Biofuels and Nanoparticles

David Kittelson
Center for Diesel Research
Department of Mechanical Engineering
University of Minnesota

Cambridge Particle Meeting

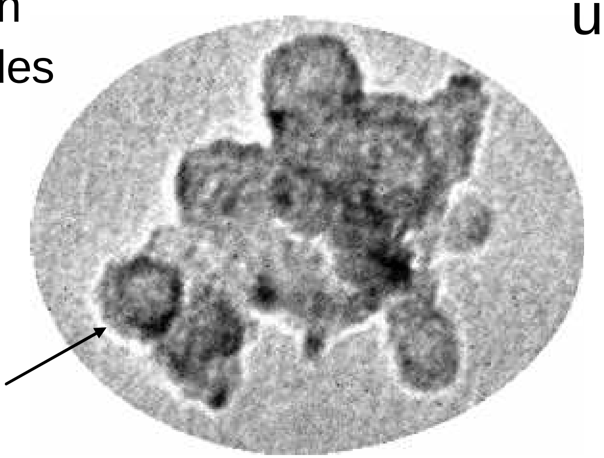
May 16, 2008

Engine, Fuel and Nanoparticle Research
Center for Diesel Research

Nanoparticle formation
- In the atmosphere
- In the engine
- sampling artifacts

Sensors for real time control of ultrafine particles and NO_x

Fundamental studies
- Role of fuel and oil composition on nanoparticle formation
- New combustion modes
  - Hydrogen assisted
  - Low temperature



C/Ce cluster

Renewable fuels, biodiesel, ethanol, to reduce CO_2 and ultrafine particles

David B. Kittelson, Professor of Mechanical Engineering
Director, Center for Diesel Research

Outline

- Introduction
- Biodiesel
- Ethanol
- Butanol
- Future work - DME

Minnesota Next Generation Energy Act

- Goal to reduce statewide GHG emissions from all sectors by at least:
  - 15% below 2005 levels by 2015
  - 30% below 2005 levels by 2025
  - 80% below 2005 levels by 2050
- Our group has been asked by the Minnesota legislature to come up with a plan to meet these goals in the transportation sector
- Renewable fuels will play a major role

Status of Minnesota Fuel Policies

- State Policy on Biodiesel
  - Current Standard: 2% Biodiesel blend
  - Future Goal: 20% blend by 2015
- State Policy on Ethanol
  - Current Standard: 10% Ethanol blend in gasoline
  - Future Goal: 20% blend by 2013 with 5% from cellulosic
  - The Next Generation Energy Initiative increases E85 gas stations from 300 to 1800 by the year 2010
  - Current production 1.1 billion gallons /year – 1/3 of our gasoline needs, most exported

Center for Diesel Research and Combustion Lab
Current Biodiesel Research

- Biodiesel (methyl esters)
  - Backup power generation
  - Marine engines
  - Automotive engines
    - » Emission measurements
    - » Fundamental particle characterizations
- Raw seed oils
  - Atomization
  - Combustion properties
  - Fundamental particle characterizations
- Biodiesel and raw seed oils in gas turbines

Soybeans the Main US Biodiesel Feedstock: Soy Methyl Ester (SME) Biodiesel Production

100 lbs. of soybean oil

+

10 lbs. methanol

=

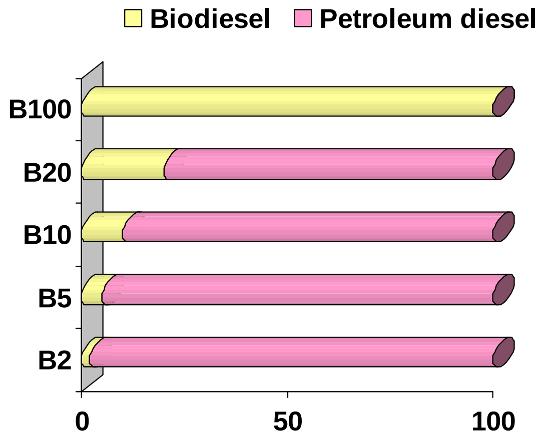
100 lbs. soy biodiesel (B100)

+

10 lbs. of glycerin

Biodiesel may also be made from animal fat, restaurant grease, canola, rapeseed, palm, etc.

Biodiesel Blends and Emissions



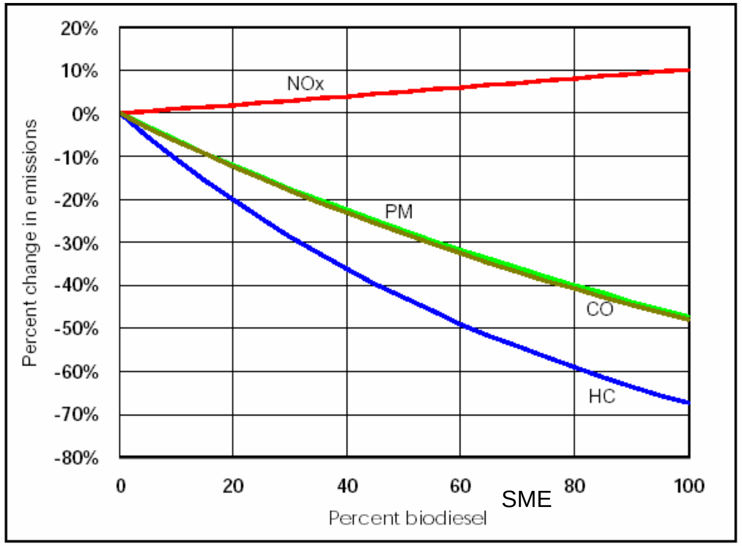
B100 = 100% biodiesel

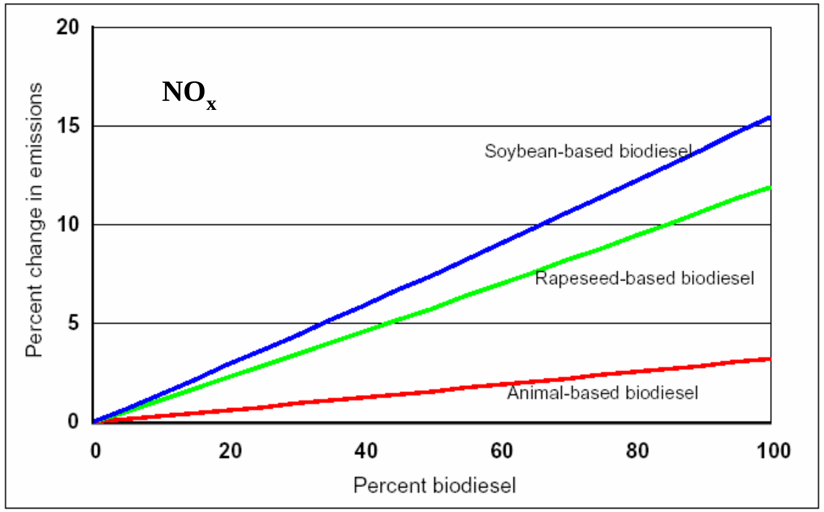
B20 = 20% biodiesel + 80% petroleum diesel

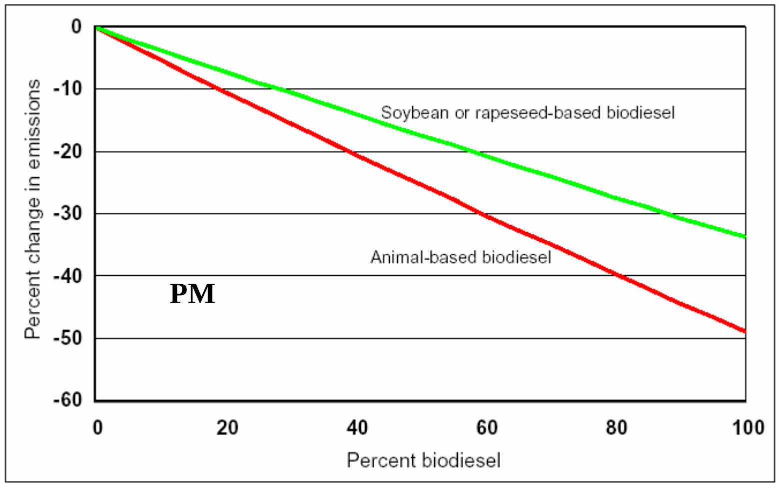
B10 = 10% biodiesel + 90% petroleum diesel

B5 = 5% biodiesel + 95% petroleum diesel

B2 = 2% biodiesel + 98% petroleum diesel





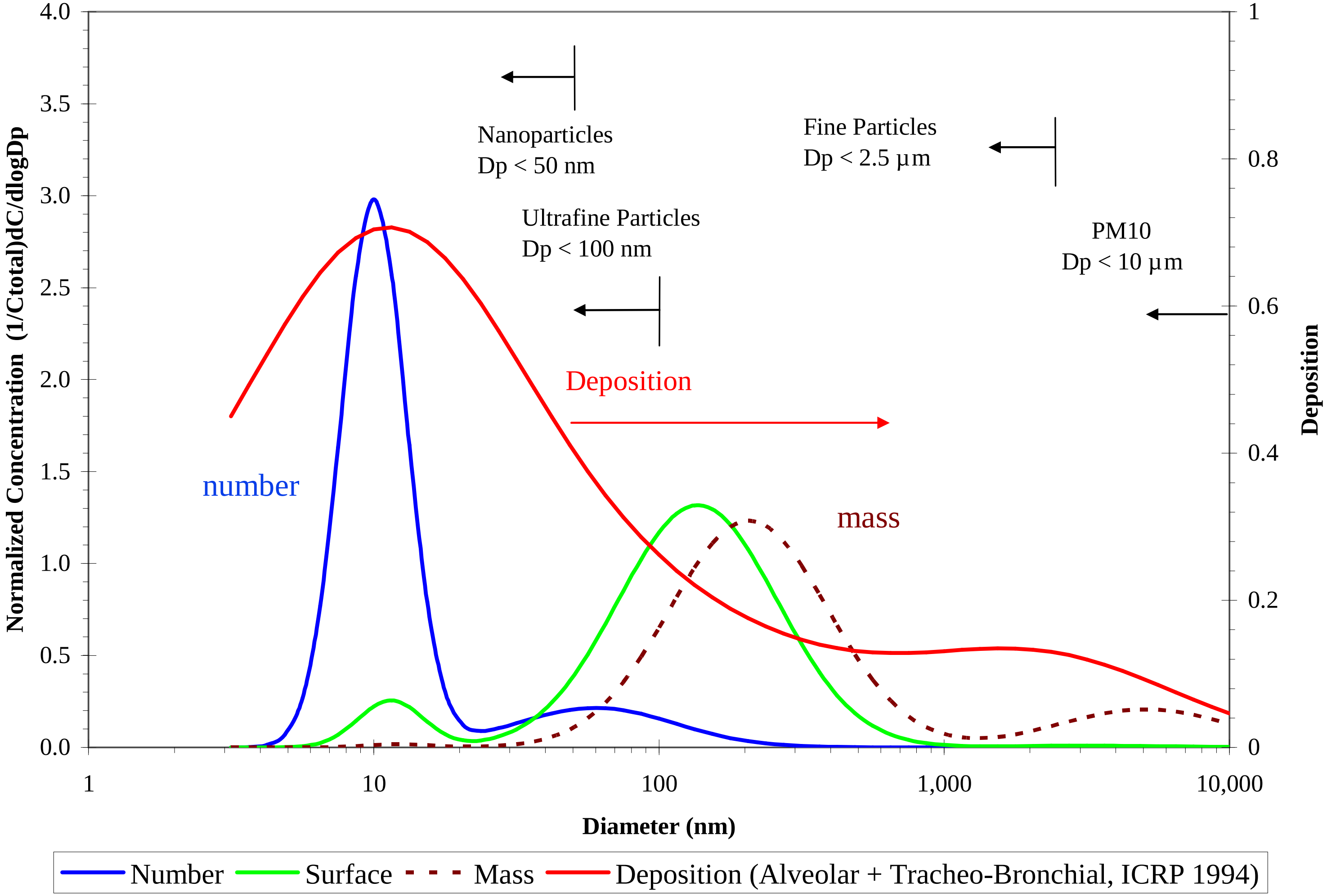


UNIVERSITY OF MINNESOTA

Data from USEPA 2002

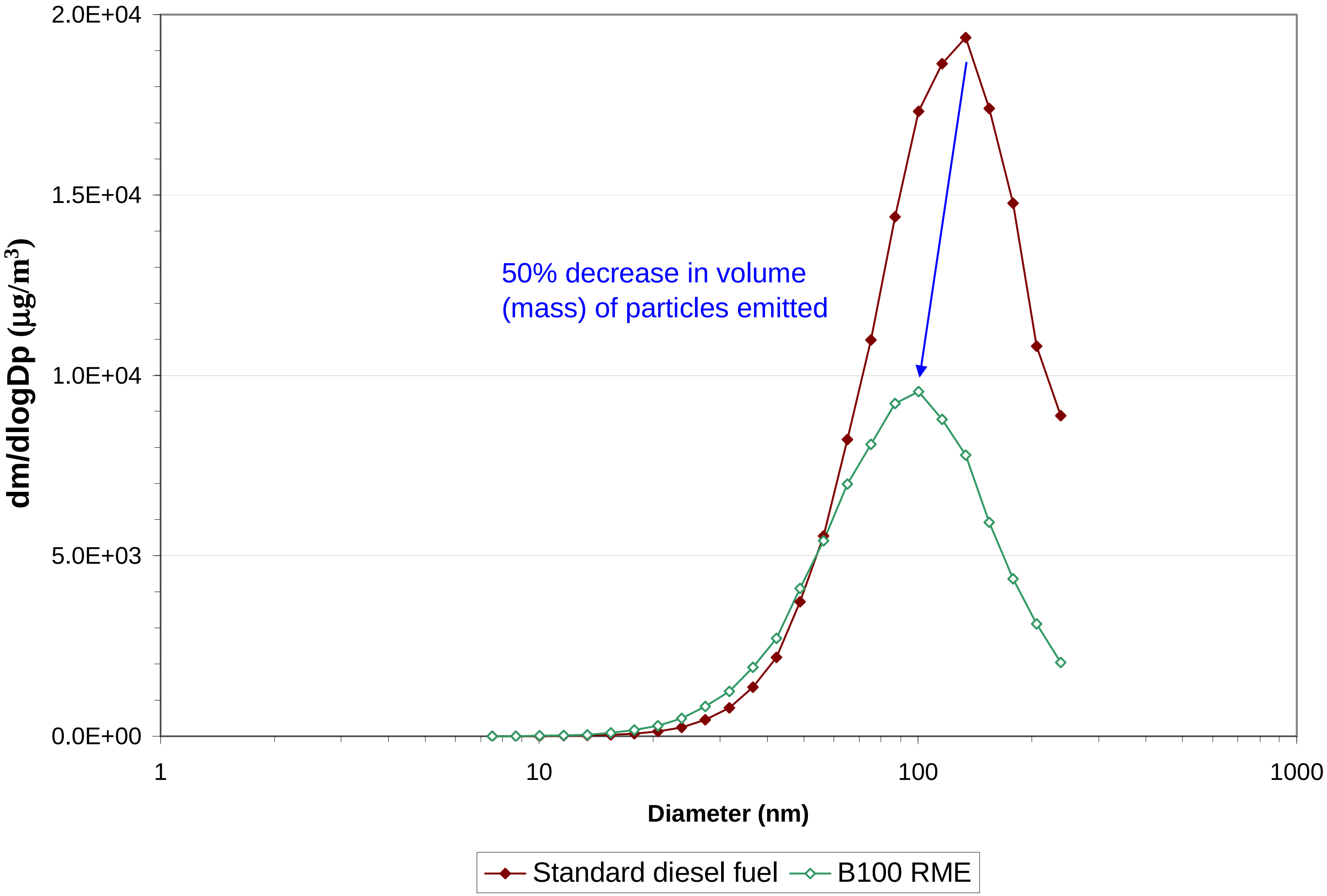
Center for Diesel Research

Engine particle size distributions, lung deposition efficiency – biodiesel makes smaller particles



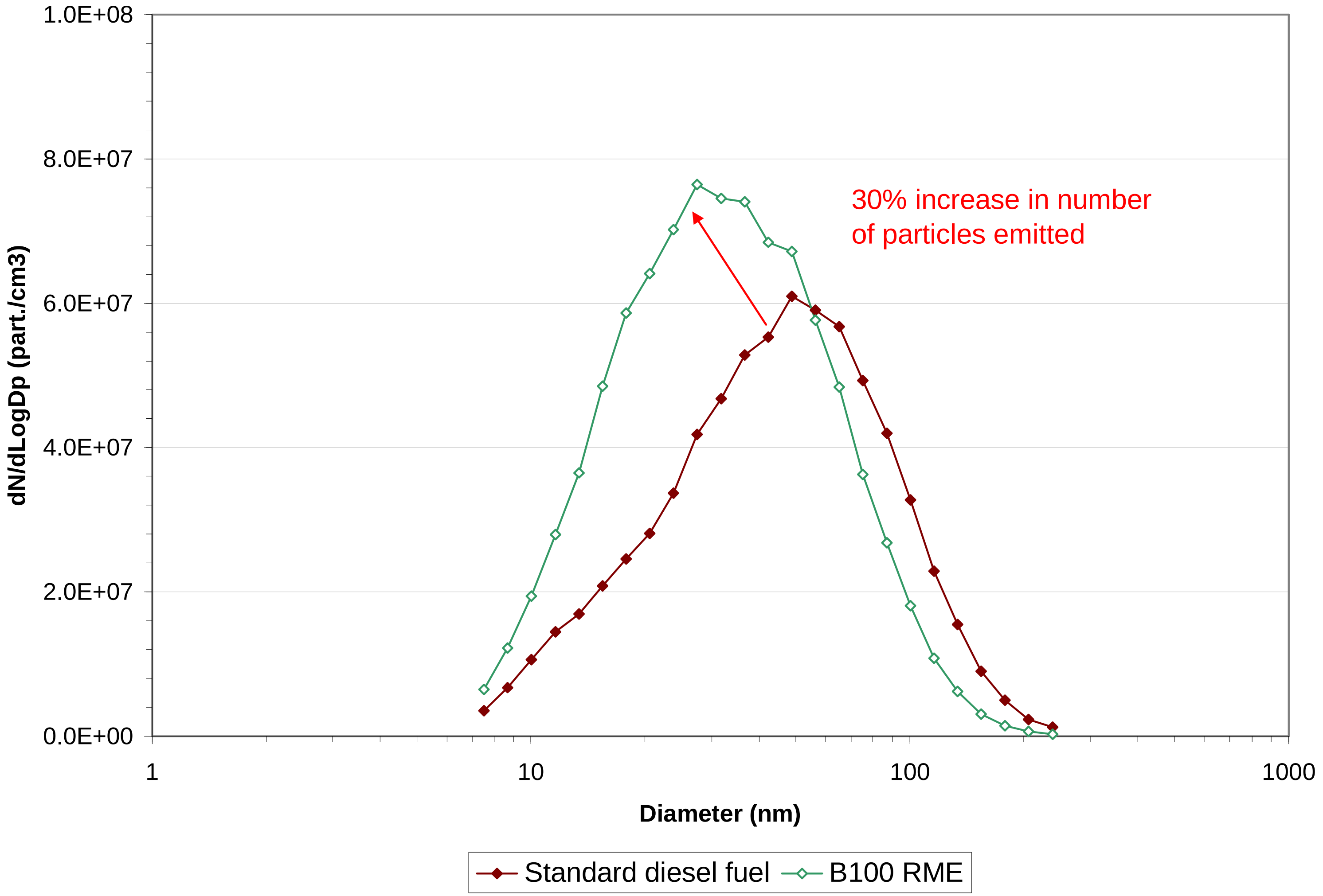
Kittelson, D.B. 1998. "Engines and Nanoparticles: A Review," J. Aerosol Sci., Vol. 29, No. 5/6, pp. 575-588, 1998

Mass distributions, light-duty engine, multimode cycle, B100 RME



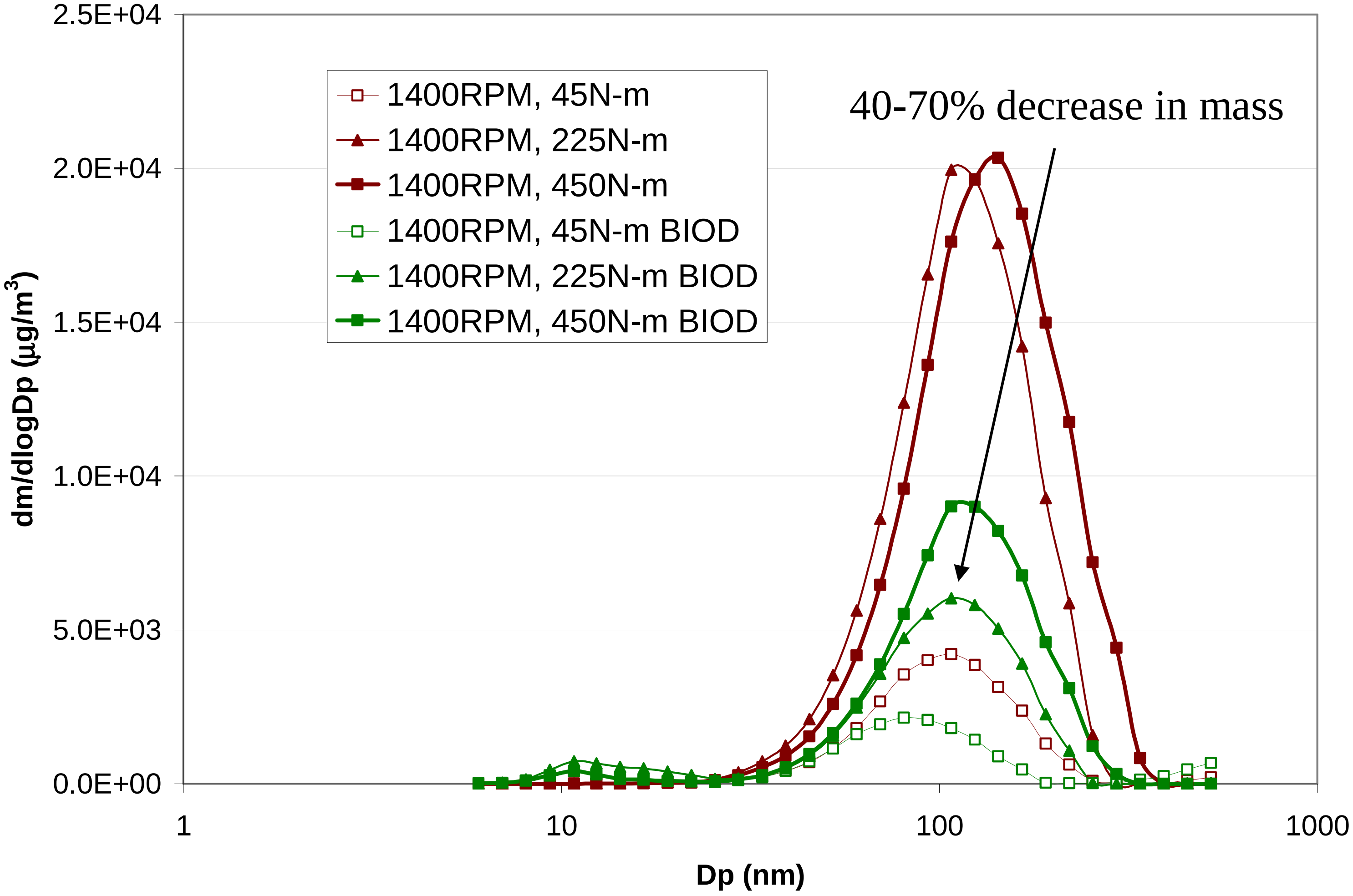
Zarling, Darrick, Todd Taubert, Robert Waytulonis, Matthew Sirek, and David Kittelson, 2001. “Fuel Effects on the Formation of Ultra-fine Particulate Emissions from a VW 1.9-L TDI Diesel Engine,” Final Report submitted to Volkswagen AG, 2001.

Number distributions, light-duty engine, multimode cycle, B100 RME



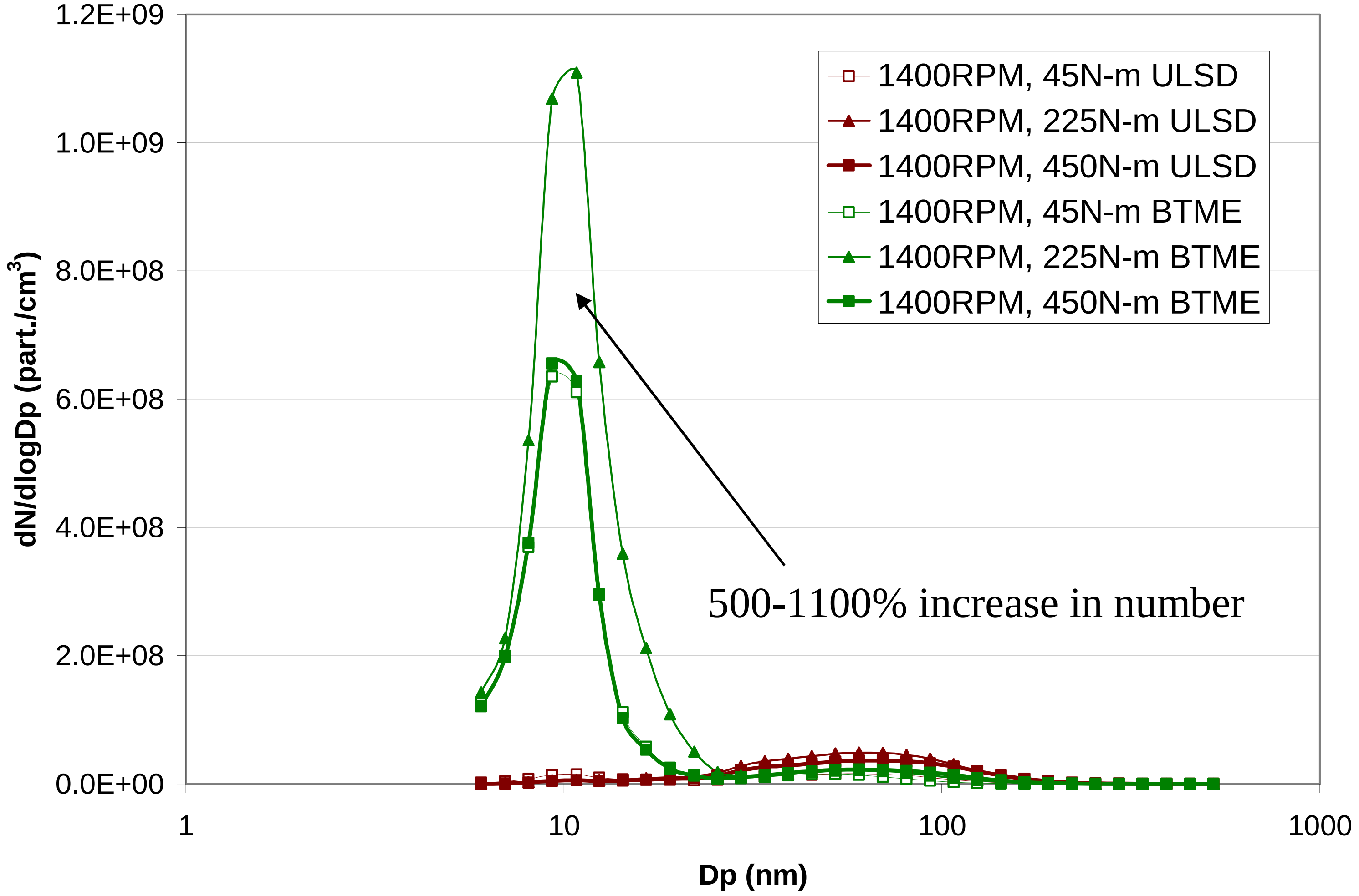
Zarling, Darrick, Todd Taubert, Robert Waytulonis, Matthew Sirek, and David Kittelson, 2001. "Fuel Effects on the Formation of Ultra-fine Particulate Emissions from a VW 1.9-L TDI Diesel Engine," Final Report submitted to Volkswagen AG, 2001.

Mass distributions, medium-duty engine, ULSD and Beef Tallow Methyl Ester (BTME)

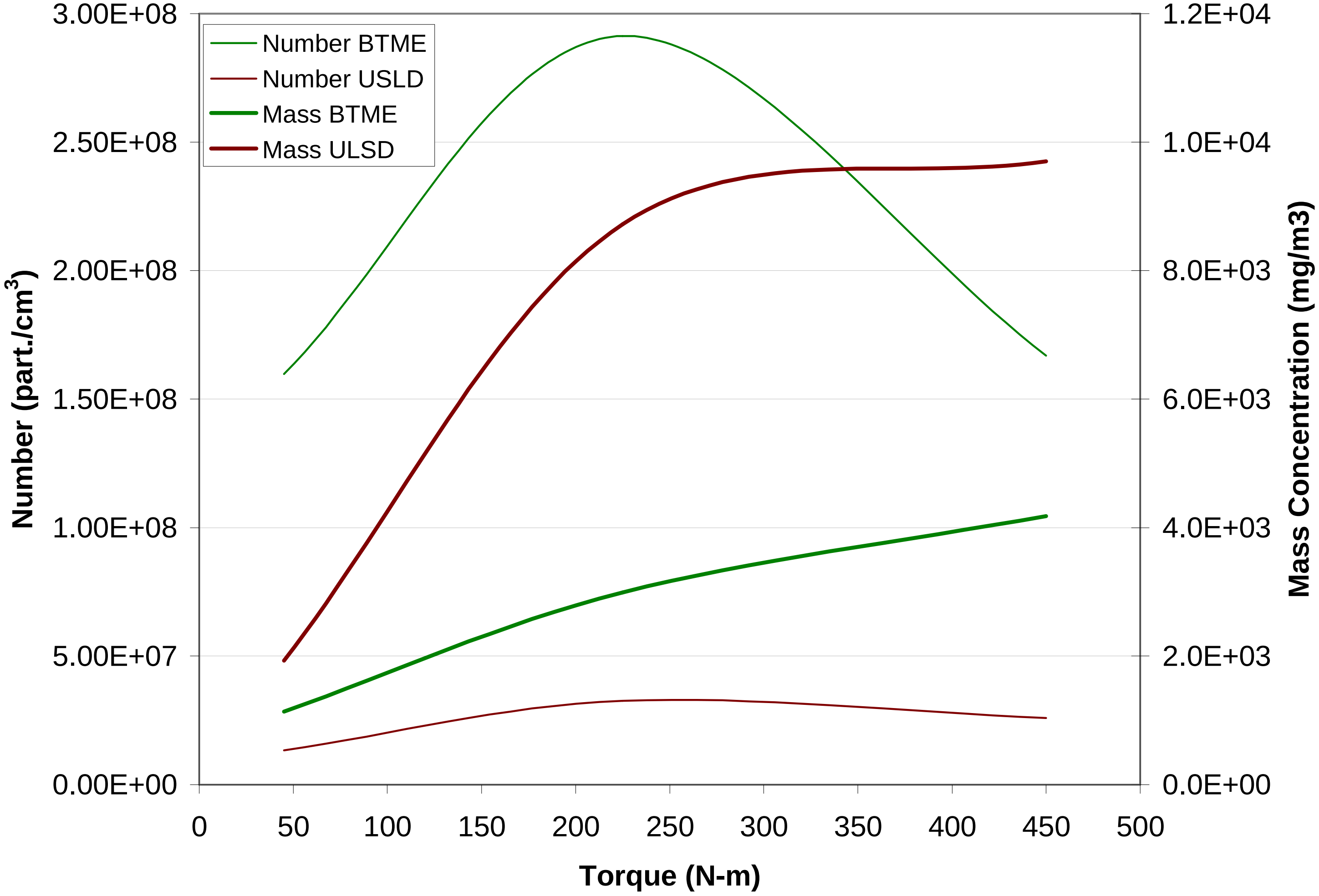


*BTME and USLD results obtained by ME 4431 lab, Spring Semester 2008, Aaron Collings, TA

Number distributions, medium-duty engine, ULSD and Beef Tallow Methyl Ester (BTME)



Mass and Number Concentrations, Medium-Duty Engine, ULSD and BTME



UNIVERSITY OF MINNESOTA

Center for Diesel Research

Comparison between biodiesel and petroleum particles

- Engine to engine variation
- Biodiesel particles are
  - Smaller
  - Contain more volatile material, especially in the smallest size range
  - Contain much less soot
- Much of this volatile material is partially burned fuel
- A well designed oxidizing catalyst removes most of this volatile material
- All this applies to current engines, what about advanced engines with aftertreatment?

Center for Diesel Research and Combustion Lab Ethanol Research

- Ethanol (E85) performance and particle emissions in Otto (gasoline) engine
- Ethanol (E20) spark ignition fleet tests – to help support 2013 E20 mandate in Minnesota
- Ethanol (E100) combustion in Diesel engine enhanced with hydrogen injection
- Ethanol (E100) as fuel in homogeneous charge compression ignition (HCCI) engine
- Hydrogen from reformed ethanol as a Diesel combustion modifier

Fundamental studies of ethanol blends in SI engine (E0 –E85)

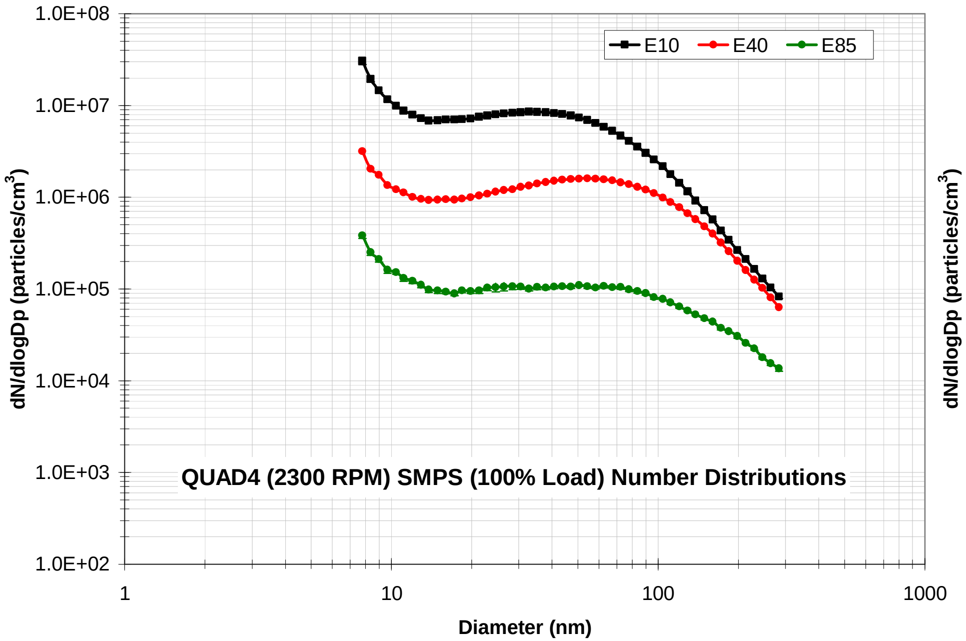
- Overall particle emissions – size and number*
- Optical properties of soot particles – light absorption and scattering characteristics*
- Kinetics of oxidation of ethanol soot**
- Single particle mass spectrometer measurements of unregulated particle emissions***

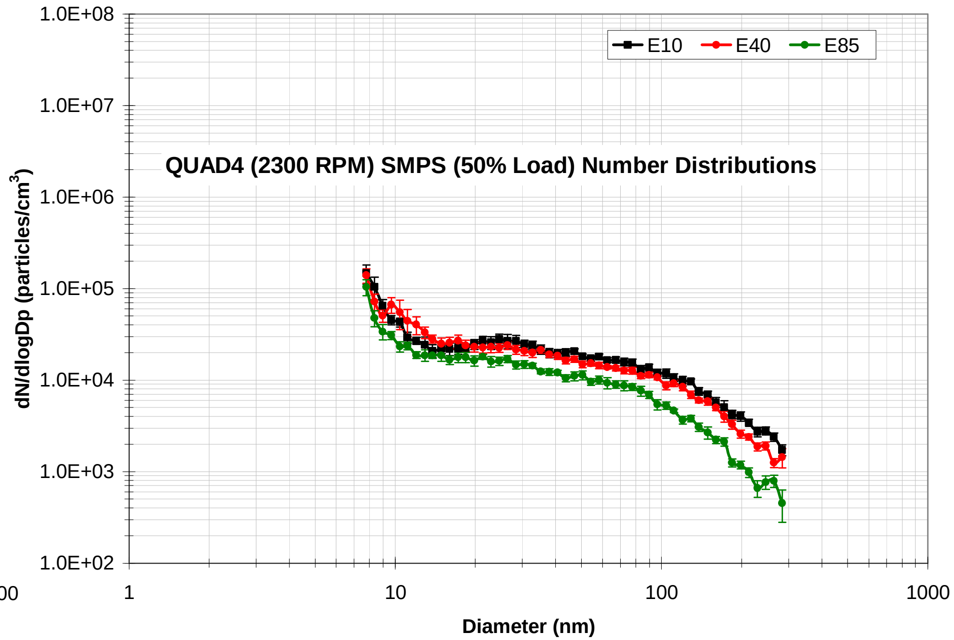
*Drayton, Marcus K.; Henry M. Ajo, Jeffrey T. Roberts, and David B. Kittelson, 2008. "The Influence of Fuel Ethanol Content on Spark Ignition Engine Nano-Particulate Emissions and Black Carbon Composition," in preparation for submission to SAE.

**Ajo, Henry M.; Marcus K. Drayton, David B. Kittelson, and Jeffrey T. Roberts, 2008. "The Effects of Ethanol as an Oxygenate Additive on Soot Nanoparticulate Matter Oxidation Kinetics, in preparation for submission to EST.

***Dutcher, Dabrina D.; Marcus Drayton, Mark R. Stolzenburg, Juan M. Medrano, Deborah S. Gross, David B.Kittelson, and Peter H. McMurry, 2008. "Bio-Fuel Combustion: a Single Particle Perspective, Part 1: Ethanol" submitted to Environmental Science and Technology.

Influence of ethanol blends on ultrafine and nanoparticle emissions*





- At high loads the particle emissions are strongly dependent upon the ethanol content of the fuel with 1 to 2 orders of magnitude decrease with E85
- At lighter loads the effect is much smaller, but this doesn't matter because nearly all emissions are at high load – E10 emissions go up by about a factor of 1000 during hard acceleration

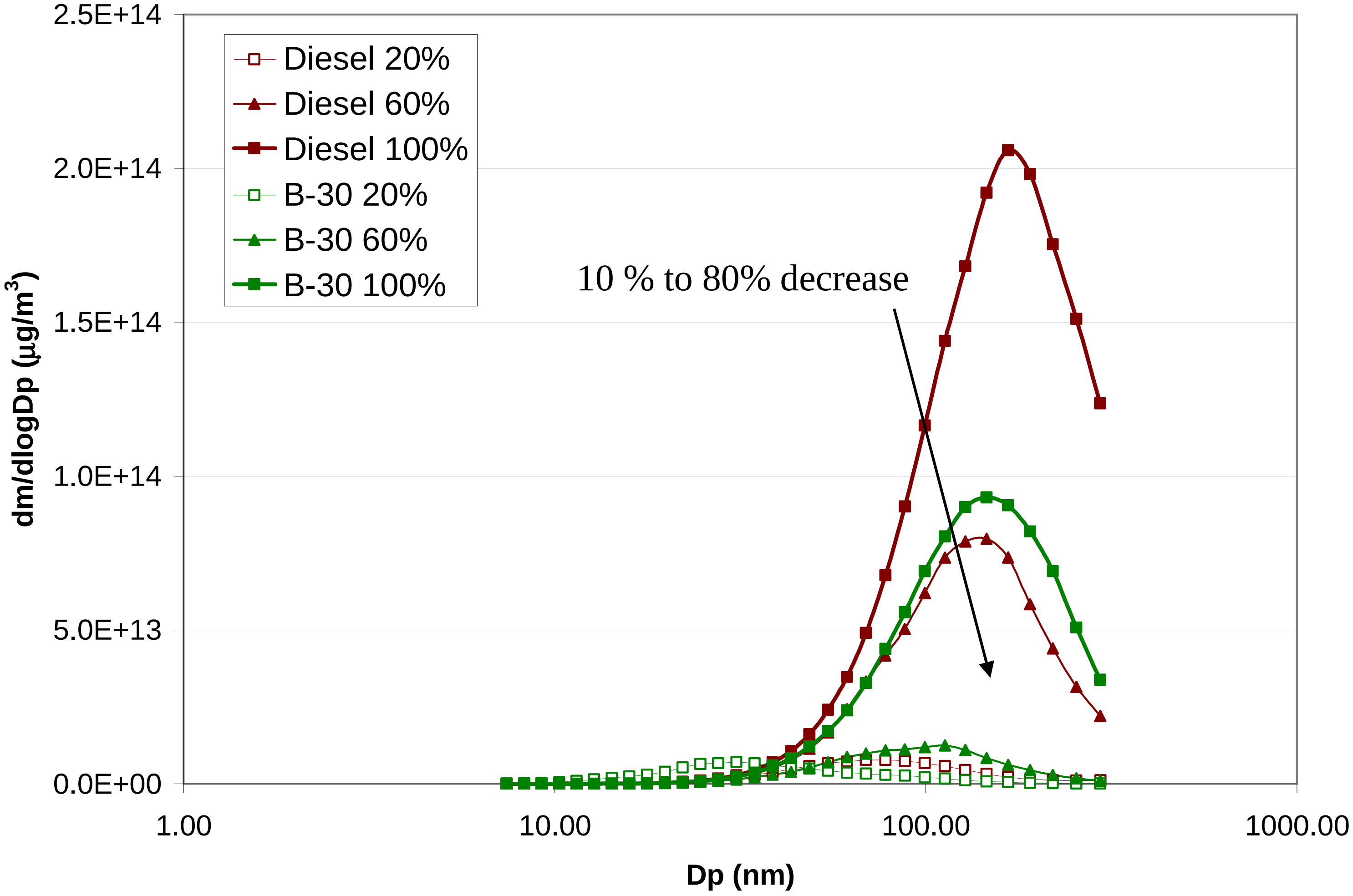
*Drayton, Marcus K.; Henry M. Ajo, Jeffrey T. Roberts, and David B. Kittelson, 2008. "The Influence of Fuel Ethanol Content on Spark Ignition Engine Nano-Particulate Emissions and Black Carbon Composition," in preparation for submission to SAE.

Butanol*

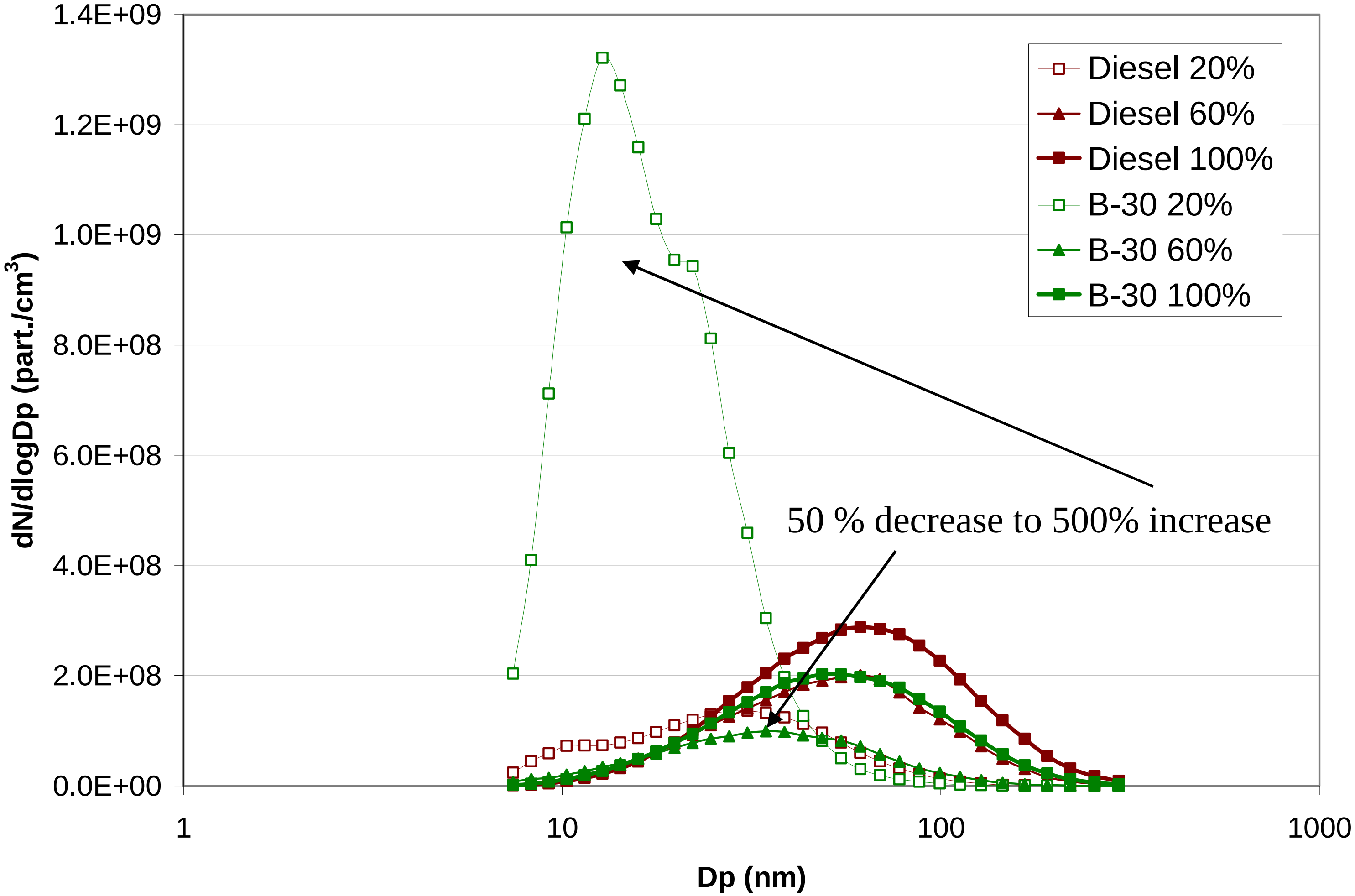
- BP is promoting the use of butanol as a gasoline fuel extender
- We decided to test butanol blends in both gasoline and Diesel engines
  - Gasoline test results being processed
  - Preliminary Diesel tests reported here for 30% butanol blend with ULSD
    - 20 to 50% NOx reductions
    - Particle results reported below

*Olson, Andre, M.S. Thesis in preparation, University of Minnesota, 2008.

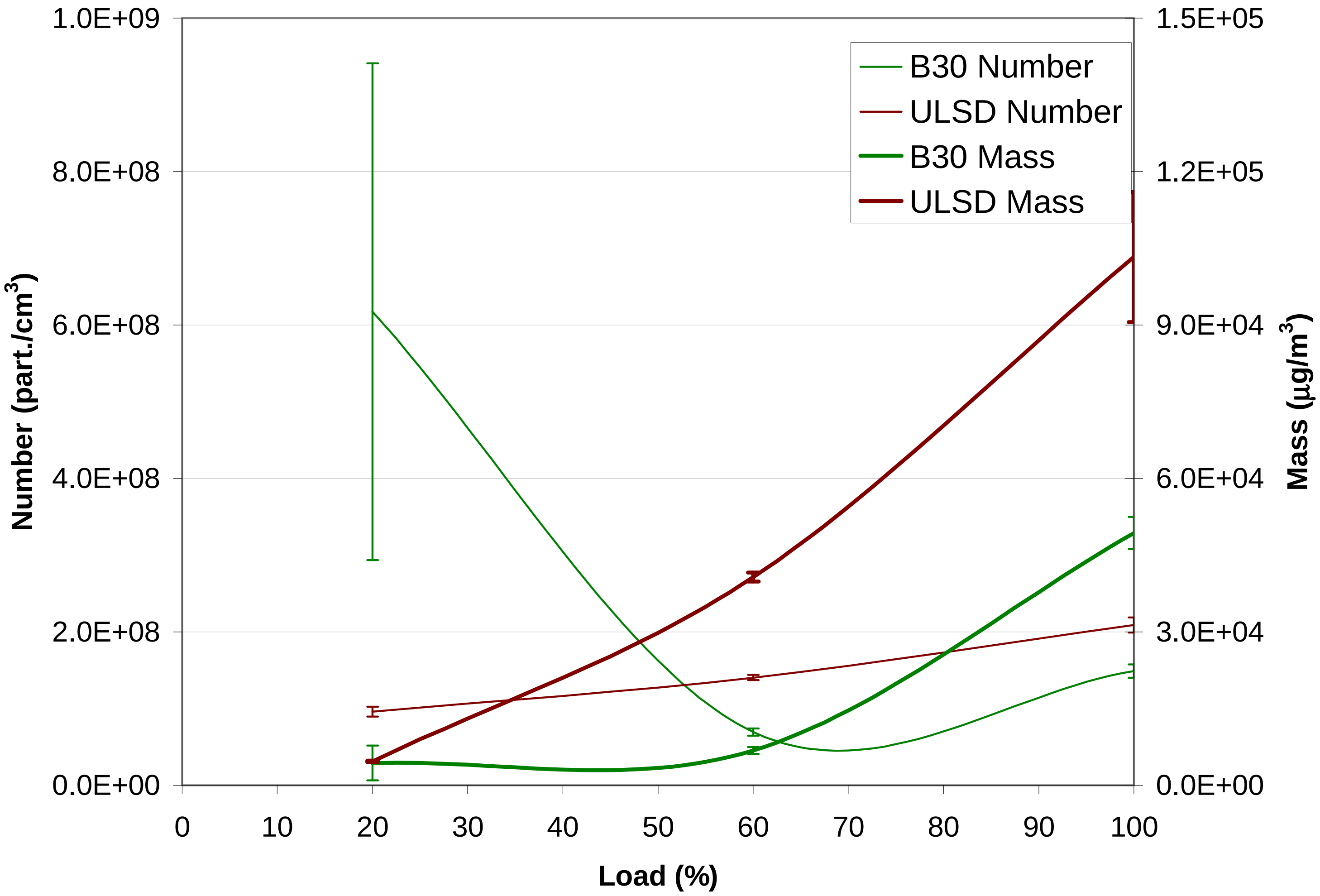
Mass distributions, small RV generator, ULSD and 30% butanol in ULSD



Number distributions, small RV generator, ULSD and 30% butanol in ULSD



Total number and mass concentrations, small RV generator, ULSD and 30% butanol in ULSD



UNIVERSITY OF MINNESOTA

Hydrogen assisted combustion*

- Objectives
  - Investigate the influence of port fuel injection of hydrogen on performance and emissions of a light-duty Diesel engine running with USLD and biodiesel as primary fuels
  - Initial work with pure hydrogen, but final goal will be to test with gases expected from autothermal reforming of ethanol or glycerin
- Test conditions
  - VW TDI engine
  - Timed port fuel injection of hydrogen
  - 1700 rpm, variable load
- Summary results
  - Up to 40% of fuel energy supplied as hydrogen
  - Slight decrease in engine efficiency
  - Reduced PM emissions
  - Little change in NO_x, but increase in NO_2/NO ratio

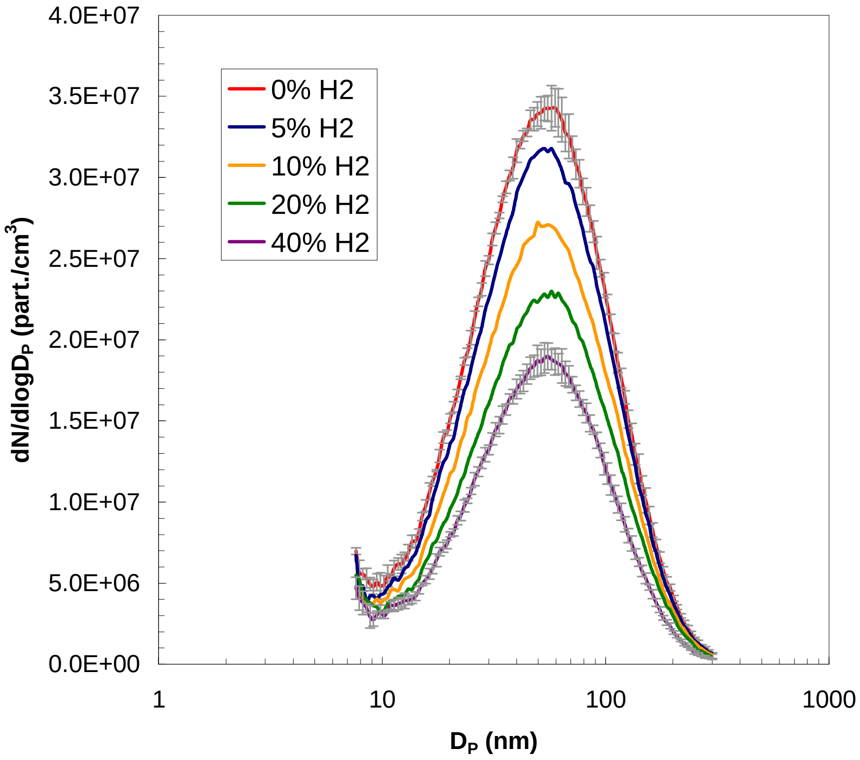
*Bika, Anil Singh; Luke M. Franklin, and David B. Kittelson, 2008. "Emissions Effects of Hydrogen as a Supplemental Fuel with Diesel and Biodiesel," SAE paper number 08PFL-971

Hydrogen injection system installed on VW TDI engine

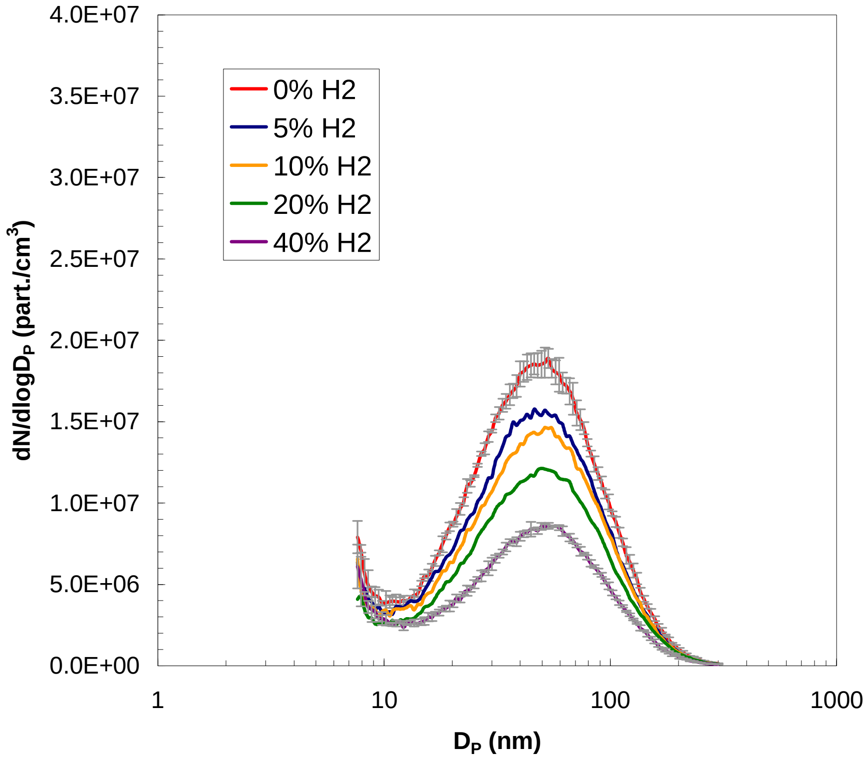
- Engine test stand
- Hydrogen injection system

Number size distributions showing influence of % hydrogen energy input

Diesel 1700 rpm, 80 N-m (40% load)



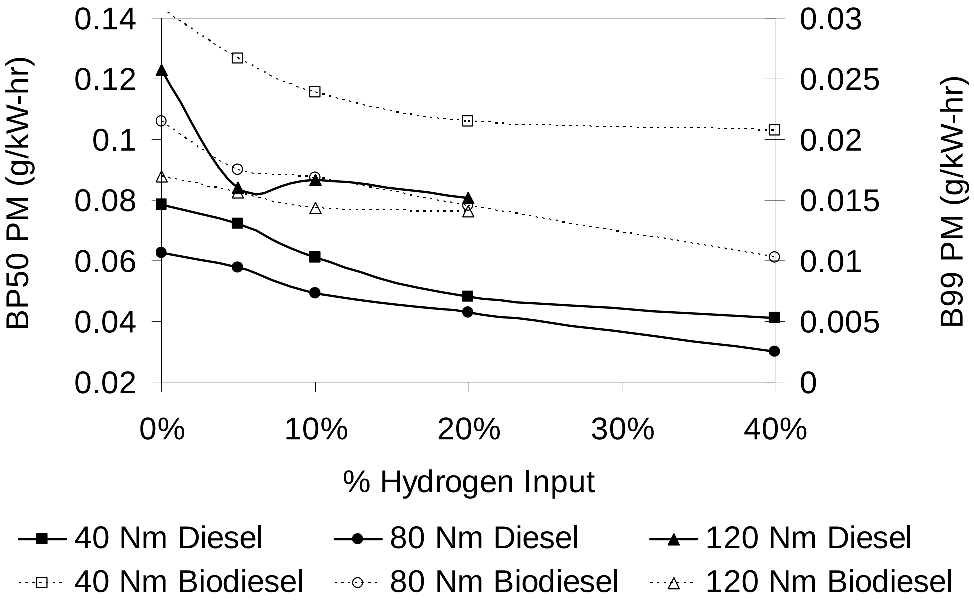
Biodiesel 1700 rpm, 80 N-m (40% load)

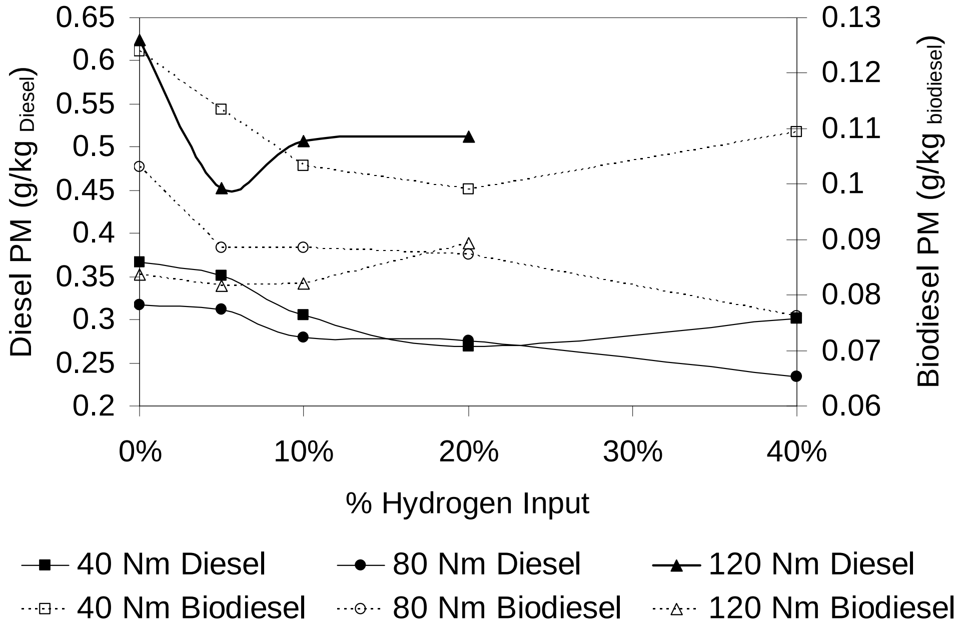


Influence of hydrogen on particle mass emissions

Brake specific emissions are reduced significantly by H_2. Note that biodiesel emissions levels are much lower

But emissions per kg of liquid fuel are only reduced slightly. Most of decrease due to less diffusion burning.





Influence of hydrogen addition on NO_x and NO_2 emissions

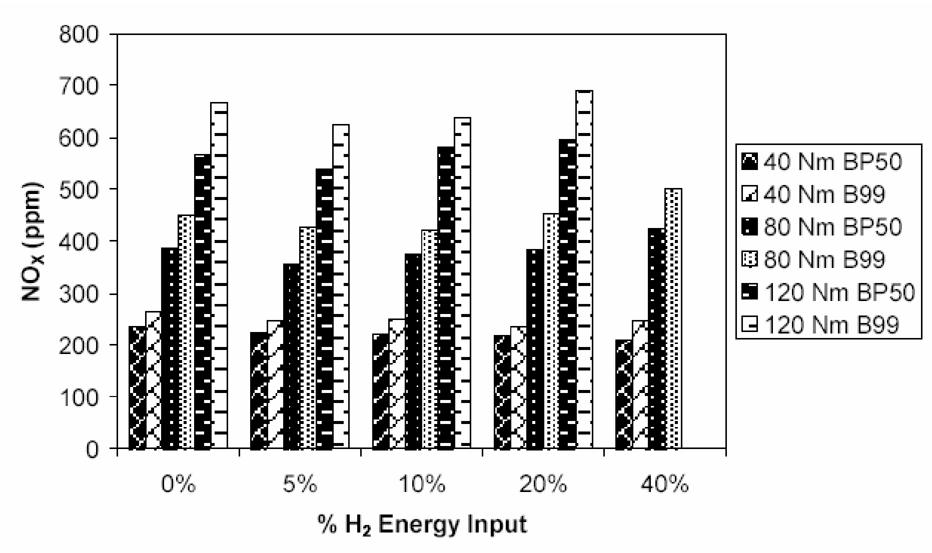
The NO_2/NO_x ratio increases with H_2

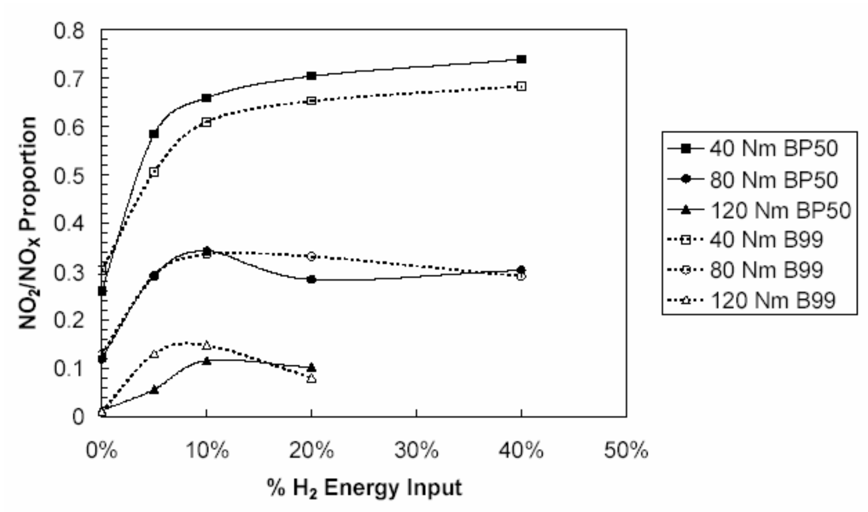
The likely reactions for the NO_2 increase are:

$HO_2 + NO \leftrightarrow NO_2 + OH$ (1)

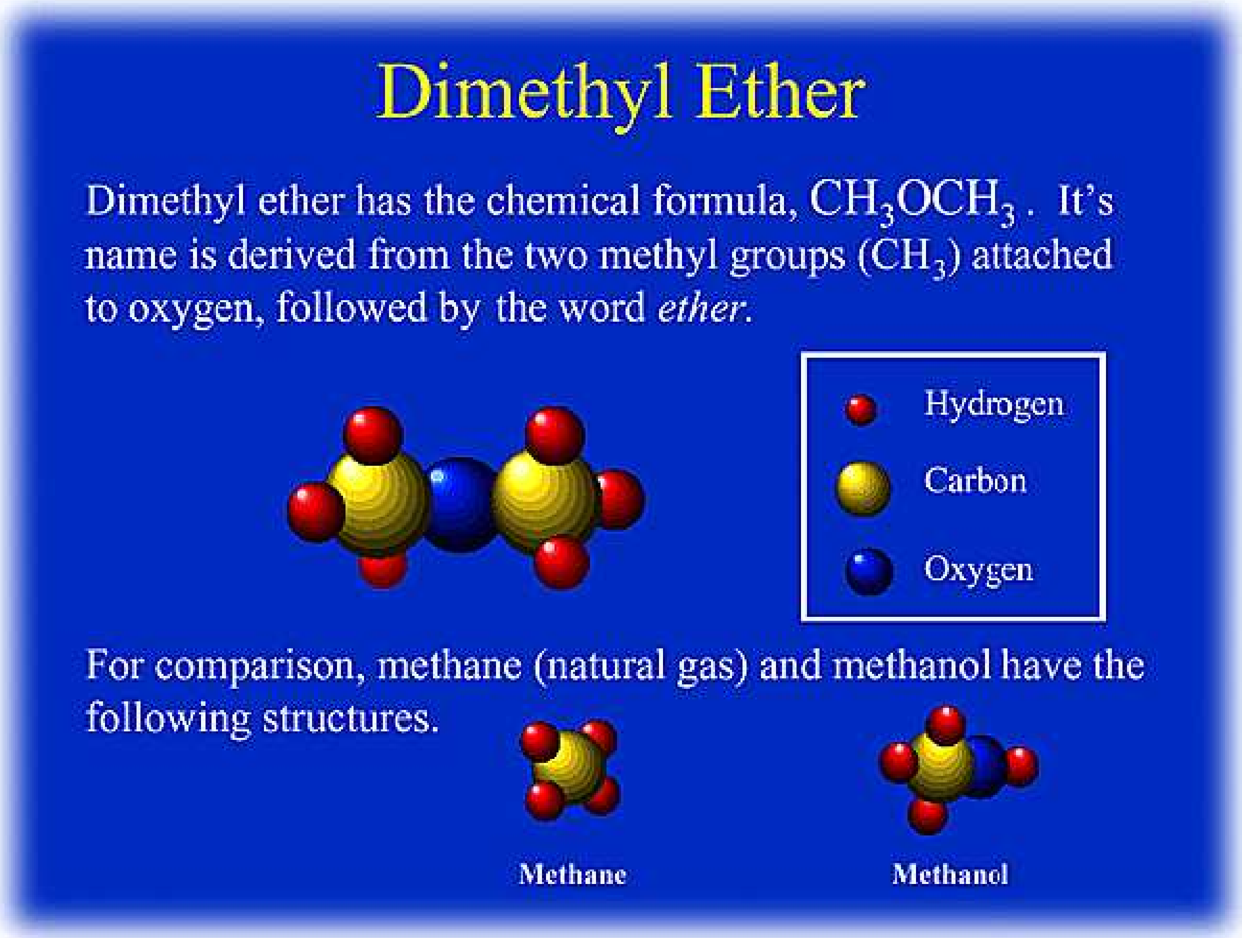
$NO + O + M \leftrightarrow NO_2 + M$ (2)

NO_x emissions are higher with biodiesel but are not changed significantly by H_2





DME - A second generation renewable fuels for Diesel engines

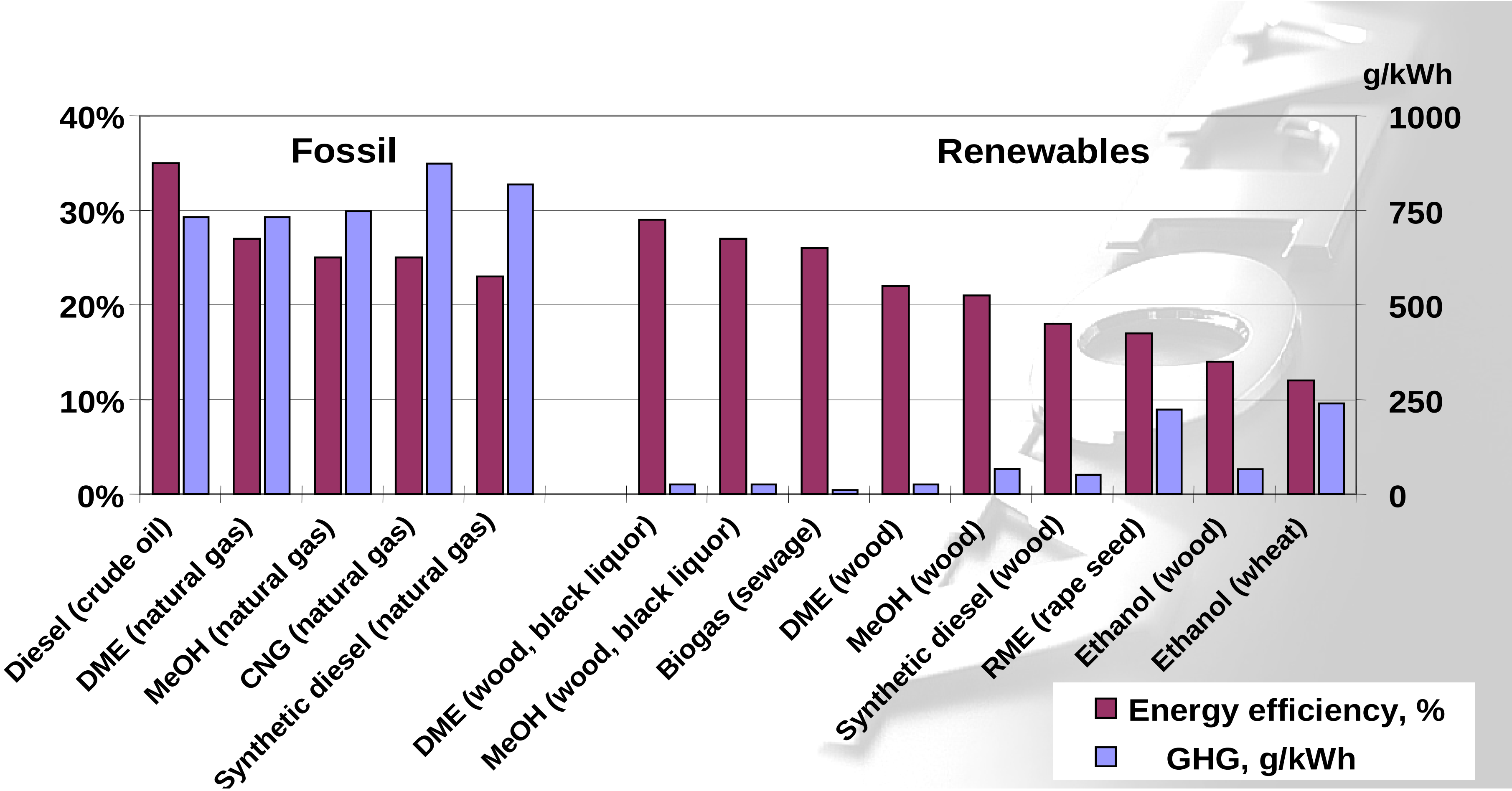


DME properties

- DME is a strong candidate for a longer term future fuel.
- Fuel properties
  - Energy dense and liquid at low pressure
  - Non-toxic, biodegradable and harmless to the atmosphere
  - Best well-to-wheel energy efficiency from bio source, 25% better than synthetic diesel (Fischer-Tropsch)
  - Highest efficiency, lowest global warming potential and cost of the biomass to liquid (BTL) fuels
  - Close to CO_2 neutral if produced from biomass
- Engine behavior
  - Very low exhaust emissions (soot-free combustion, Euro 5)
    - » Eliminates need for particle traps
    - » Allows low NO_x engine optimization
  - Requires substantial engine modification, mainly to fuel system

”Well-to-wheel” analysis (Volvo study)
Energy efficiency and Greenhouse gases

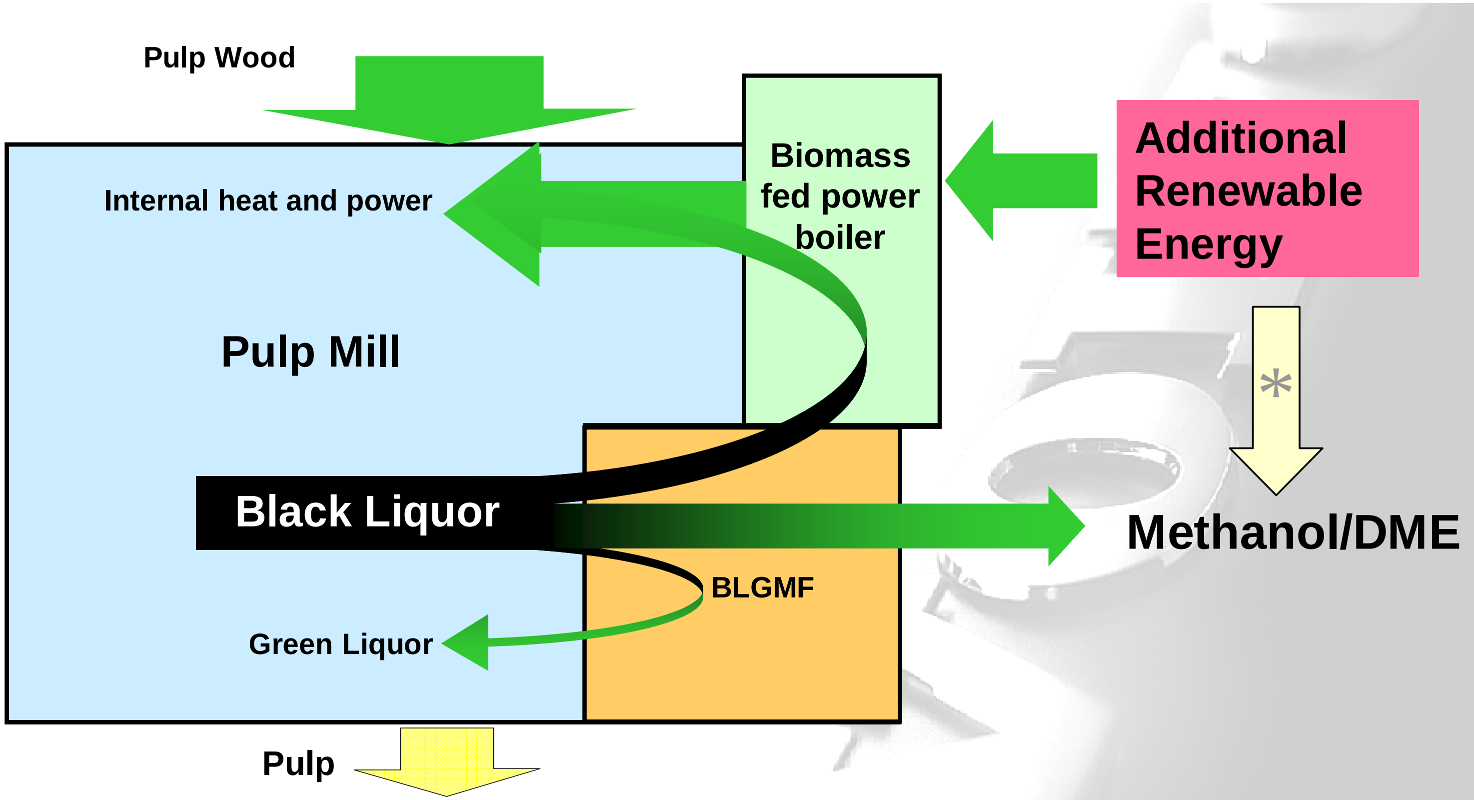
Courtesy - Anders Röj, Volvo Technology Corporation, Fuels and Lubricants



These figure include production, transport, and end use. Ethanol figures are based on European practice from wood or wheat

Black liquor to engine fuels - Ideal use of low grade biomass

Courtesy - Anders Röj, Volvo Technology Corporation, Fuels and Lubricants



$$\text{Production Efficiency} = \frac{\text{Methanol/ DME}}{\text{Additional Renewable Energy}} > 65\%$$

(Source: Chemrec)

DME prospect in Minnesota

- CDR is seeking funding for DME research
  - Seeking guidance from Volvo Technology in obtaining funding
  - We have funding to set up DME fuel storage and distribution in the lab if other funding available
- Minnesota company, Rational Energy, seeking funding to build DME plant
  - 250 ton DME per day from corn stover or corn cobs
  - Initial market propane replacement
  - Negotiating with UM and Metro Transit for engine tests and bus demonstration
  - If all corn cobs in Minnesota were converted to DME, we could replace about 60% of Diesel fuel in MN
- With soot free combustion, DME is still likely to make particles from the lube oil – in fact it is an ideal for studying nanoparticle formation by lube oil.

Acknowledgements

We would like to thank our many sponsors including

University of Minnesota Initiative for Renewable Energy and the Environment
Minnesota Department of Agriculture
National Biodiesel Board
MN Soybean Producers
AURI
Xcel Energy
Great Lakes Governors
Volkswagen
Volvo
Deere Power Systems
And many others