Nanoparticle Emissions from a Second Generation Biofuel: DME

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Performance and Emissions of a Second Generation Biofuel – DME: Project Overview

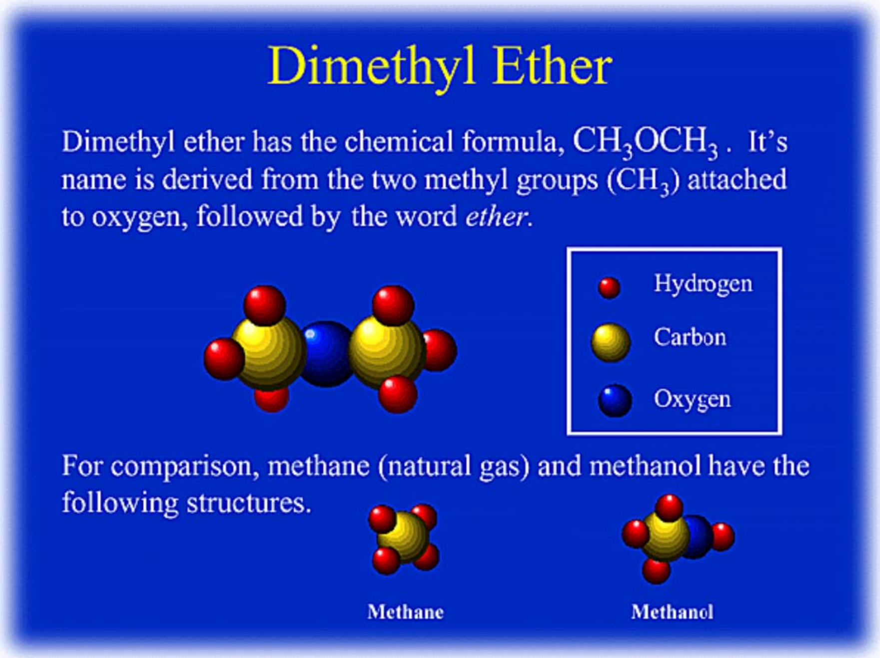
- The University of Minnesota received a three year grant from IREE to investigate the performance and emissions of dimethyl ether, a second generation biofuel.
- Investigators –
  - David Kittelson, Win Watts, David Bennett, Mechanical Engineering, , University of Minnesota, Twin Cities
  - Steven Taff, Applied Economics, University of Minnesota, Twin Cities
- Sponsored by the University of Minnesota Initiative for Renewable Energy and the Environment (IREE) with addition support from General Motors, Chemrec, and USEPA
- The program involves a variety of informal collaborators including
  - Pennsylvania State University
  - Johnson-Matthey
  - Volvo
  - Rational Energies

University of Minnesota DME program

- Background
- DME production in a Minnesota pulpmill
  - Economics
  - Production potential
- DME engine program
  - Fuel system development
  - Solid and semi-volatile nanoparticle emissions
    - Particle emission measurement system
    - Influence of lubricating oil and lubricity additive
    - Conclusions

DME Basics

- What is DME?



Source: International DME Association

- DME Properties
  - Physical properties similar to propane
- DME Uses
  - Cosmetic propellant
  - Propane replacement
  - Diesel fuel
    - High efficiency
    - Soot free combustion
    - Fuel system modifications required
  - Fuel cell fuel
  - Gas turbine fuel

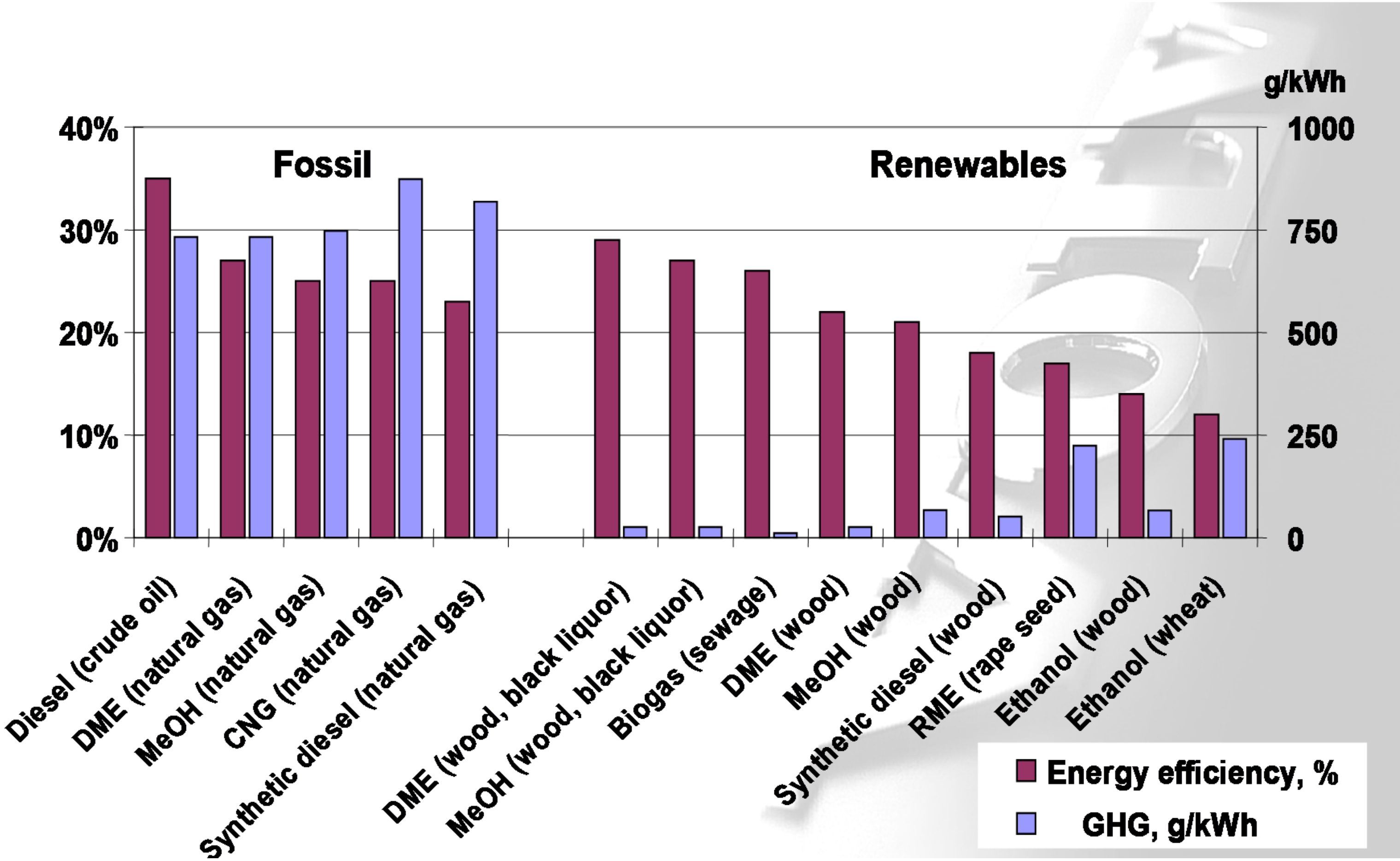
Environmental benefits of dimethyl ether

- Environmental
  - DME has the highest well-to-wheel energy efficiency and the lowest greenhouse gas emissions (GHG) of any biomass-based fuel.
  - Does not lead to stratospheric ozone depletion
  - Significant reduction in end use emissions
    - Soot free combustion
    - Low NOx emissions
- Health
  - Virtually non-toxic
  - Not a carcinogen or mutagen
  - Not a groundwater pollution threat
- Safety
  - Like LPG
  - Heavier than air
  - Visible flame

Current Status

- Most of the DME worldwide is made from natural gas or coal
- In the US, DME is used as a nontoxic, non-ozone depleting cosmetic propellant
- DME is widely used in China as a propane replacement for cooking and heating
  - Current production about 40 million gallons/year
  - Planned production by 2020 about 800 million gallons/year, this corresponds to about, nearly half the current US use
- The first bio DME pilot plant has been built by Chemrec at a paper mill in Piteå, Sweden.
- Oberon fuels has announced small scale plants (3000-10,000 gal DME /day) for conversion of biomass, solid waste, methane/CO_2 to DME
- Volvo, Isuzu, Shanghai Diesel and Nissan, have been testing prototype DME vehicles for several years
  - Shanghai announced plans to introduce fleets of DME trucks, buses, and taxis
  - Volvo has announced production of DME fueled trucks in the U.S. starting 2015

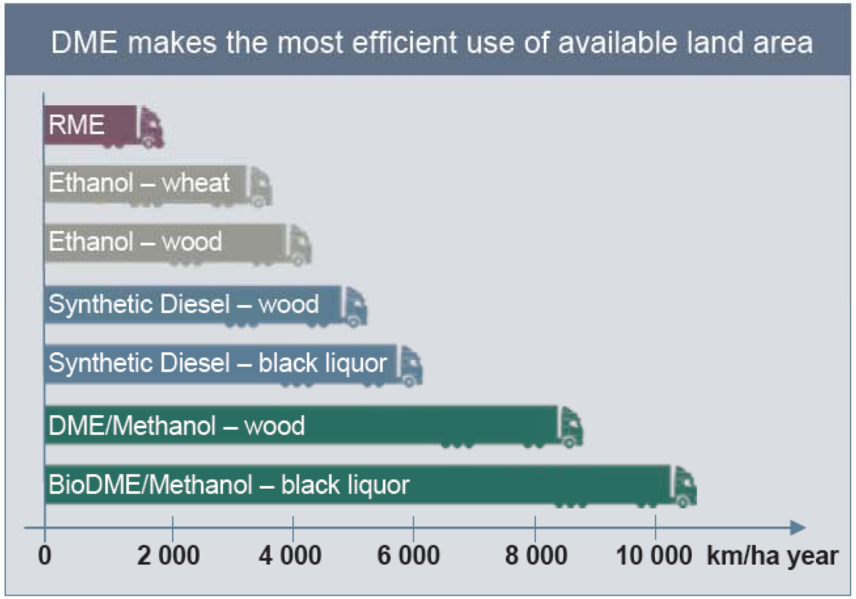
Fuel comparison - efficiency and greenhouse emissions



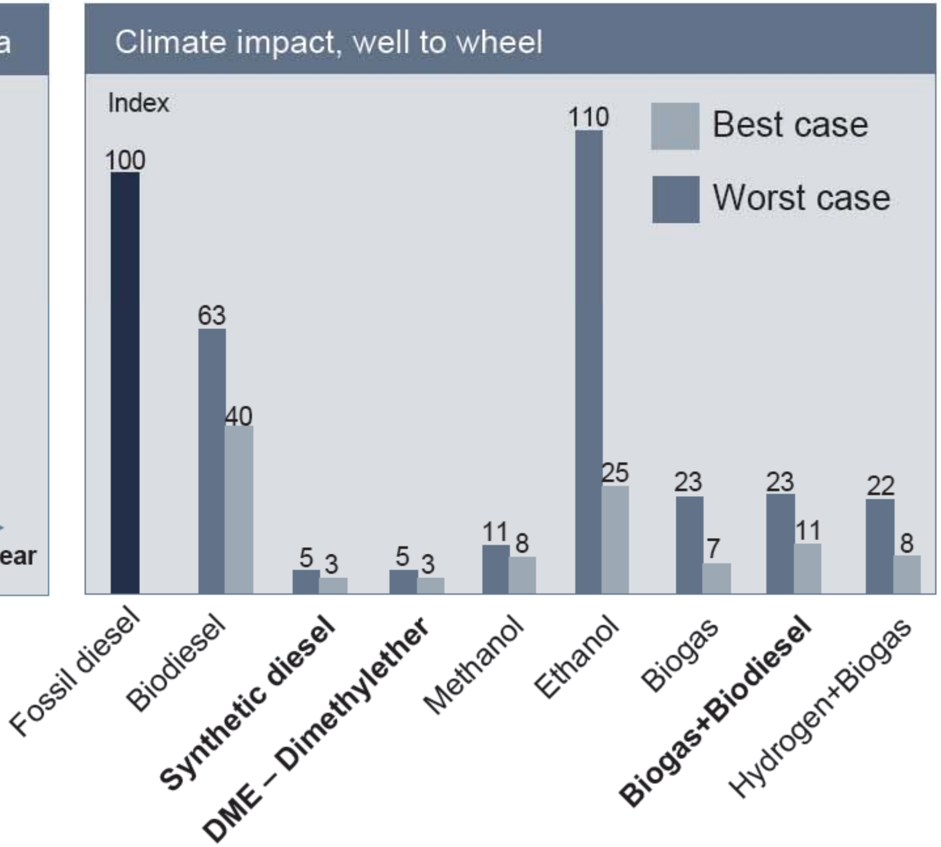
Source: Volvo Technology Corporation. These estimates include production, transport, and end use GHG emissions. KEY: DME dimethyl ether; MeOH methanol; CNG compressed natural gas; RME rapeseed methyl ester; GHG greenhouse gas.

Efficiency in focus

Efficient use of land area



Minimal greenhouse gas emissions

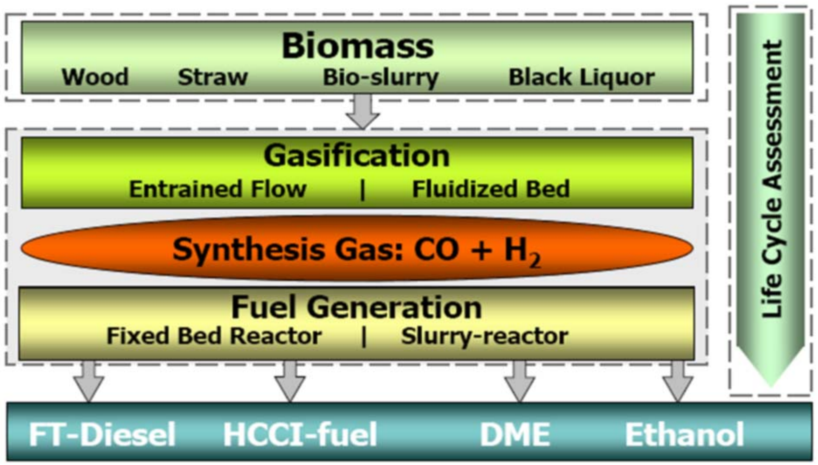


Heavy duty DME vehicles -from advanced engineering to customer field test, Niklas Gustavsson, Environmental & Public Affairs, AB Volvo

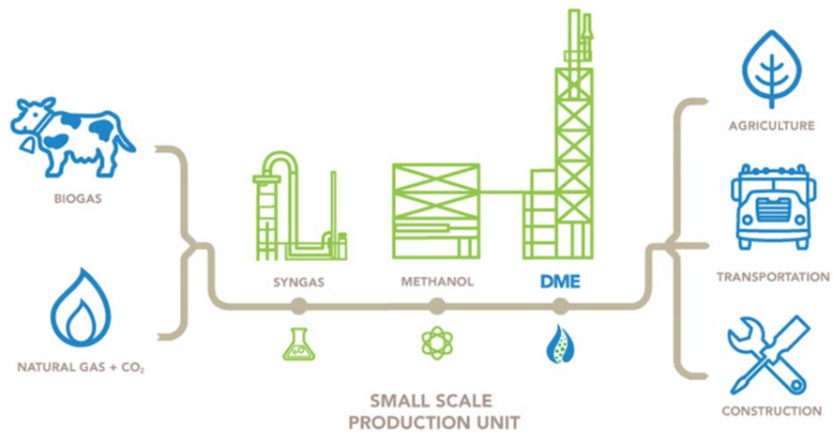
DME Production

- Unlike current ethanol and biodiesel, DME is produced by thermochemical processes.
- It can be produced from virtually any carbon containing feedstock, coal, natural gas, biomass, and even CO_2. Examples below
  - Large scale thermochemical biomass to fuel processes (Source: RENEW, 2008)
  - Small scale biomass or fossil to DME process (Oberon Fuels 2014)

RENEW



Oberon



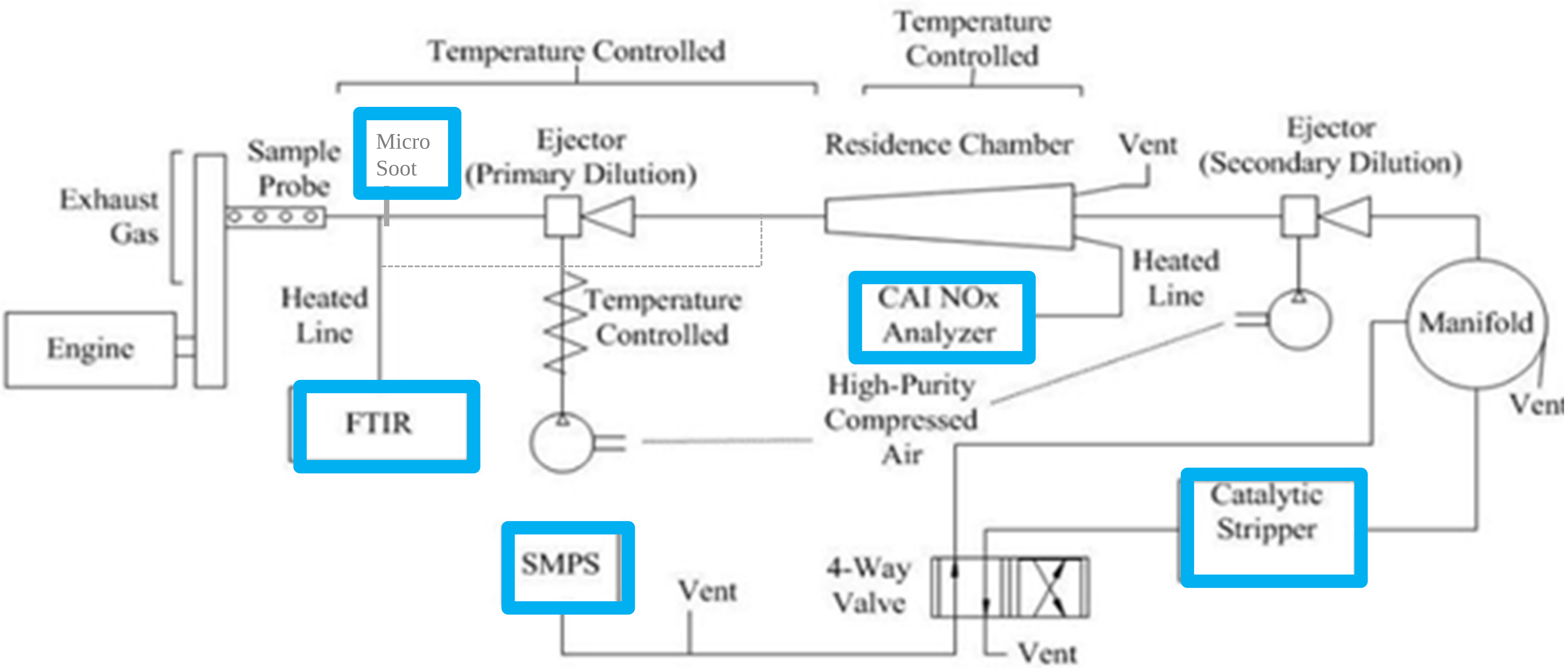
Engine Specifications

Model	Navistar VT275
Type	4-stroke, direct injection diesel
Configuration	V6, pushrod operated four valves/cylinder
Compression Ratio	18:1
Aspiration	Naturally Aspirated
Injection System	Electro-hydraulic (HEUI)
Injector Type	Sturman

Modified to run on DME

- One of six cylinders is isolated, acts as a single-cylinder research engine
- Dummy injector opposite the firing injector used to stabilize rail pressure
- Altered Sturman injector for DME fuel (from US EPA)

Experimental Setup-Dilution Tunnel



Primary DR = 9, secondary = 20, T primary -= 25 C

DME test matrix and regulated emissions

Test matrix

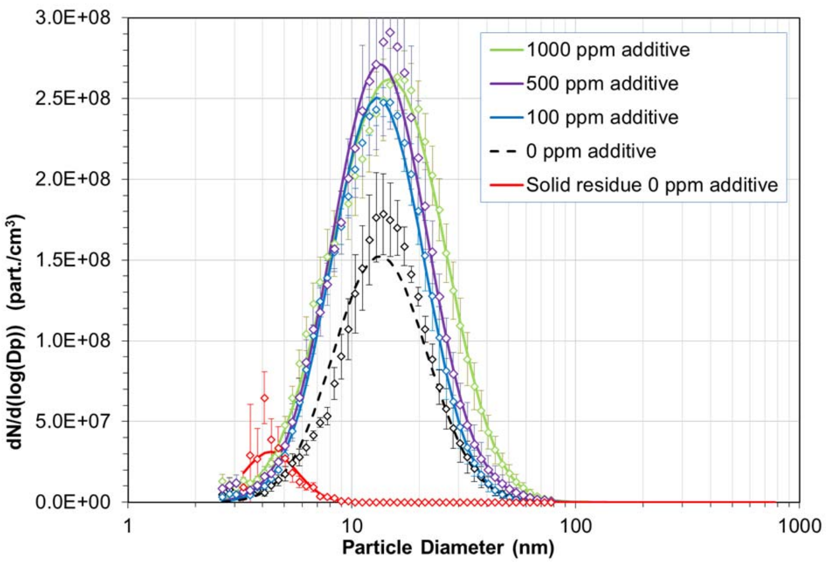
Fuel	Additive concentration (ppm)	DMA	Load (*bar)	SMPS (scans/day)	Test Days
DME	1000	Nano	4, 6, 8	9	3
DME	500	Nano	4, 6, 8	9	3
DME	100	Nano	4, 6, 8	9	3
DME	0	Nano	4, 6, 8	9	1
Diesel	n/a	Nano	4, 6, 8	9	3
Diesel	n/a	Long	4, 6, 8	9	3

Regulated emissions

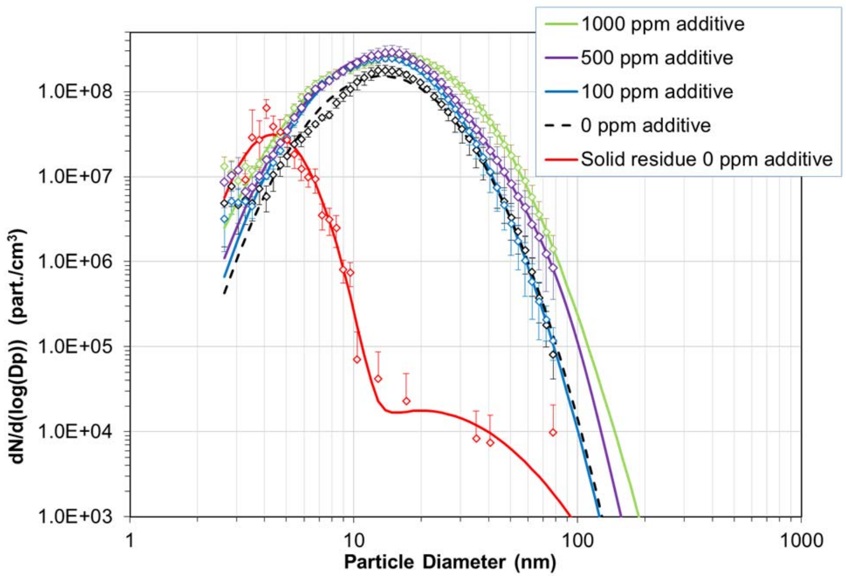
Engine Load	4 bar		6 bar		8 bar	
Fuel	ULSD	DME	ULSD	DME	ULSD	DME
ITE (%)	48	45	48	45	47	44
NO x (g/kWh)	3.8	1.7	5.9	3.1	8.1	3.7
CO (g/kWh)	1.00	1.45	0.42	0.45	0.27	0.36
Soot (mg/m^3)	0.13	-	0.2	-	0.49	-

Influence of additive concentration, 8 bar IMEP

Number size distribution, linear scale



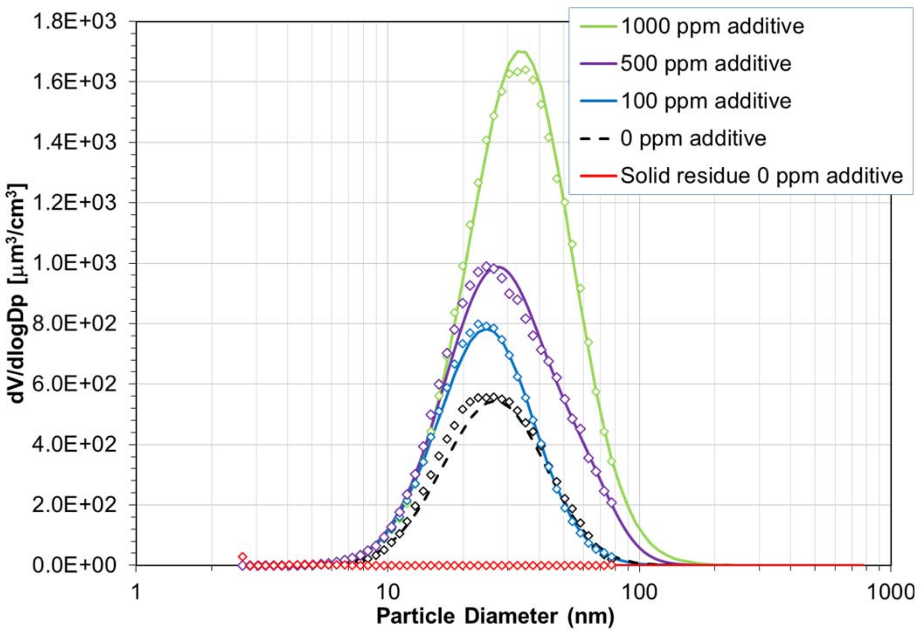
Number size distribution, log scale



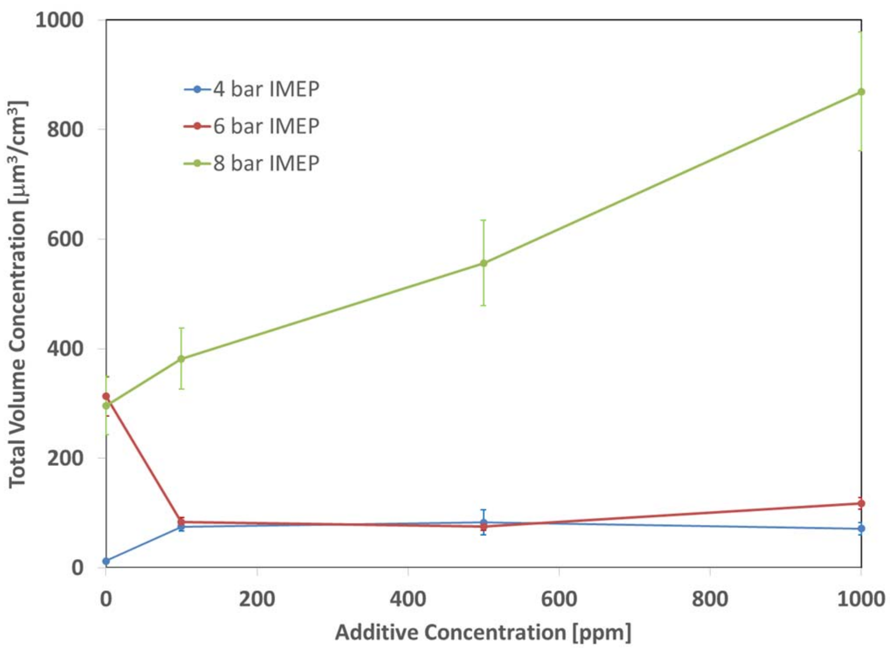
Solid particle measurements were made using the catalytic stripper

Influence of additive concentration

Volume (mass) size distribution, 8 bar IMEP

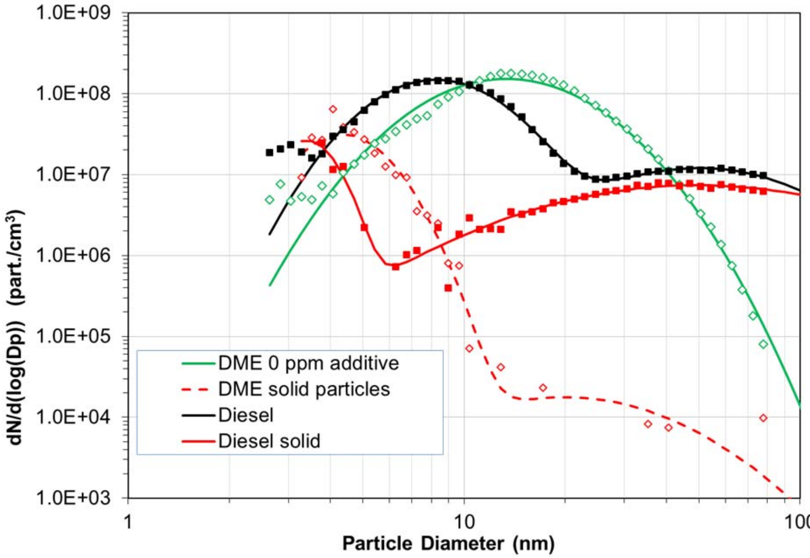


Total volume (mass) concentrations, 4, 6, 8 bar IMEP

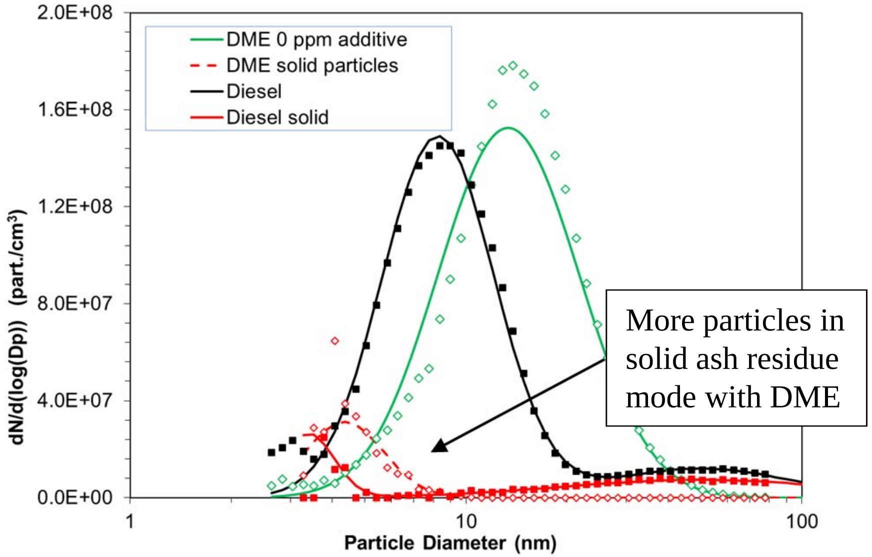


Comparison of DME and diesel fuel size distributions, 8 bar IMEP

DME with 500 ppm additive and diesel fuel, 8 bar IMEP



DME with 500 ppm additive and diesel fuel, 8 bar IMEP



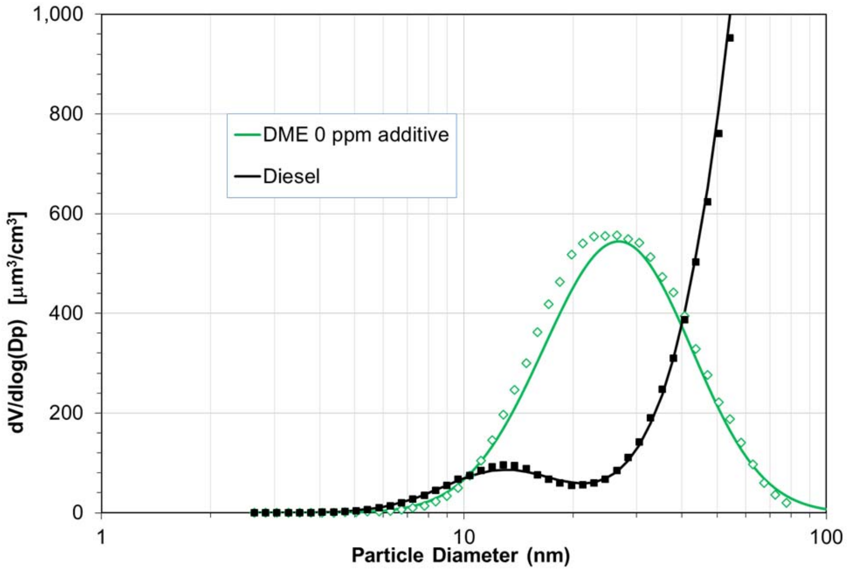
PMP solid PN emissions, EU standard = 8 x 10^{11} particle/kWh

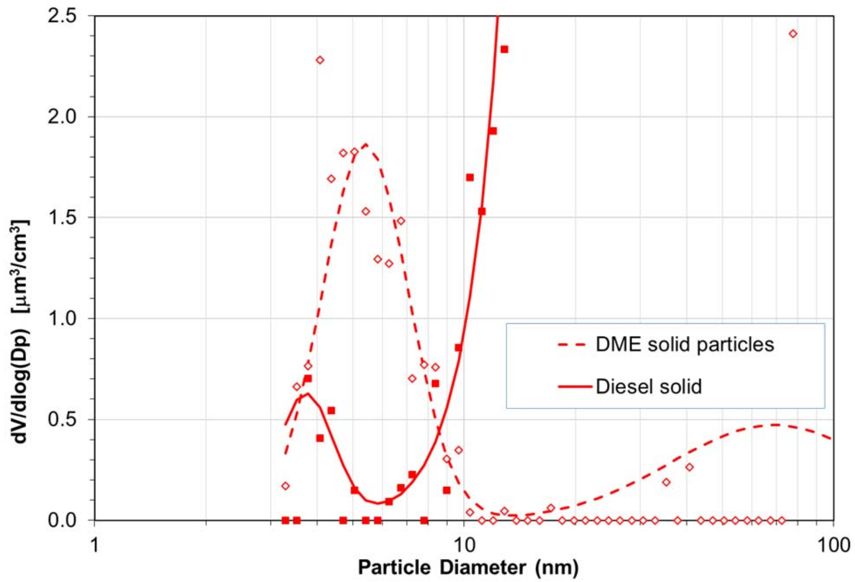
DME 3.4 x 10^{9} (99.99% below 23 nm); Diesel 1.6 x 10^{13} (78% below 23 nm)

Here is an example of suppression of nucleation by diesel soot particles

Much smaller semi-volatile nucleation mode with diesel

Much smaller solid (ash) nucleation mode with diesel

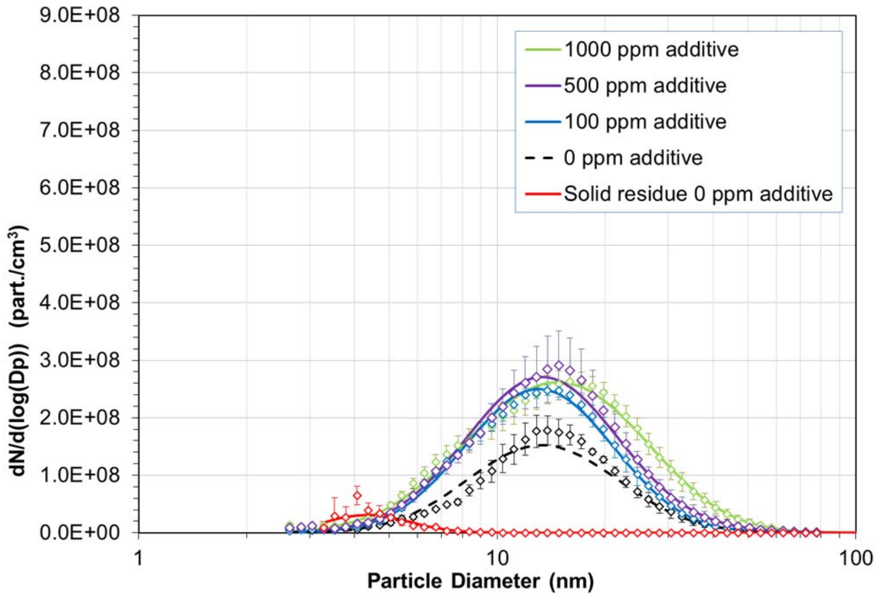




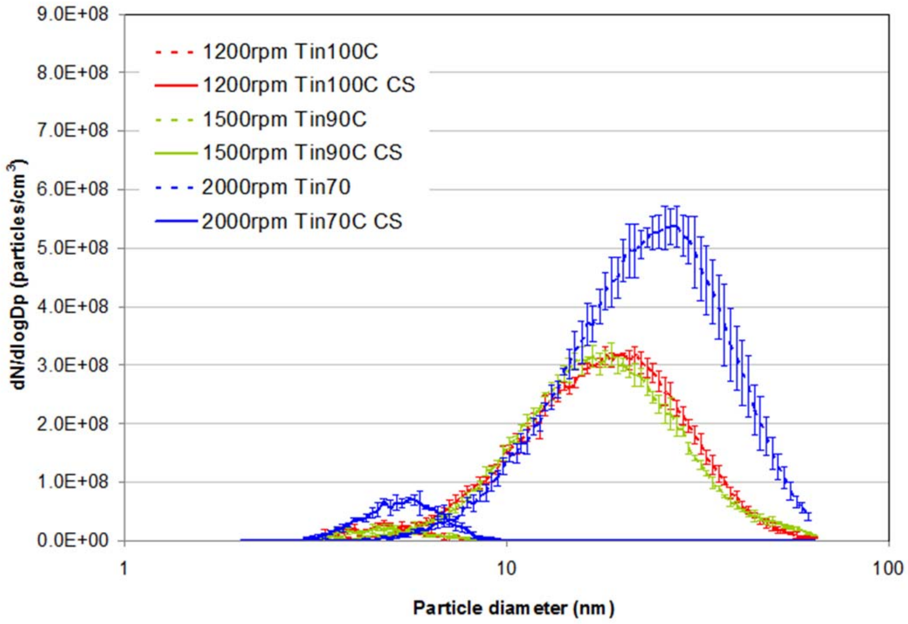
8 bar IMEP diesel compared with DME with no lubricity additive
The main source of semi-volatile material and ash is the lube oil

Comparison with other soot free combustion modes – HCCI combustion of ethanol

DME



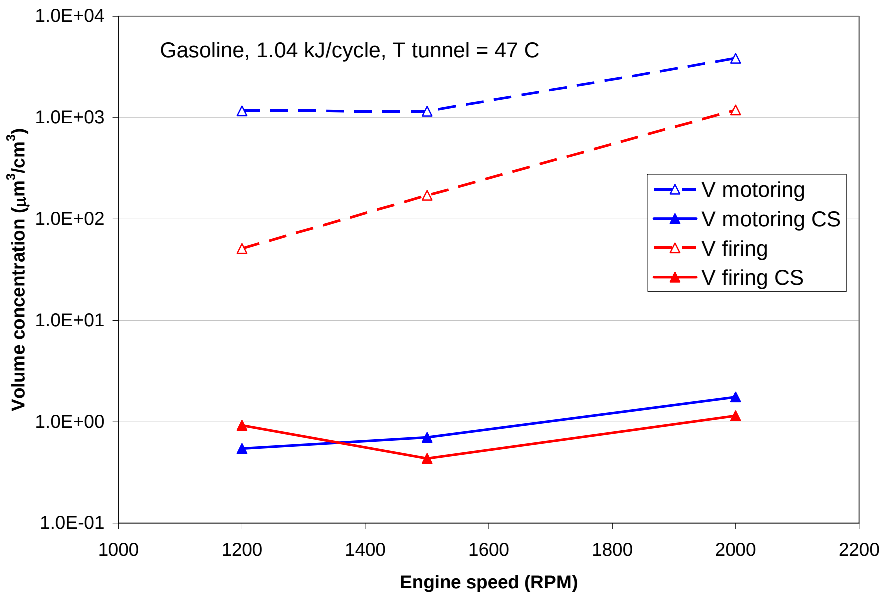
Ethanol HCCI



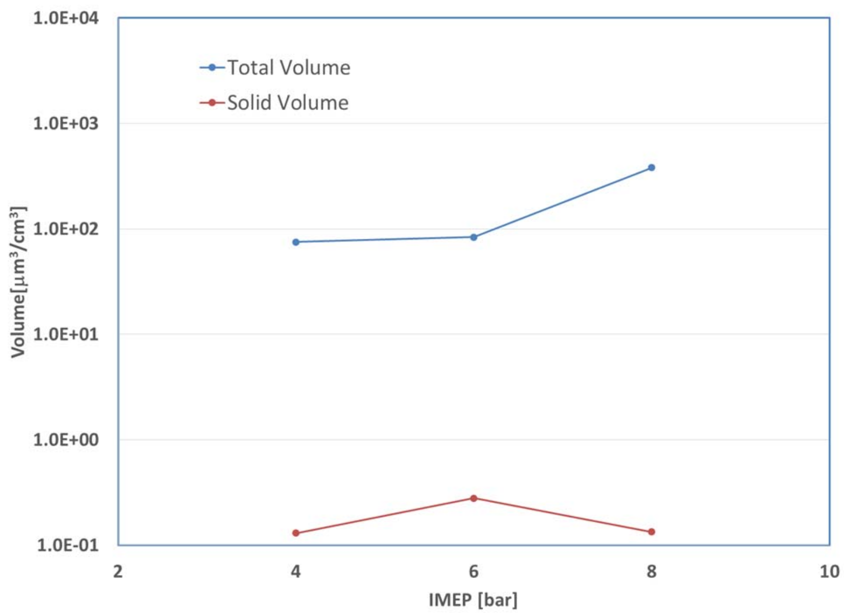
In both case the lube oil is the likely main source of the semi-volatile and ash particles

Total and solid particle volume emissions, soot free modes, motoring and firing

Gasoline HCCI



DME



Conclusions - DME

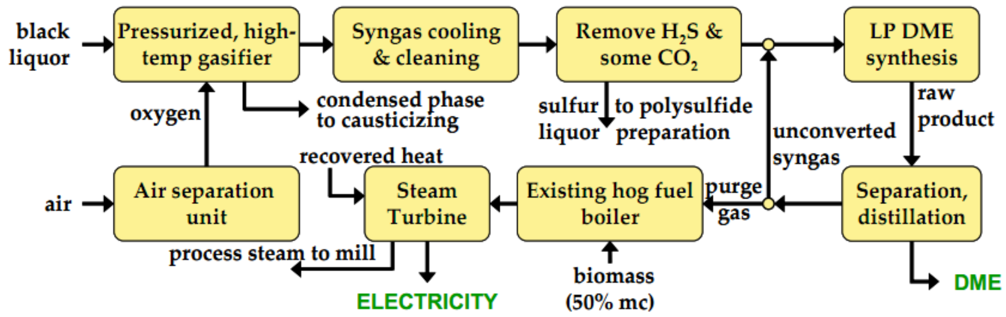
- DME and diesel performance and emissions measured with single cylinder conversion of Navistar V6
- Test run at 4, 6, and 8 bar naturally aspirated
- DME produced relatively large, higher than comparable diesel, concentrations of semi-volatile nucleation mode particles
  - At typical lubricity additive concentration, lube oil and lubricity additive contribute roughly equally to PM
  - These particles were effectively removed by the catalytic stripper in the sample stream, and could be removed by a suitable DOC on the engine
- A small solid core remained downstream of the catalytic stripper
  - Nearly all these particles were smaller than 10 nm
  - DME led to formation of many more of these tiny particles than diesel fuel
  - However solid particle emissions as measured by the EU PMP method were more than two orders of magnitude below the EU standard.
- Although it appears that most of the particles formed in soot free engines of the type examined here come from lube oil, these lube oil emissions are much lower than those associated with hot motoring

Questions?

- Contact information for further questions - kitte001@umn.edu

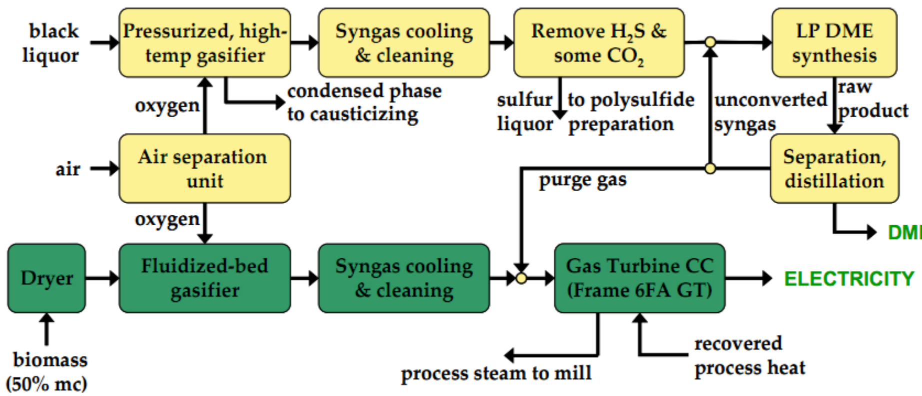
Three Possible Pathways for DME Production

a)

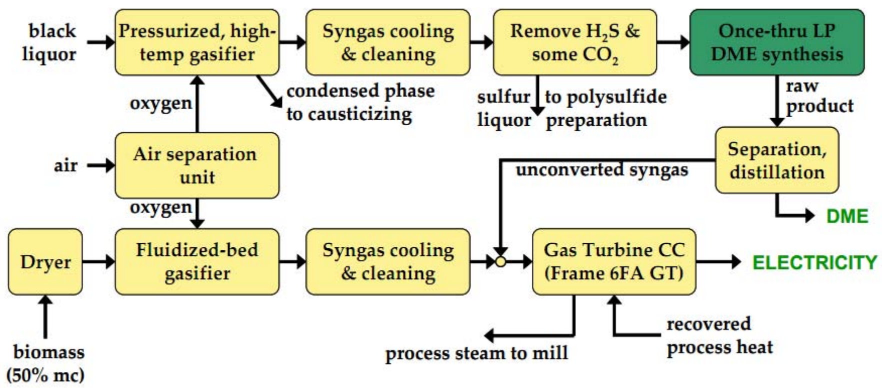


Configurations with Gas Turbine Combined Cycle

b)



c)



Source: Larson, et al., A Cost-Benefit Assessment of Gasification-Based Biorefining in the Kraft Pulp and Paper Industry, Vol. 1, Main Report, 2006

Model Pulp Mills

Mill Capacity: 1,580 US tons pulp/day

Input Value	Tomlinson	DME a	DME b	DME c
Capital Cost, 2011$ (million)	170	315	520	324
DME production, gal/day (thousand)	0	199	199	88
Net electricity production, MW/day	64.3	87.4	87.4	991

Minnesota paper mills with the potential to integrate DME production

Boise Inc.
Location: International Falls, MN
Pulping method: Kraft Process
Total daily pulp capacity: 1,100 US tons
Age of the current recovery boiler: 10 years
Projected daily DME production: 61,000 - 138,000 gallons

Sappi Fine Paper North America
Location: Cloquet, MN
Pulping method: Kraft Process
Total daily pulp capacity: 1,400 US tons
Age of current recovery boiler: 20 years
Projected daily DME production: 78,000 - 177,000 gallons

Preliminary pulpmill economic analysis: Install a DME plant to replace current recovery boiler

DME sales price set with same value per MJ as EIA Diesel fuel projections

Production Capacity: 70-82%

Percentage of investment from equity: 50%

Percentage of investment from debt: 50%

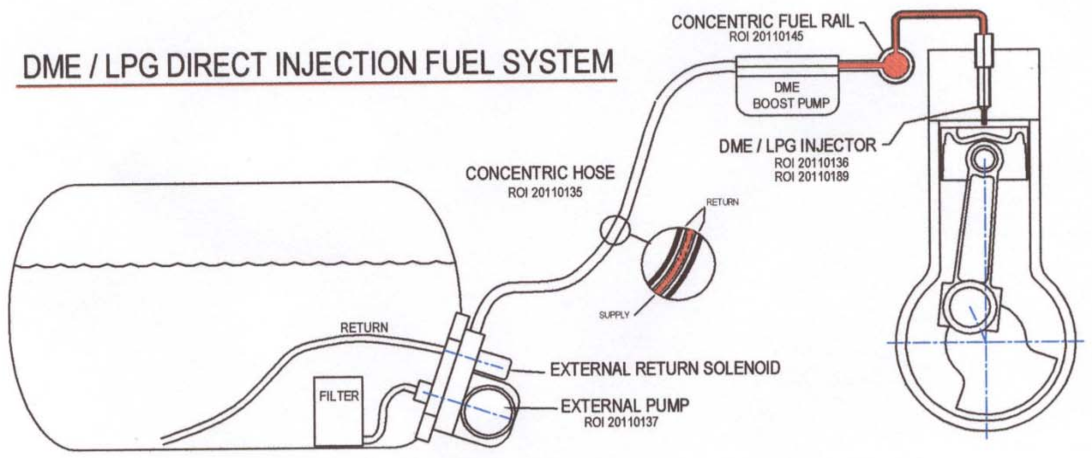
	DME a	DME b	DME c
Net present value	416M – 454M	310M – 361M	348M – 405M
Internal rate of return	20-22%	13-14%	14-16%
Years to pay off investment	4	7	7

Projected DME Supplies in Minnesota Pulpmills

- DME Daily Production: 139,000 – 315,000 gallons /day
- If both mills adopts DME production
  - DME could displace 2-6% of our current Diesel fuel use
- Going beyond pulpmills - Minnesota if all existing biomass resources were used to produce DME
  - We could produce about 1.2 times our current Diesel fuel need or
  - Nearly 5 times our propane needs.

Fuel system development – joint propane DME

- The engine fuel system development has a dual focus
  - Propane direct injection for spark ignition engines
  - DME direct injection Diesel engines
  - The pumping structure for the transfer pump is thus designed to be used singularly for propane and doubled in series for DME
- Fuel system features
  - External transfer pump
  - Self centering injector for reduced tip wear
  - Improved tip sealing
  - New measures for keeping fuel cool including concentric fuel lines



Fuel system design issues: particle contamination

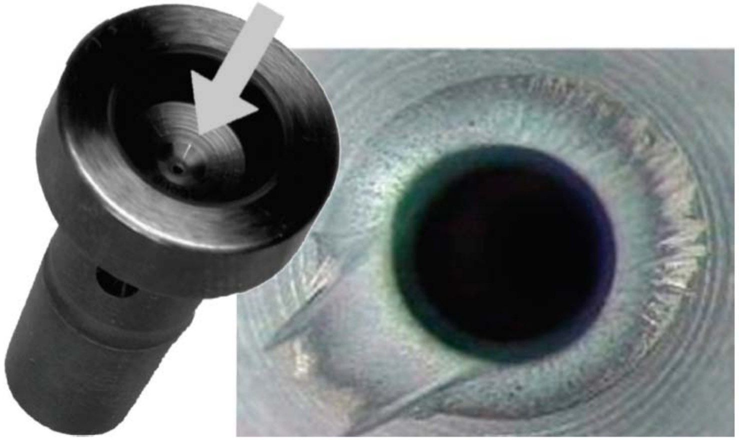
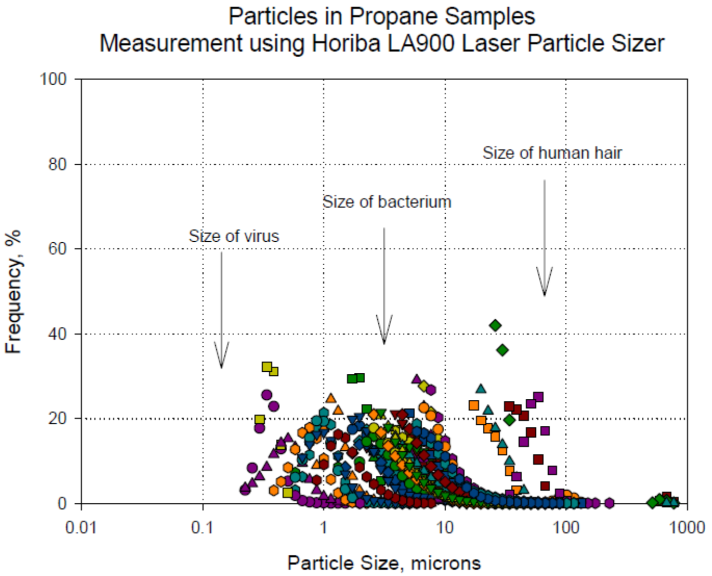


Fig. 4: ball valve seat of injector CRI2, eroded by particles in the fuel

From:von Stockhausen A, Mangold MP, Eppinger D, Livingston TC. Procedure for determining the allowable particle contamination for diesel fuel injection equipment (FIE). SAE International Journal of Fuels and Lubricants. 2009;2(1):294-30.



from: Water And Solid Contaminant Control In Lp Gas, PERC Docket 11353, Volume 1, May 2006

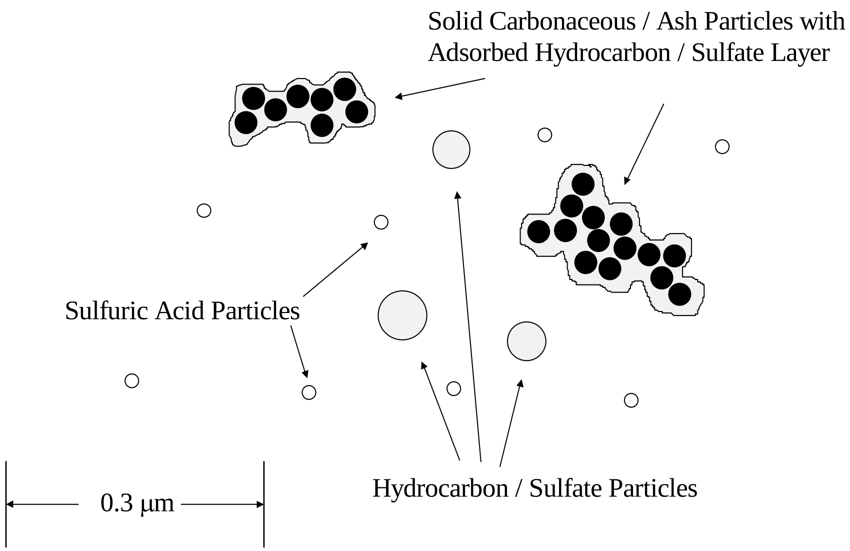
- Fuel contaminant particles growing concern with high pressure common rail diesel injection – leading to nozzle erosion, poor sealing
- Potentially an even greater problem with propane and DME
- Typical LPG shipping equipment leads to significant particulate contamination – iron, iron sulfide
- Filters below 3 micron are not commercially available; 1 micron are OEM specials (Donaldson) .

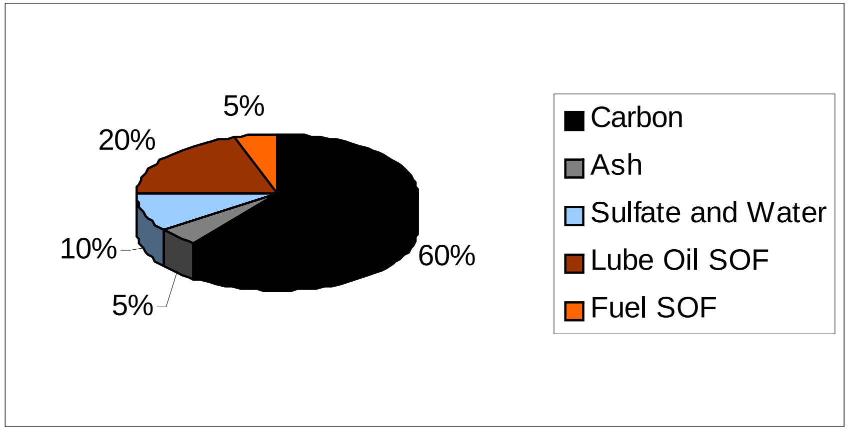
Soot free and low soot engines / fuels

- There are several fuels coming into use that lead little or no soot formation including:
  - DME
  - Hydrogen, methanol, methane (with proper fuel control)
  - Syngas, producer gas
- Low temperature combustion also produces little or no soot – there are a variety of so called low temperature combustion concepts including:
  - HCCI, (Homogeneous Charge Compression Ignition), PCCI or PCI (Premixed Charge Compression Ignition), and RCCI (Reaction Controlled Compression Ignition)
  - *All rely on control of the temperature – mixing history to avoid passing through regions of soot and NOx formation.*
- But all of these processes and fuels still emit PM, especially in the nanoparticle range
  - These particles are formed mainly from lubricating oil and / or lubricity additives
  - They are mainly volatile and are very difficult to sample correctly
  - Lube oils also contain metallic additives that lead to solid ash particles in the exhaust

Typical Composition and Structure of Diesel Particulate Matter - without aftertreatment

- Solid particles are typically carbonaceous chain agglomerates and ash and usually comprise most of the particle mass
- Volatile or semi-volatile matter (sulfur compounds and organics (OC or SOF)) typically constitutes 30% (5-90%) of the particle mass, 90% (30-99%) of the particle number
- Carbon and sulfur compounds derive mainly from fuel
- SOF or OC and ash derive mainly from oil
- Most of the volatile and semi-volatile materials undergo gas-to-particle conversion as exhaust cools and dilutes – very sensitive!





With DME or other soot free engine concepts the soot is eliminated

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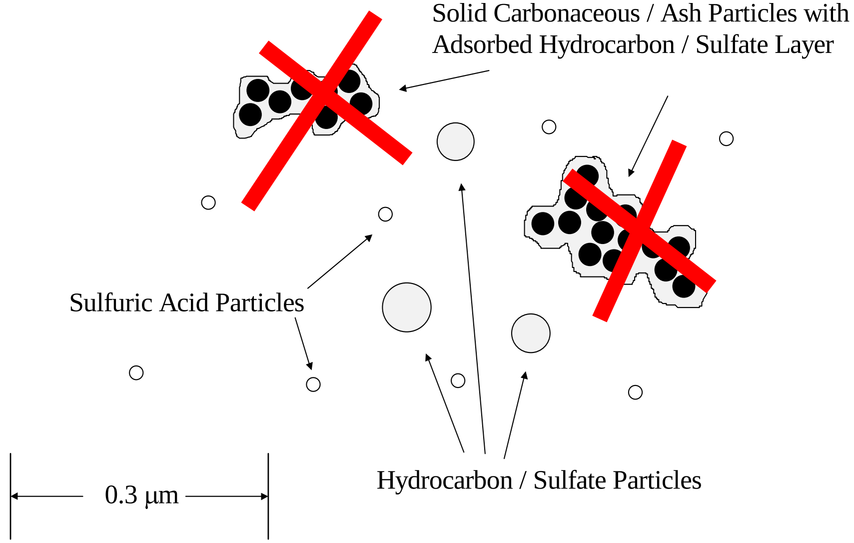
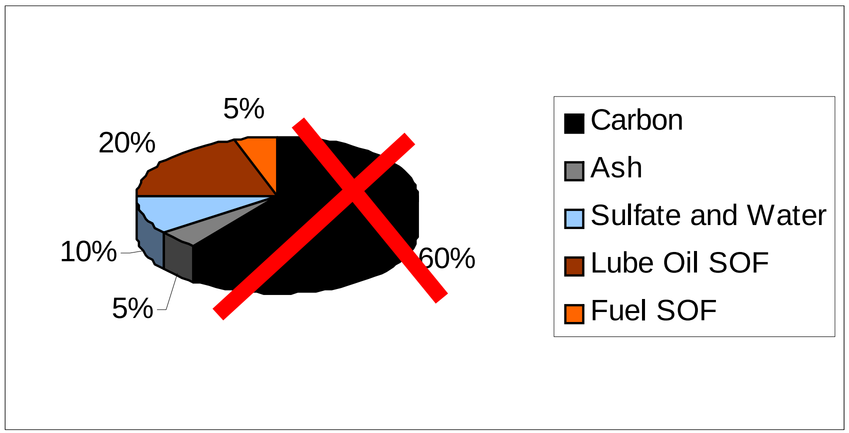
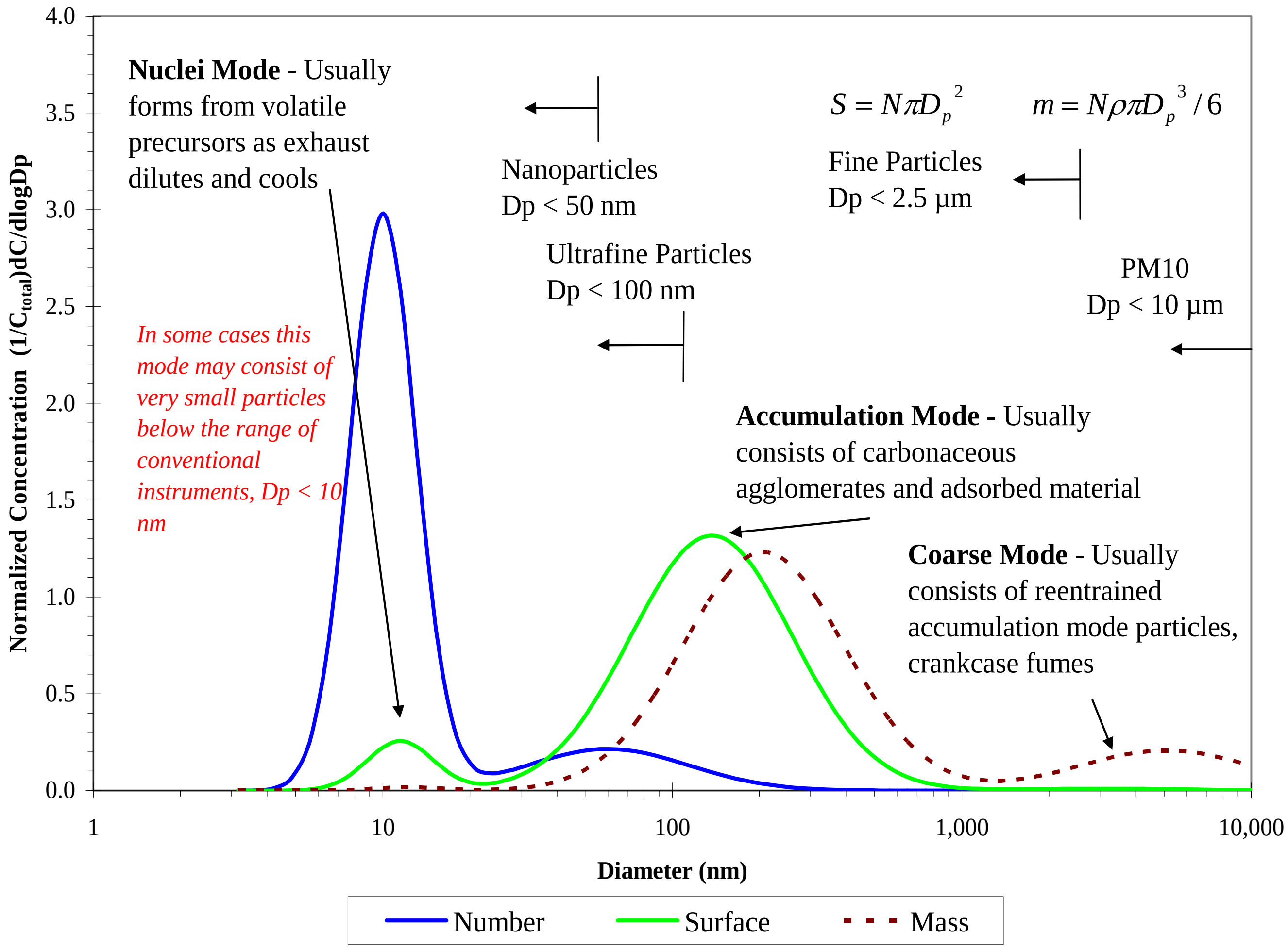
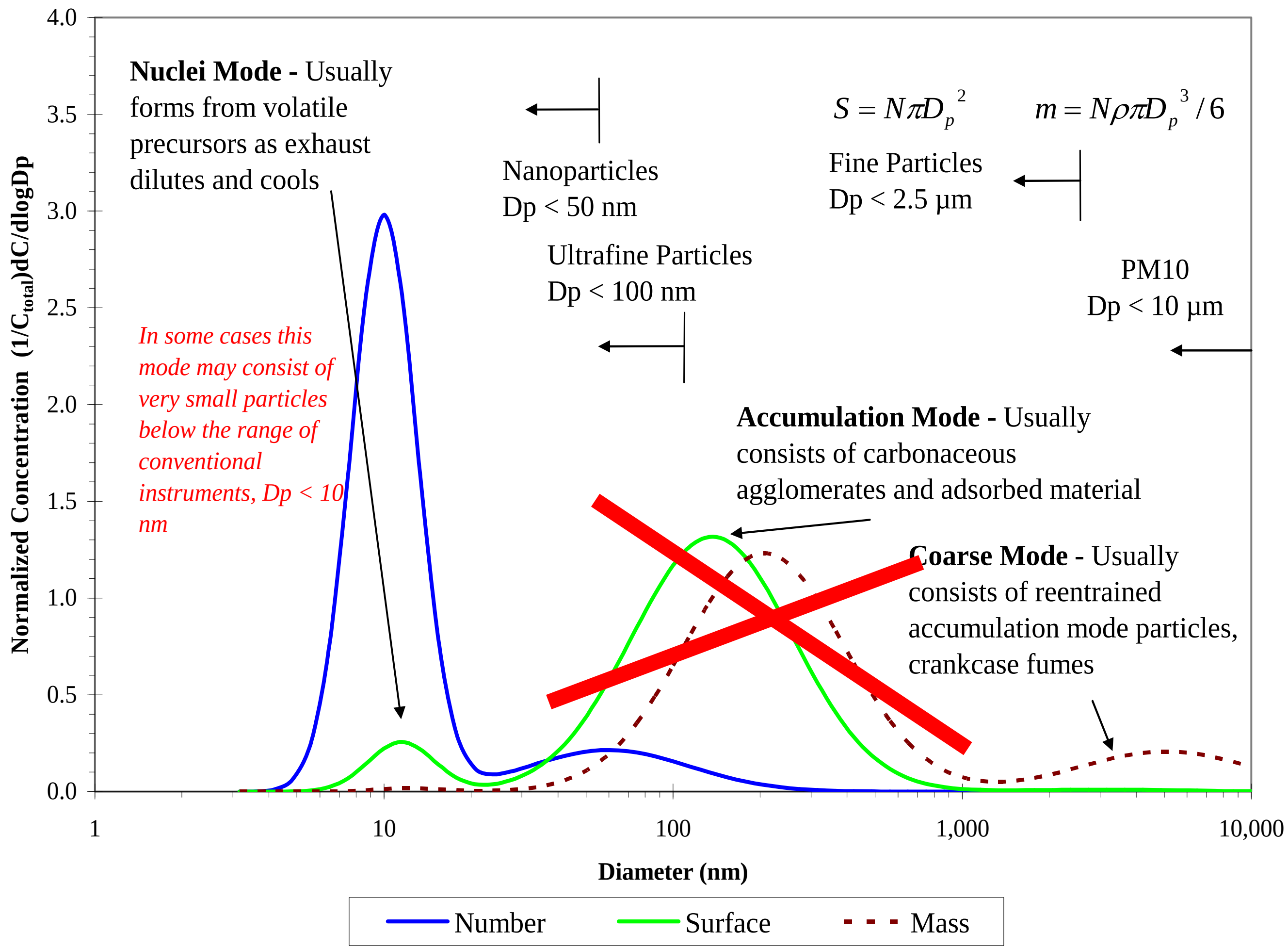




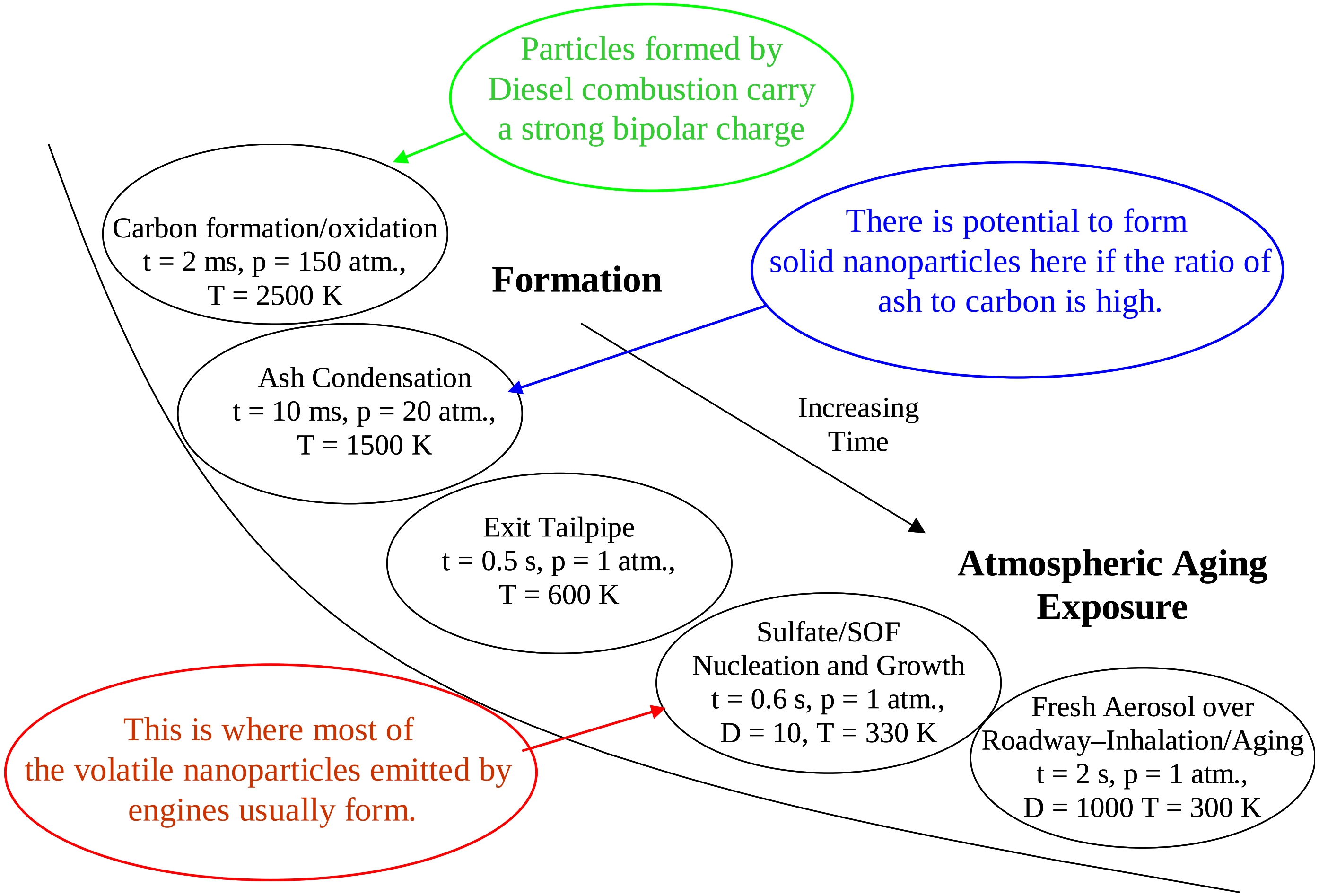
Typical Diesel engine exhaust particle size distribution by mass, number and surface area – without aftertreatment



With DME or other soot free engine concepts the soot is eliminated – where does the adsorbed HC from lube oil go?

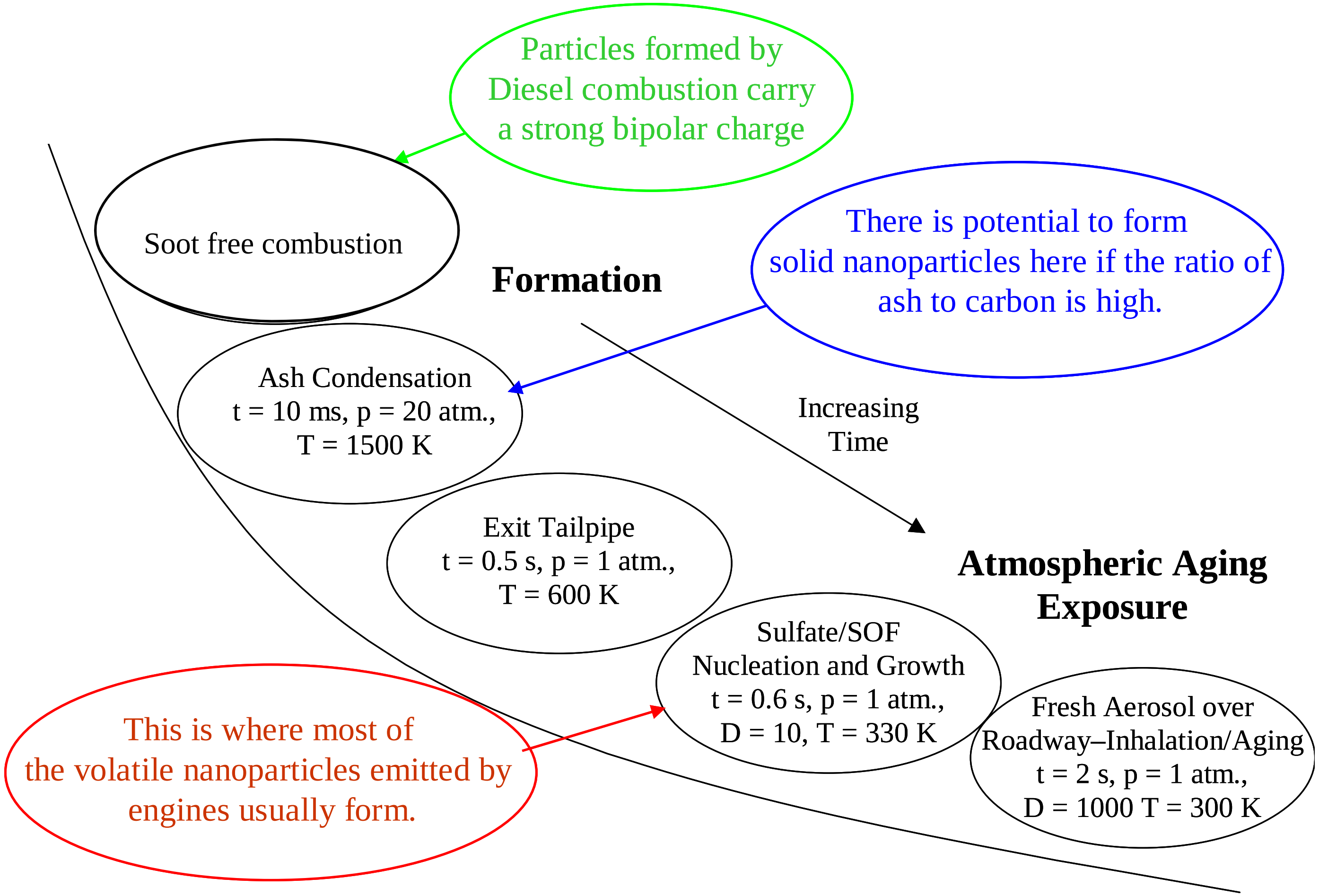


Particle formation history – 2 s in the life of an engine exhaust aerosol



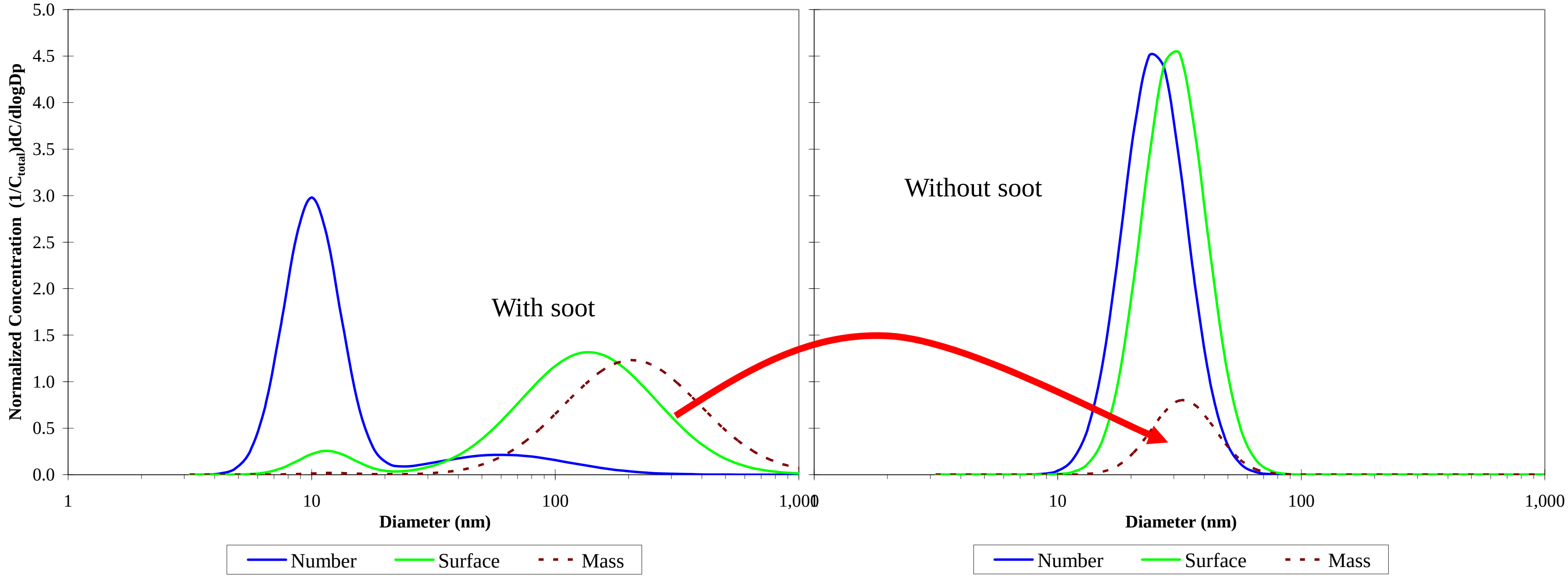
Kittelson, D. B., W. F. Watts, and J. P. Johnson 2006. “On-road and Laboratory Evaluation of Combustion Aerosols Part 1: Summary of Diesel Engine Results,” Journal of Aerosol Science 37, 913–930.

Particle formation history – 2 s in the life of an engine exhaust aerosol – soot free



Kittelson, D. B., W. F. Watts, and J. P. Johnson 2006. "On-road and Laboratory Evaluation of Combustion Aerosols Part 1: Summary of Diesel Engine Results," Journal of Aerosol Science 37, 913–930.

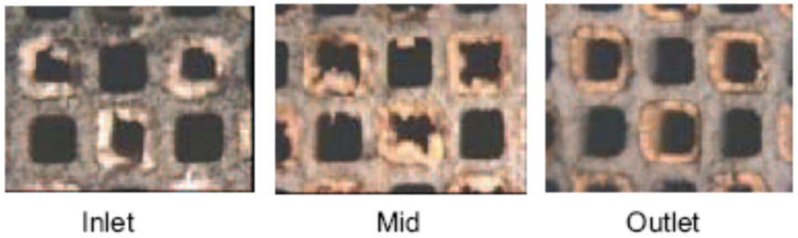
Here are the submicron regions of the size distributions with and without soot



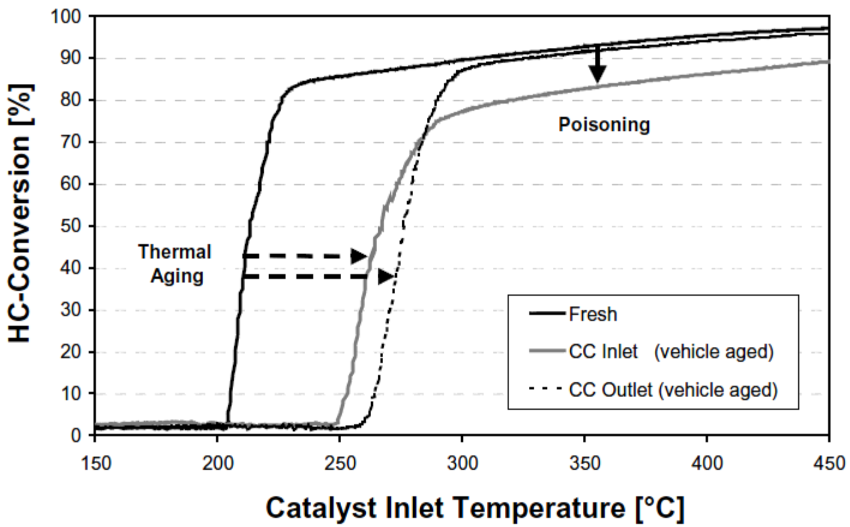
- The accumulation mode is assumed to contain 30% adsorbed hydrocarbon from the lube oil
- This all transfers to the nucleation mode when the soot is removed
- This results in more and larger nucleation mode particles
- Any solid ash associated with the soot mode also transfers into the nucleation mode

Importance of ash emissions

- Diesel engines - build-up and plugging of DPF
- Gasoline engines
  - Deposition in 3-way catalyst leads to poisoning
  - Same issues as diesel if GPF used
  - Solid nanoparticle emissions if GPF not used, especially with metallic additives
- Soot free engines
  - Deposition in aftertreament catalyst
  - Solid nanoparticle emissions

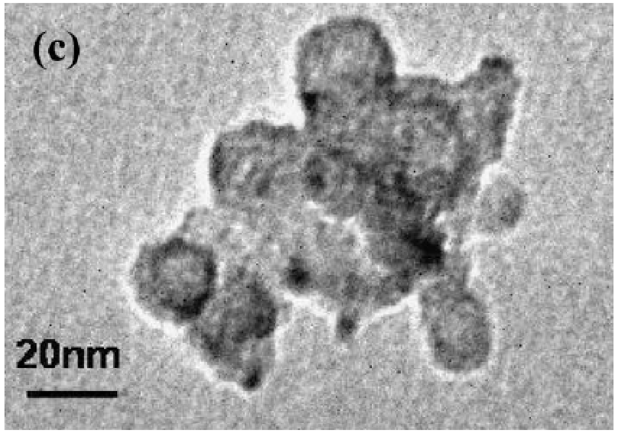


Ash distribution in exhaust filter channels (Heibel and Bhargava, 2007)



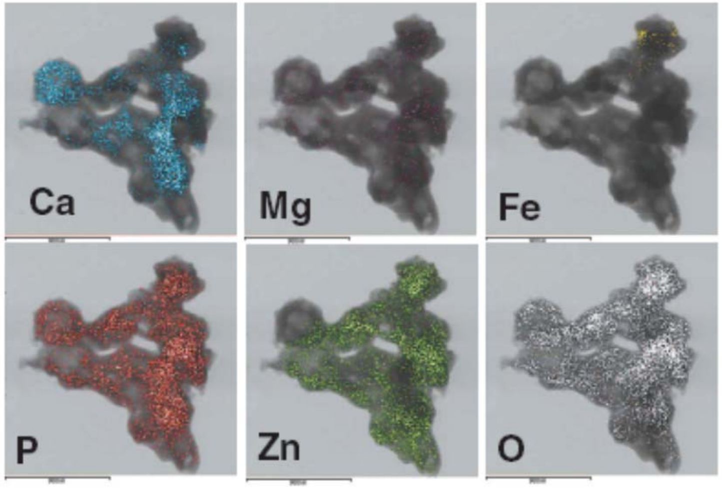
3-way catalyst poisoning by ash deposits (Franz, et al., 2005)

Engine ash emissions

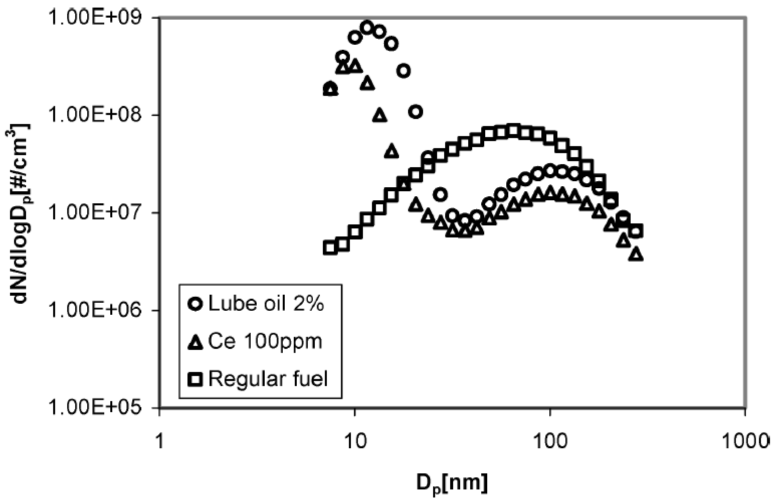


Jung, et al., 2005

- Non-combustible fraction of exhaust aerosol
- From metallic additives and engine wear metals
- Metallic particles tend to ‘decorate’ carbonaceous exhaust particles
- Form separate particles at sufficiently high metal to soot ratios



Sappok and Wong, 2007

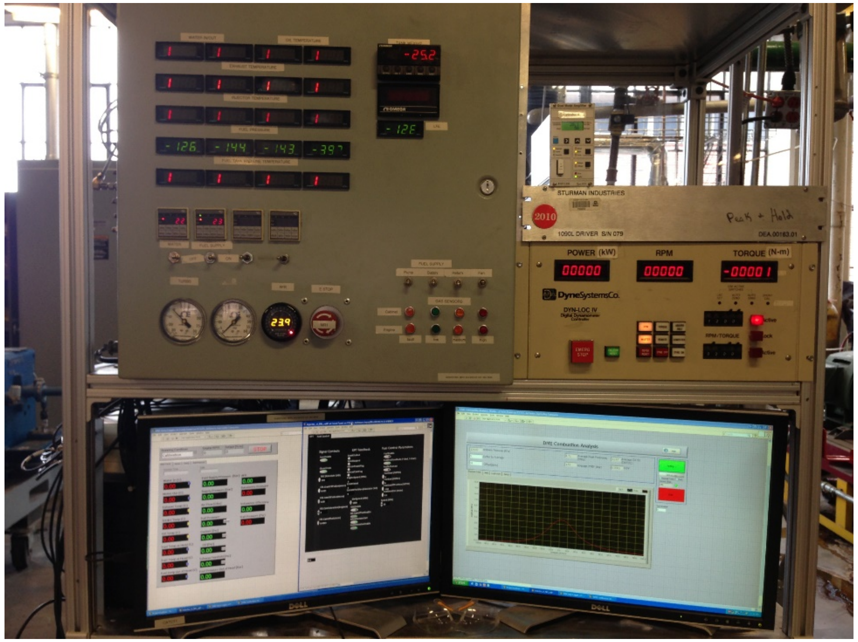


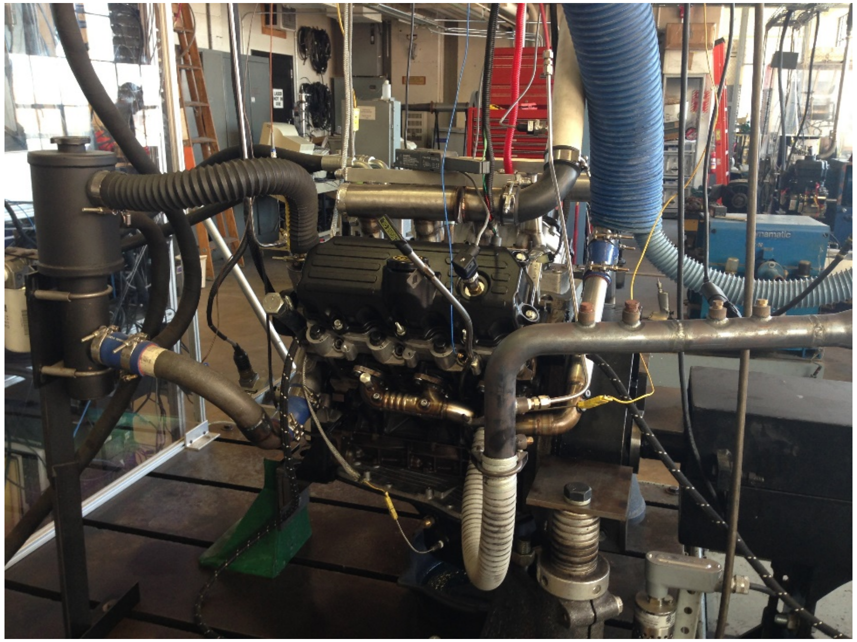
Jung and Kittelson, 2005

Particles from soot free engines

- Volatile particles
  - Lube oil, partially burned lube oil
  - Lubricity additives, partially burned lubricity additives
  - Partial oxidation products from fuel
  - These particles are extremely difficult to sample in a representative way
- Solid particles
  - Ash from metallic additives
  - Soot from lube oil
  - Wear particles

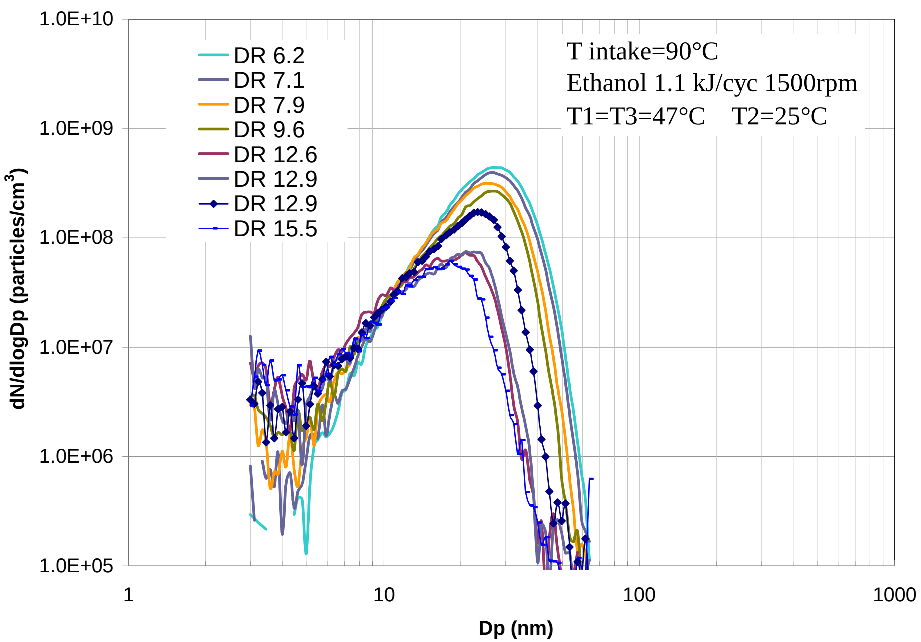
Engine layout

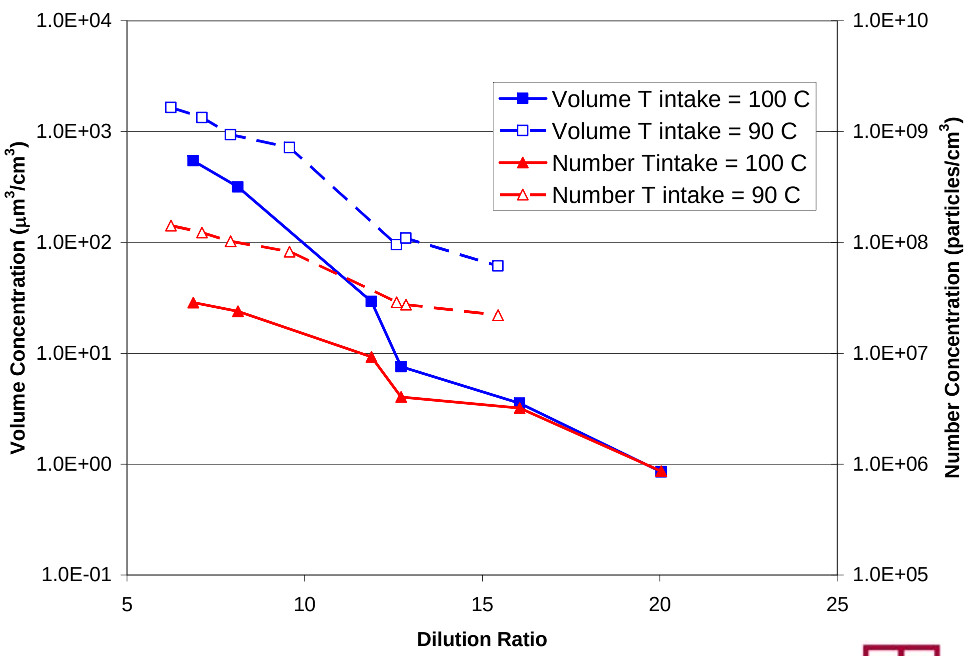




Dilution sensitivity tests showed strong dependence on dilution ratio

- We decided to standardize first stage dilution temperature – which is the critical one, to 47 C
- Both total number and total volume (mass) are very sensitive to dilution conditions but volume (mass) is most sensitive due to effect of both changing number and size
- There is no stable region for DR but the curve is "relatively" flat at DR = 15 so that is where we have mainly tested
- What happens is atmosphere, what do we breathe?
- At low dilution ratios mass emissions exceed US 2010 HD standards, however these volatile should be relatively easy to control with oxidation catalyst.





Results shown are for ethanol HCCI

Center for Diesel Research

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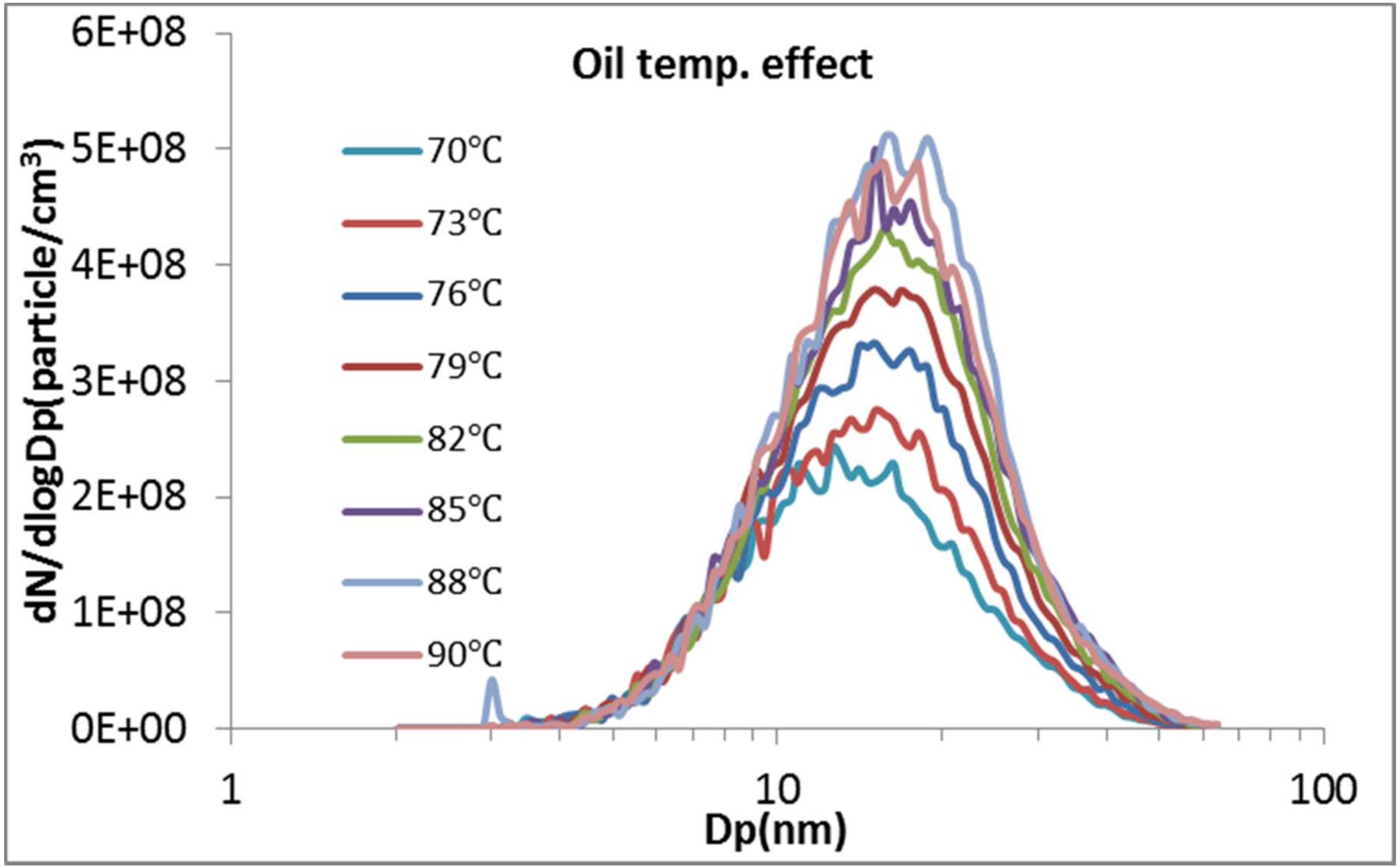
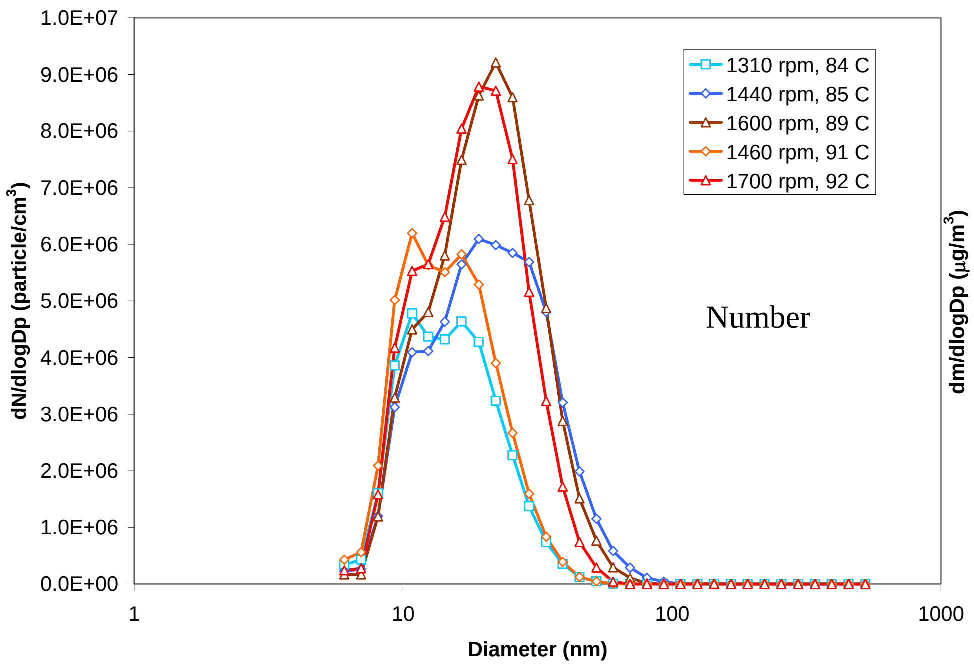
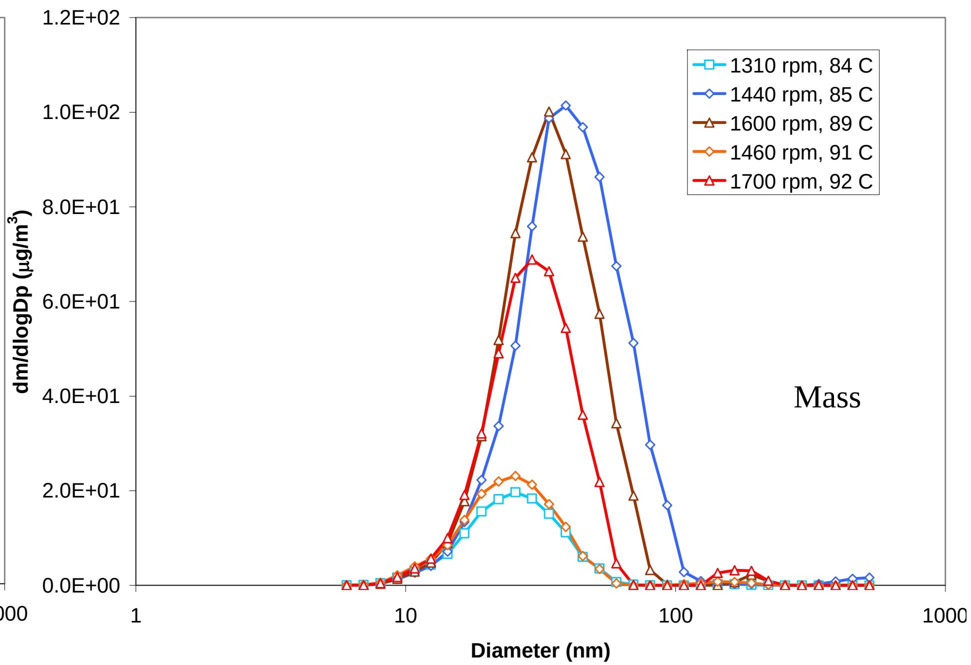
Conclusions

- Preliminary analysis of the economics of DME production in a pulpmill biorefinery look attractive – why isn't it happening?
- Joint propane DME fuel system development underway
- Most of the PM emissions from DME and other non-sooting fuels or engine concepts likely formed from the lube oil or lubricity additive
  - These emissions may be significant compared to US 2010 and Euro VI levels
  - Fortunately it is likely that they can be controlled with good DOC technology
  - Impact of solid ash emissions unclear
- We are looking for partners


Oil temp. effect
6E+08
5E+08
4E+08
3E+08
2E+08
1E+08
0E+00
dN/dlogDp(particle/cm3)
70°C
73°C
76°C
79°C
82°C
85°C
88°C
90°C
1
10
100
Dp(nm)

Hot motoring particle emissions, DME engine





- Preliminary results, lubrication oil still stabilizing
- Similar to HCCI test results
- Emissions increase with oil temperature and speed
- These will be partially burned out with under fired conditions

Sources of particulate emissions other than soot

- **US 2010 PM stnd – 0.013 g/kWh, Euro VI – 0.01 g/kWh**
- Sulfates from sulfur in fuel and lube oil
  - With modern ultralow S fuel at least as much sulfate comes from the oil as from the fuel
- Partially burned heavy hydrocarbons, i.e., organic carbon (OC)
  - Mainly from lube oil in heavy-duty engines
  - US pre-DPF (2006) heavy duty engines had to meet 0.13 g/kWh standard with typical actual emissions in the range of 0.08 and of this 25 to 50% or **0.025 to 0.05 g/kWh** OC
  - Lube oil consumption for such engines typically 0.05 to 0.15% of fuel consumption or 0.1 to 0.3 g/kWh
  - If we assume all the consumed oil enters the cylinder this implies a combustion efficiency ranging from about 50 to 90%. Remember fuel combustion efficiency for a Diesel is usually greater than 99%
- In a DME engine 100-200 ppm lubricity additive would input 0.03 to 0.06 g/kWh HC to the engine but since this is mixed with the fuel it is likely to be much more completely consumed than the lube oil
- HC Impurities in the DME likely to behave in a similar manner to lubricity additive
- Ash
  - Lube oil is 0.5 - 1 % metal which leads to corresponding solid ash emissions – not much mass but very tiny
  - Metal contaminants in DME would go directly to solid ash, 10 ppm to at least 0.003 g/kWh
- **Lube oil OC the likely major source of PM in soot free engines – fortunately this can be controlled quite effectively with a DOC**

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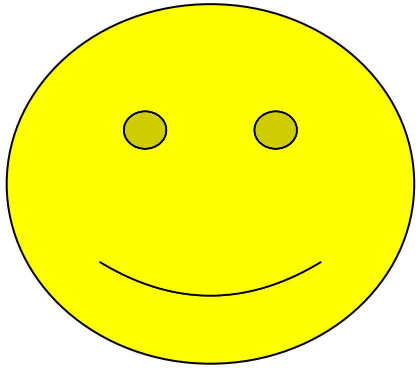

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