Co-Optimization of Fuels &
Engines (Co-Optima), DOE

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A numerical study on the sooting tendencies of bio-derived fuels for spark-ignition engines

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- Biofuel: fuels produced from biomass that can replace petroleum fuels
- Advantages^[1]
 - Various source material
 - Sustainability
 - Reduction of greenhouse gas emissions
- Barriers to the realization of biofuels' implementation target^[2]
 - Shortage of feedstocks
 - Higher costs than traditional fuels
 - Variations in performance

[1] A. Demirbas, *Energ. Source Part B* 12 (2017) 47-55

[2] Y. Oh et al, *Bioresource Technol.* 257 (2018) 320-333

❑ Co-Optimization of Fuels & Engines (Co-Optima)

→ Fuels intended to enable high-efficiency, low-emissions engines

→ Fuel screening using a tiered process

[1] Technical Report. U.S. Department of Energy, Washington, DC. 2018. DOE/GO-102018-4970.

Alcohol

ethanol

n-propanol

i-propanol

i-butanol

Ketone

cyclopentanone

Alkene

diisobutylene

Furan mixture

R = H, -CH₃

Aromatic

- Potential to increase the efficiency of SI engines, meet key fuel-quality requirements, and be commercially available by 2025-2030
- YSI has been measured to characterize sooting tendencies.

[1] Technical Report. U.S. Department of Energy, Washington, DC. 2018. DOE/GO-102018-4970.

(1) Predict YSIs of the promising blendstocks using numerical simulations

- YSI has never been computed for those fuels
- Efficiently predict YSIs using a perturbation-based approach
- Validate the ability of a kinetic model

(2) Quantify the effects of chemical kinetic uncertainties on YSI predictions

- Quantify impact of PAH growth reactions on YSI
- Identify the most sensitive reactions to YSI predictions
- Quantify rate constant uncertainties on YSI Predictions

[1] Technical Report. U.S. Department of Energy, Washington, DC. 2018. DOE/GO-102018-4970.

❑ Yield Sooting Index (YSI)^[1]

- It defines sooting tendency based on soot yield
- Measure of **max soot volume fraction** ($f_{v,max}$)
- YSI is defined as a linear function of $f_{v,max}$

$$\text{YSI}(\text{dopant}) = A \times f_{v,max}(\text{dopant}) + B$$

YSI = 36.0 for *n*-heptane,

YSI = 170.9 for toluene

Measure $f_{v,max}$
along the
centerline

Test compound, 0.1 % by mole
Methane, 40 % by mole
Nitrogen, balance

[Yale co-flow burner]

[1] C.S. McEnally, L.D. Pfefferle, *Combust. Flame* 148 (2007) 210-222

YSI is easy to be modeled computationally

- Only one 2D flame simulation is required to calculate YSI
- YSI computation for each test compound is efficient (1D simulations along the flame centerline)
- Agreement with experimental YSIs for aliphatic, aromatic compounds, surrogate fuels

1	2-heptanone	7	Ethynylbenzene
2	2-octanone	8	Ethylbenzene
3	trimethylpentane	9	Indene
4	Benzene	10	1-methylnaphthalene
5	Methylbenzene	11	2-ethylnaphthalene
6	Ethenylbenzene	12	1-ethylnaphthalene

[1] Y. Xuan, G. Blanquart, *Combust. Flame* 160 (2013) 1657-1666

[2] C.S. McEnally et al., *Proc. Combust. Inst.* 37 (2019) 961-968

Co-Optima chemical model has been developed for transportation fuels by LLNL, NUI Galway, and KAUST teams^[1]

- Co-Optima model can handle Co-Optima fuels
 - C₁-C₅ alcohols
 - Ester (methyl acetate, ethyl acetate, methyl butanoate)
 - Ketone (cyclopentanone, 2-butanone)
 - Furan (2-methylfuran, 2,5-dimethylfuran)
 - Alkene (di-isobutylene)
- Validated against ignition and flame propagation for a broad range of Φ , T, P
- A reduced model generated by removing the low temperature chemistry
- 1172 species, 7517 reactions
- Hydrocarbon growth up to naphthalene

[1] M. Mehl et al., 10th U.S. National Combustion Meeting (2017), LLNL-CONF-725343.

List of Co-Optima Fuels Considered

#	Name	Family group	#	Name	Family group
1	Methanol (CH ₄ O)	Alcohols	11	2-methyl-1-butanol (C ₅ H ₁₂ O)	Alcohols
2	ethanol (C ₂ H ₆ O)	Alcohols	12	methyl acetate (C ₃ H ₆ O ₂)	Esters
3	<i>n</i> -propanol (C ₃ H ₈ O)	Alcohols	13	ethyl acetate (C ₄ H ₈ O ₂)	Esters
4	<i>iso</i> -propanol (C ₃ H ₈ O)	Alcohols	14	methyl butanoate (C ₅ H ₁₀ O ₂)	Esters
5	<i>n</i> -butanol (C ₄ H ₁₀ O)	Alcohols	15	2-butanone (C ₄ H ₈ O)	Ketones
6	2-butanol (C ₄ H ₁₀ O)	Alcohols	16	cyclopentanone (C ₅ H ₈ O)	Ketones
7	2-methyl-1-propanol (C ₄ H ₁₀ O)	Alcohols	17	2-methylfuran (C ₅ H ₆ O)	Furans
8	<i>tert</i> -butanol (C ₄ H ₁₀ O)	Alcohols	18	2,5-dimethylfuran (C ₆ H ₈ O)	Furans
9	<i>n</i> -pentanol (C ₅ H ₁₂ O)	Alcohols	19	2,4,4-trimethyl-1-pent ene (C ₈ H ₁₆)	Alkenes
10	3-methyl-1-butanol (C ₅ H ₁₂ O)	Alcohols	20	2,4,4-trimethyl-2-pent ene (C ₈ H ₁₆)	Alkenes

Reference fuels:

- 2,4,4-trimethyl-2-pentene (the most sooting fuel)
- methanol (the least sooting fuel)

- Good agreement for most species, worst prediction for 25DMF
- Furans and alkenes are sootiest
- Alcohols and esters and ketones are least sooty

Co-Optima Model:

naphthalene

Expanded Model:

naphthalene

growth
→

cyclopenta[cd]pyrene

Polycyclic Aromatic
Hydrocarbons
(PAHs)

- Two different PAH sub-mechanisms agree to within 1.8 %
- Soot yield increases when using the Expanded Model, but the effects are canceled out when converting it to a relative sooting tendency (YSI)

❑ Regular sensitivity analysis in combustion chemistry

- Calculate sensitivity coefficients (S) pertinent to a quantity of interest
- Reveals which are the main control parameters in the chemical model

This approach cannot be directly used in YSI

❑ Sensitivity analysis in YSI

- Calculate sensitivity coefficients in doped and undoped flames
- Calculate relative sensitivity coefficients: $S_{rel,j} = (S_{doped,j} - S_{undoped,j}) / (|S_{undoped,j}| + \varepsilon)$
- List of sensitive reactions in 2,5-DMF doped flame

	Reactions	$S_{rel,j}$
R1	2,5-DMF $\rightarrow$ CH ₃ CHCCH(CO)CH ₃	-6.42E+06
R2	2,5-DMF + CH ₃ $\rightarrow$ DMF252J + CH ₄	6.18E+06
R3	2,5-DMF (+M) $\rightarrow$ DMF252J + H (+M)	4.18E+06
R4	2,5-DMF + H $\rightarrow$ DMF252J + H ₂	3.86E+06
R5	2,5-DMF + H $\rightarrow$ 2-MF + CH ₃	-2.33E+06
R6	2,5-DMF + H $\rightarrow$ 1,3-C ₄ H ₆ + CH ₃ CO	-2.14E+06

- R2-R4 forming effective soot precursor, C_5H_5 : positive S_{rel}
- R1, R5, R6 forming less effective soot precursors: negative S_{rel}

Reference Fuels

(a) Methanol

(b) 2,4,4-Trimethyl-2-pentene

Target Fuel

(c) 2,5-DMF

- Randomly perturb the sensitive reaction rates altogether within a factor of 2 [50%, 200%]
- 500 randomly perturbed flame simulations
- Re-calculate YSI using the mean soot production rates ± 2 standard deviations
- Good agreement under the first bullet point

- YSIs of 20 bio-fuels were numerically predicted.
- PAH growth reactions had little impact on YSI.
- A modified sensitivity coefficient was introduced.
- Rate constant uncertainties on YSI of 2,5-DMF was quantified.