Experimental Study and Structural Group Analysis for Soot Reduction Tendency of Oxygenated Fuels

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Motivation

- Synthetic oxygenated fuels become increasingly attractive
  - Beneficial effects on greenhouse gas emissions if made from biodiesel
  - Significant potential for the reduction in particulate and NO_x emissions from diesel engines

Photo by Brett Hampton

		No. 2 Diesel Fuel	Bio Diesel
Chem. Form.		C_8 to C_{25}	C_{12} to C_{22}
W [g/mol]		~200	~292
Composition [weight %]	C	87	77
	H	13	12
	O	0	11

Energy Efficiency and Renewable Energy
US Department of Energy

- Structural differences compared to petroleum-based fuels
  - Primarily aliphatic compounds containing oxygen moieties
- Observations
  - Particulate emission reductions depend on:
    - the amount of oxygen in the fuel
    - the oxygenate's structure

Smoke Point Experimental Database

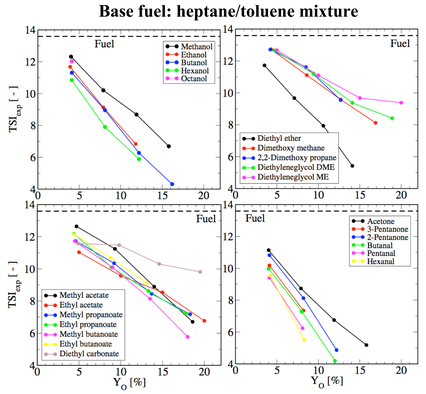
Smoke point lamp
Koehler Instrument Company, Inc

- Smoke Point (SP): Maximum flame height at which a given fuel will burn without smoking
- ASTM standard for aviation turbine fuel and kerosene
- Data from A. Boehman *et al.* (Penn State University)
- Base fuels
  - *n*-Heptane (65 vol%), Toluene (35 vol%)
  - Ultra-low sulphur diesel fuel BP15
- Oxygenated fuels
  - Alcohols, aldehydes, esters, ethers, ketones...

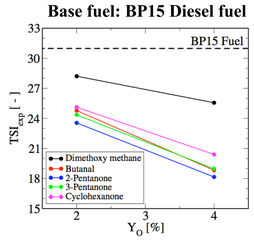
Threshold Sooting Index: $$\mathrm{TSI} = a\left(\frac{\mathrm{MW}}{\mathrm{SP}}\right) + b$$

Higher Smoke Point ⟷ Lower TSI ⟷ Less Soot

Base fuel: heptane/toluene mixture



Base fuel: BP15 Diesel Fuel

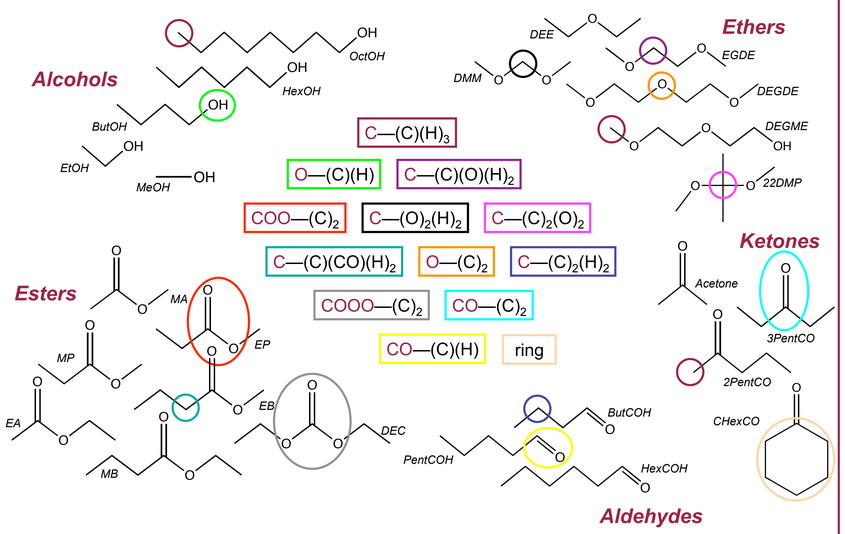


TSI variations due to:
- Replacement of aromatic base fuel ➡ "Dilution" effect
- Efficient use of oxygenated groups

Linear variations of TSI with mass fraction of oxygen Y_O in mixture

Group Additivity

- Assumption: Properties of a molecule may be estimated from the contribution of the individual building blocks in the molecule
  - Building blocks = atoms, bonds, groups...
- Nearest neighbor approach
  - Group = polyvalent atom with all of its ligands



Least-Square Optimization

$$\mathrm{TSI}_{\mathrm{sim}} = \sum_{i=1}^{n_{S,\mathrm{mix}}} X_i \left(\sum_{j=1}^{n_{G,i}} N_{j,i} C_j^{\mathrm{TSI}} \right) \quad \text{with} \quad \begin{cases} X_i & \text{Molar fraction of species } i \text{ in mixture} \\ N_{j,i} & \text{Number of groups } j \text{ in species } i \\ C_j^{\mathrm{TSI}} & \text{TSI contribution of group } j \end{cases}$$

Fuel contributions

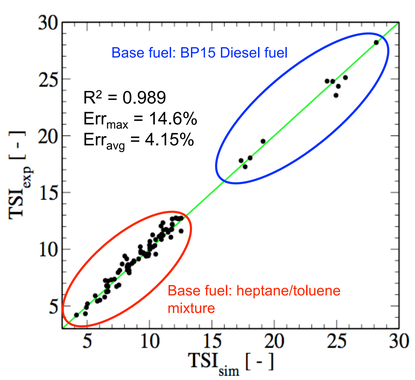
Group	Contribution
Hept./Tol.	13.53
Diesel BP15	31.23

Mid-group contributions

Group	Contribution
C—(C)2(H)2	0.32
C—(O)2(H)2	0.97
C—(C)(O)(H)2	0.26
C—(C)(CO)(H)2	-0.59
O—(C)2	-0.80
CO—(C)2	-1.73
COO—(C)2	-1.84
COOO—(C)2	0.21
C—(O)2(H)2	1.55
Ring	6.12

End-group contributions

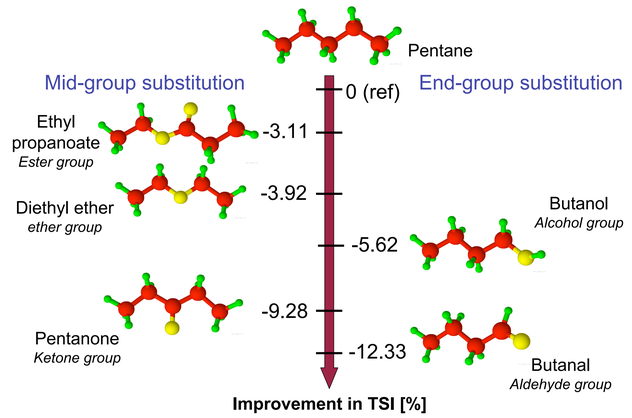
Group	Contribution
C—(C)(H)3	1.48
O—(C)(H)	0.28
CO—(C)(H)	-2.99



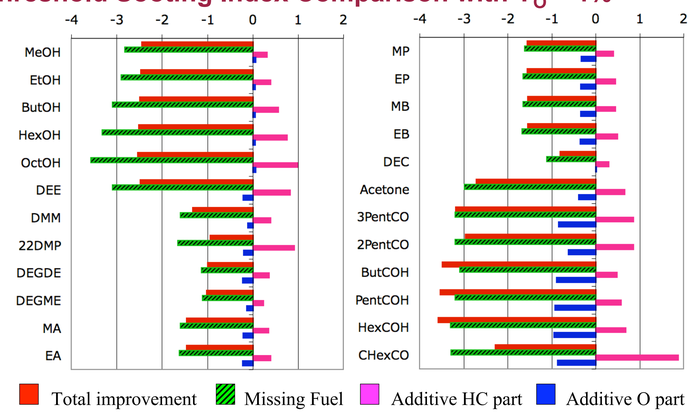
Analysis

Functional Group Efficiencies

- Compare TSI between:
  - A mixture base fuel/oxygenate with $Y_O = 4\%$
  - A mixture base fuel/pentane with the same liquid volume of additive



Threshold Sooting Index Comparison with $Y_O = 4\%$



- "Dilution" effect by substituting aliphatic chains for sooting toluene
- Oxygen-containing groups not equally effective: aldehyde and ketone most efficient oxygenated groups

Additional Comments

- Effect of oxygen-containing moieties in additives on sooting tendency of fuel successfully identified by group additivity theory
- Contradictory experimental data from literature explained by group analysis
- Method cannot explain everything, for example, the overall negative effect of short oxygenated additives in diffusive combustion mode.

➡ A more fundamental, chemical understanding of soot reduction mechanisms is necessary