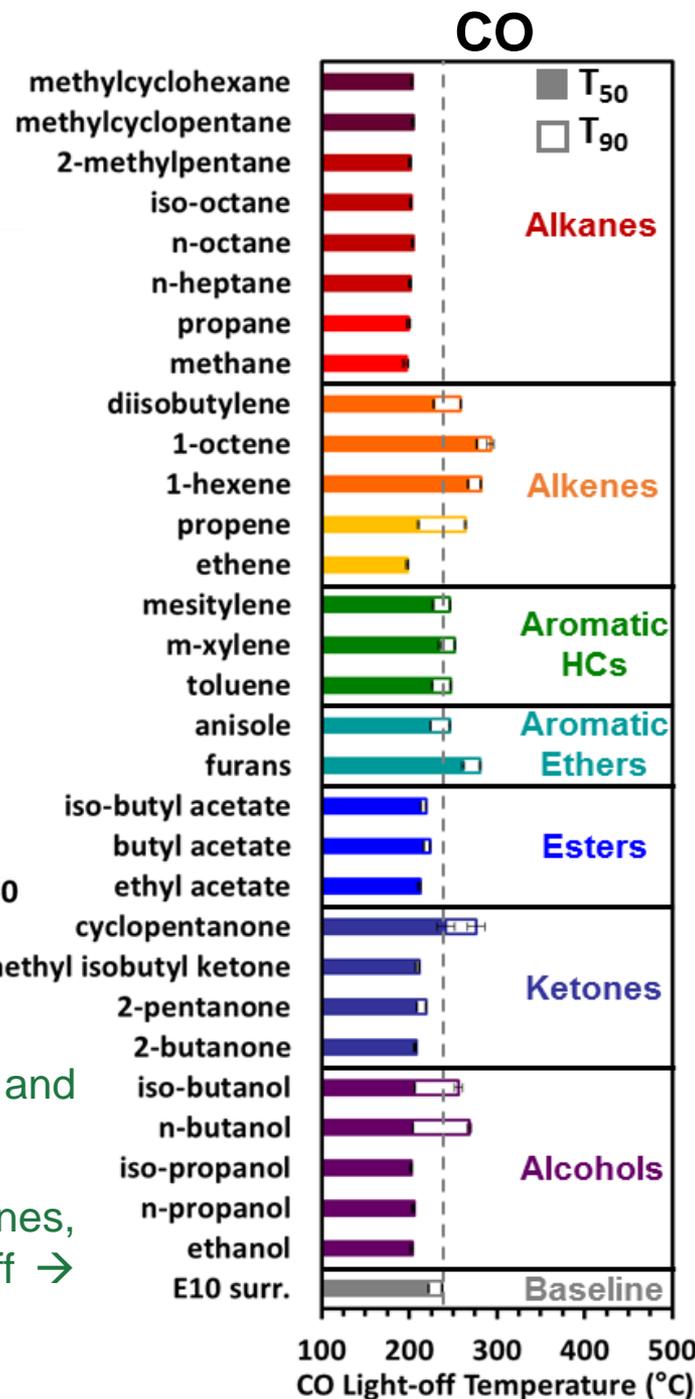
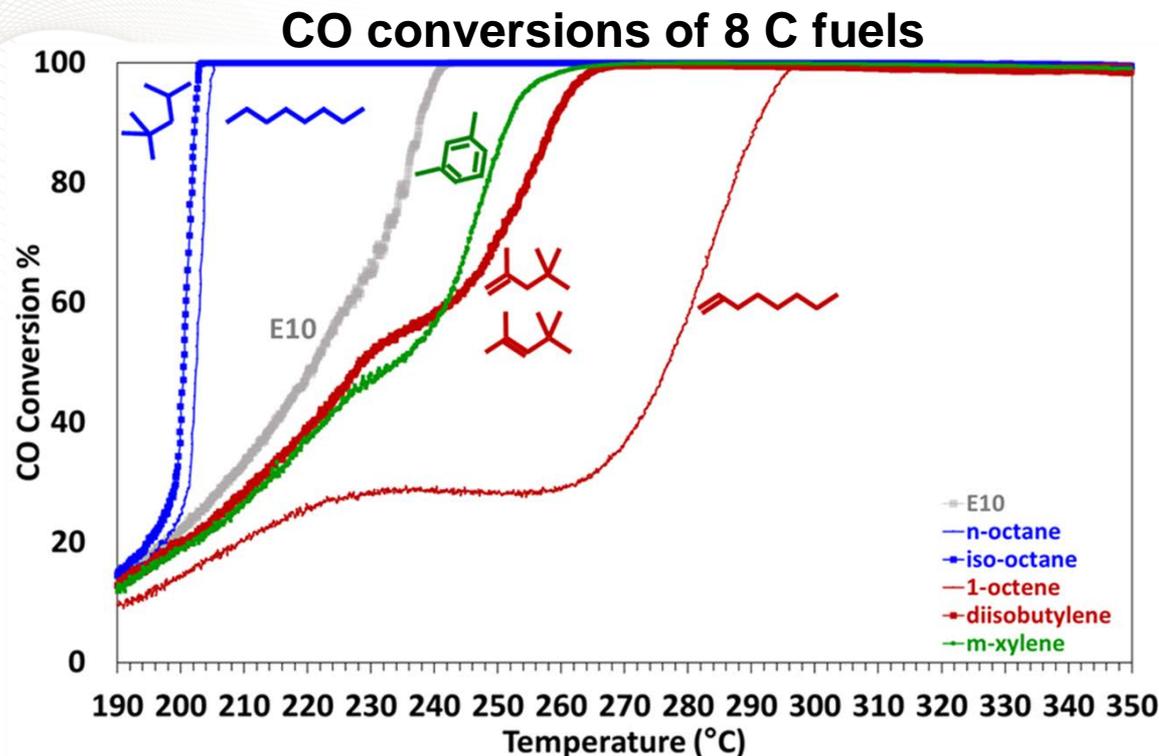


Comparison of T_{50} and T_{90} based on different functional groups: impact on total NO_x conversion

- NO_x T_{50} s comparable across different fuels because CO and H_2 reduce a significant fraction of NO_x
- NO_x T_{90} s follow trends similar to the HC conversions: at $\lambda = 1$, high HC conversions are required to achieve high NO_x conversions



Comparison of T_{50} and T_{90} based on different functional groups: impact on CO conversion



- Alcohols, straight-chain ketones, alkanes, esters and cycloalkanes have minimal effect on CO light-off
- Aromatic hydrocarbons, aromatic ethers, cyclic ketones, and alkenes have a significant impact on CO light-off → inhibition of CO oxidation until the HC reacts

Pure component light-off curves are only a starting point; next phase of investigation will focus on measuring the light-off temperatures for fuel blends

- Real-world fuels will be complex multicomponent blends
- Next phase of experiments and analysis will focus on light-off temperature measurement for fuel blends and their effects on CO and NO_x light-off

Conclusions

- Oxygenates light off early except aromatic ethers which behave more like the non-oxygenated aromatic hydrocarbons
- Light-off curves of the alkanes and alkenes spread over a wide range of temperatures and are strongly dependent on their structure:
 - For linear alkanes, increase in no. of C lowers the light-off temperature where as for linear alkenes we observe the opposite trend: increase in no. of C pushes the light-off to higher temperatures
- Overall trends in reactivity on the TWC:
C₂, C₃ alcohols > linear, branched ketones > long-chain alkanes > esters, cycloalkanes > **E10 surrogate** > aromatic ethers, non-oxygenated aromatic hydrocarbons > C₃₊ alkenes > short-chain alkanes
- CO and total NO_x conversion impacted depending on specific fuel light-off characteristics

Thank you!