

**Biodiesel and Renewable
Diesel Emissions Study
VOC, Carbonyl & N₂O Emissions**

Christopher Brandow
Dec 8, 2010

Acknowledgements

MLD Southern Branch
Organic Analysis

Richard Ong
Michael Okafor
Yong Yu
Lyman Dinkins
Christine Maddox
Richard Ling
Paul Rieger

Engines and Fuels

Make/model/year	Emission Control Devices	Test fuels	Analyses
2000 Freightliner C15 Caterpillar		ULSD diesel, Soy-based biodiesel (S20, S50, S100), Animal-based (A20, A50, A100), Renewable diesel (R20, R50, R100)	VOC Carbonyl N2O
2006 International ISM 370	EGR	ULSD diesel, Soy-based biodiesel (S20, S50, S100), Animal-based (A20, A50, A100),	VOC Carbonyl
2008 Freightliner Mercedes Benz MBE 4000	DOC, DPF, EGR	ULSD diesel, Soy-based biodiesel (S20, S50, S100), Animal-based (A20, A50, A100),	VOC Carbonyl

Emissions Analyses

- Speciated non-methane hydrocarbons (NMHC)
- Carbonyl compounds
- Nitrous Oxide (N₂O)

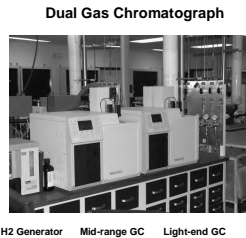
Instrumentation

Analysis	Sample Container	Instrument
NMHC	Tedlar Bag	Gas Chromatograph (GC) with flame ionization detector (FID)
Carbonyls	DNPH* Cartridge	High performance liquid chromatograph (HPLC) with UV detector
N ₂ O	Tedlar Bag	Fourier transform infrared spectrometer (FTIR)

* Sampling cartridge impregnated with 2,4-dinitrophenylhydrazine

Speciated Non-Methane Hydrocarbon Analysis

- Tedlar bag samples analyzed by 2 GC/FIDs, connected in parallel
 - Light-end GC: C1 to C5 HCs
 - Mid-range GC: C6 to C12 HCs
- Liquid nitrogen trapping of sample yields FID detection limits to very low ppbC

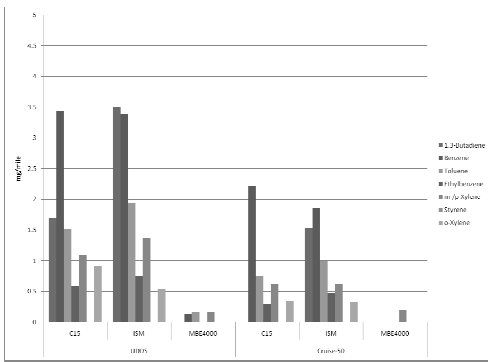


Speciated Non-Methane Hydrocarbon Analysis

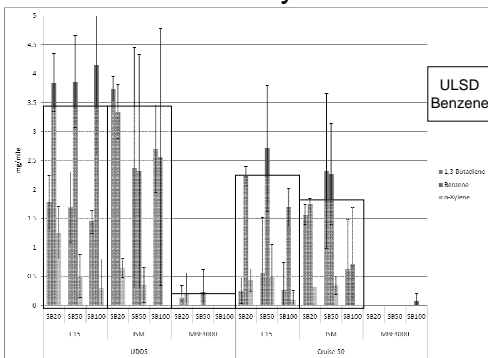
- Compounds reported for this study:

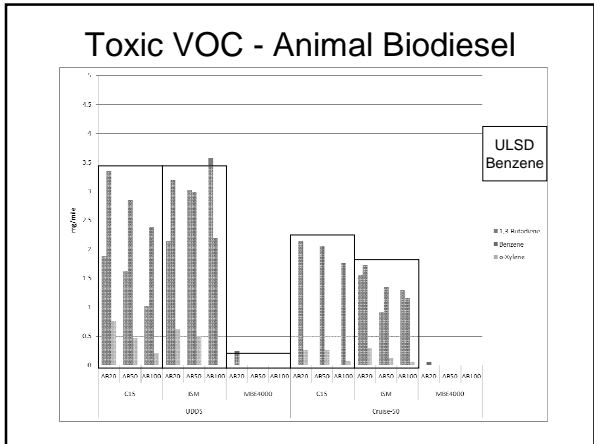
1,3-butadiene
benzene
toluene
ethylbenzene
m-p-xylene
styrene
o-xylene

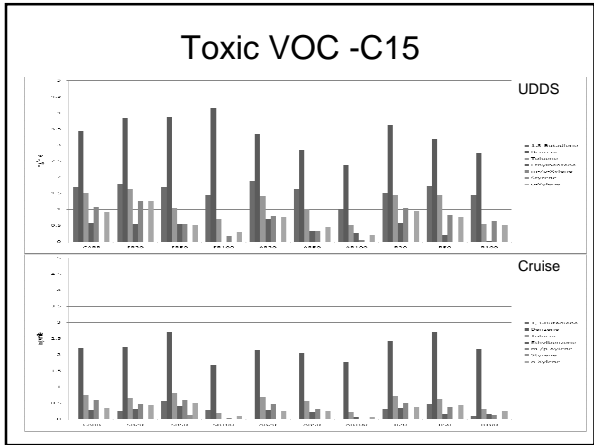
Toxic VOC - ULSD

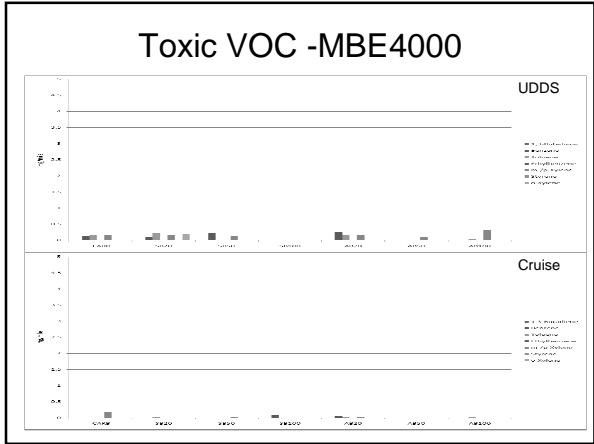


Toxic VOC - Soy Biodiesel



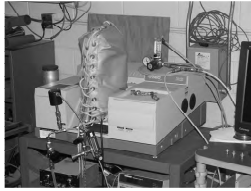




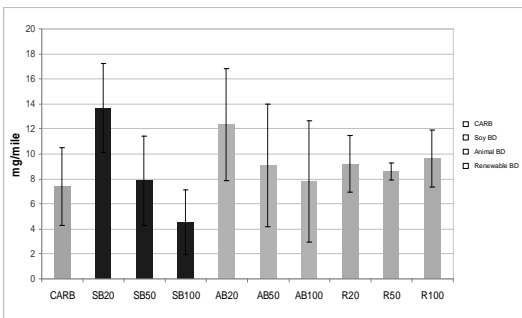


NITROUS OXIDE ANALYSIS

- Tedlar bag samples analyzed by Fourier transform infrared spectroscopy (FTIR)
 - 10-Meter, folded path IR cell



N₂O – C15 Engine



Carbonyl Analysis (Aldehydes and Ketones)

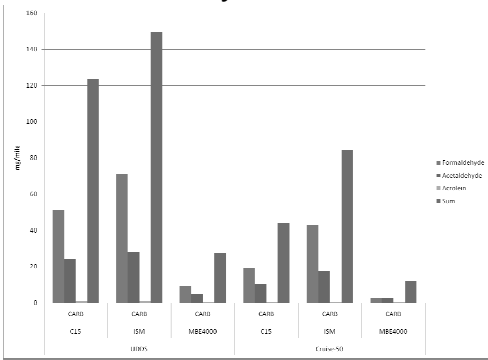
- Carbonyl group derivatized by DNPH in sampling cartridge*
- Cartridges flushed with solvent to extract carbonyl compounds
- Solution analyzed by high performance liquid chromatograph (HPLC) with UV detection



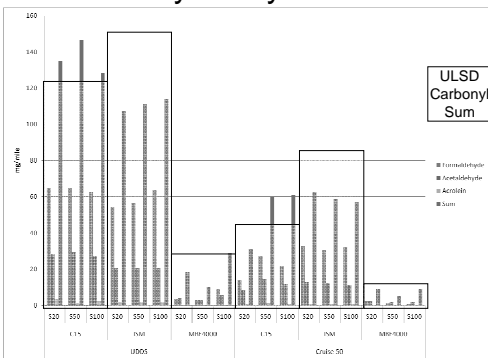
Carbonyl Analysis (Aldehydes and Ketones)

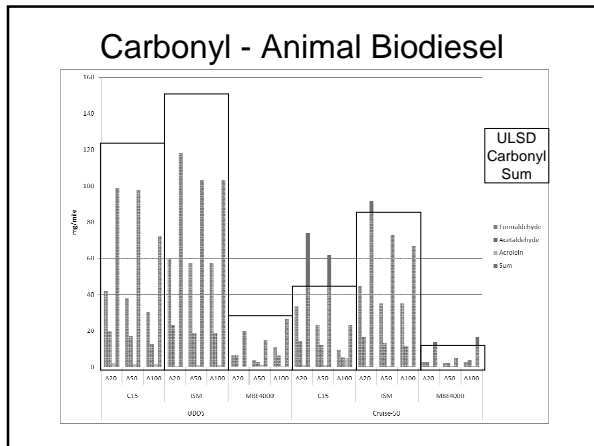
- This method measures:
 - formaldehyde
 - acetaldehyde
 - acrolein*
 - 10 Other carbonyls (to C₆)

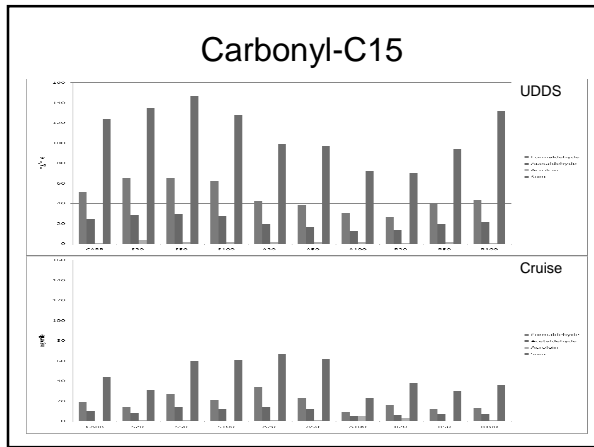
Carbonyl - ULSD

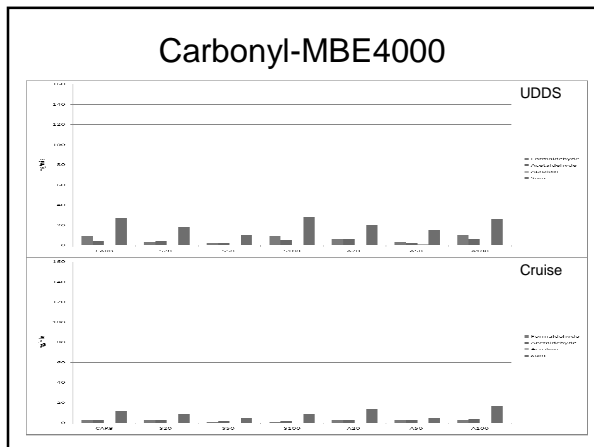


Carbonyl - Soy Biodiesel









Summary - VOC

- Soy Biodiesel
 - No significant VOC increase versus ULSD Fuel
 - No trend with regard to increasing Biodiesel fractions
- Animal Biodiesel
 - Modest VOC decrease versus ULSD Fuel
 - VOC reduced with increasing Biodiesel fractions
- Renewable Biodiesel
 - Modest VOC decrease in UDDS cycle versus ULSD fuel but not in cruise
 - VOC reduced with increasing Biodiesel fraction in UDDS but not in cruise

Summary – N2O

- No significant change in N2O emissions is observed for any fuel blend

Summary - Carbonyl

- Soy Biodiesel
 - No significant changes versus ULSD Fuel
 - No trend with regards to increasing Biodiesel fractions
- Animal Biodiesel
 - Modest decrease versus USLD Fuel in UDDS Cycle only
 - emissions reduced with increasing Biodiesel fractions.
- Renewable Biodiesel
 - No significant changes versus ULSD

Summary - Engines

- VOC
 - C15 and ISM engines perform similarly to each other under all fuel scenarios
 - MBE4000 emits ~ <1/10th of the average of C15 and ISM engines
- Carbonyls
 - C15 and ISM engines perform similarly to each other under all fuel scenarios
 - MBE4000 emits ~ <1/6th of the average of C15 and ISM engines
