

Low sooting tendencies of individual polyoxymethylene ethers as alternative diesel fuels

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Yale

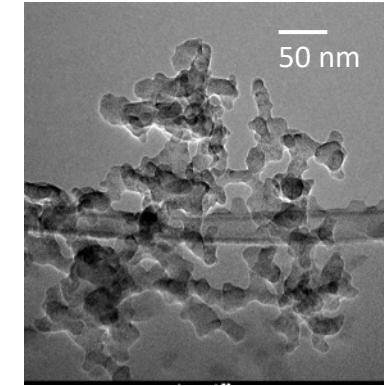


Colorado
State
University



Why should we care about soot emission?

- Soot emitted from combustion is the second largest source of climate change¹;
- Atmospheric particulates, including emitted soot, cause 4.6 million annual global deaths²;
- Soot has a short atmospheric lifetime (under 5.5 days³); therefore, emission reductions have an immediate effect;
- Biofuels usually have a lower tendency to form soot than their hydrocarbon counterparts due to the presence of oxygen atoms.



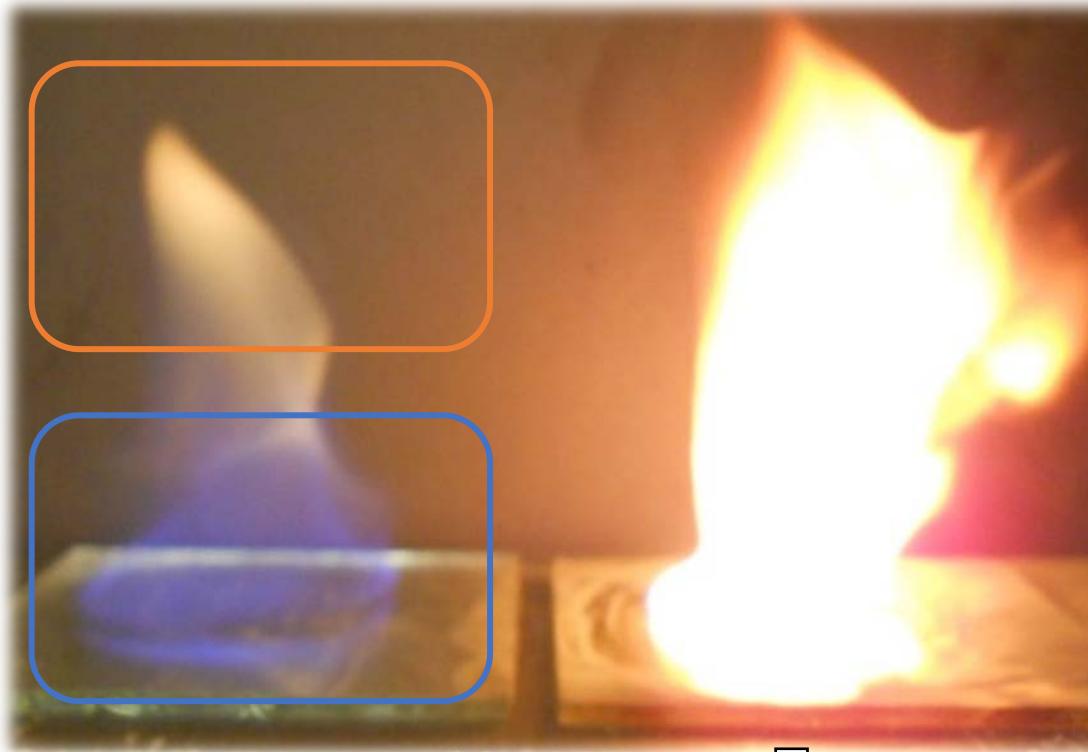
TEM image of soot particles from a flame (photo: J. Zhu)

Different fuels have different sooting tendencies

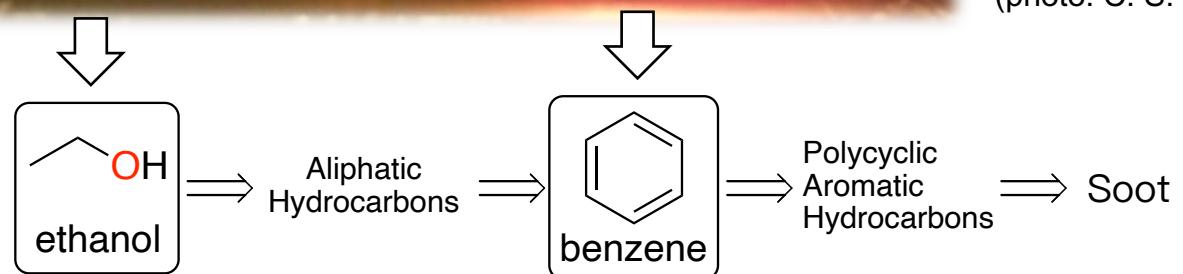
Blackbody radiation from soot particles



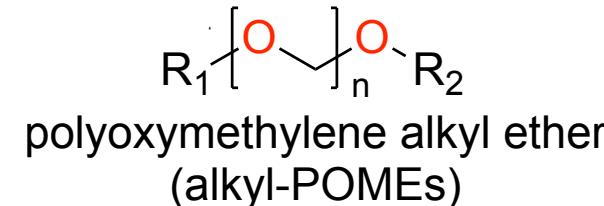
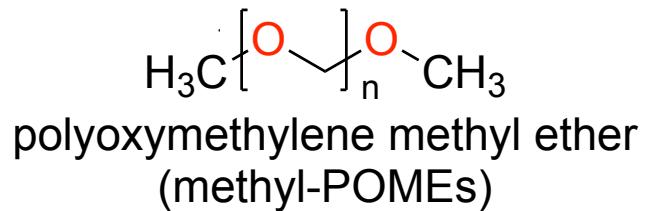
Chemiluminescence from intermediates CH^*



Pool fires of ethanol (left) and benzene (right)
(photo: C. S. McEnally)



Polyoxymethylene ethers (POMEs) as alternative diesel fuels



Biomass \rightarrow CH₃OH \rightarrow methyl-POMEs $\xrightarrow{\text{C2-C4 alcohol}}$ alkyl-POMEs¹



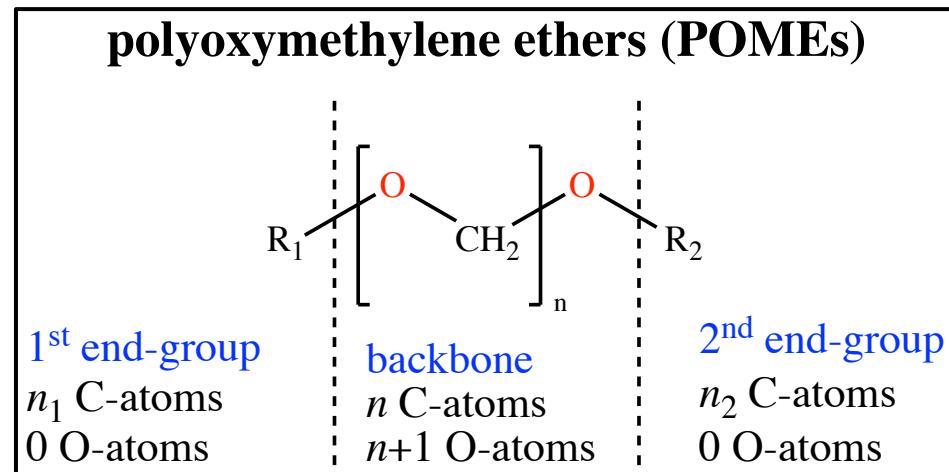
(photo: J. Zhu)

- Objectives:
 1. Quantify the sooting tendencies and the soot-energy tradeoff of alkyl-POMEs;
 2. Establish structure-soot relationships and explain these relationships by numerical simulations and reaction pathways.

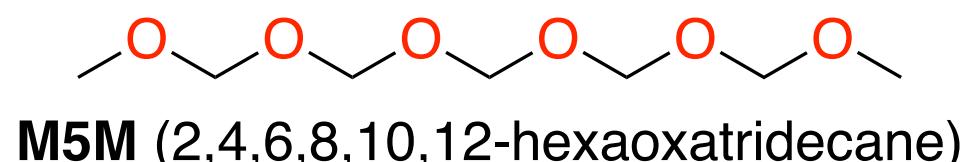
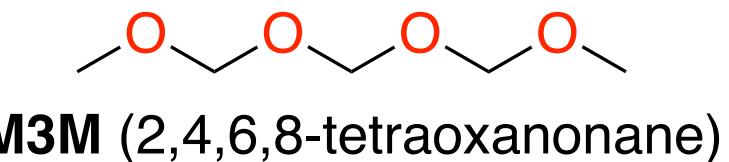
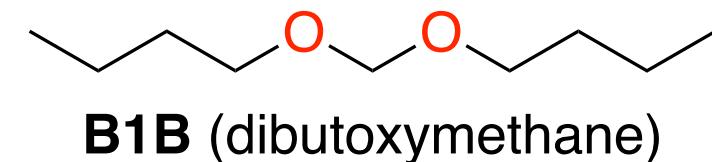
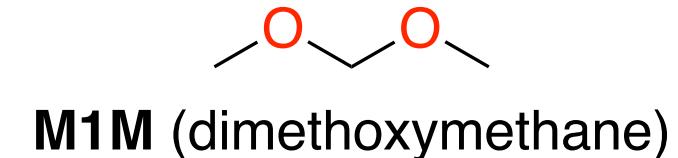
MACROMOLECULAR CHEMISTRY: THE SECOND CENTURY

1. Arellano-Treviño et al. Synthesis of butyl-exchanged polyoxymethylene ethers as renewable diesel blendstocks with improved fuel properties. Accepted by *ACS Sustainable Chemistry & Engineering*
2. Bartholet et al. *Fuel* 295 (2021): 120509.

POME nomenclature



- **Alkyl Index (AI)** = $n_1 + n_2$
- **Oxymethylene Index (OI)** = n
- Nomenclature = $\text{R}_1 n \text{R}_2$ (For R_1 and R_2 , "M" = methyl, "E" = ethyl, "P" = n-propyl, "B" = n-butyl)
- Increase AI: $\text{M1M} \xrightarrow{\text{n-BuOH}} \text{B1B}$
- Increase OI: $\text{M1M} \rightarrow \text{M3M} \rightarrow \text{M5M}$



How do we quantify the sooting tendencies of POMEs?

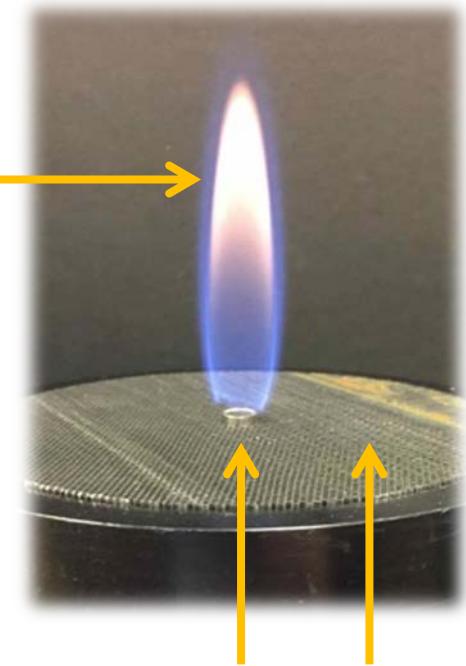
1. Sequentially dope 3000 ppm of a test compound (TC), water (W), and n-heptane (HEP) in the fuel;
2. Measure the maximum soot concentration of each flame with line-of-sight spectral radiance (LSSR);
3. Rescale to **Yield Sooting Index (YSI)**¹;

$$\text{YSI}_{\text{TC}} = \text{YSI}_{\text{HEP}} - (\text{YSI}_{\text{HEP}} - \text{YSI}_{\text{W}}) \times \frac{\text{LSSR}_{\text{HEP}} - \text{LSSR}_{\text{TC}}}{\text{LSSR}_{\text{HEP}} - \text{LSSR}_{\text{W}}}$$

where $\text{YSI}_{\text{W}} \equiv 0$, $\text{YSI}_{\text{HEP}} = 36.0^*$

The mole-based YSI is defined such that $\text{YSI}_{\text{benzene}} = 100$ and the YSI of a fuel that produces no soot is around 0.

*For $\text{YSI}_{\text{TC}} < 36.0$ except P1P, we used water and n-heptane ($\text{YSI}_{\text{W}} = 0$, $\text{YSI}_{\text{HEP}} = 36.0$) with 3000 ppm of dopants;
For $\text{YSI}_{\text{TC}} > 36.0$, we used n-heptane and toluene ($\text{YSI}_{\text{HEP}} = 36.0$, $\text{YSI}_{\text{TOL}} = 170.9$) with 1000 ppm of dopants;

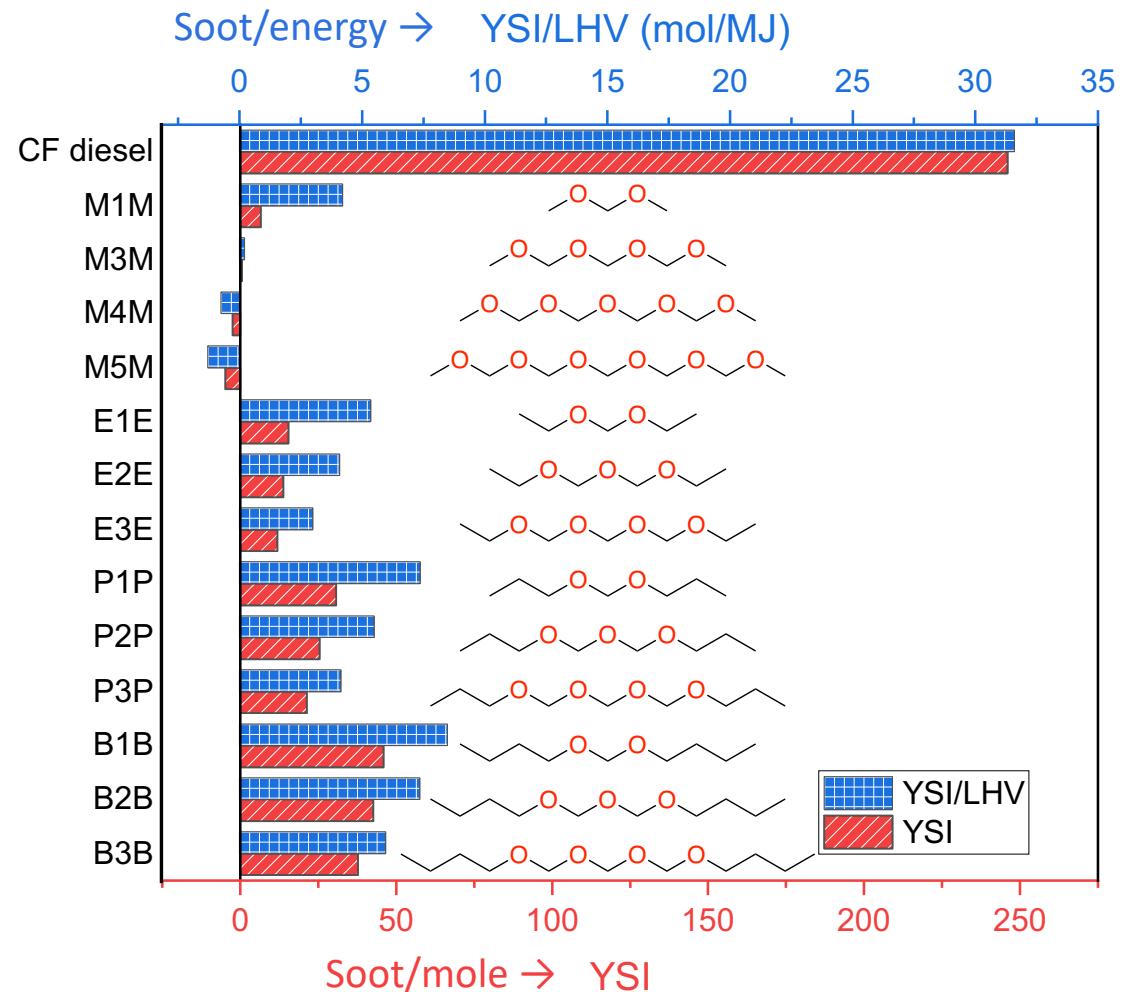


Fuel: Methane
Oxidizer: Air
Nitrogen
Test Compound
(photo: C. S. McEnally)

1. McEnally et al. *Proceedings of the Combustion Institute* 37.1 (2019): 961-968.

YSI and YSI/LHV of POMEs

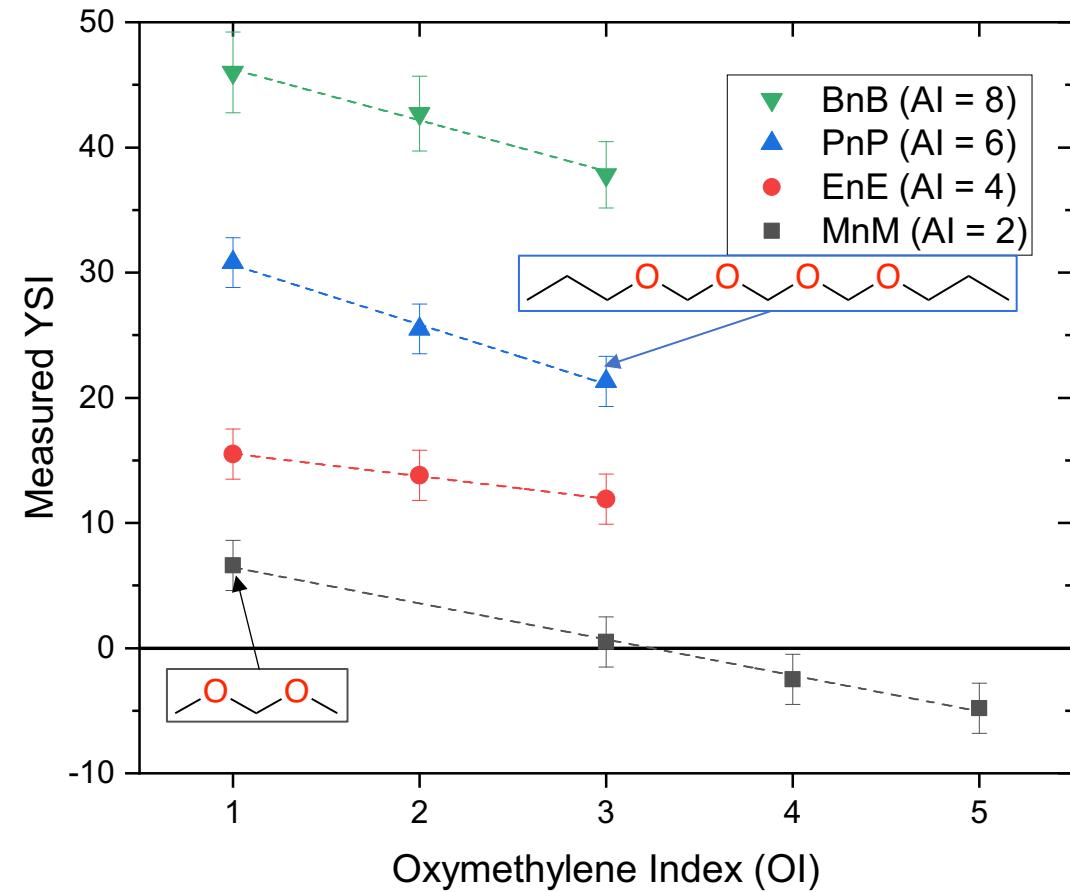
- Both soot/energy and soot/mole follow the same trend: MnM < EnE < PnP < BnB;
- All the POMEs have much lower soot/energy and soot/mole than a certification diesel (CF diesel¹).



1. Mueller et al. *Energy & Fuels* 30.2 (2016): 1445-1461.

Structure-YSI relationship

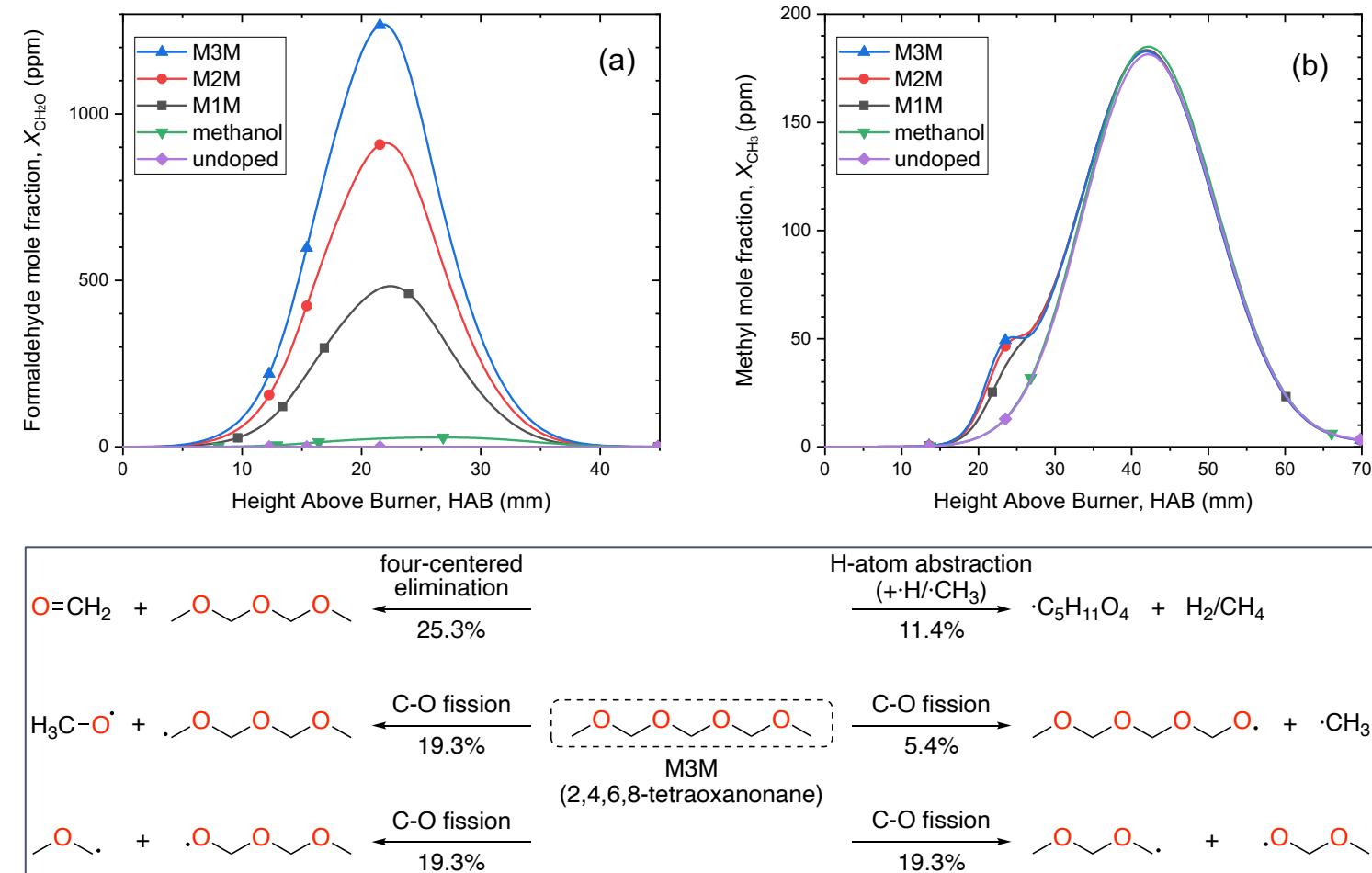
1. For a given AI, YSI decreases with OI;
2. For a given OI, YSI increases with AI;
3. For MnM, $YSI_{M1M} > 0$ while $YSI_{M4M} & YSI_{M5M} < 0$.



Simulation result

- CFD flame simulations with kinetic mechanisms¹ was used to explain structure-property relationships;
 - As OI of MnMs increases, more CH_2O is formed;
 - MnMs decompose to $\cdot\text{CH}_3$ at lower HAB compared to methane;
 - Initial decomposition of M3M is dominated by unimolecular reactions.

Simulated centerline profile of the flames with $X_{\text{dopant}} = 1000 \text{ ppm}$



Simplified reaction pathways



- E2E $\Rightarrow C^* + 3 C=O + C=C + *H$ (6 total products, 3 carbon in hydrocarbons)
 1. CCOCOCOCOC $\rightarrow 2/8 C^* + *COOCOCOC \rightarrow \dots \Rightarrow C^* + 3 C=O + C=C + *H$
 2. CCOCOCOCOC $\rightarrow 2/8 CC^* + *OCOCOCOC \rightarrow \dots \Rightarrow H^* + C=C + 3 C=O + *C$
 3. CCOCOCOCOC $\rightarrow 2/8 CCO^* + *COOCOCOC \rightarrow \dots \Rightarrow C^* + 3 C=O + C=C + *H$
 4. CCOCOCOCOC $\rightarrow 2/8 CCOC^* + *OCOCOCOC \rightarrow \dots \Rightarrow H^* + C=C + 3 C=O + *C$
- $R-(O-CH_2)_{OI}-O-R \Rightarrow (OI+1) CH_2O + (AI/2 - 1) C_2H_4 + \cdot CH_3 + \cdot H$

Simplified reaction pathways

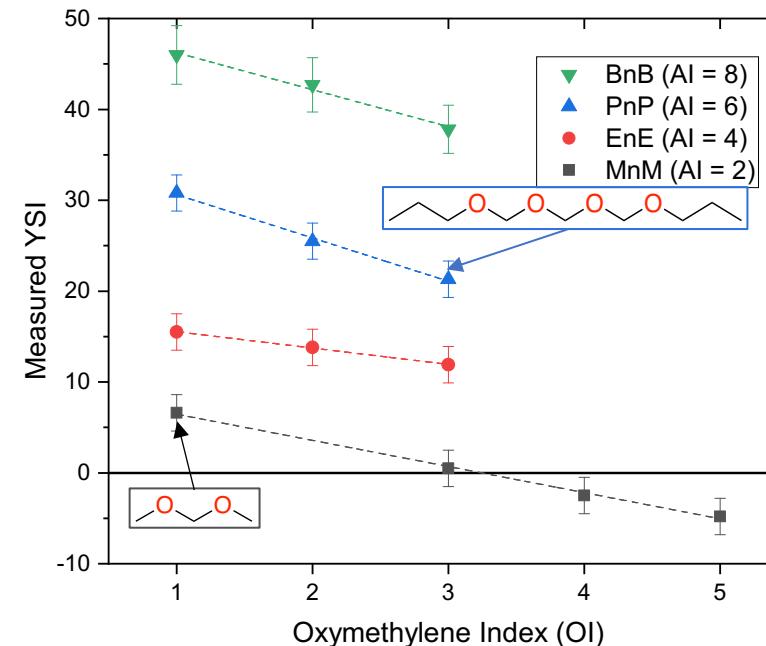


large **dilution effect**
— CH_2O does not
lead to soot

large **chemical effect**
— C_2H_4 leads strongly
to soot

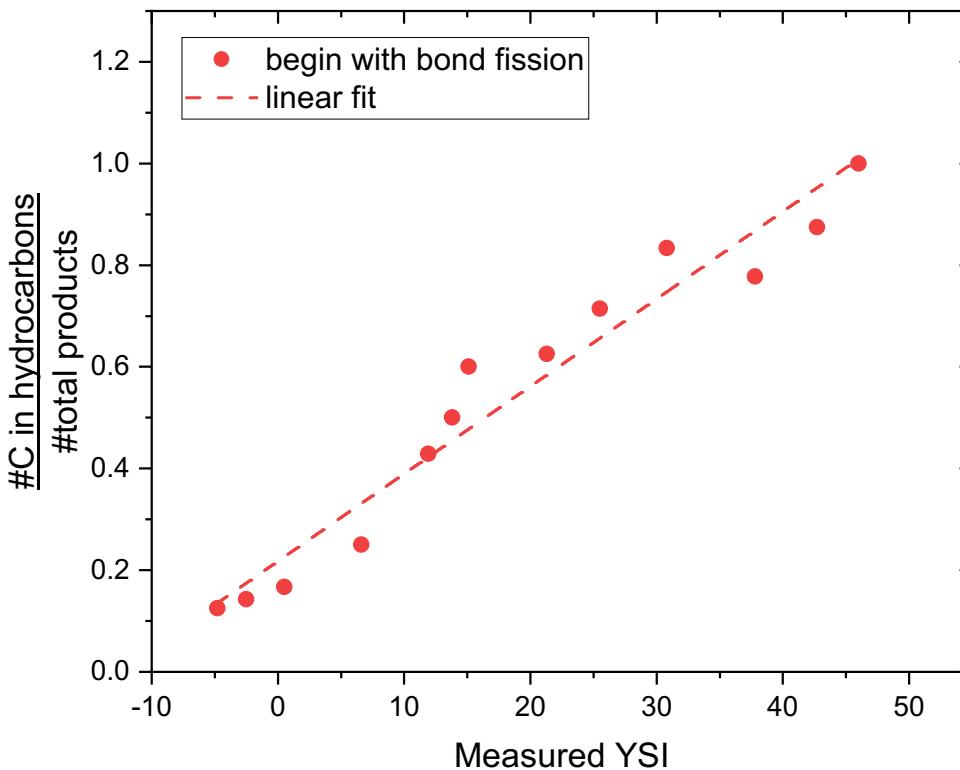
small **chemical effect**
— $\cdot CH_3$ leads weakly
to soot

1. $OI \uparrow, CH_2O \uparrow$ (**dilution effect**), $YSI \downarrow$;
2. $AI \uparrow$, aliphatic hydrocarbons such as $C_2H_4 \uparrow$ (**chemical effect**), $YSI \uparrow$;
3. For M4M & M5M, **dilution effect** of $CH_2O > \text{chemical effect}$ of $\cdot CH_3$, $YSI < 0$.



Simplified reaction pathways

- $YSI \sim \frac{\text{chemical effect}}{\text{dilution effect}} = \frac{\#C \text{ in hydrocarbons}}{\#\text{total products}}$



Conclusion

1. Both soot/mol and soot/energy of POMEs follow the same trend: MnM < EnE < PnP < BnB << certification diesel;
2. The sooting tendency of POMEs decreases with OI and increases with AI;
3. Numerical simulation shows that more CH_2O is formed as OI of MnMs increases and the initial decomposition of M3M is dominated by unimolecular reactions;
4. Simplified reaction pathways based on simulation show that:
 - 1) OI \uparrow , $\text{CH}_2\text{O} \uparrow$, more dilution and less soot;
 - 2) AI \uparrow , aliphatic hydrocarbons \uparrow , more soot;

Other POME talks from our collaborators

- Synthesis:

Present by Stephen Lucas and Fan Liang Chan, "Extended alkyl terminated polyoxymethylene ethers as a potential renewable diesel fuel blendstock: synthesis approaches and physicochemical property characterization"

Present by Martha Arellano-Trevino, "Butyl-terminated polyoxymethylene ethers as renewable diesel blendstocks with improved fuel properties"

- Mechanisms:

Present by Jatinder Sampathkumar and Katherine Lockwood, "Combined experimental and theoretical approach for understanding molecular structure effects on targeted fuel properties"

- LCA/TEA:

Presented by Dan Gaspar, "Screening and identification of diesel bio-blendstocks to improve performance and reduce emissions"

Acknowledgements



Co-Optimization
of
Fuels & Engines

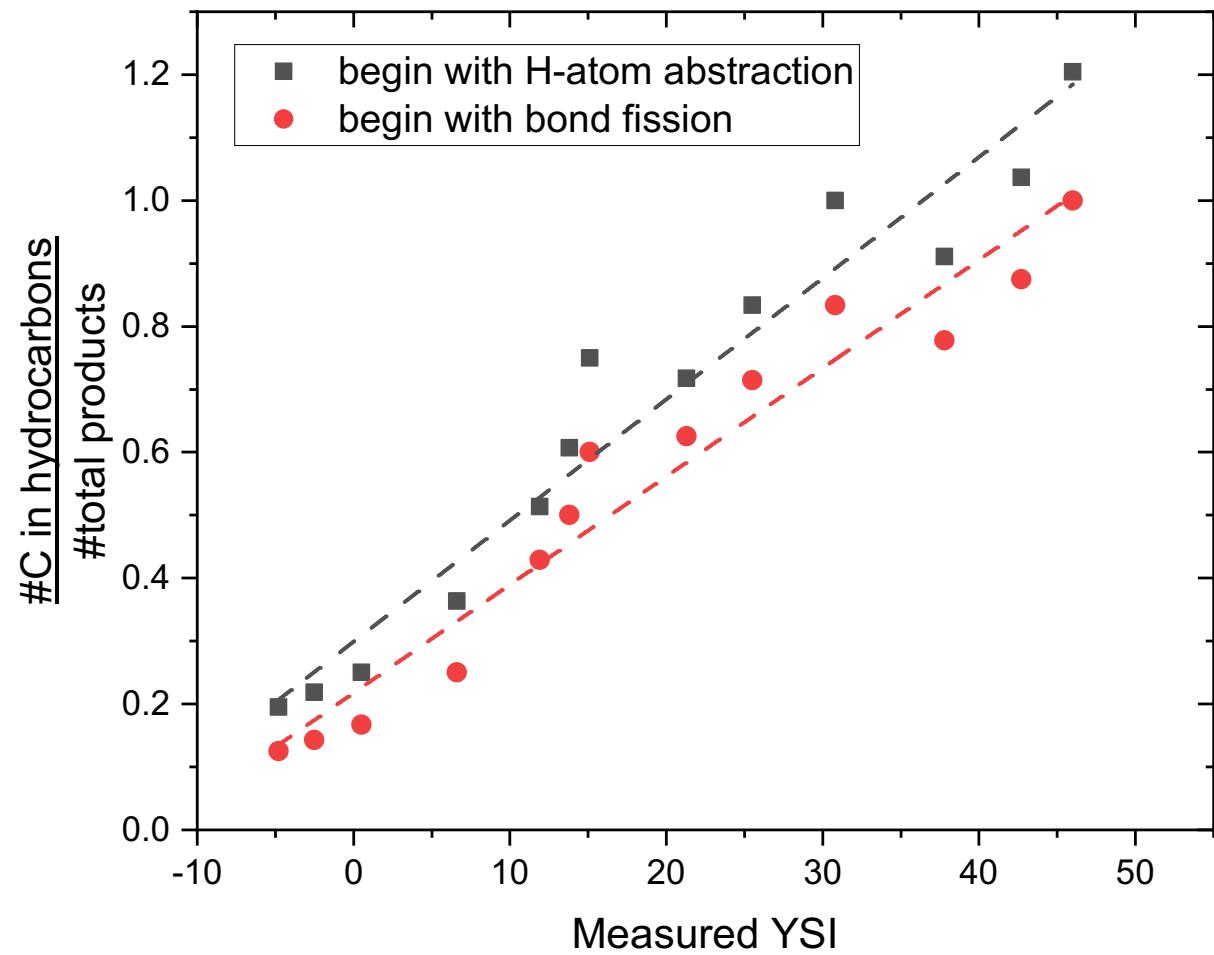
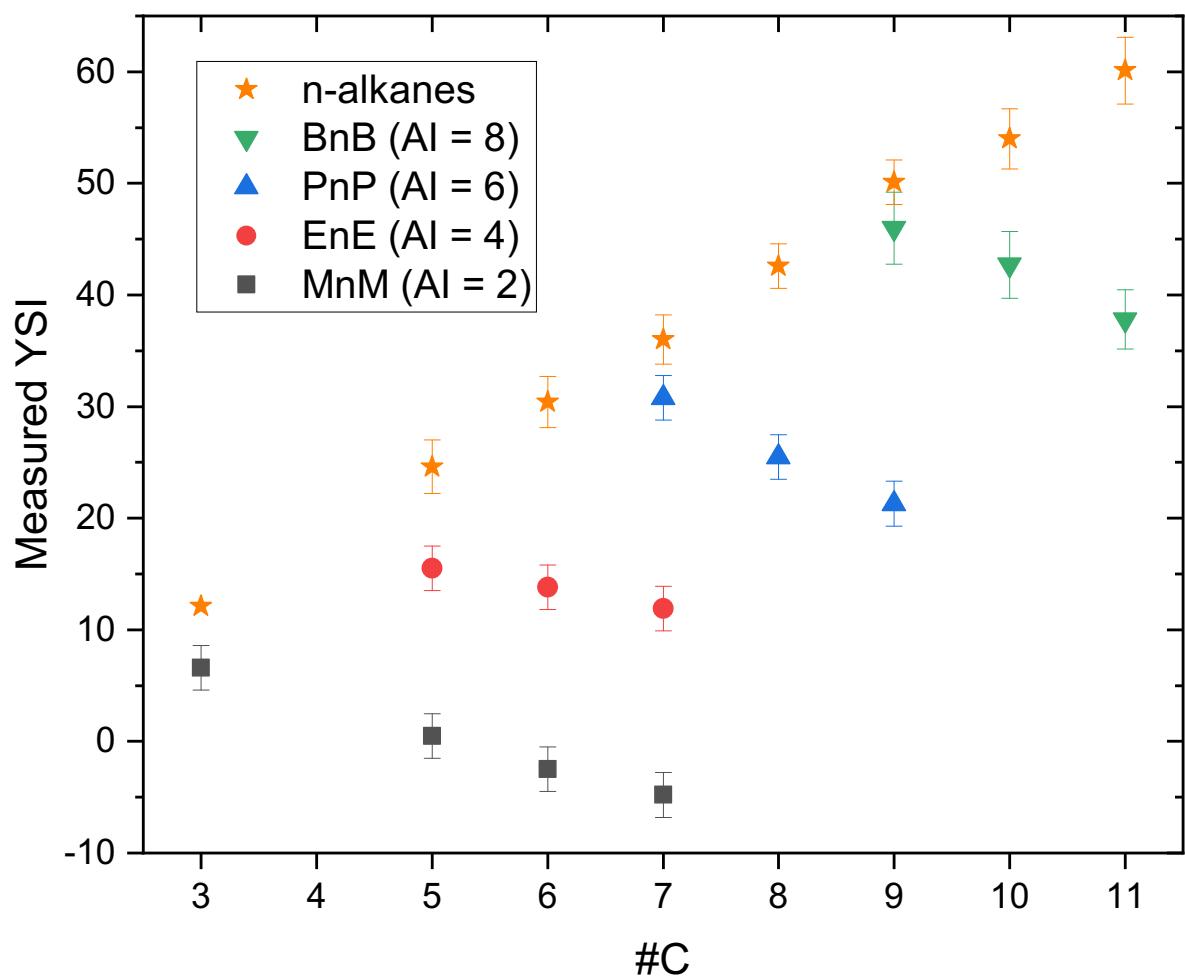


Prof. Nicole Labbe
UC Boulder



Dr. Daniel Ruddy
NREL

Back-up slides



Back-up slides

1. Simple bond fission followed by beta scission;
2. Assume the C-O and C-C bond fissions happen simultaneously and are much faster than other reactions (C-H breaks if it's the only beta bond).
 - Rate constants of C-C fission is much higher than other reactions;
 - 88% n-propyl (CCC*) and 94% n-butoxyl (CCCO*) react via C-C fission.

reaction	k (rxn-dependent)	T (K)	A (rxn-dependent)	n (-)	Ea (kJ/mol)	source*
CCC* → C=C + C*	4.81E+09	2000	6.15E+17	-4.75	160	JPCA 121.6 (2017): 1261-1280.
CCC* → C=CC + H*	6.32E+08	2000	7.66E+17	-5.3	180	JPCA 121.6 (2017): 1261-1280.
CCCO* → CCC* + C=O	1.57E+12	2000	2.92E+13	0.47	63.5	JPCA 117.9 (2013): 1890-1906.
CCCO* → C*CCCO	6.51E+10	2000	1.28E+08	3.63	11.3	PCCP 12.28 (2010): 7782-7793.
CCCO* → CC*CCO	2.94E+10	2000	1.19E+06	6.2	28.1	PCCP 12.28 (2010): 7782-7793.

Back-up slides

iP1iP \Rightarrow C* + CC=O + C=O + C=CC + *H (5 #total products, 4 C# in hydrocarbons)

1. CC(C)OCOC(C)C \rightarrow 4/8 C* + CC*OCOC(C)C \rightarrow C* + CC=O + *CO(C)C \Rightarrow C* + CC=O + C=O + C=CC + *H
2. CC(C)OCOC(C)C \rightarrow 2/8 CC*C + *OCOC(C)C \rightarrow H* + CC=C + O=C + *OC(C)C \Rightarrow H* + CC=C + O=C + O=CC + *C
3. CC(C)OCOC(C)C \rightarrow 2/8 CC(C)O* + *CO(C)C \rightarrow C* + CC=O + C=O + *C(C)C \Rightarrow C* + CC=O + C=O + C=CC + *H

P1P \Rightarrow C* + 2 C=O + 2 C=C + *H (6 #total products, 5 C# in hydrocarbons)

1. CCCOCOCOCCC \rightarrow 2/8 C* + *CCOCOCOCCC \Rightarrow C* + 2 C=O + 2 C=C + *H
2. CCCOCOCOCCC \rightarrow 2/8 CC* + *COCOCOCCC \Rightarrow H* + 2 C=O + 2 C=C + *C
3. CCCOCOCOCCC \rightarrow 2/8 CCC* + *OCOCOCCC \Rightarrow C* + 2 C=O + 2 C=C + *H
4. CCCOCOCOCCC \rightarrow 2/8 CCCO* + *COCCC \Rightarrow H* + 2 C=O + 2 C=C + *C