Biofuels and Nanoparticles

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Engine, Fuel and Nanoparticle Research
Center for Diesel Research

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

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

Sensors for real time control of ultrafine particles and NO\textsubscript{x}

Renewable fuels, biodiesel, ethanol, to reduce CO\textsubscript{2} and ultrafine particles

C/Ce cluster
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
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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

Data from USEPA 2002
Engine particle size distributions, lung deposition efficiency – biodiesel makes smaller particles

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

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

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

40-70% decrease in mass

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*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)

500-1100% increase in number

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


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.
**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

10 % to 80% decrease
Number distributions, small RV generator, ULSD and 30% butanol in ULSD

![Graph showing number distributions with Diesel and B-30 blends](image-url)

- Diesel 20%
- Diesel 60%
- Diesel 100%
- B-30 20%
- B-30 60%
- B-30 100%

50% decrease to 500% increase
Total number and mass concentrations, small RV generator, ULSD and 30% butanol in ULSD
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\textsubscript{x}, but increase in NO\textsubscript{2}/NO ratio

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

NO$_x$ emissions are higher with biodiesel but are not changed significantly by H$_2$

The NO$_2$/NO$_x$ ratio increases with H$_2$

The likely reactions for the NO$_2$ increase are:

\[ \text{HO}_2 + \text{NO} \leftrightarrow \text{NO}_2 + \text{OH} \quad (1) \]

\[ \text{NO} + \text{O} + \text{M} \leftrightarrow \text{NO}_2 + \text{M} \quad (2) \]
DME - A second generation renewable fuels for Diesel engines

**Dimethyl Ether**

Dimethyl ether has the chemical formula, $\text{CH}_3\text{OCH}_3$. It’s name is derived from the two methyl groups ($\text{CH}_3$) attached to oxygen, followed by the word *ether*.

For comparison, methane (natural gas) and methanol have the following structures.

- **Methane**
- **Methanol**
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 figures 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

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.
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