On the Manipulation of Particle Nanostructure

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TU/e

I: Introduction

Background:

A study has been performed into the impact of oxygenates (e.g. $C_xH_yO_z$ molecules blended with diesel fuel) and engine characteristics on the particle formation process

Main conclusions from literature research

1. *Trivial:* An elevated oxygen concentration in the particle synthesis zone, either via fuel oxygen or improved fuel/air mixing (e.g. modern engine), leads to lower particle emissions

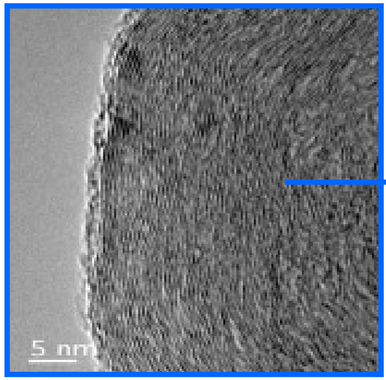
2. *Non-trivial:* An elevated oxygen concentration in the particle synthesis zone, either via fuel oxygen or improved mixing process (e.g. modern engine), alters the particle nanostructure

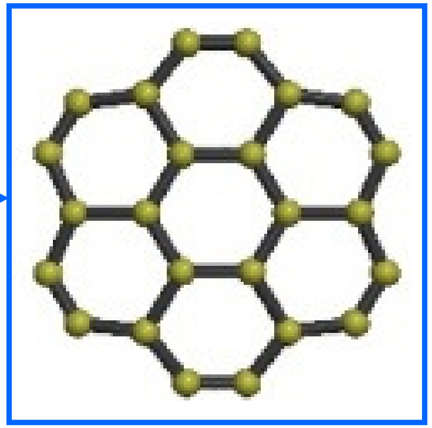
Fuel oxygen: R.L. Vander Wal, *Combustion and Flame 136, pp. 129-140, 2004*

Modern engine: D.S. Su, *Topics in Catalysis 30/31, pp. 241-245, 2004*

II: Particle nanostructure

Particle nanostructure as formed in oxygen-lean environment:





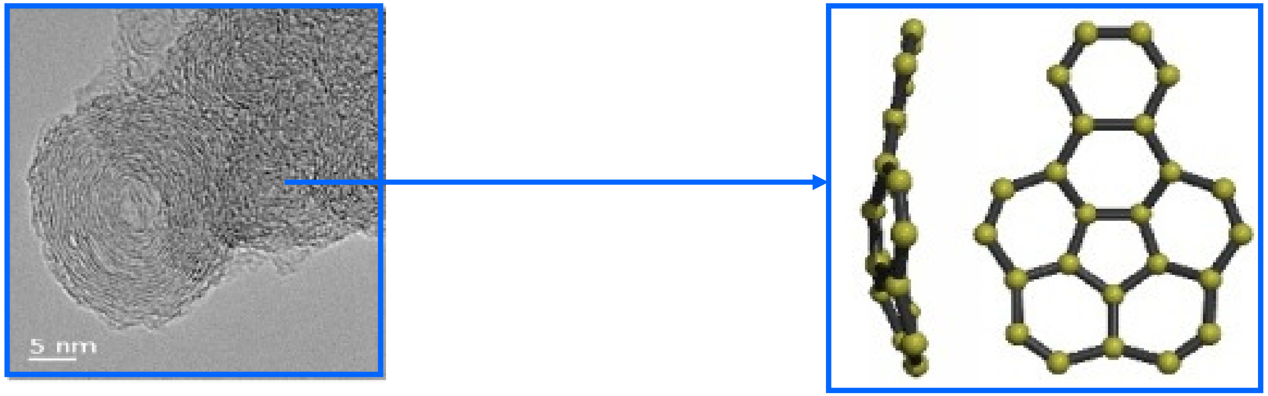
R.L. Vander Wal, *Combustion and Flame 136, pp. 129-140, 2004*

Characteristics

- Composed from layered poly-aromatics hydrocarbons (PAH) which are predominantly planar (i.e. 2D)
- PAH are held together by VanderWaals (VDW) forces
- Overall structure is crystalline (i.e. ordered) and "black"

II: Particle nanostructure

Particle nanostructure as formed in oxygen-rich environment:



R.L. Vander Wal, *Combustion and Flame 136, pp. 129-140, 2004*

Characteristics

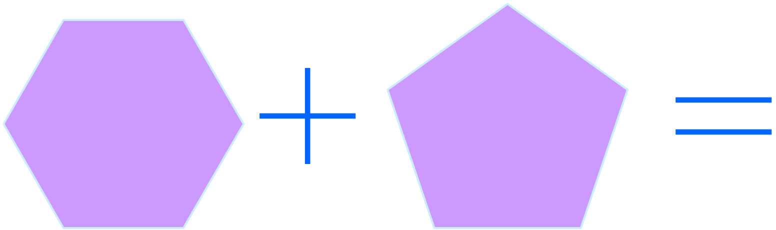
- Composed from PAH which are predominantly curved (i.e. 3D)
- PAH are held together by VDW forces
- Overall structure is more amorphous (i.e. disordered) and "grey"

II: Particle nanostructure

How do the PAH become curved?

Curvature results from contamination of the hexagonal PAH by a number of pentagonal unsaturates (e.g. cyclopentadienyl radicals)

T.S. Norton, *Proc. Combust. Inst. 23, pp. 179–185, 1990*



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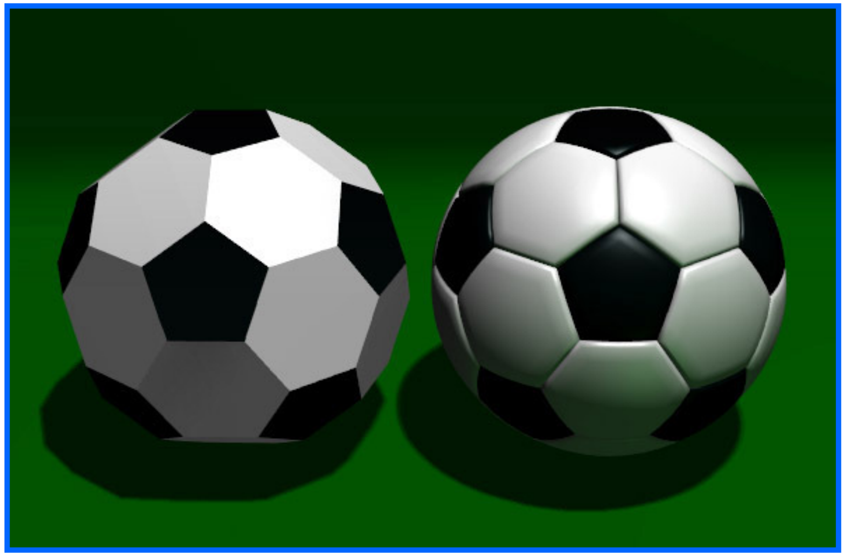


III: Interlude

Some interesting facts on the Day Gecko

- Day Gecko is a small reptile indigenous to South Africa
- It is able to cling upside down to polished glass and to support full body weight with a single toe
- Gecko feet properties studied extensively for application in for example tires and “gecko” tape

III: Interlude

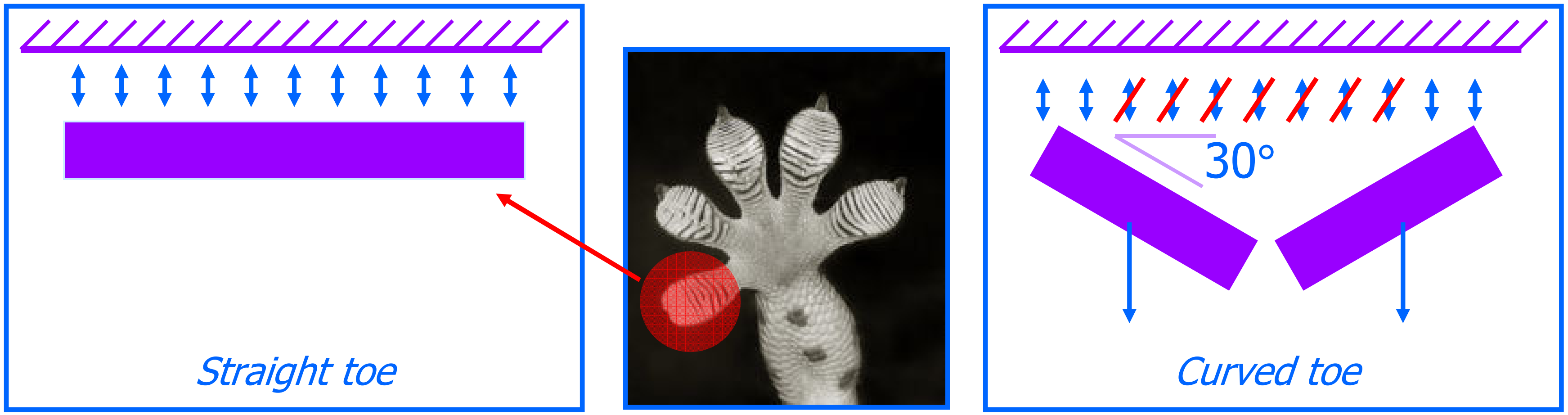
How do Geckos “Stick” ?

- Strong attraction is due to Van der Waals (VDW) force
- For a given object mass, VDW increases with surface area
- Gecko feet are covered in millions of microscopic hairs which split into hundreds of tips (Ø 200 *nm*), resulting in an enormous surface area

III: Interlude

How do Geckos “fall” ?

- VDW force decreases rapidly with intermolecular distance
- To release their feet Geckos, curl their toes, breaking the binding when the toe is at a 30° angle with the contact surface



IV: Implications of curvature *1-2*

Main conclusions "*II: particle nanostructure* "

Particles are basically held together by VDW forces

Oxygen-rich synthesis conditions appear to promote curvature in PAH

Main conclusion "*III: Gecko Interlude*"

VDW force between two surfaces attenuates rapidly with decreasing "approachability" and is therefore lower between curved (i.e. 3D) surfaces

IV: Implications of curvature

Hypothesis based on aforementioned conclusions

Promoting curvature in PAH will manifest in a weaker nanostructure and will therefore yield lower particle emissions

Literature data discloses that the burn-rate of a curved vs. crystalline particle nanostructure is a factor 5 higher

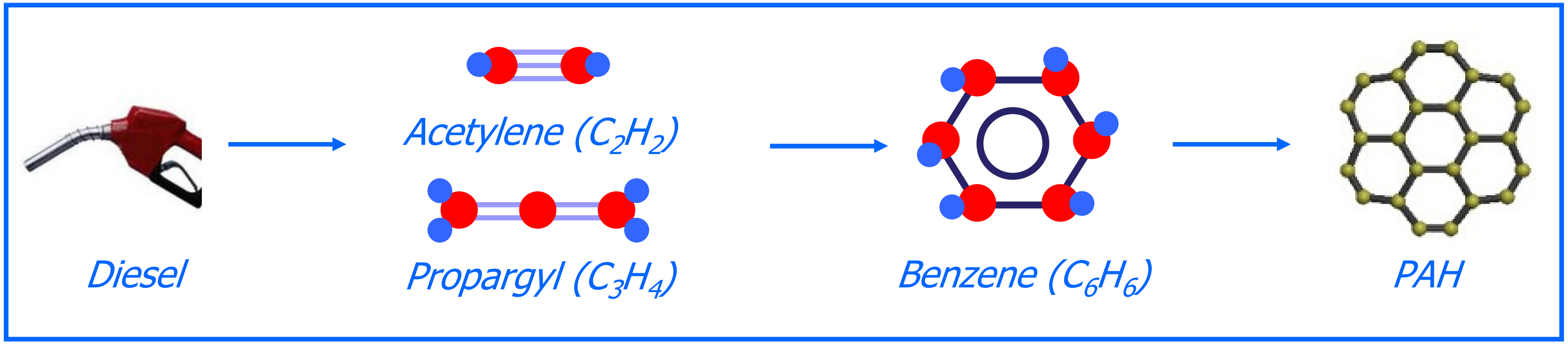
R.L. Vander Wal, *Combustion and Flame 134, pp. 1-9, 2003*

-> Main research question <-

How can one boost the degree of curvature in PAH?

V: Formation of curvature in PAH

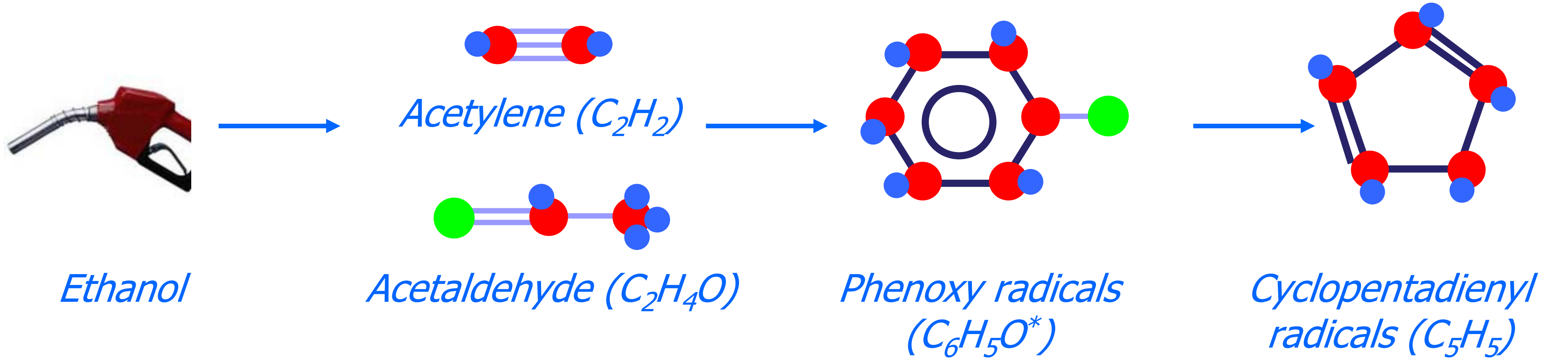
Principal pathway to planar PAH



1. Diesel pyrolysis -> unsaturated C_2-C_3 species
2. Recombination of unsaturated C_2-C_3 species -> first aromatic ring
3. Subsequent growth via C_2H_2 addition and H abstraction -> PAH

V: Formation of curvature in PAH

Probable pathway to curved PAH



T.S. Norton, *Proc. Combust. Inst. 23, pp. 179–185, 1990*

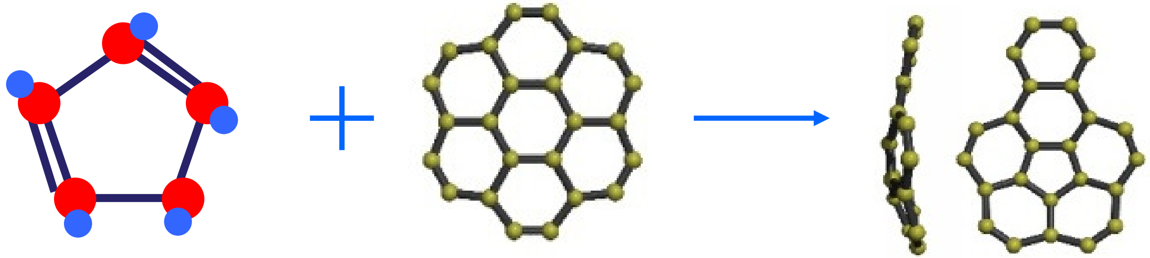
1. Ethanol pyrolysis -> C_2 species *w* and *w/o* O-group

2. Recombination of both types of C_2 species -> phenoxy radicals

3. Decomposition of phenoxy radicals -> cyclopentadienyl radicals

V: Formation of curvature in PAH

Probable pathway to curved PAH



Cyclopentadienyl radicals (C_5H_5) — *Planar PAH* — *Curved PAH*

T.S. Norton, *Proc. Combust. Inst. 23, pp. 179–185, 1990*

4. Cyclopentadienyl radicals can be rapidly incorporated into larger PAH and will inherently induce curvature

VI: Promotion of curvature in PAH

Brief summary of contents thus far

Curvature in PAH is beneficial for the particle burn-rate

Oxygen-rich synthesis conditions appear to promote curvature in PAH

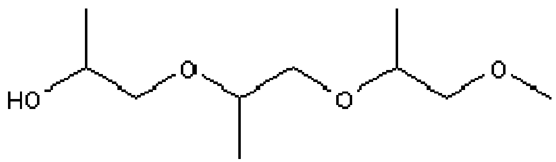
Although precise pathway is uncertain, phenoxy radicals appear pivotal

-> Approach <-

Select an oxygenate (e.g. cyclohexanone) which resembles phenoxy radicals and compare the emissions performance to that of contemporary oxygenates in two test engines

VII: Experimental setup

Oxygenates to be blended with diesel fuel to 9 wt-% fuel O_2

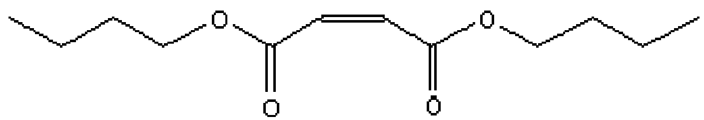


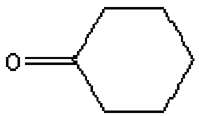
TPGME

Boiling point	515 *K*
Cetane number	75 -

DBM

Boiling point	438 *K*
Cetane number	30 -





Cyclohexanone (CHO)

Boiling point	430 *K*
Cetane number	16 -

VII: Experimental setup

Test Engine I

Engine with EGR: DAF *PEC* 6-cylinder 9.2 *liter*

Speed	1650 *RPM*
Fuel injection pressure	~ 800 *bar* *(PLD)*
Start of fuel injection (actuation)	-13 *dCA aTDC*
Intake pressure	1.47 *bar*
Load (IMEP)	8.4 *bar*

NB Exhaust gas recirculation (EGR) is a well-known method to reduce NO_x emissions

V: Experimental setup *3-3*

Test Engine II

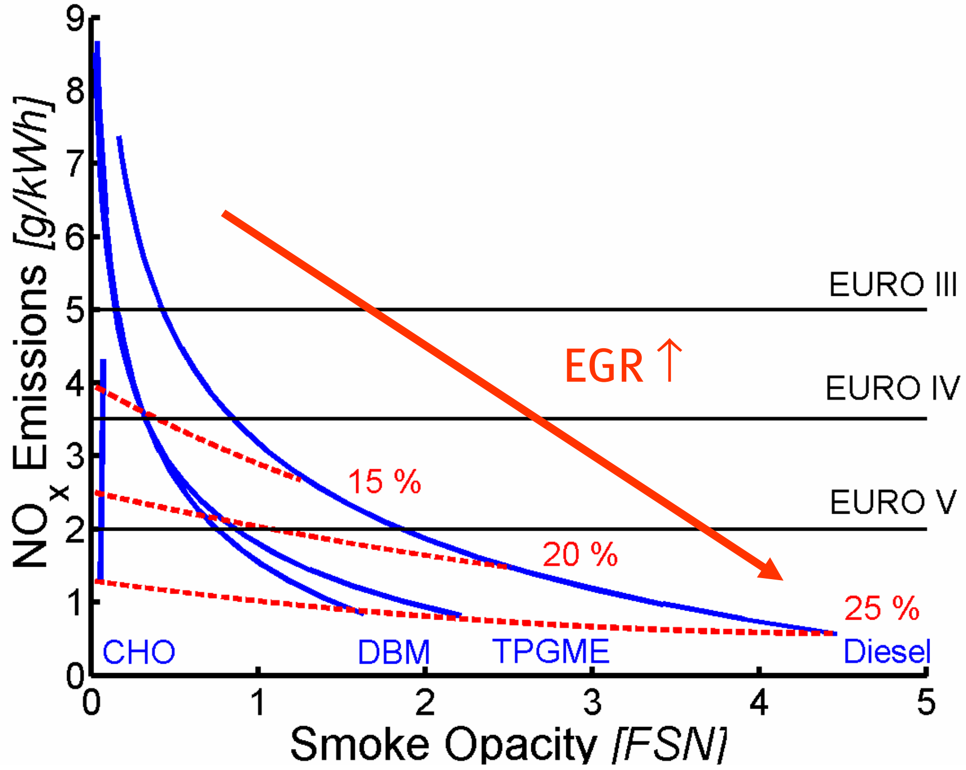
Optically accessible (e.g. Bowditch-type) engine: DAF *WS* 6-cylinder 11.6 *liter*

Speed	1400 *RPM*
Fuel injection pressure	1200 *bar* *(common rail)*
Start of fuel injection (actuation)	-13 *dCA aTDC* *(skip-fired @ 1:30)*
Intake pressure	1.4 *bar*
Load (IMEP)	~ 5 *bar*

Assumption: light emitted from the combustion is attributed to particle radiation

VIII: Results & Discussion

Test engine I: EGR sweep @ 9 *wt-%* fuel oxygen



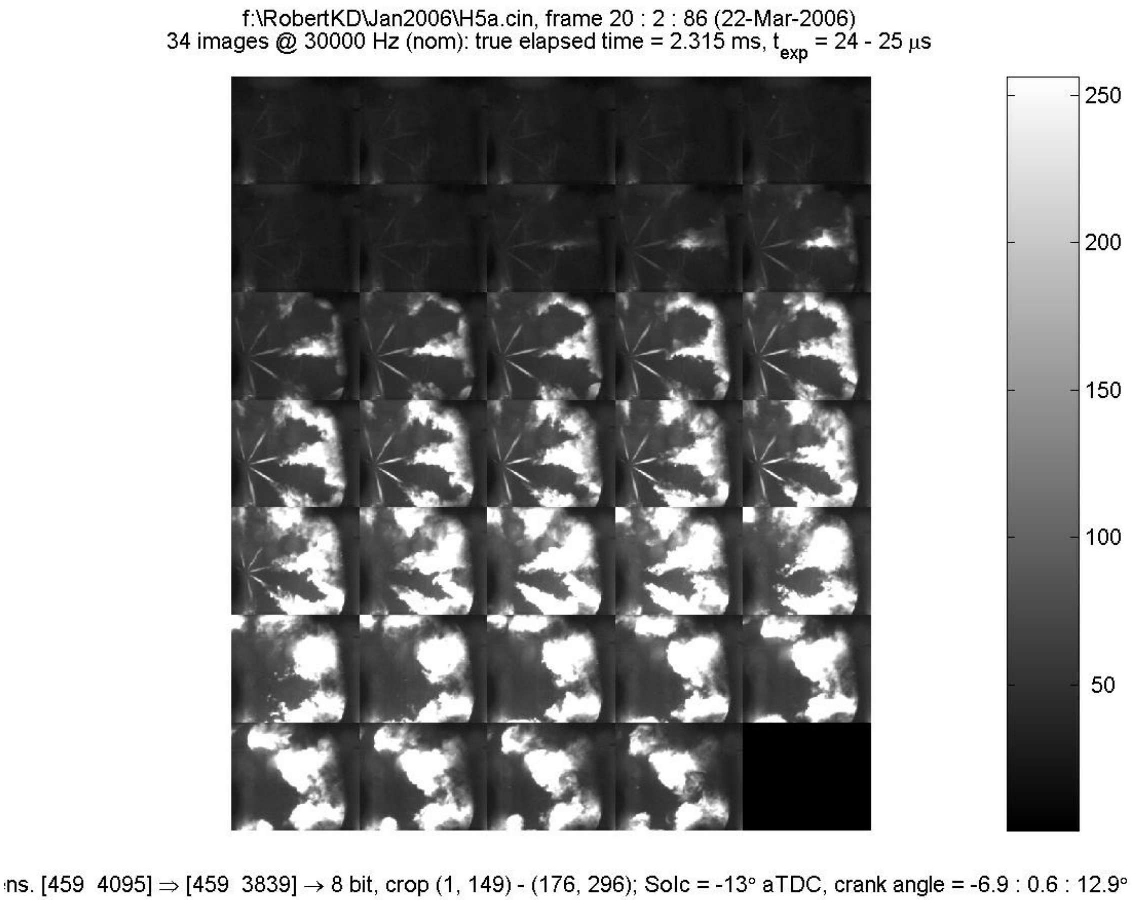
At all EGR levels fuel oxygen leads to lower particle emissions (smoke)

NO_x decreases with EGR for all fuels

Particle emissions (smoke) increase rapidly with EGR for all fuels (except cyclohexanone)

VIII: Results & Discussion

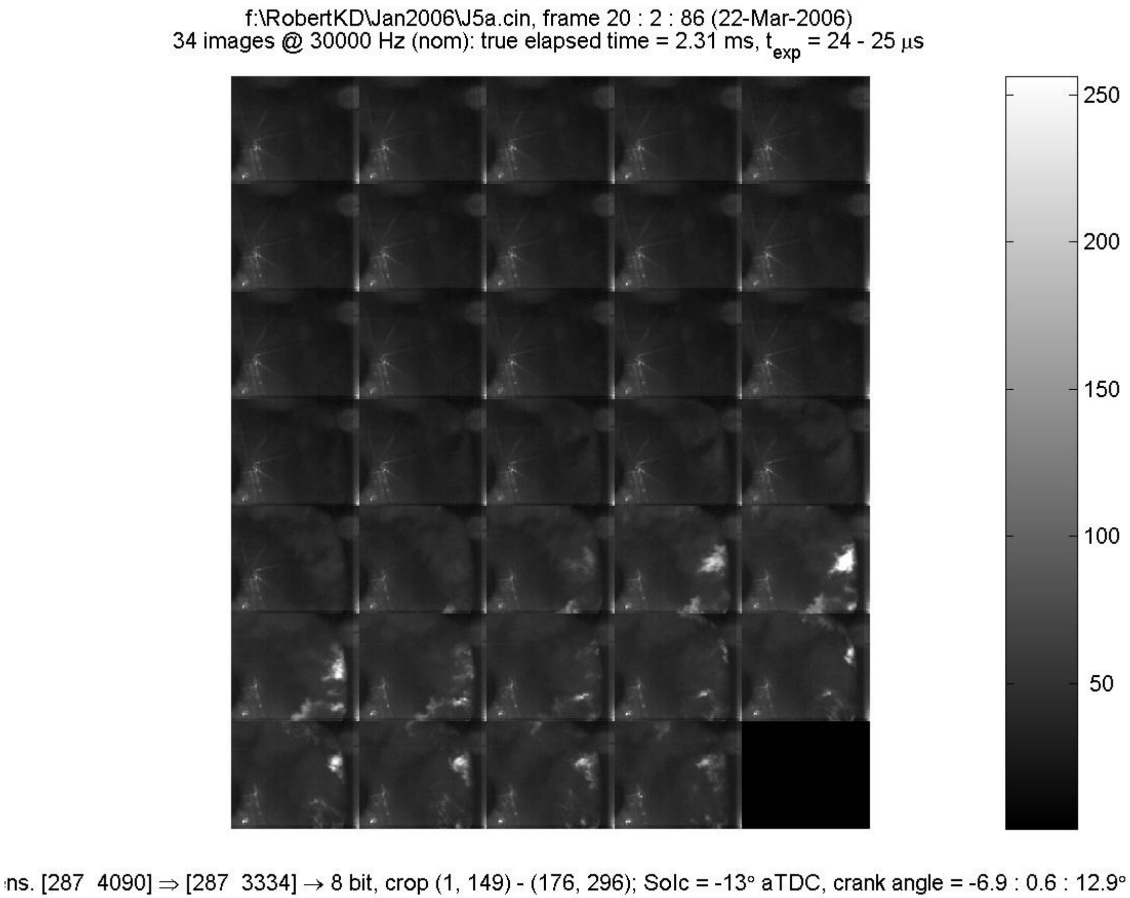
Test engine II: Soot luminosity for TPGME @ 9 *wt-%* fuel O_2



Speed	1400 *RPM*
Fuel injection pressure	1200 *bar (common rail)*
Start of fuel injection (actuation)	-13 *dCA aTDC (skip-fired @ 1:30)*
Intake pressure	1.4 *bar*
Load (IMEP)	~ 5 *bar*

VIII: Results & Discussion

Test engine II: Soot luminosity for CHO @ 9 *wt-%* fuel O_2



Speed	1400 *RPM*
Fuel injection pressure	1200 *bar (common rail)*
Start of fuel injection (actuation)	-13 *dCA aTDC (skip-fired @ 1:30)*
Intake pressure	1.4 *bar*
Load (IMEP)	~ 5 *bar*

VIII: Results & Discussion

Main conclusions test engine I

- At equal fuel oxygen content there is a clear distinction in oxygenate performance, especially at low NO_x values
- With cyclohexanone the "Diesel Dilemma" (i.e. PM/NO_x trade-off), typically encountered when applying EGR, appears to vanish

Main conclusion test engine II

- The absence of radiation suggests that the strength of cyclohexanone is not enhanced particle oxidation but rather improved particle suppression

VIII: Results & Discussion

5-5

Future work

TU/e has recently applied for a patent describing the use of cyclic oxygenates like cyclohexanone in automotive fuels

Further testing of cyclic oxygenates in research Diesel engine (emissions & performance) and Eindhoven High Pressure Cell (spray & flame behavior)

Presentation + paper of work has been submitted and will be presented at the JSAE conference in Kyoto (July 2007)

IX: Final thought

It may prove more (cost) efficient to sabotage the particle formation process, rather than to reduce its feedstock by improving the fuel/air mixing process