

Oxygenates for Diesel Emissions Reduction

Ed Owens
Southwest Research Institute

7th Diesel Engine Emissions Reduction Workshop
Portsmouth, Virginia

DOE Fuel Evaluation Projects at SwRI

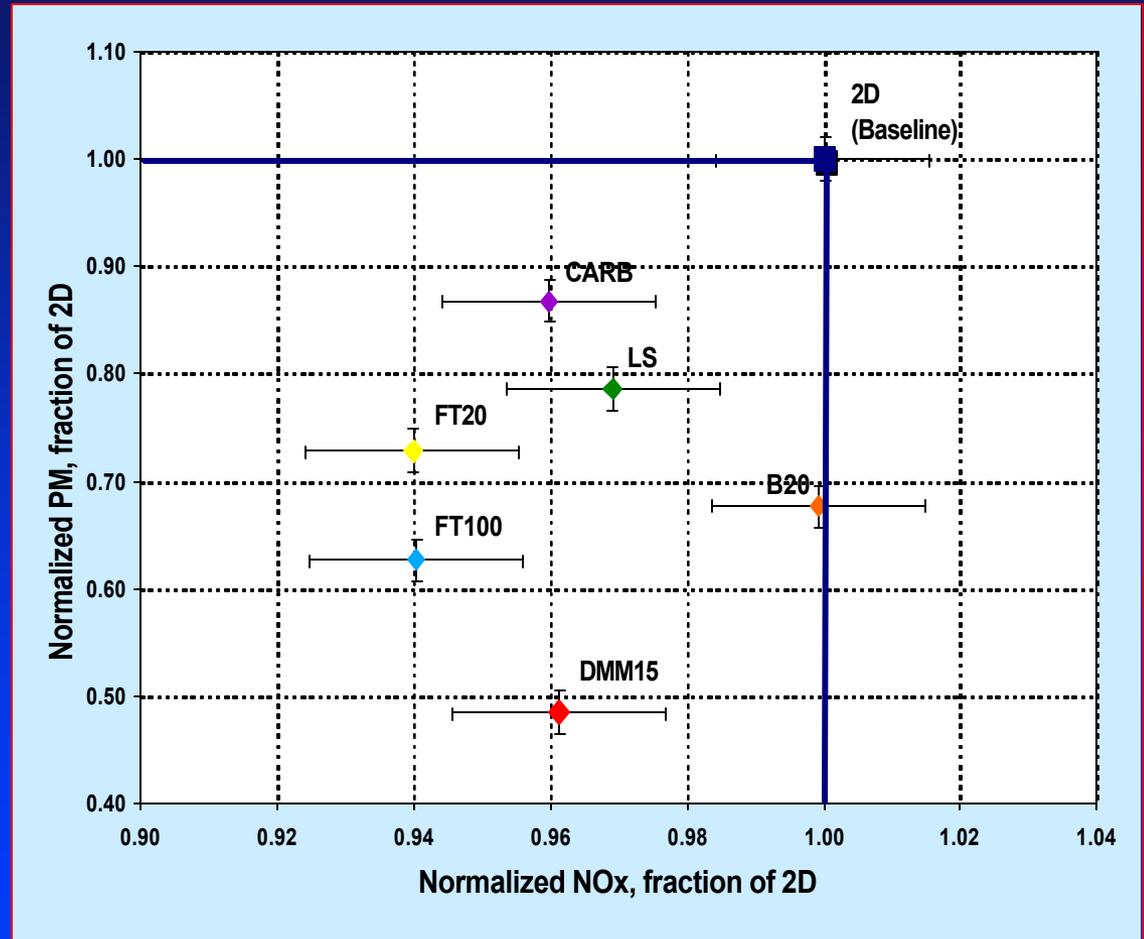
- Fuels Screening Study
- In-vehicle Fuels Evaluations
- Characterization of Toxicologically Relevant Compounds from Diesel Exhaust
- Lubricant contribution to PM
- Oxygenates for Advanced Petroleum-Based Diesel Fuels

All these projects included oxygenates



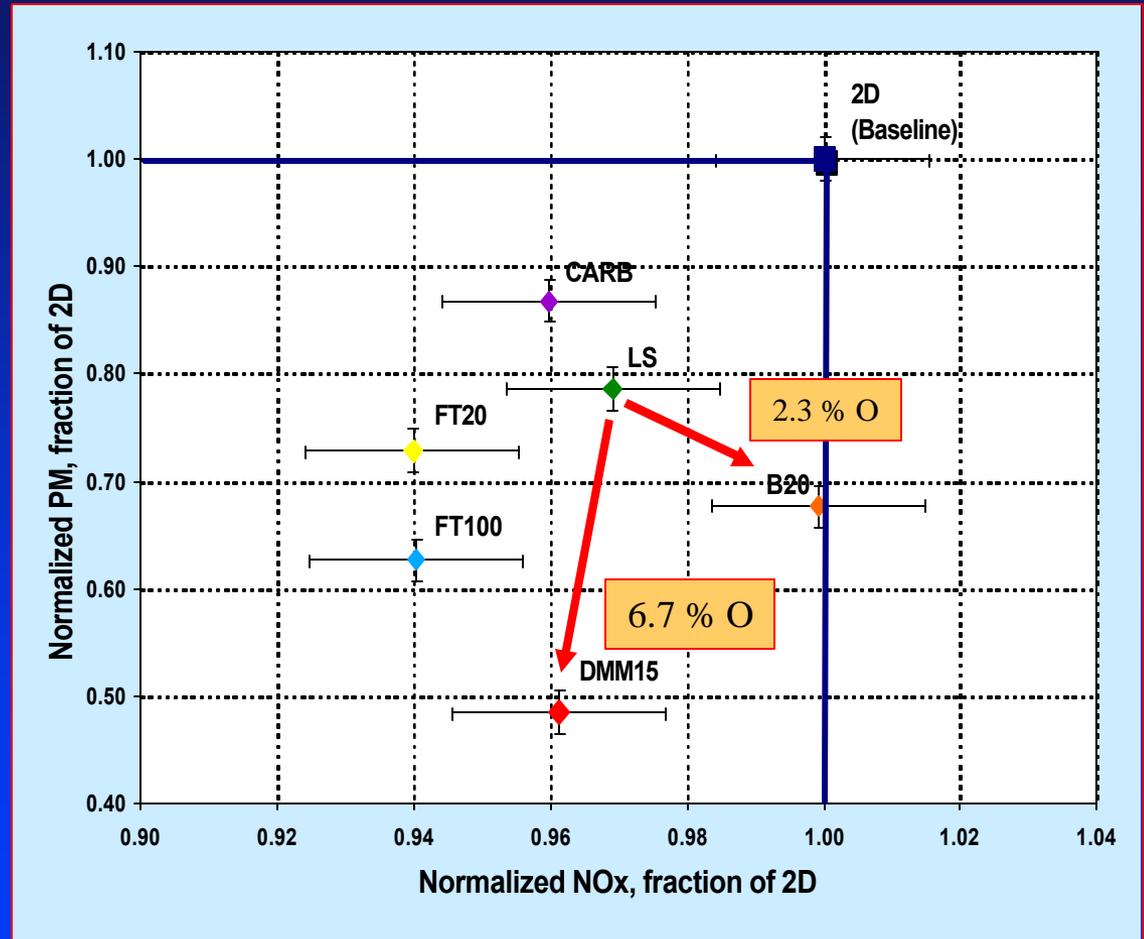
Fuels Screening Study Results

- DaimlerChrysler 2.2l light-duty diesel
- Over 50% PM reduction with DMM in Swedish Class 1 fuel.

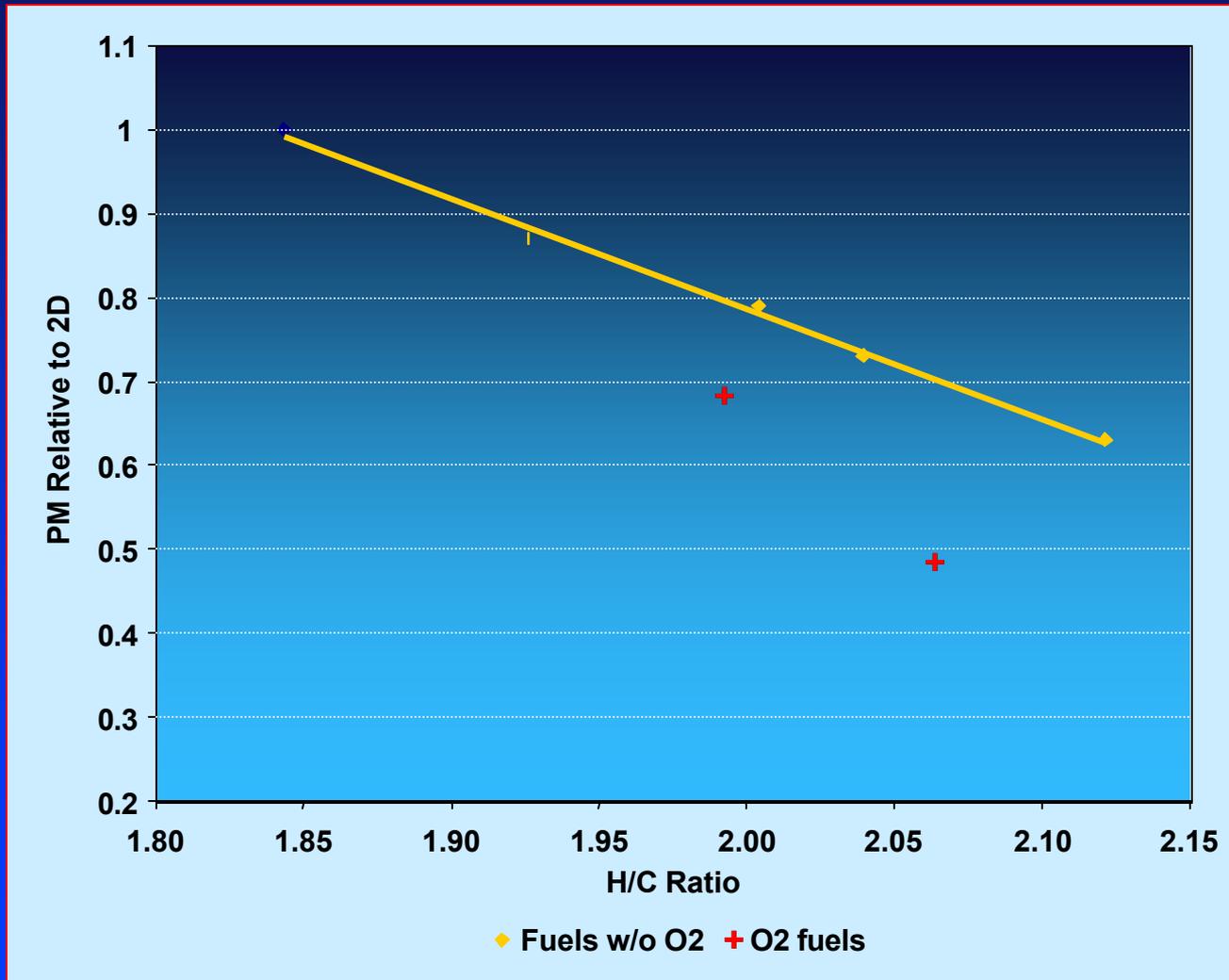


Fuels Screening Study Results

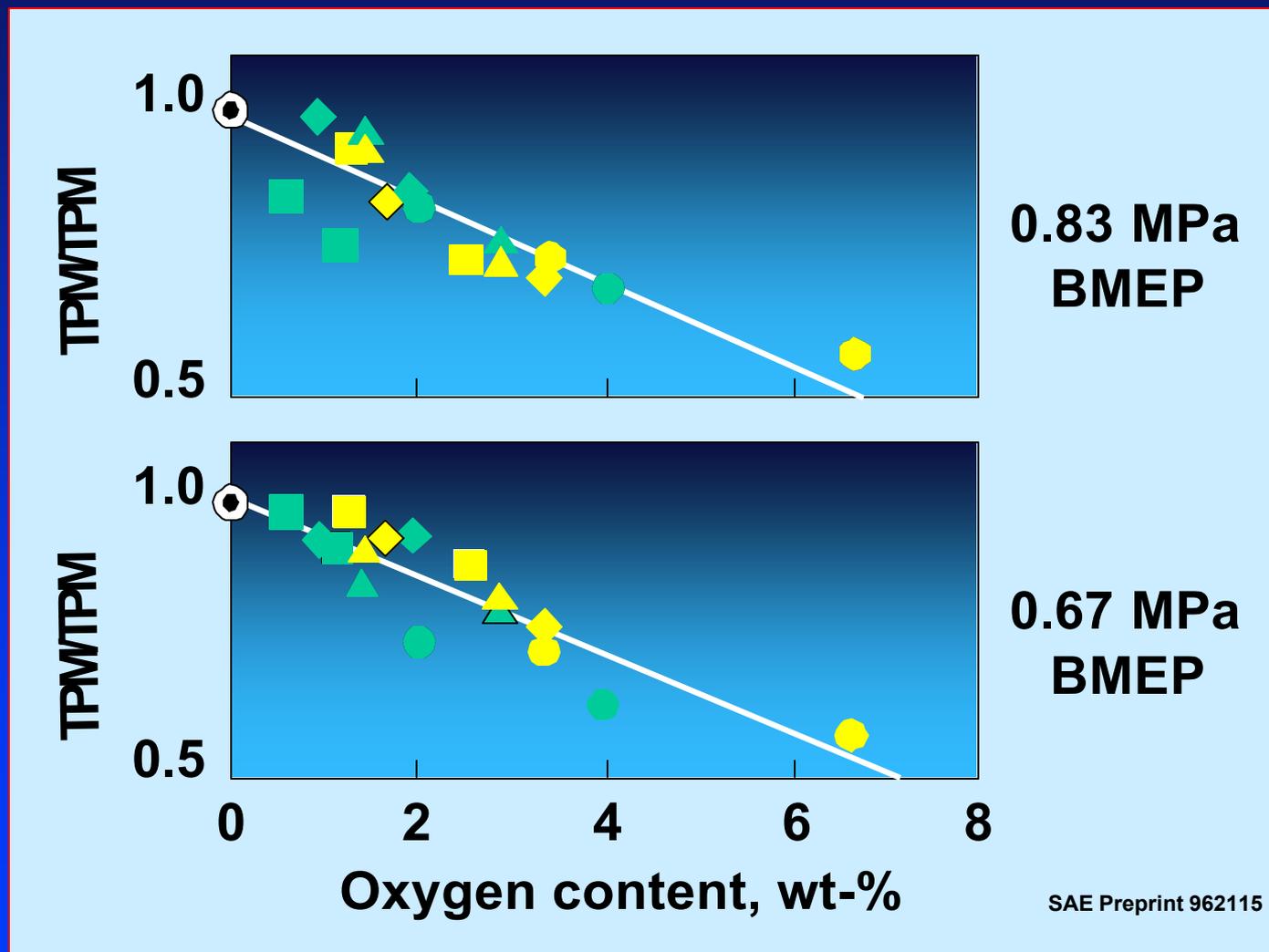
- Oxygen added as DMM and as bio-diesel (methyl esters) reduced PM
- NO_x impact inconsistent



Particulate Emissions Correlated with Hydrogen/Carbon Ratio



Total Particulate Mass Reduction with Oxygen Miyamoto et.al.

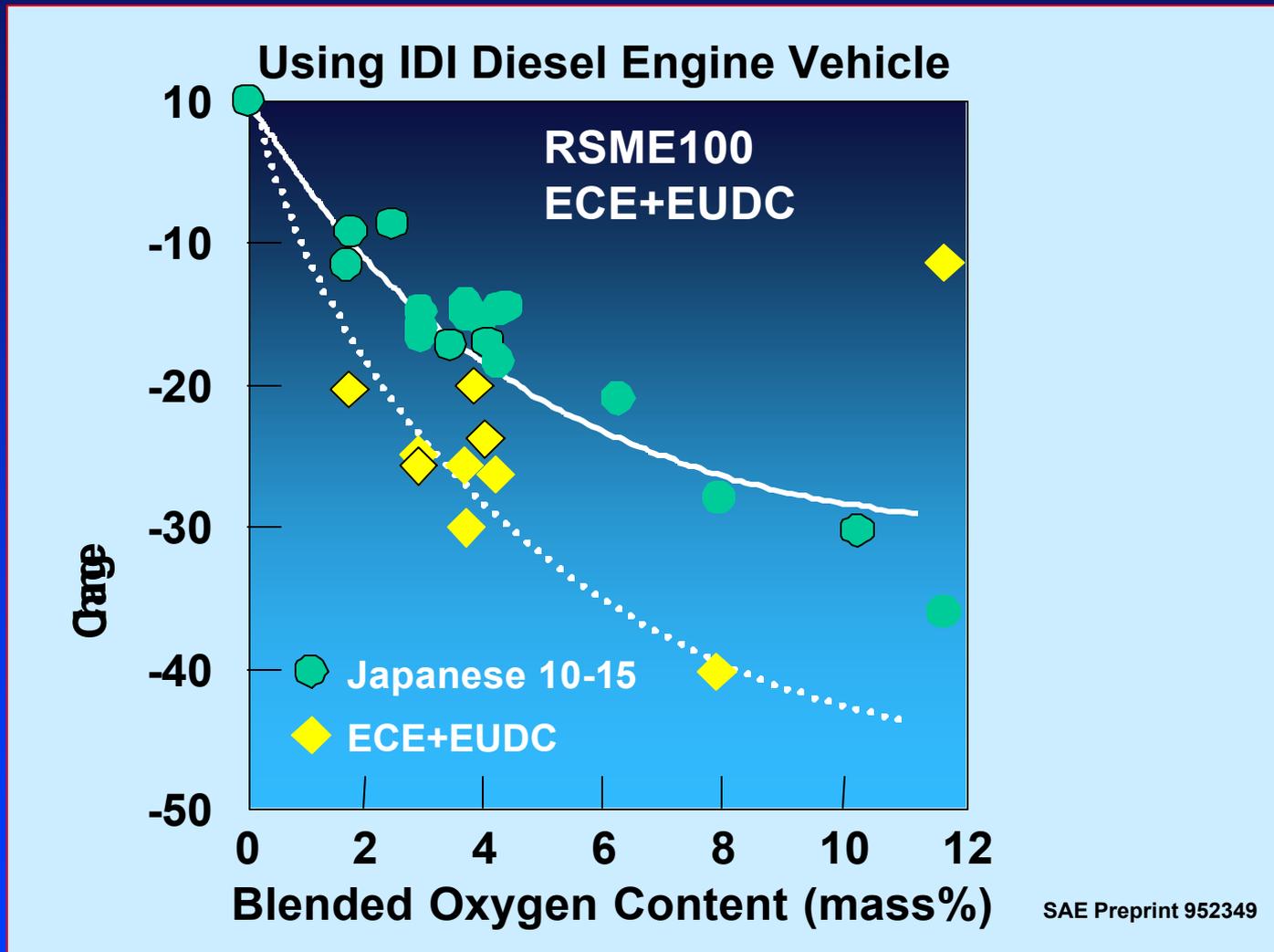


SAE Preprint 962115



Oxygen Impact on Particulate Emissions

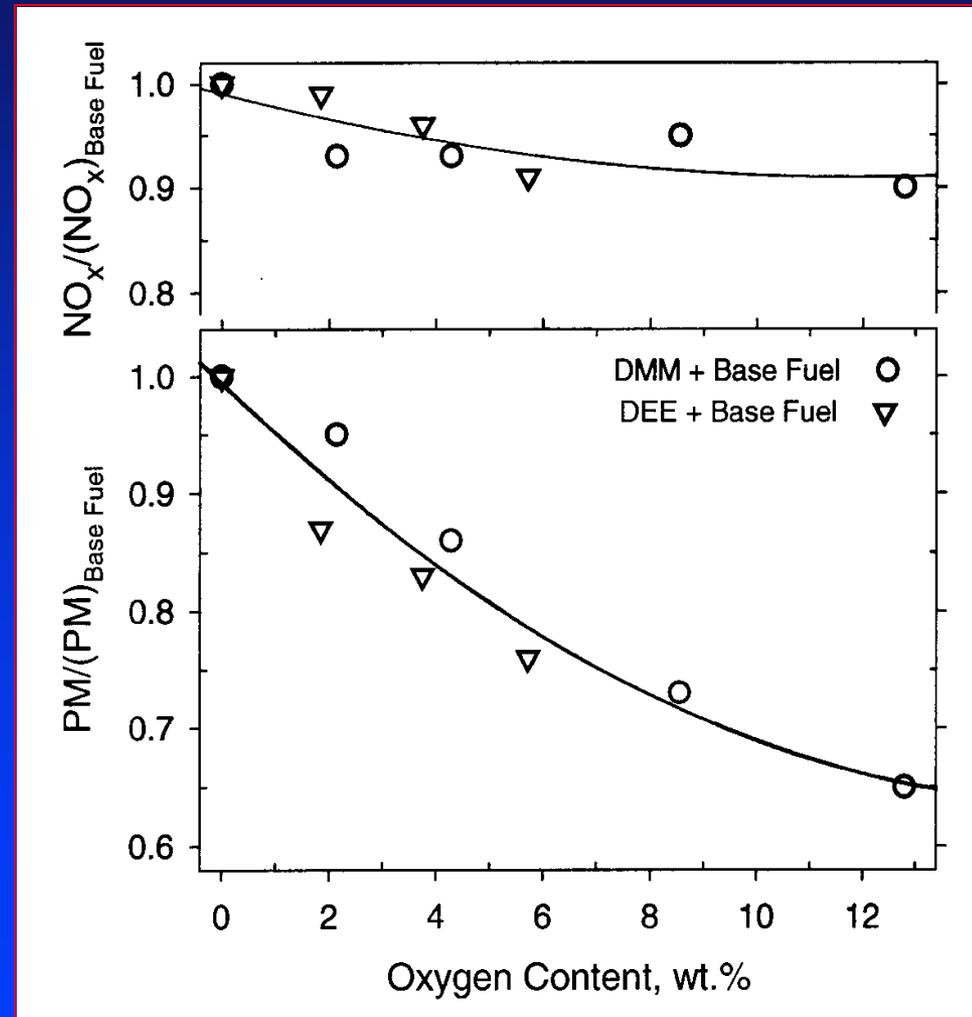
Tsurutani et.al.



Cheng & Dibble

SAE 1999-01-3606

- Engine: Cummins 5.9 liter DI turbodiesel
- Di-methoxy methane and di-ethyl ether in diesel fuel
- Observed NO_x and PM reduction.
- Molecular structure not significant



In-Vehicle Fuels Evaluation

- Evaluate emissions from original phase I fuels.
- European configuration Mercedes C220 diesel
- U.S. and European procedures
 - Federal Test Procedure (FTP)
 - US06 aggressive driving cycle
 - ECE + EUDS cycles

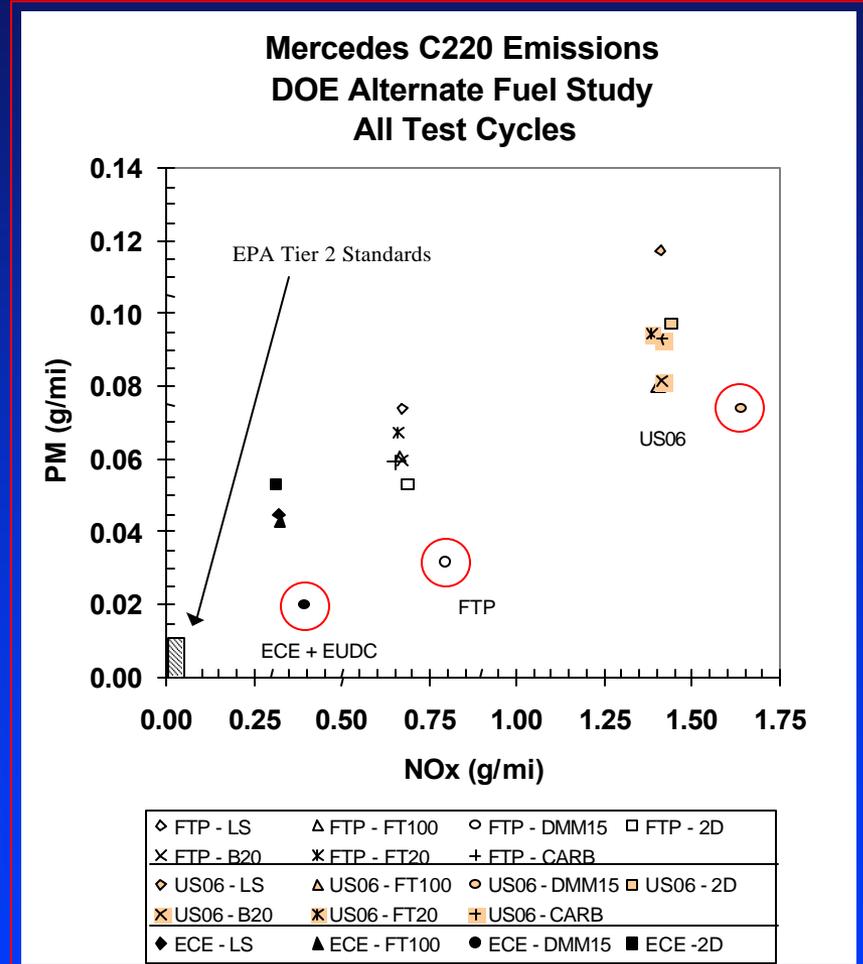


Continuous gaseous emissions before & after catalyst, plus particulate measurement.

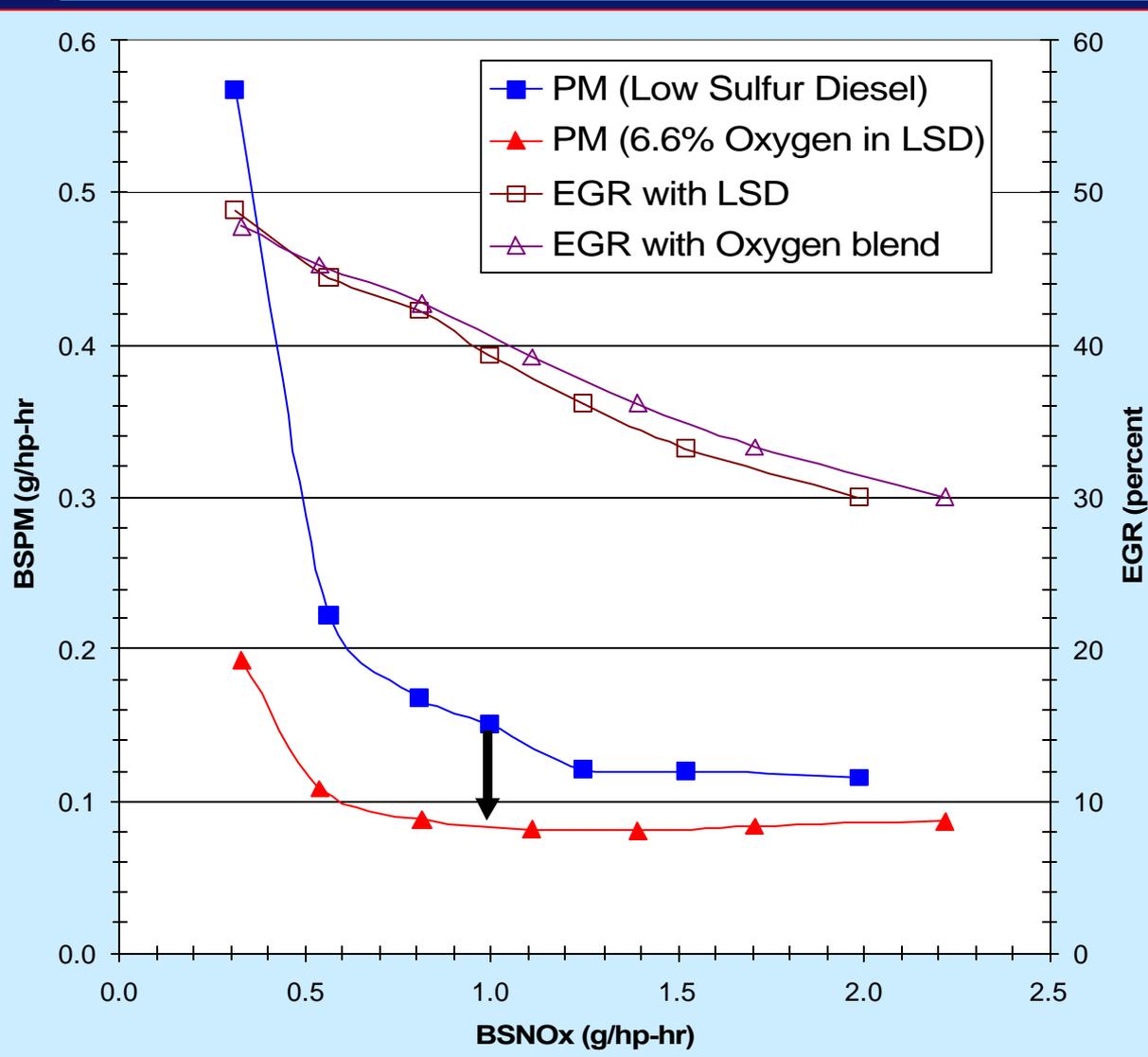
Vehicle Evaluation of Fuel Effects

- NO_x increase observed with reduced PM.
- DMM15 consistently lower PM than other fuels.
- Unlike earlier work, some NO_x increase with DMM15.

DMM15 oxygenate consistently lowest PM former.



Adding Oxygen with DMM reduces PM at all EGR Rates

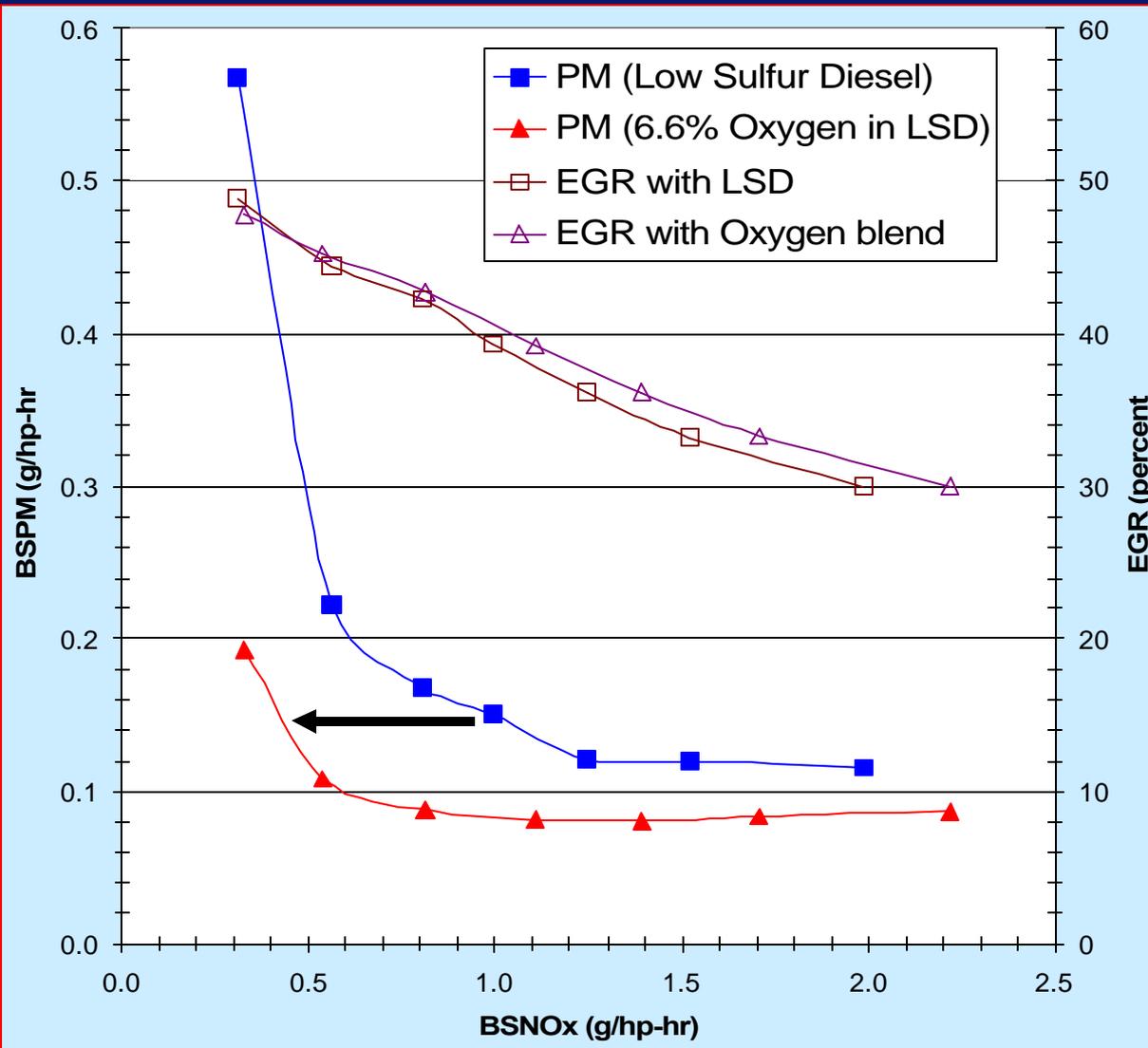


- DMM lowers PM at all EGR rates.
- At 1.0 specific NO_x, oxygen reduces PM by > 45 %.

Yost et al., US DOE FY2000 Progress Report for Advanced Automotive Fuels



Oxygen Seems to Increase Usable EGR Levels



- DMM lowers PM at all EGR rates.
- At 1.0 specific NO_x, oxygen reduces PM by > 45 %.
- By increasing EGR, oxygen can reduce NO_x by > 50 %.



Oxygenate Summary

- Adding oxygenated compounds to diesel fuel can substantially reduce PM emissions.
 - 3 - 5 percent PM for each 1 % oxygen
 - Possible improved EGR tolerance
 - Useful in existing and new designs
- Role of molecular structure unclear.
- Mechanisms of PM reduction unclear.



Oxygenate Summary

- Changes in NO_x emissions inconsistent.
- Particulate size distribution with oxygenates substantially unchanged.
- Are (currently) unregulated emissions changed?
- What about cost and materials compatibility?
- Low molecular weight oxygenates unsuitable for existing diesel fuel distribution system.

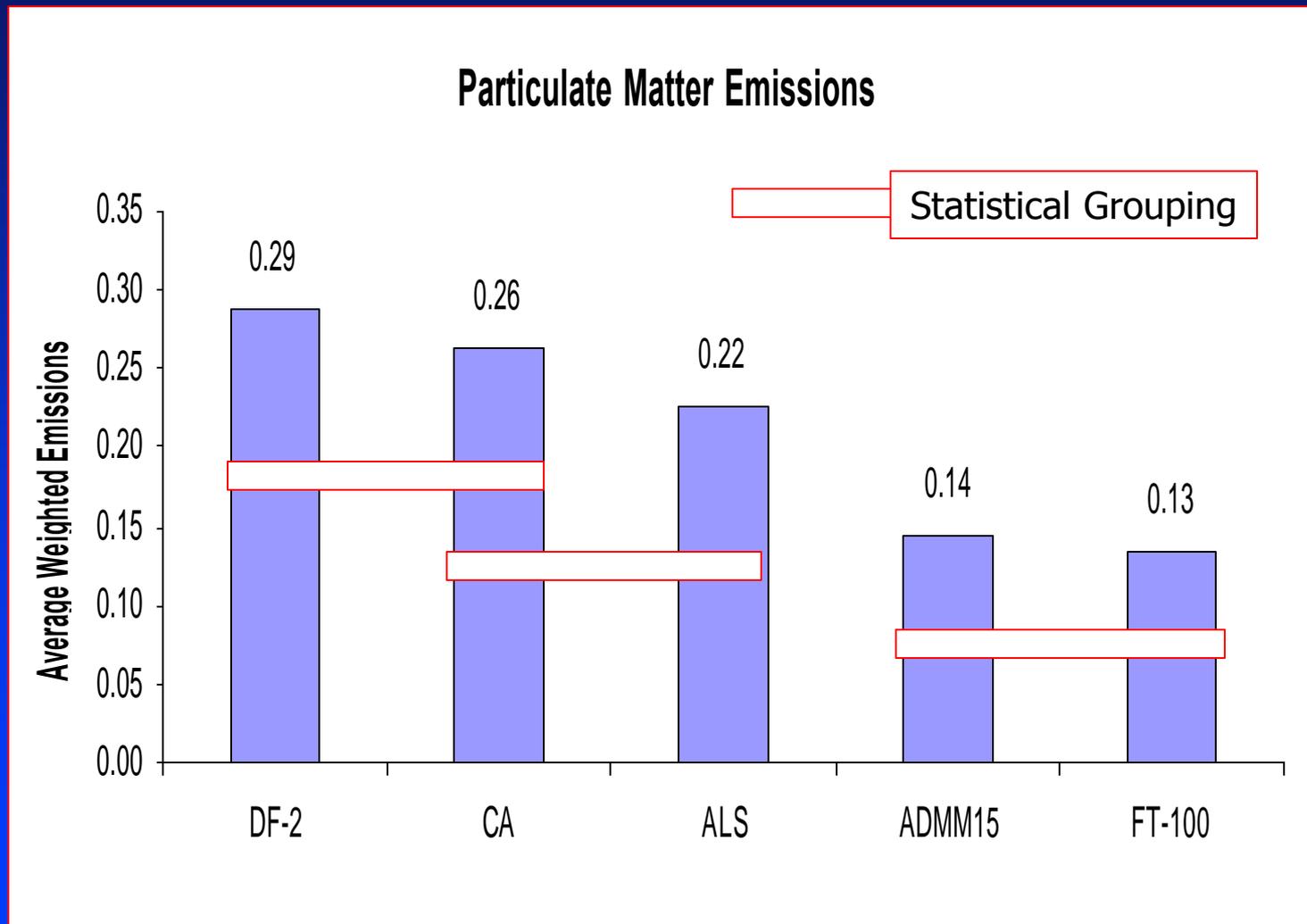


Chemical Characterization of Toxicologically Relevant Compounds from Diesel Emissions

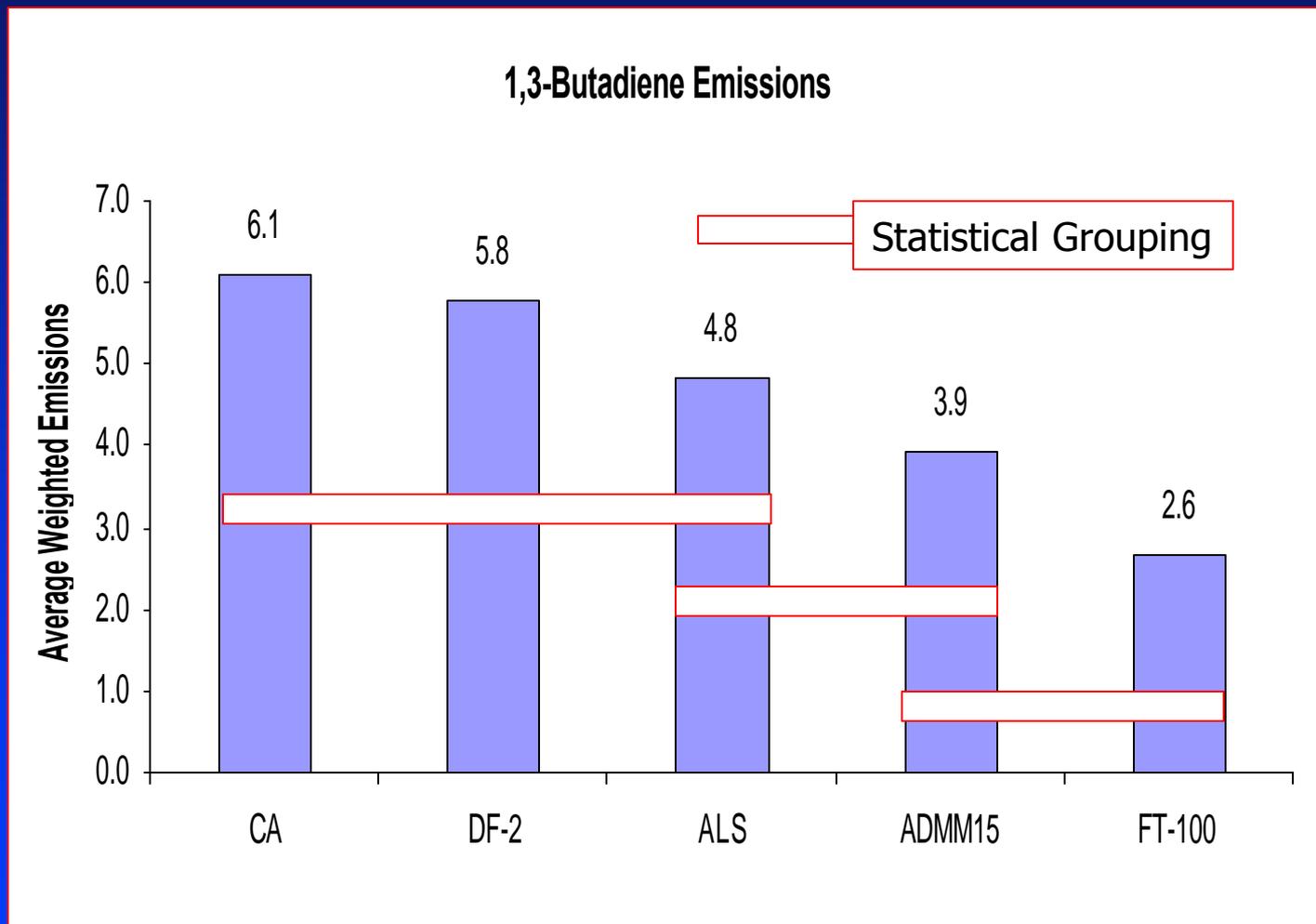
- Measure Engine Out Compounds Collected from a Matrix of Operating Conditions and Fuels
 - Polycyclic Aromatic Hydrocarbons (PAH) from the Soluble Organic Fraction of the Particulate Matter (PM)-Seventeen (17) Compounds
 - Gas Phase PAH-Eleven (11) Compounds
 - Other Gaseous Toxins (4)
 - HC, CO, CO₂, NO_x, PM, SOF



Test Fuel Weighted Average Particulate Matter Mass Emissions (g/kWh)



Test Fuel Weighted Average 1,3-Butadiene Emissions (mg/kWh)



Typical Soluble Toxics Emissions Ranking

Rank	Naphthalene	Acenaphthylene	Acenaphthene	Fluorene	Phenanthrene	Anthracene
Highest	DF-2	CA	DF-2	DF-2	DF-2	DF-2
	CA	DF-2	CA	CA	CA	CA
	FT-100	FT-100	FT-100	ADMM15	FT-100	FT-100
	ADMM15	ADMM15	ADMM15	FT-100	ALS	ADMM15
	ALS	ALS	ALS	ALS	ADMM15	ALS
Lowest						

Typical Soluble Toxics Emissions Ranking

Rank	Fluoranthene	Pyrene	Benzo[a]-anthracene	Chrysene
Highest   Lowest	DF-2	DF-2	DF-2	DF-2
	ALS	ALS	CA	CA
	CA	CA	ALS	ALS
	FT-100	FT-100	FT-100	FT-100
	ADMM15	ADMM15	ADMM15	ADMM15

Oxygenates for Advanced Petroleum-Based Diesel Fuels

Objectives:

Identify compounds to blend with diesel fuel which:
have high oxygen content, compatible with diesel
fuel infrastructure, and substantially reduces PM
emissions.

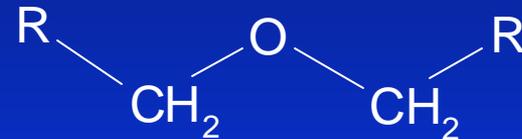
How Oxygen can be Bound in Molecules

- Oxygen attachment impacts fuel properties

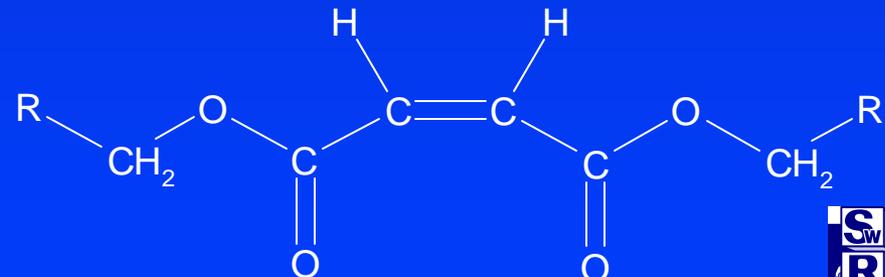
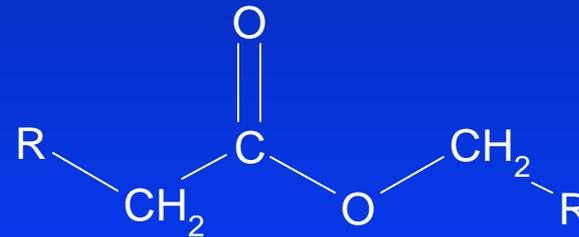
- Alcohol groups lower cetane number.



- Ether groups higher cetane number.



- Ester groups have high oxygen content.



Screening criteria

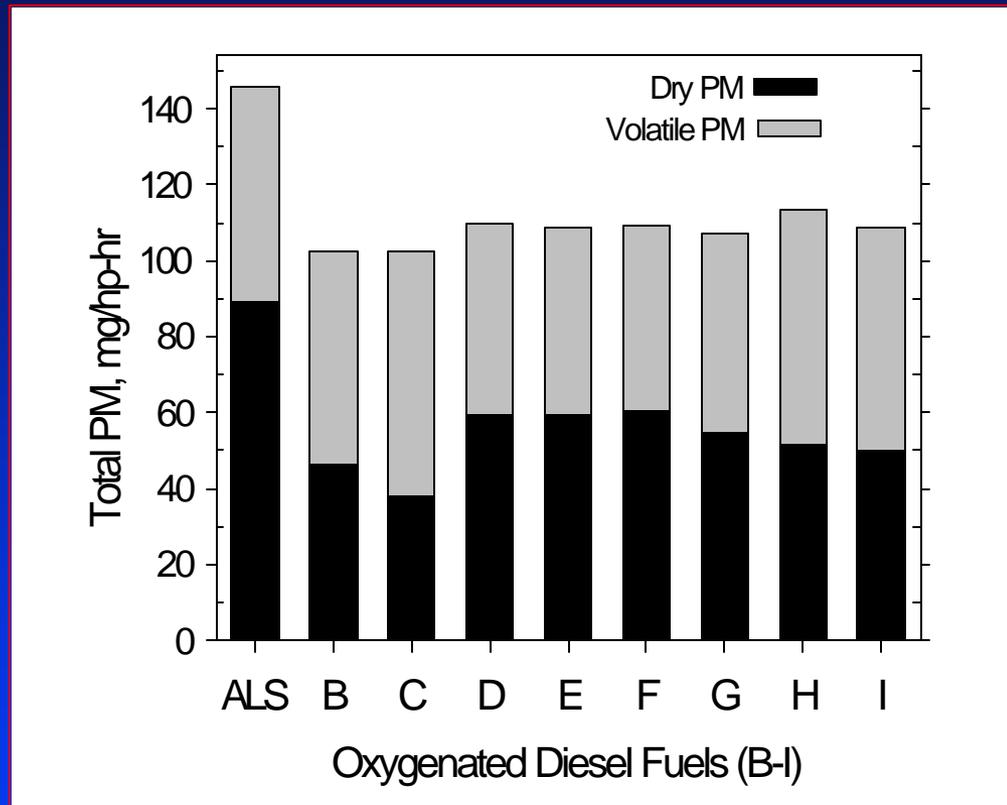
- 71 oxygenate compounds identified from the literature.
- Flash point -- eliminated 28
- Low oxygen content -- eliminated 3
- Soluble in diesel fuel -- eliminated 28
- Odor -- eliminated 1
- Corrosivity -- eliminated 8



Oxygenate candidates for Engine Evaluations

Fuel Code	Oxygenate Compound	Percent Oxygen
B	Tri-propylene glycol mono-methyl ether	19.8
C	1-methoxy-2-propanol	17.9
D	Di-propylene glycol mono-methyl ether	19.4
E	2-ethoxy ethyl acetate	16.7
F	2-ethoxy ethyl ether	21.9
G	Di-ethyl adipate	18.8
H	Tributyrin	18.4
I	Di-butyl maleate	21.6

OM611 Engine PM Emissions



- Single condition tests, with timing revision for each fuel
- Substantial reductions in non-volatile PM
- No change to small increase in volatile PM

Compounds Selected for Further Testing

- Tripropylene glycol monomethyl ether



- Di-butyl maleate



Oxygen-Containing Fuels

- While issues like toxicity, biodegradability, material compatibility and cost were considered, much additional work needed.
- Additional evaluations to be conducted at SwRI and elsewhere with these compounds.

