13th ETH Conference on Combustion Generated Nanoparticles, June 22nd-24th 2009

Title: Particulate emissions from a dual-fuel compression ignition engine utilising ethanol fumigation

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Extended summary:

Particle emissions, volatility and the concentration of reactive oxygen species (ROS) were investigated for a Pre-Euro I, 4-cylinder, Ford 2701C compression ignition engine to study the potential health impacts of employing ethanol fumigation technology. The dual-fuel system fitted to the test engine enabled vapourised ethanol to be delivered to the intake manifold. Engine testing was performed in two separate experimental campaigns. The first was conducted at 2000 rpm, full load, and the second at intermediate speed (1700 rpm) using four different load settings. For a particular load setting, all tests were conducted at the same brake load, so that any change in emissions was only due to the change in fuel, and not due to the different power output of the engine.

A Scanning Mobility Particle Sizer (SMPS) was used to determine particle size distributions, a Volatilisation Tandem Differential Mobility Analyser (V-TDMA), pre-selecting 80 nm accumulation mode particles, was used to explore particle volatility, and a new profluorescent nitroxide probe, BPEAnit, was used to investigate the particle-related reactive oxygen species (ROS) concentrations emitted by the test engine. BPEAnit is a weakly fluorescent compound, but it exhibits strong fluorescence upon radical trapping or redox activity [1]. This makes it a powerful optical sensor for radicals and redox active compounds, and can assist in determining the potential toxicological impact of particle emissions.

Particulate mass was significantly reduced, and the concentration of gas phase hydrocarbons increased considerably, with ethanol fumigation. Both of these factors contributed to the formation of a nucleation mode at full load operation with a 40% ethanol substitution. Previous research on ethanol blends [2-4]; using ethanol substitutions lower than that used in this study, demonstrate a reduction in the accumulation mode particle concentration, and a shift to smaller particles, without the presence of a nucleation mode.

Particle size was correlated with the peak combustion pressure and the ethanol fumigation percentage. As a result, fragmentation of agglomerates due to increased combustion pressures, and oxidation of the particle surface due to OH radicals emerge as two hypotheses that could explain the smaller particles that arise from ethanol fumigation technology.

The V-TDMA results showed that the percentage of volatile particles was increased by ethanol fumigation. Furthermore, particles were internally mixed at full load operation and were externally mixed at all other loads. Volatilisation curves indicated the presence of organic material, either derived from fuel or lubricating oil. The particle volume fraction remaining, plotted against the thermodenuder temperature, generally exhibited a more rapid decrease for tests involving ethanol.

Particle-related ROS emissions increased with decreasing engine load, for both neat diesel and ethanol tests, although ROS emissions were higher for the tests involving ethanol fumigation, except at idle mode. In addition, higher ROS concentrations were associated with the formation of a nucleation mode in the particle size distributions.

In conclusion, the smaller particles, the increased volatility, and the significant increase in ROS emissions from ethanol fumigation may provide a substantial barrier to the uptake of fumigation technology using ethanol as a supplementary fuel.

Acknowledgements:

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References:

[1] Fairfull-Smith KE, Bottle SE. The synthesis and physical properties of novel polyaromatic profluorescent isoindoline nitroxide probes. European Journal of Organic Chemistry 2008;32:5391-5400.

[2] Di YG, Cheung CS, Huang ZH. Experimental study on particulate emission of a diesel engine fueled with blended ethanol-dodecanol-diesel. Journal of Aerosol Science 2009;40(2):101-112.

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[4] Lapuerta M, Armas O, Herreros JM. Emissions from a diesel-bioethanol blend in an automotive diesel engine. Fuel 2008;87(1):25-31.

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Zürich, 22nd-24th June 2009

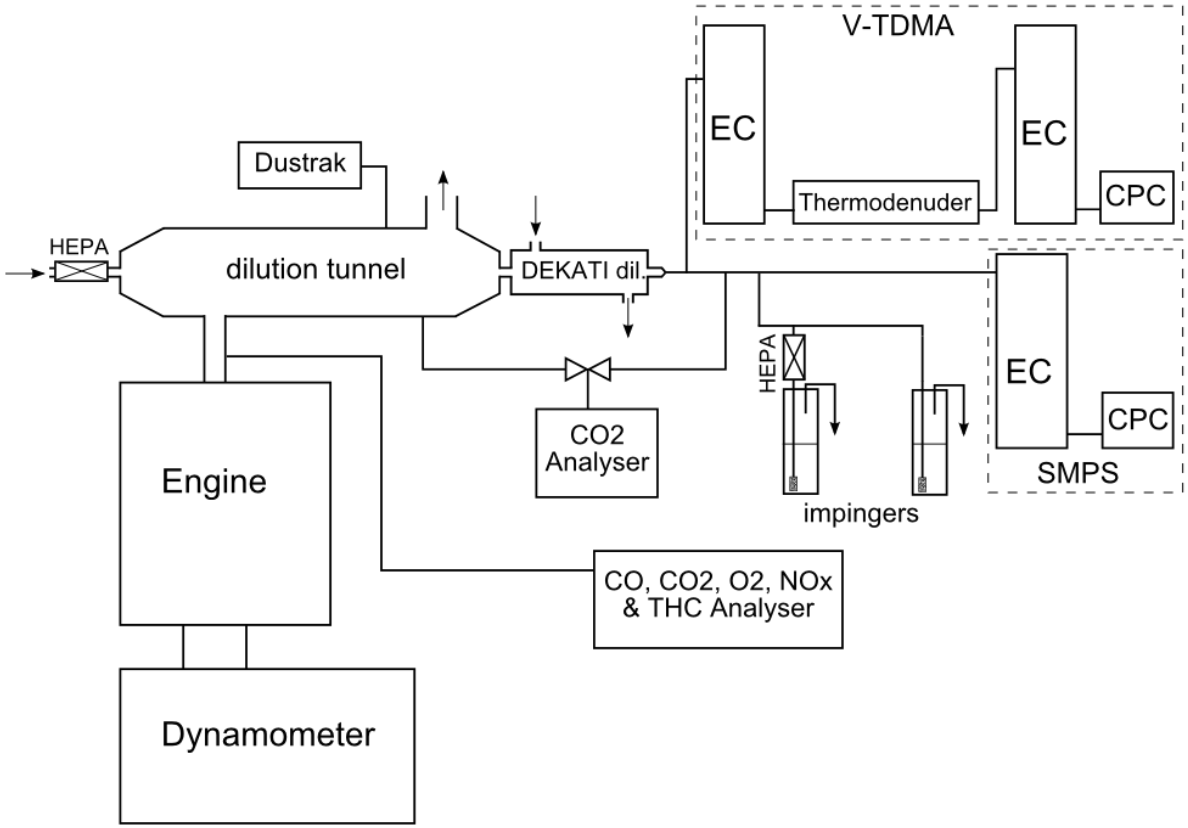
In today's talk...

1. Project overview and rationale
2. Methodology
- Particle emissions (SMPS)
- Particle volatility (VTDMA)
- Reactive oxygen species (Profluorescent nitroxide probes)
3. Results
4. Conclusions and future research

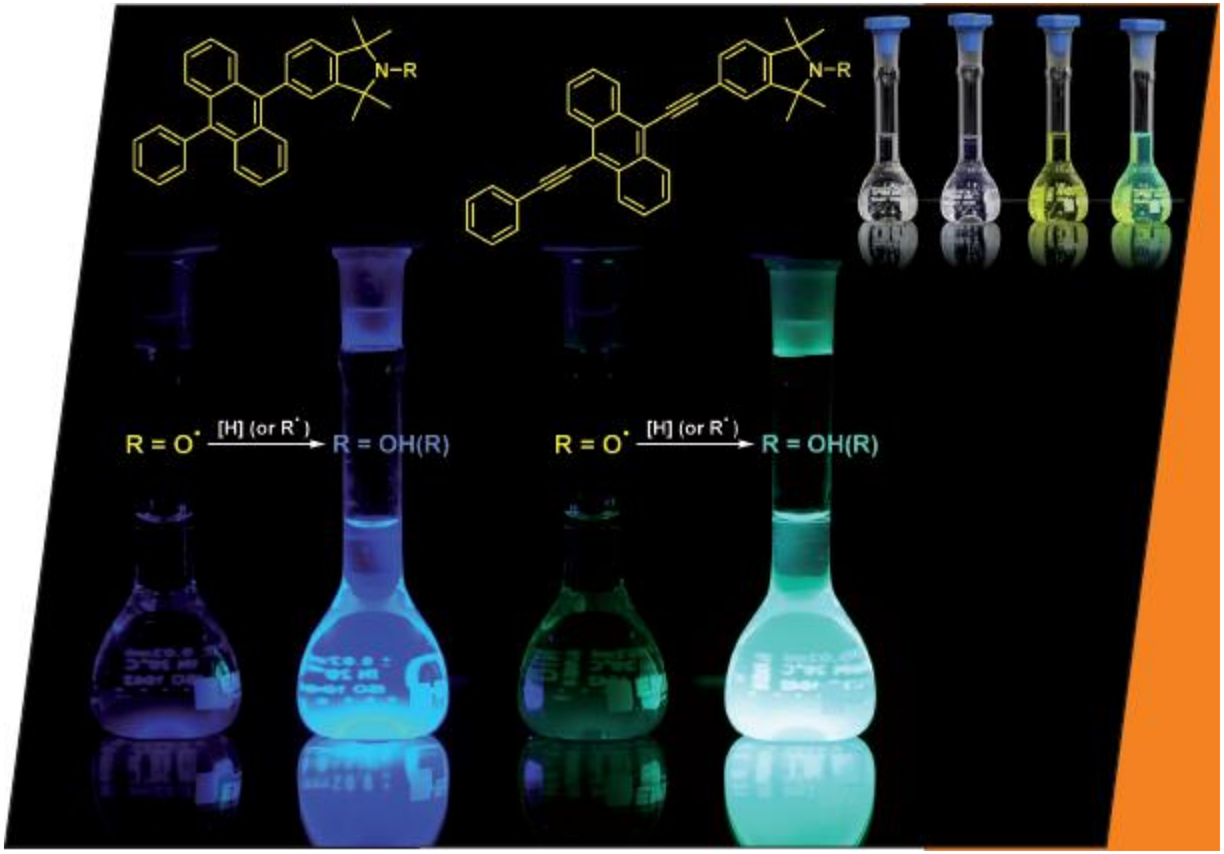
Background

- Involved with the dual-fuel engines project at QUT
- Drivers for biofuel research
- Project aim is to "optimise" compression ignition engines (using biofuels) with respect to emissions and performance
- My project investigates emissions with a major focus on particulates

Experimental configuration



Methodology: profluorescent nitroxide probes[1]



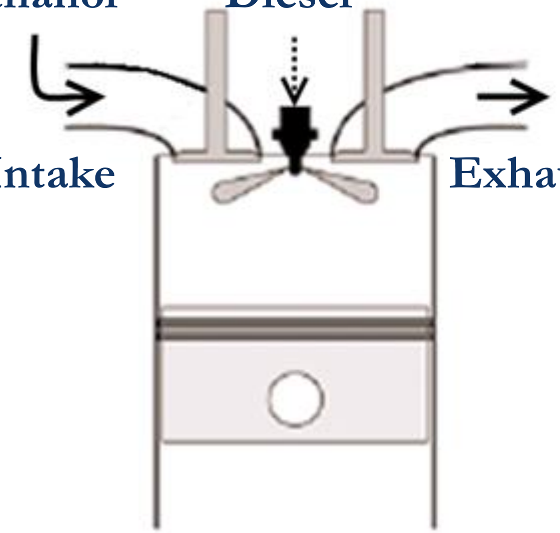
Basic idea: fluorescence exhibited upon radical trapping or redox activity

Test engine specifications

Model	**Ford** 2701C
Cylinders	4 in line
Capacity (L)	4.152
Bore × stroke (mm)	108.2 × 115
Maximum power (kW/rpm)	48/2500
Maximum torque (Nm/rpm)	228/1700
Compression ratio	15.5
Aspiration	Naturally aspirated
Emissions certification	Pre Euro I

Experiments performed on an older technology engine while new test facility was constructed (operational May 2009)

Ethanol fumigation technology



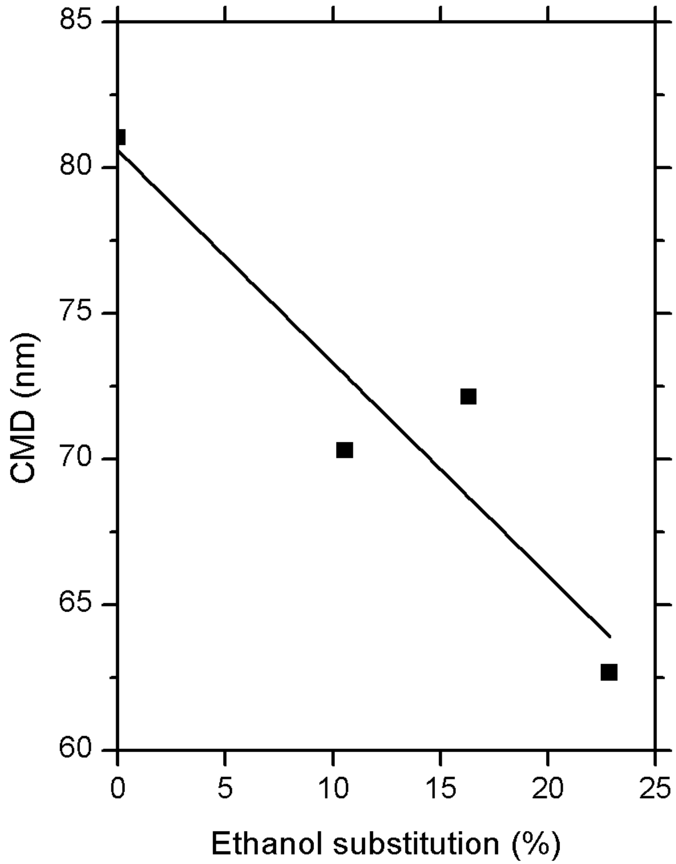
Implementation

- Diesel undergoes normal injection cycle
- Ethanol vapour added to intake manifold
- Need to reduce ethanol flow at high/load loads
- ≤ 50% energy substitution at intermediate load

Advantages (relative to ethanol blends)

- Over comes phase separation
- Limited water tolerance of blends
- Enables greater ethanol substitutions > 20-25%
- **Separate fuel tanks**: switch back to neat diesel operation if problems encountered with ethanol combustion

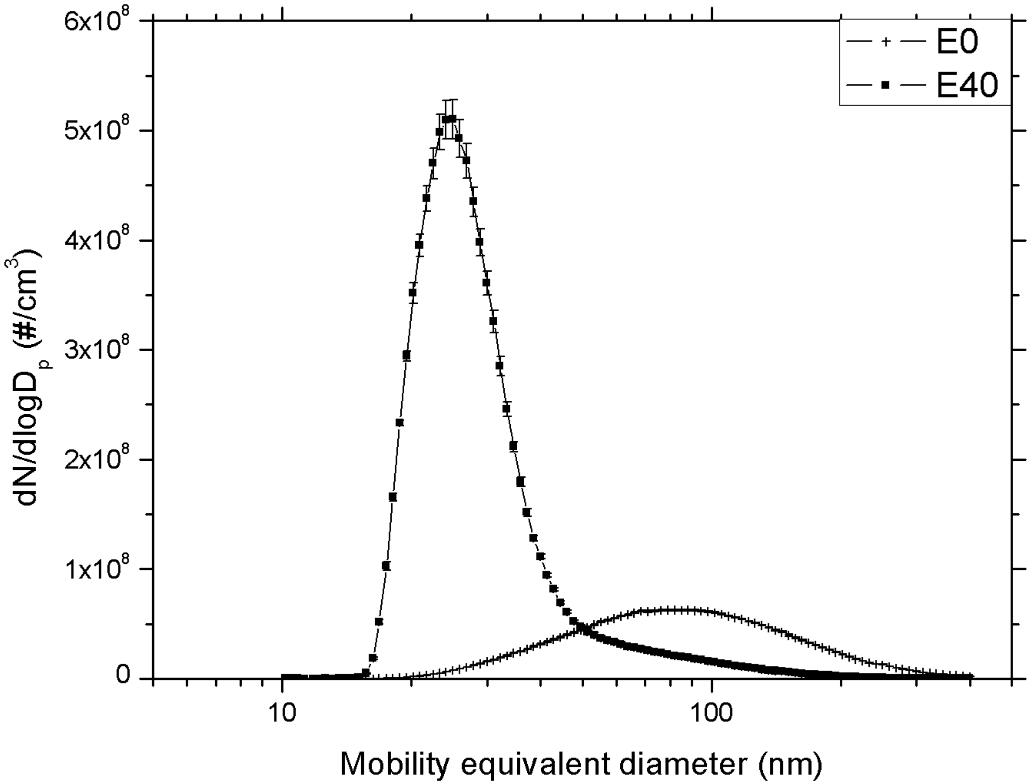
Results: low fumigation percentages



2000 rpm Full Load

- Results here consistent with other studies conducted with ethanol blends[2-4]:
- Reduction in accumulation mode particle concentrations
- Shift of count median diameter (CMD) to smaller particle diameter
- Ethanol blending technology capable of delivering 20-25% fuel energy
- What happens if we use more ethanol, like fumigation technology can???

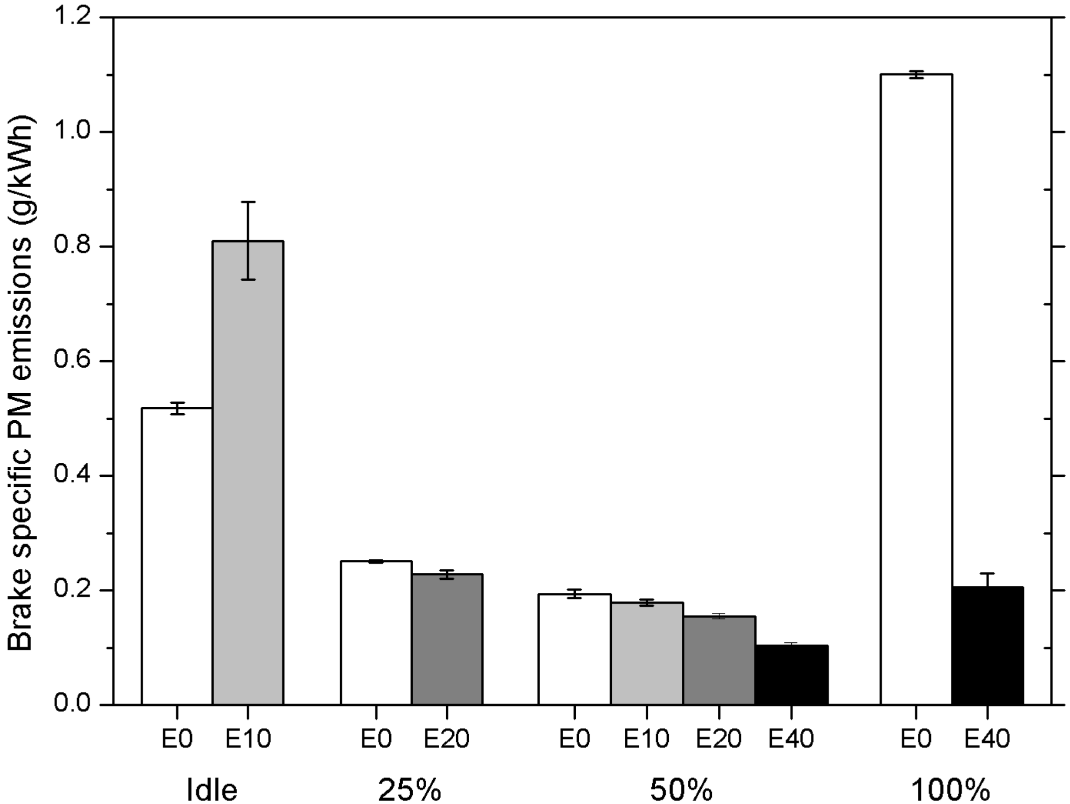
Results: high fumigation percentage



- With 40% fuel energy from ethanol we get nucleation instead!
- Why did this happen?

Intermediate Speed (1700 rpm) Full Load

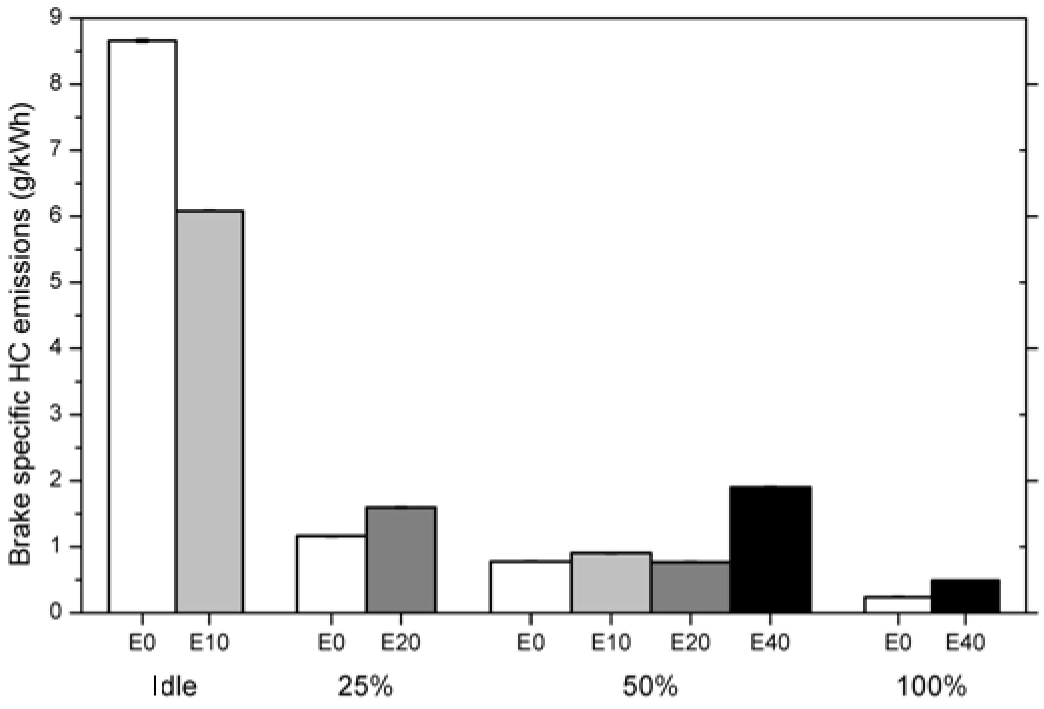
Results: PM emissions



Observation #1

- Full load PM emissions reduced five-fold by ethanol
- Accumulation mode particle surface vastly reduced

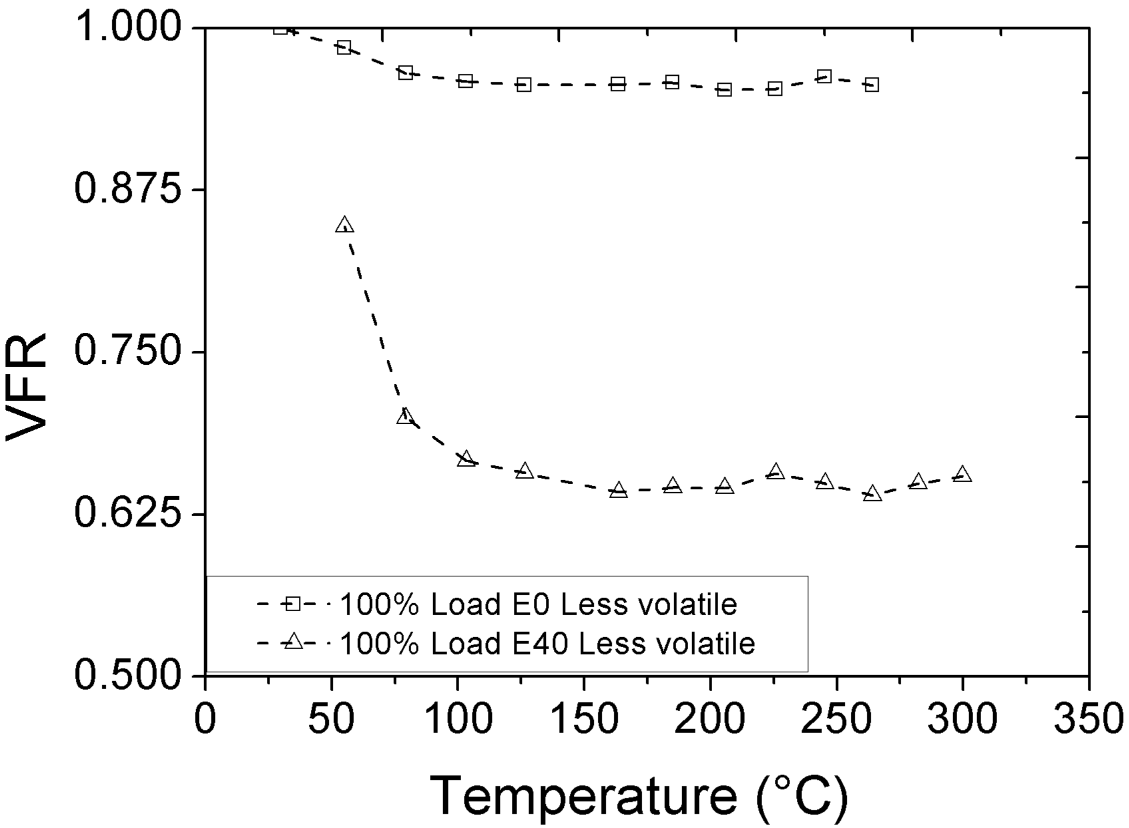
Results: HC emissions



Observation #2

- Gas phase hydrocarbons increased by ethanol fumigation

Results: volatility full load



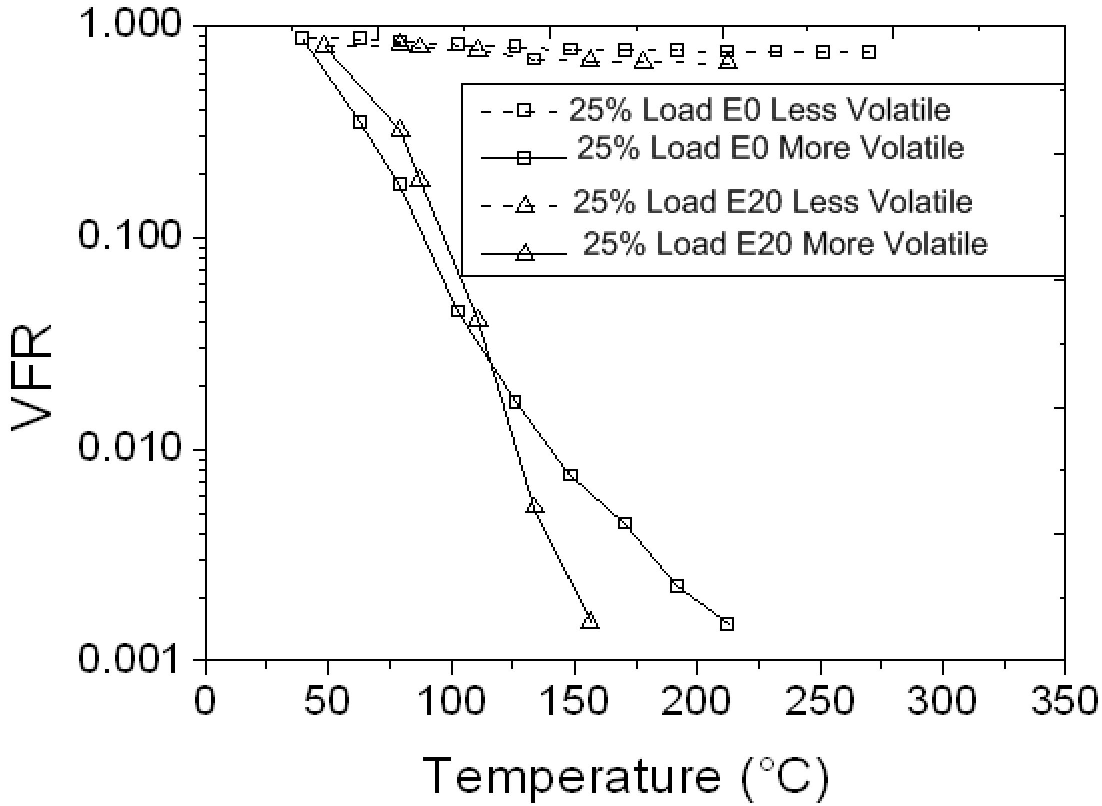
Observation #3

- A significant volume of organic material coats accumulation mode particles
- Nucleation occurs then a large amount of organic material condenses on particles

Conclusion

The presence of more volatile material, with a decreased particle surface for condensation, provides a viable mechanism for nucleation to occur

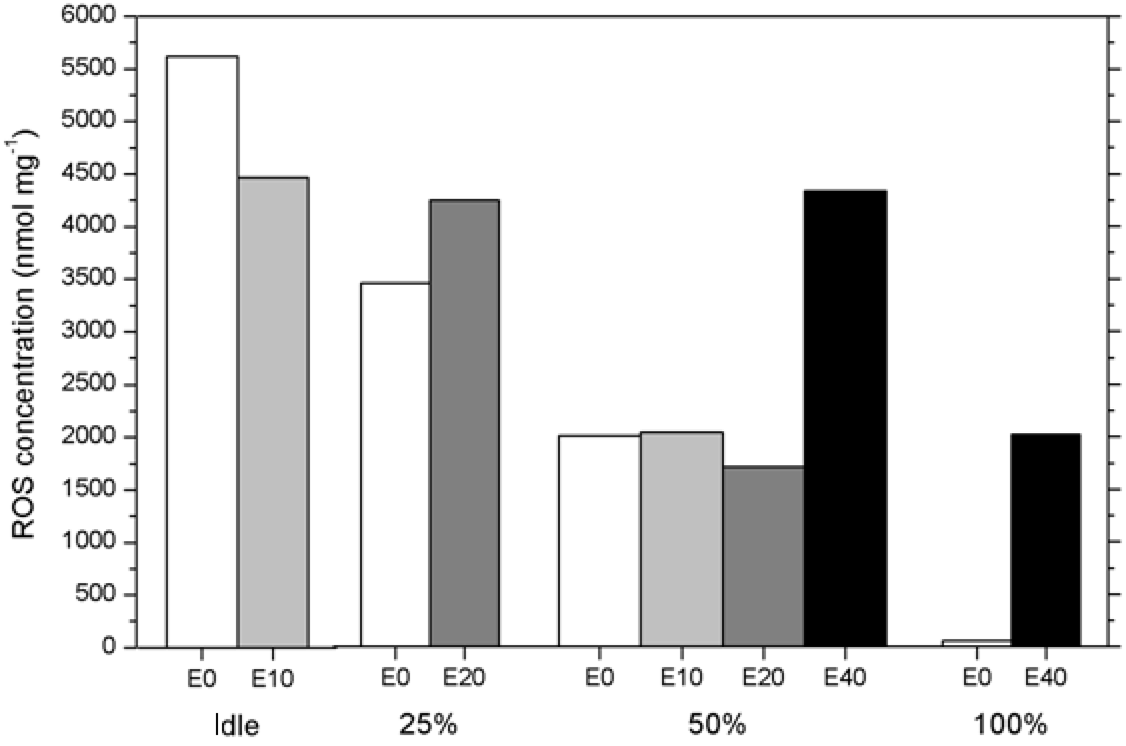
Results: volatility quarter load



Particles externally mixed at partial load

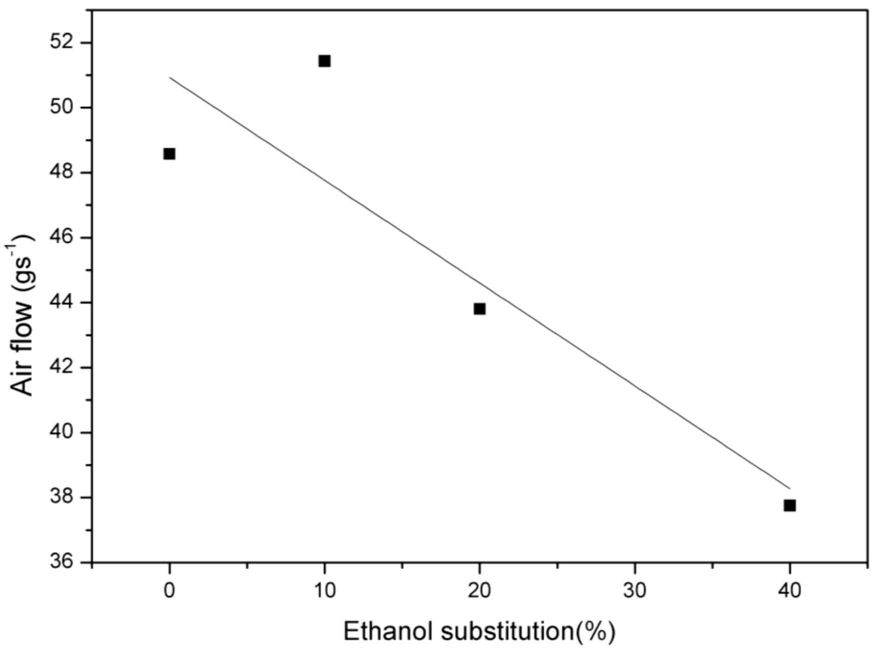
Results: reactive oxygen species

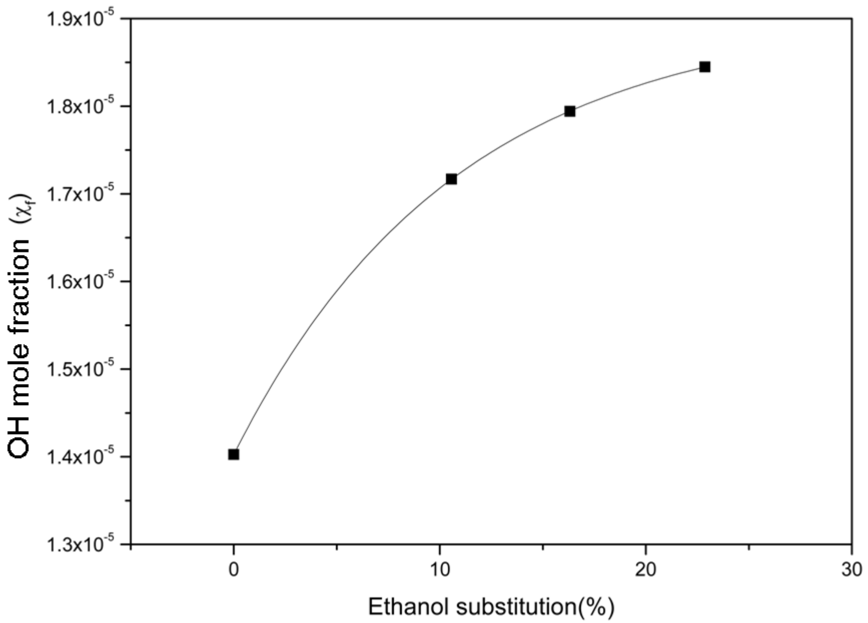
- What about the potential toxicity of particles?



- Normalised ROS emissions significantly increased by ethanol fumigation, especially at full load operation
- ROS emissions associated with the formation of a nucleation mode

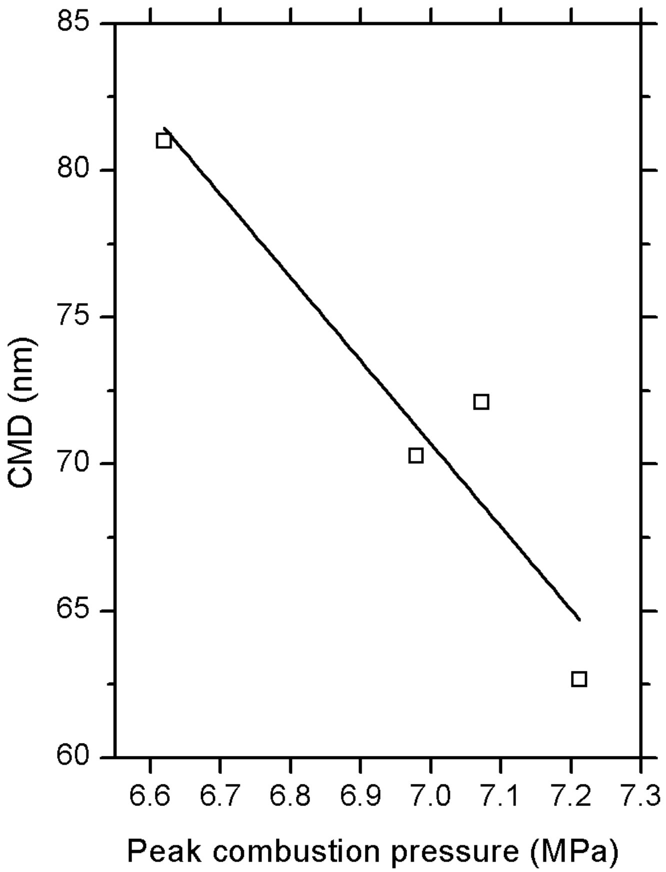
Particle size reduction mechanisms I





- Reduction in air available for combustion
- AVL Boost simulation shows an increase in OH radicals
- OH radicals known to more readily oxidise particle surface[5]

Particle size reduction mechanisms II



Observation

- Particle size also correlated with the peak combustion pressure
- Possibility of fragmentation?

Conclusions

- Ethanol fumigation:
- Produces smaller particles
- Prone to gas-particle conversion
- Increases ROS emissions
- Makes particles more volatile
- Uptake of ethanol fumigation technology might be a problem based on these results

Future directions

- More work to establish the physical cause of smaller particles with ethanol fumigation
- Oxidation due to OH radicals?
- Fragmentation due to increased pressure?
- TDMA analyses targeted at nucleation mode, not accumulation mode particles
- Comparison of ethanol blending versus ethanol fumigation particle emissions
- Testing with a more modern engine technology (Euro III)

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References

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[4] Lapuerta M, Armas O, Herreros JM. Emissions from a diesel-bioethanol blend in an automotive diesel engine. Fuel 2008;87(1):25-31.

[5] Xu F, El-Leathy AM, Kim CH, Faeth GM. Soot surface oxidation in hydrocarbon/air diffusion flames at atmospheric pressure. Combustion and Flame 2003;132(1-2):43-57.