Future sustainable fuels: Exploiting waste streams and reducing toxicity of combustion emissions

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Researcher Links UK-Russia Workshop:

Scientific and technical grounds of future low-carbon propulsion

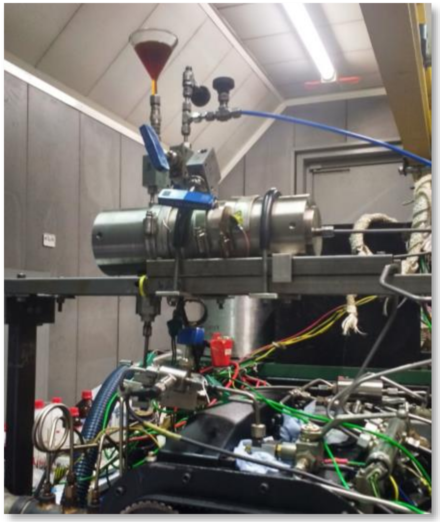
19th November 2018

EPSRC

UCL

Outline

1. Emissions requirements of future fuels
2. Methodology:
   i. Fuel molecular structure
   ii. Low volume fuel systems
3. Structure effects on ignition and NOx:
   i. Waste biomass conversion
   ii. Genetically engineered microalgae
4. Particulate matter formation and toxicity:
   i. Substructure ^{13}C labelling
   ii. Polycyclic aromatic hydrocarbons
5. Conclusions



Testing of waste coffee ground derived biodiesel

How do emissions impact on fuels?

GHG

10% of all road transport fuels from **renewable** sources by **2020**[1]

3% must be from **non-food crop** sources[2]

Air quality

Euro 6 (2014 – **2021**)
PN limit introduced
Further **NOx** and **PM reductions**

Euro 7 (**2022** –) Likely further **significant reductions** in **PN, PM** and **NOx**

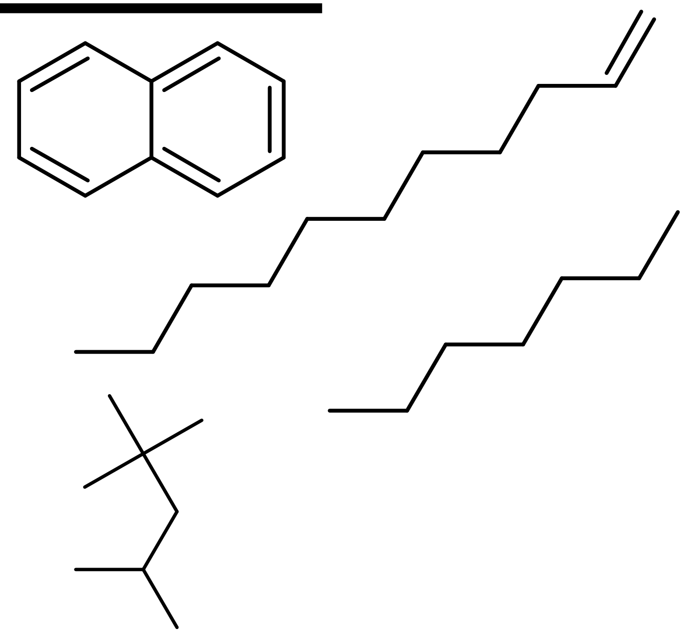
[1]Directive 2009/28/EC of the European Parliament and of the Council of 23 April 2009 on the promotion of the use of energy from renewable sources
[2]DIRECTIVE (EU) 2015/1513 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL.

Fuel molecular structure

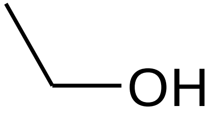
Diesel

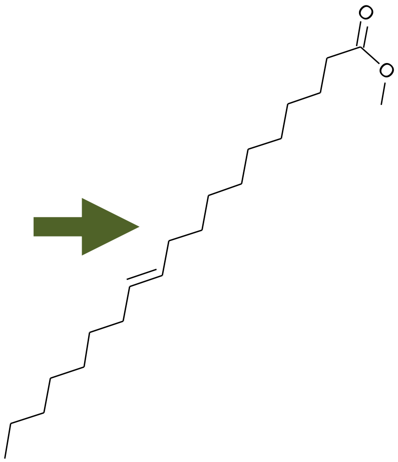
> 130 individual species

Gasoline

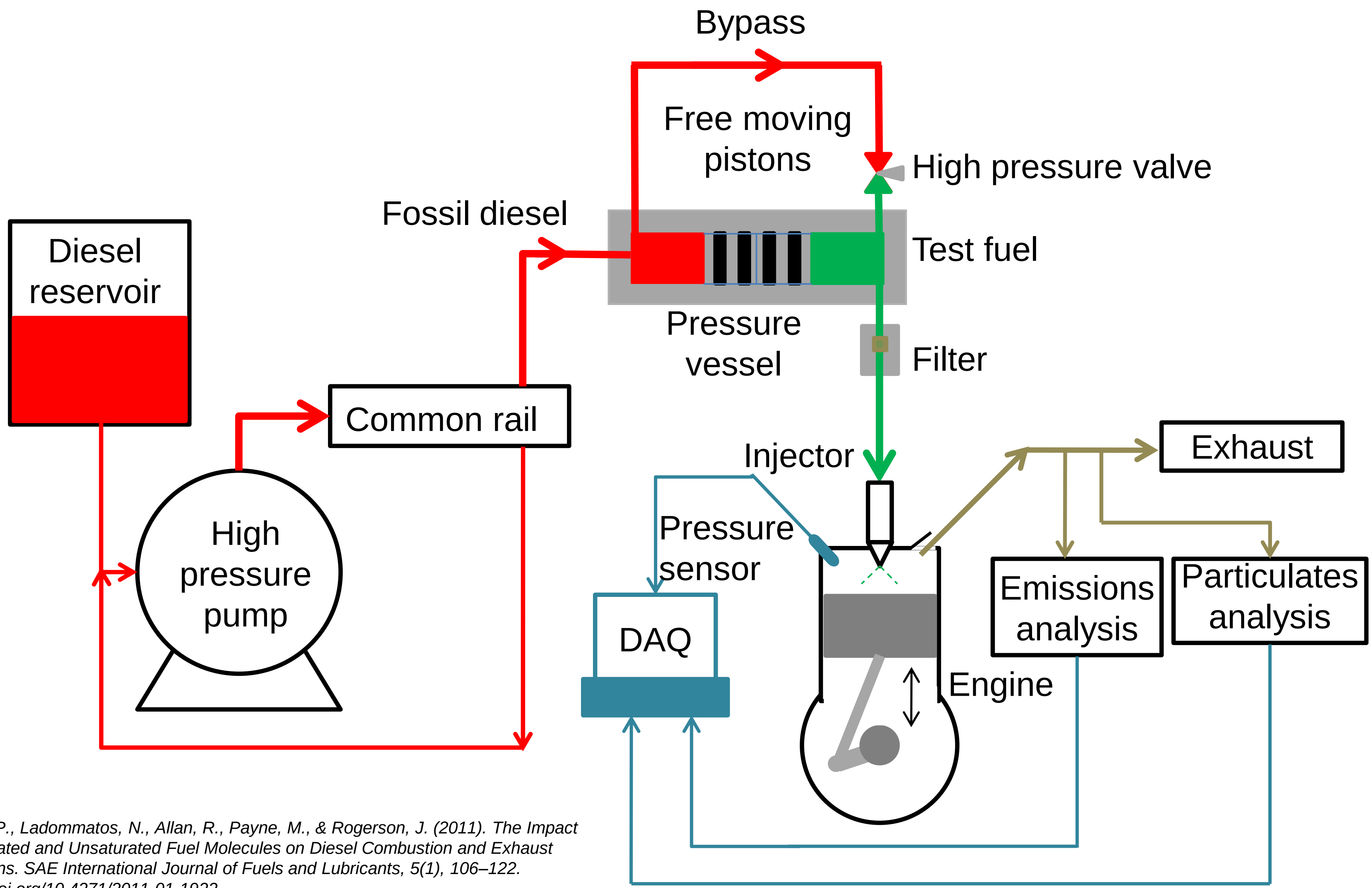


Biofuels

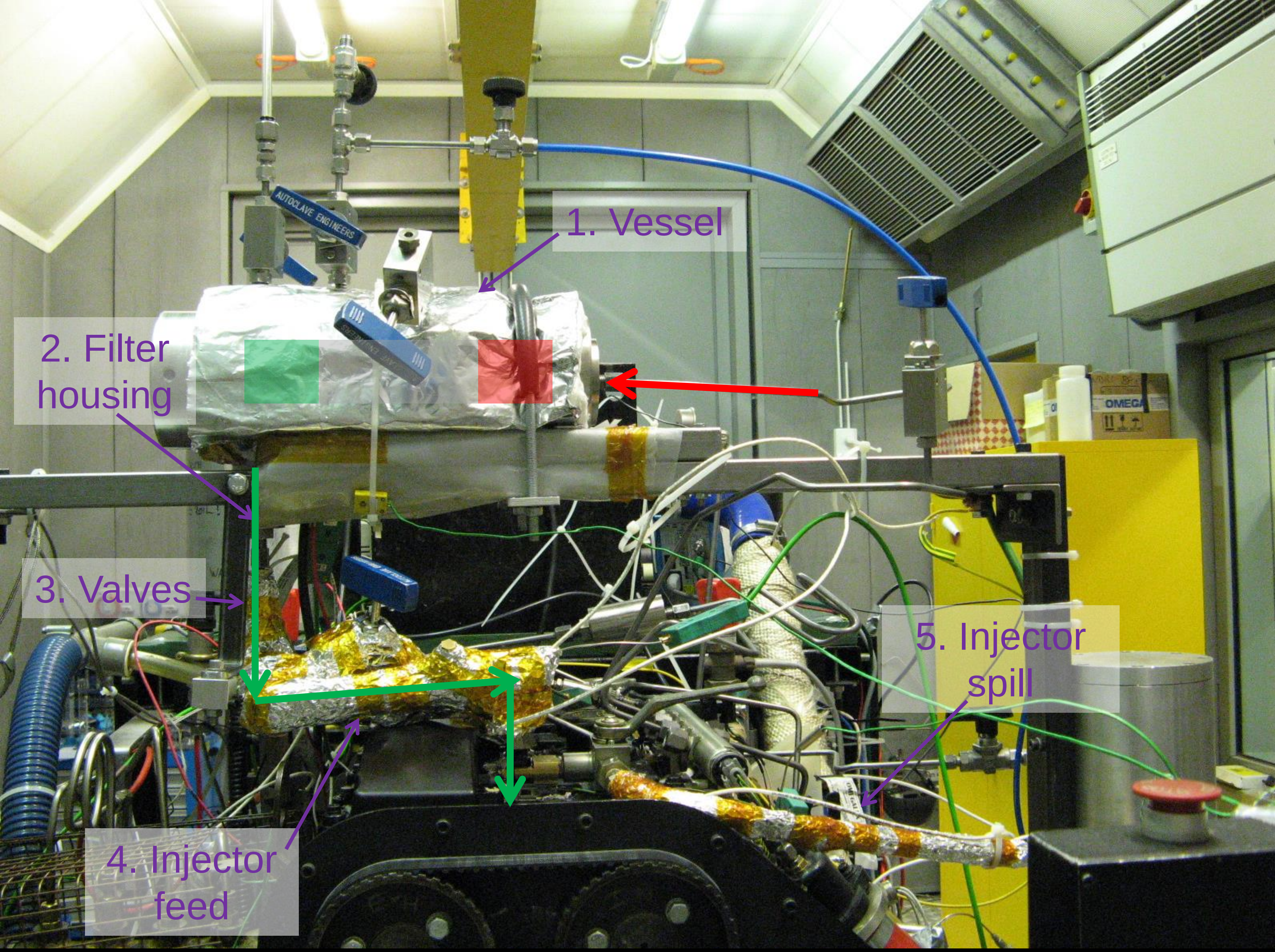




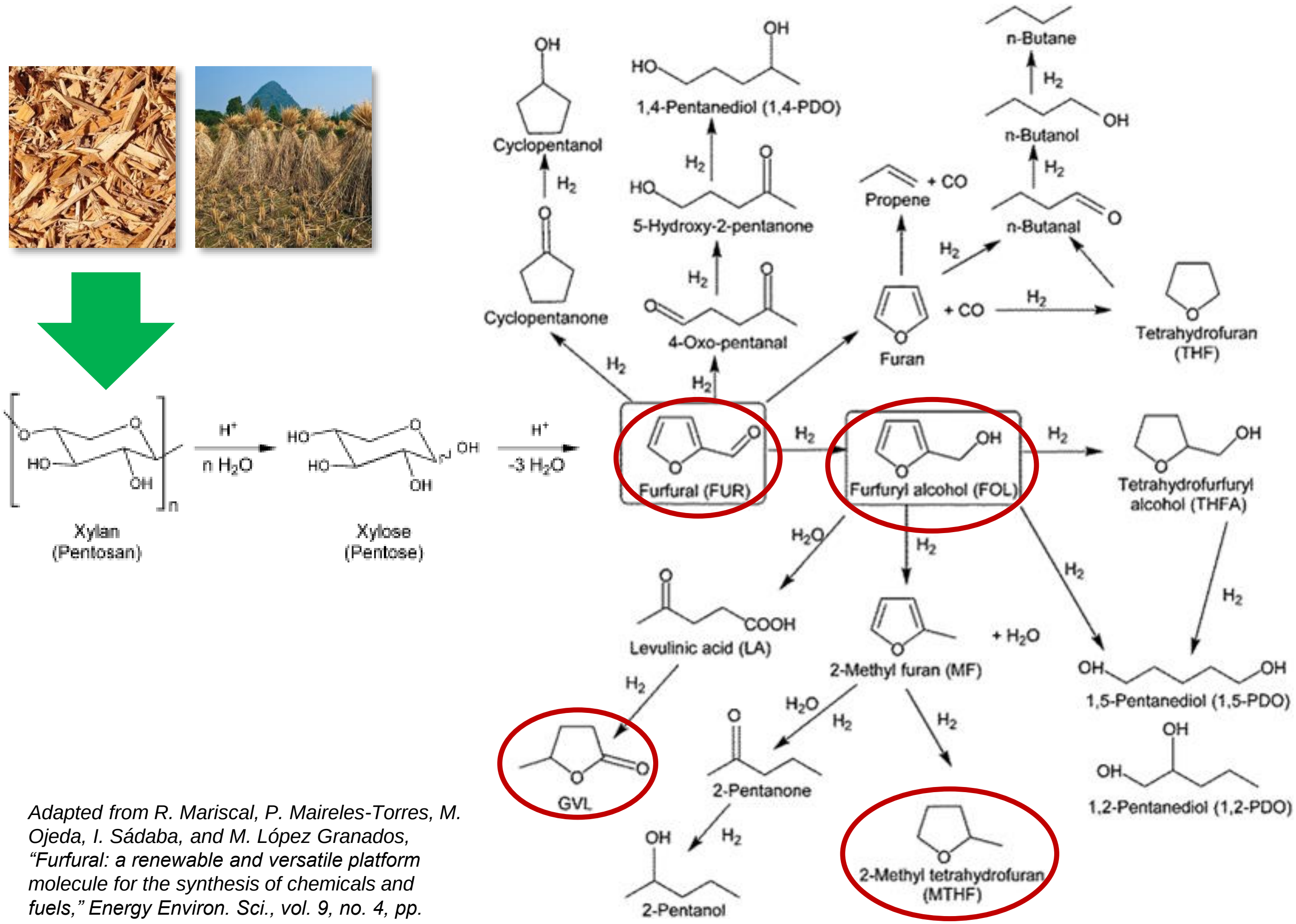
Low volume fuel system



Hellier, P., Ladommatos, N., Allan, R., Payne, M., & Rogerson, J. (2011). The Impact of Saturated and Unsaturated Fuel Molecules on Diesel Combustion and Exhaust Emissions. SAE International Journal of Fuels and Lubricants, 5(1), 106–122. https://doi.org/10.4271/2011-01-1922


1. Vessel
2. Filter housing
3. Valves
4. Injector feed
5. Injector spill

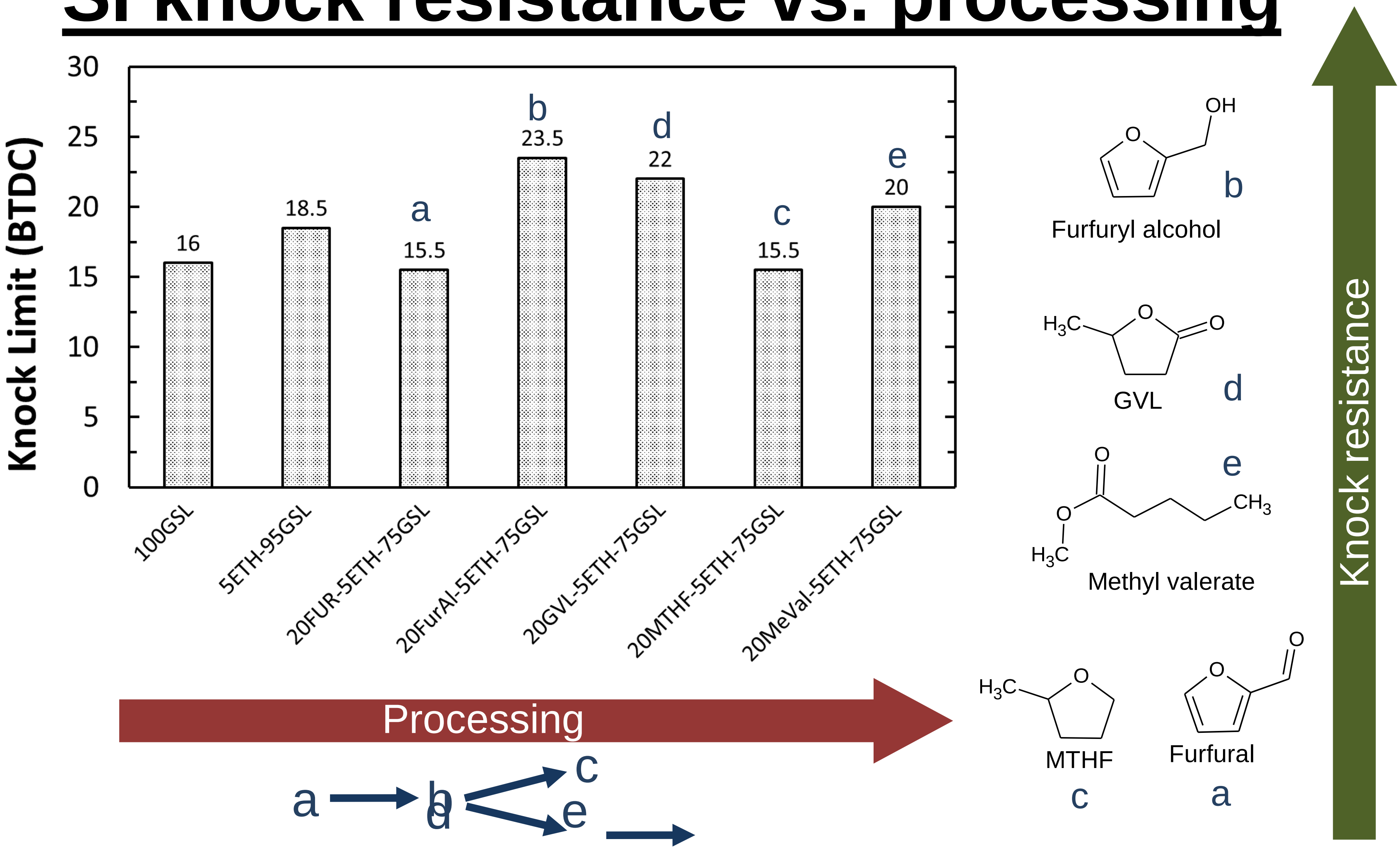
How much to process biomass?



Adapted from R. Mariscal, P. Maireles-Torres, M. Ojeda, I. Sádaba, and M. López Granados, "Furfural: a renewable and versatile platform molecule for the synthesis of chemicals and fuels," Energy Environ. Sci., vol. 9, no. 4, pp. 1144–1189, 2016. doi:10.1039/C5EE02666K.

- Additional processing:
  - Reactants (**H_2**)
  - **Energy**
- **Incremental** changes to molecular structure.
- Improvements in combustion and emissions **justified**?

SI knock resistance vs. processing



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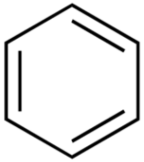
Pyrolysis products temperature effects

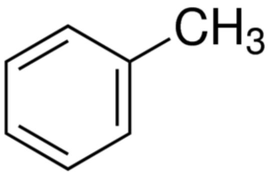
Lignocellulosic biomass

Catalytic pyrolysis

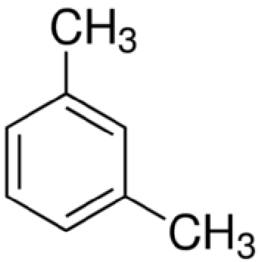
450 ºC to **600** ºC



Benzene



Toluene



M-xylene

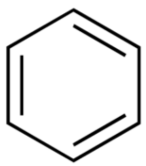
Decreasing temperature

- Aromatics comprise 80 % of liquid fraction.
- Reduced temperatures increases proportion of methyl-benzenes.

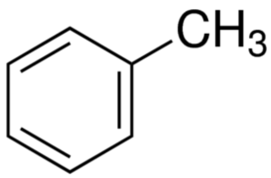
Thring RW, Katikaneni SPR, Bakhshi NN. The production of gasoline range hydrocarbons from Alcell lignin using HZSM-5 catalyst. Fuel Process Technol 2000;62:17–30.

Zhang Y, Bi P, Wang J, Jiang P, Wu X, Xue H, et al. Production of jet and diesel biofuels from renewable lignocellulosic biomass. Appl Energy 2015;150:128–37. doi:10.1016/j.apenergy.2015.04.023.

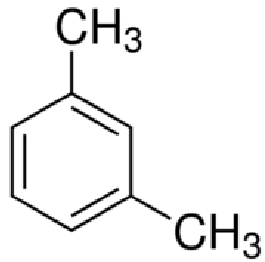
Minor changes in fuel structure



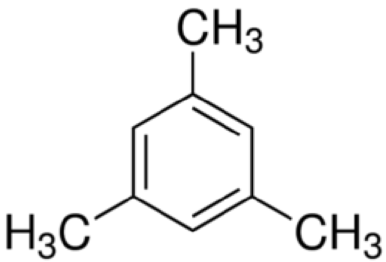
Benzene



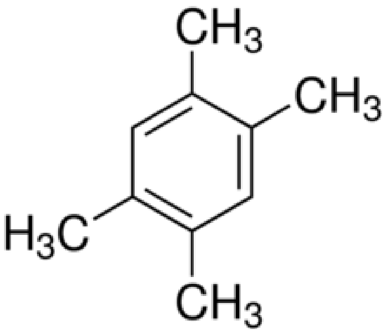
Toluene



M-xylene



1-3-5 trimethylbenzene



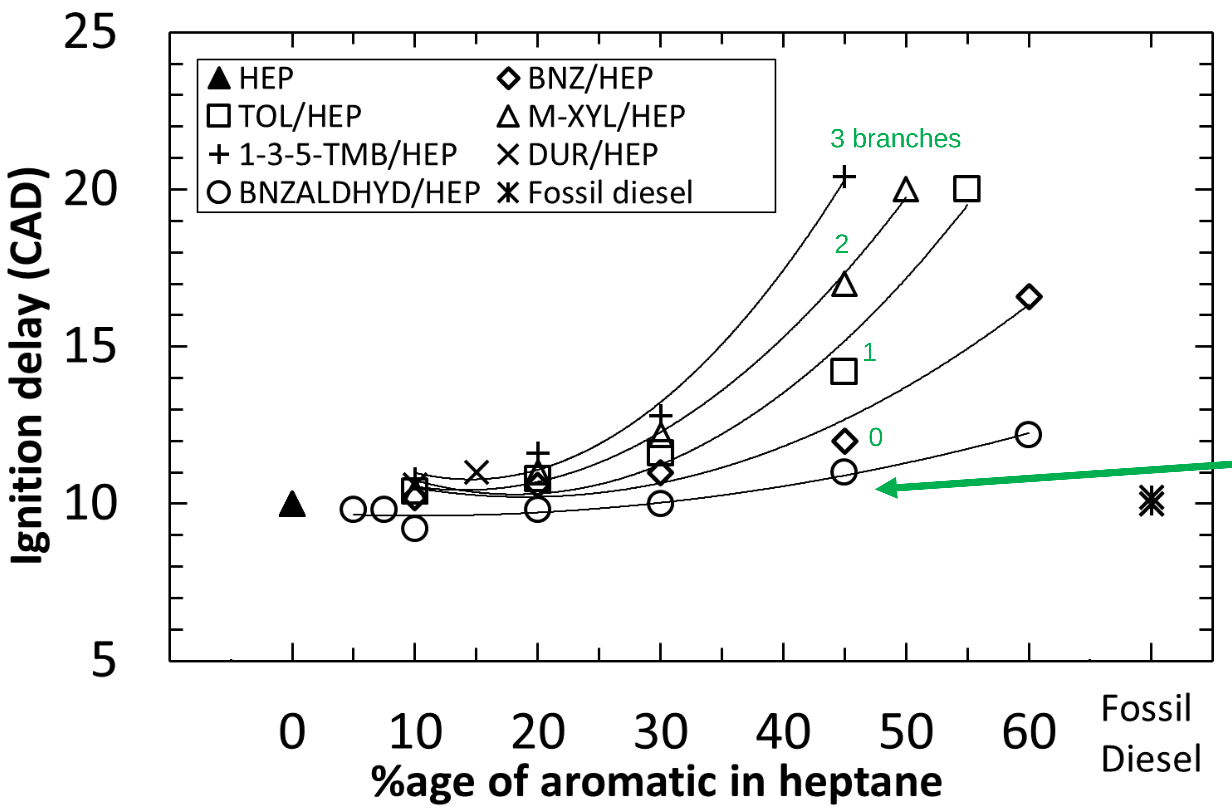
Durene

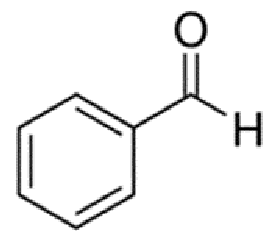
Increasing number of methyl branches on aromatic ring

Experimental conditions

- 1200 rpm
- 450 bar fuel injection pressure
- 4 bar IMEP (injection timing ~700 – 900 *μs*)
- Constant start of injection SOI = 10.0 CAD BTDC
- Constant start of combustion SOI varied for SOC at TDC

Significant effects on ignition





Benzaldehyde

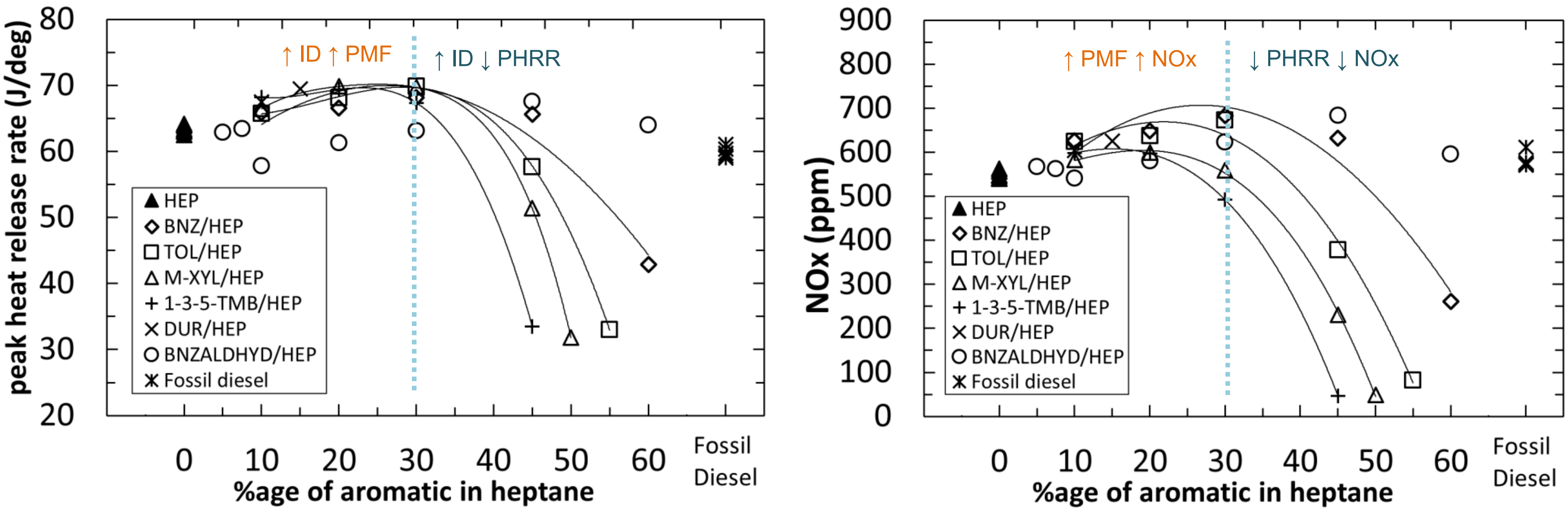
Increasing number of methyl branches

$C_6H_5CH_3 + OH^* \rightarrow C_6H_5CH_2^* + H_2O$

Talibi, M., Hellier, P., & Ladommatos, N. (2018). Impact of increasing methyl branches in aromatic hydrocarbons on diesel engine combustion and emissions. Fuel, 216. https://doi.org/10.1016/j.fuel.2017.12.045

Fuel effects on NOx emissions

- Constant injection timing



Changes to fuel structure (e.g. addition of methyl branches) → Ignition delay → Max. T / Time at T → NOx

Talibi, M., Hellier, P., & Ladommatos, N. (2018). Impact of increasing methyl branches in aromatic hydrocarbons on diesel engine combustion and emissions. Fuel, 216. https://doi.org/10.1016/j.fuel.2017.12.045

Micro-algae GM for fuel design

Light

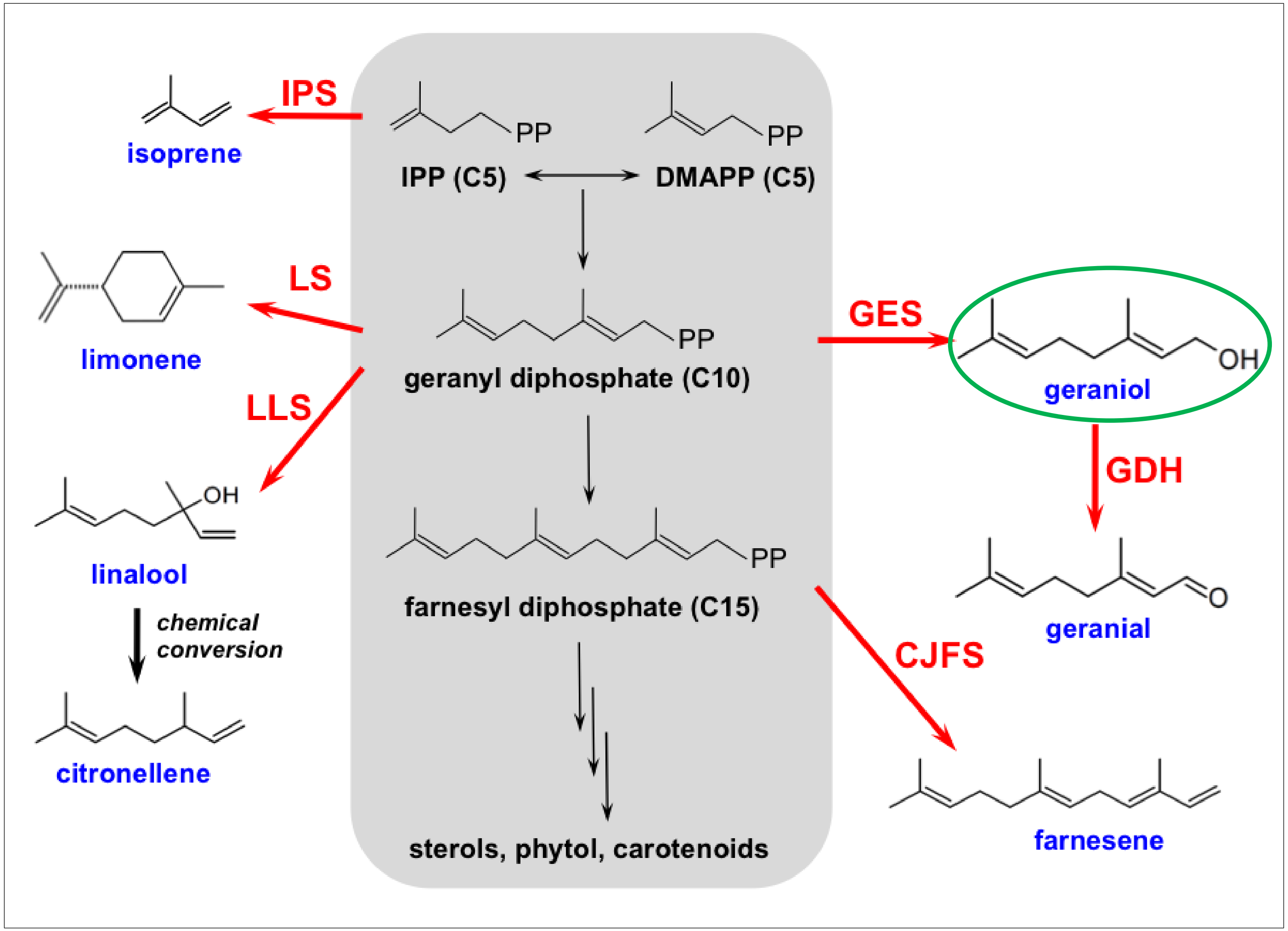
CO_2 (flue gas)

Nutrients (waste water)

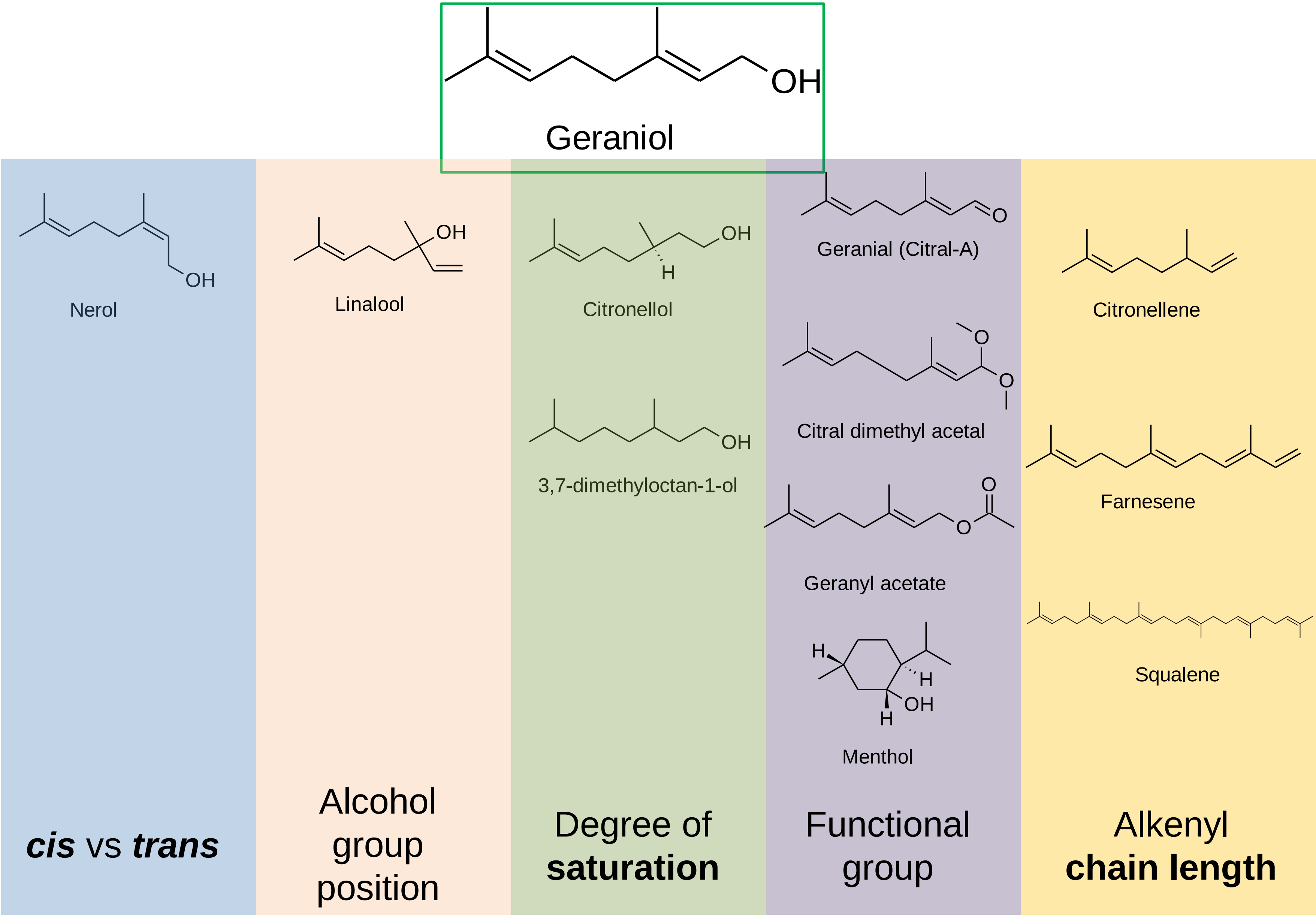
2 – 3 µm

Triglycerides

Designer hydrocarbons / oxygenates



P. Hellier, L. Al-Haj, M. Talib, S. Purton and N. Ladommatos, "Combustion and emissions characterisation of terpenes as biofuels produced by the micro-algae Synechocystis", Fuel, Volume 111, September 2013, Pages 670-688



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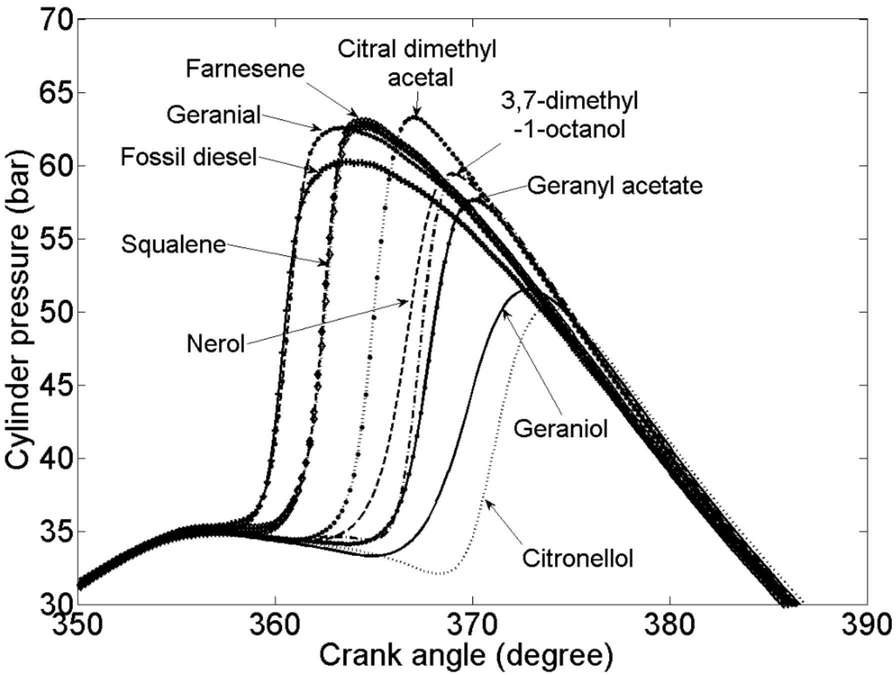
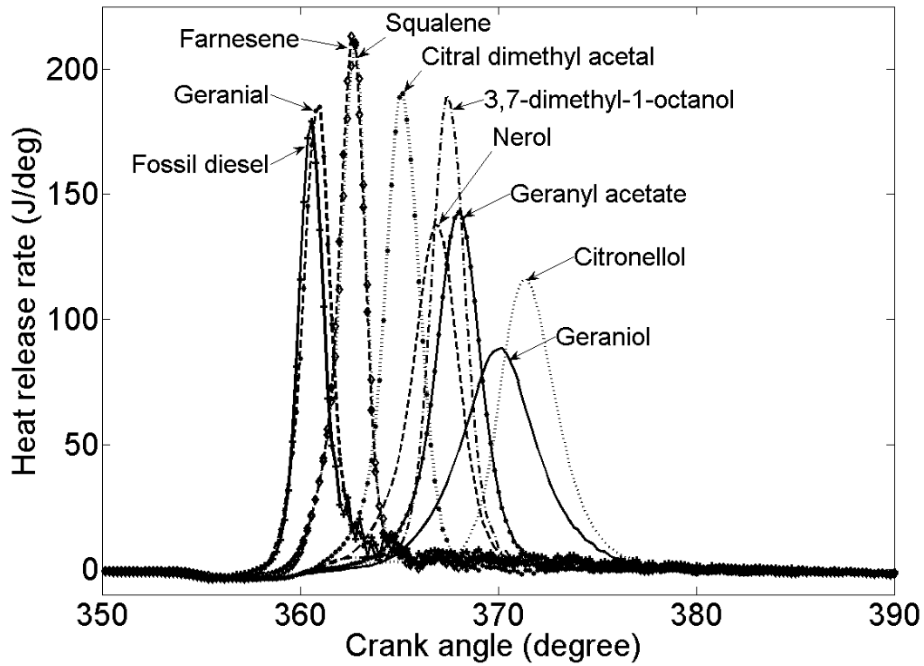
Combustion phasing





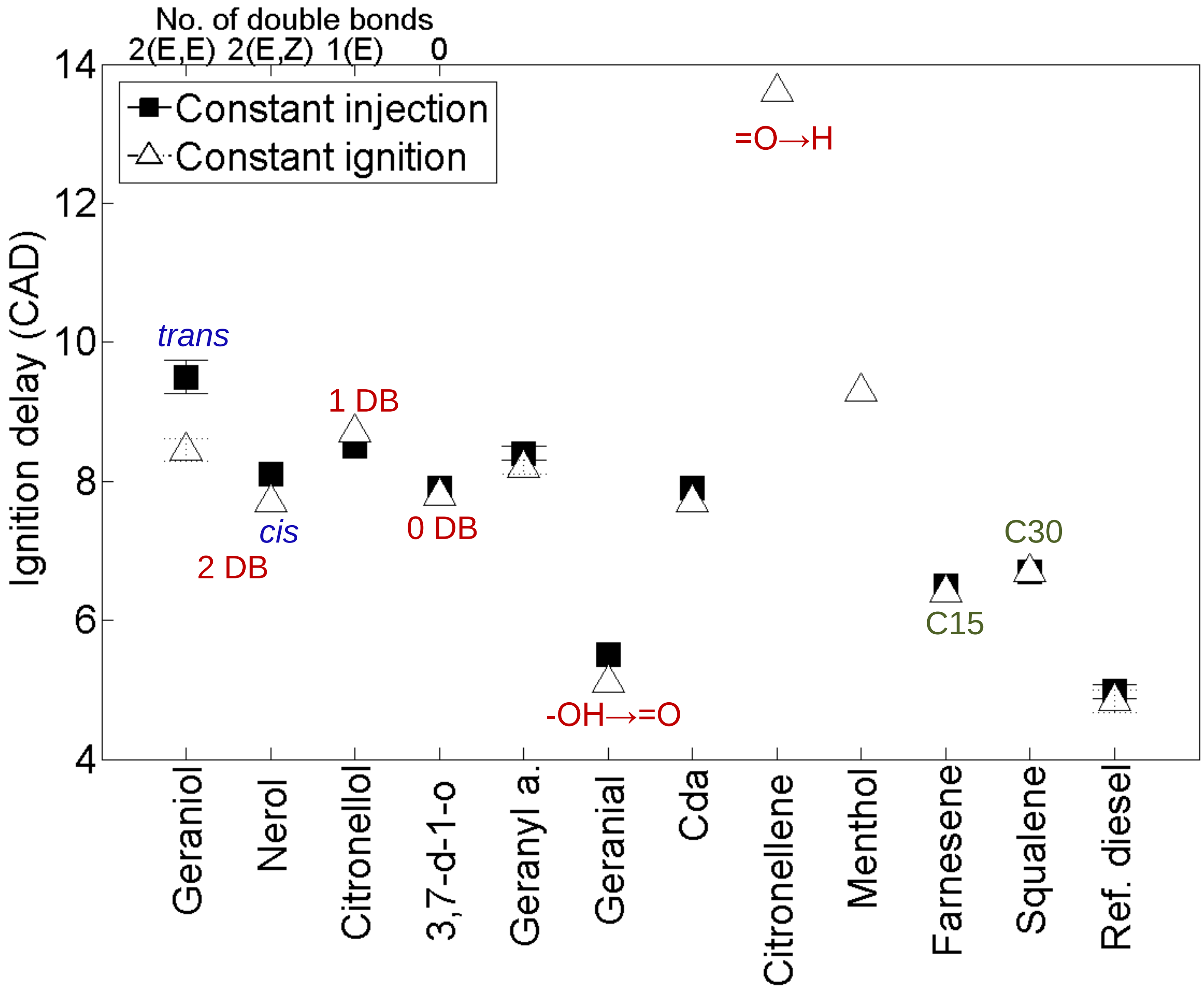
Experimental conditions

- 1200 rpm
- 450 bar fuel injection pressure
- 4 bar IMEP (injection timing ~700 – 900 *μs*)
- Constant start of injection SOI = 7.5.0 CAD BTDC

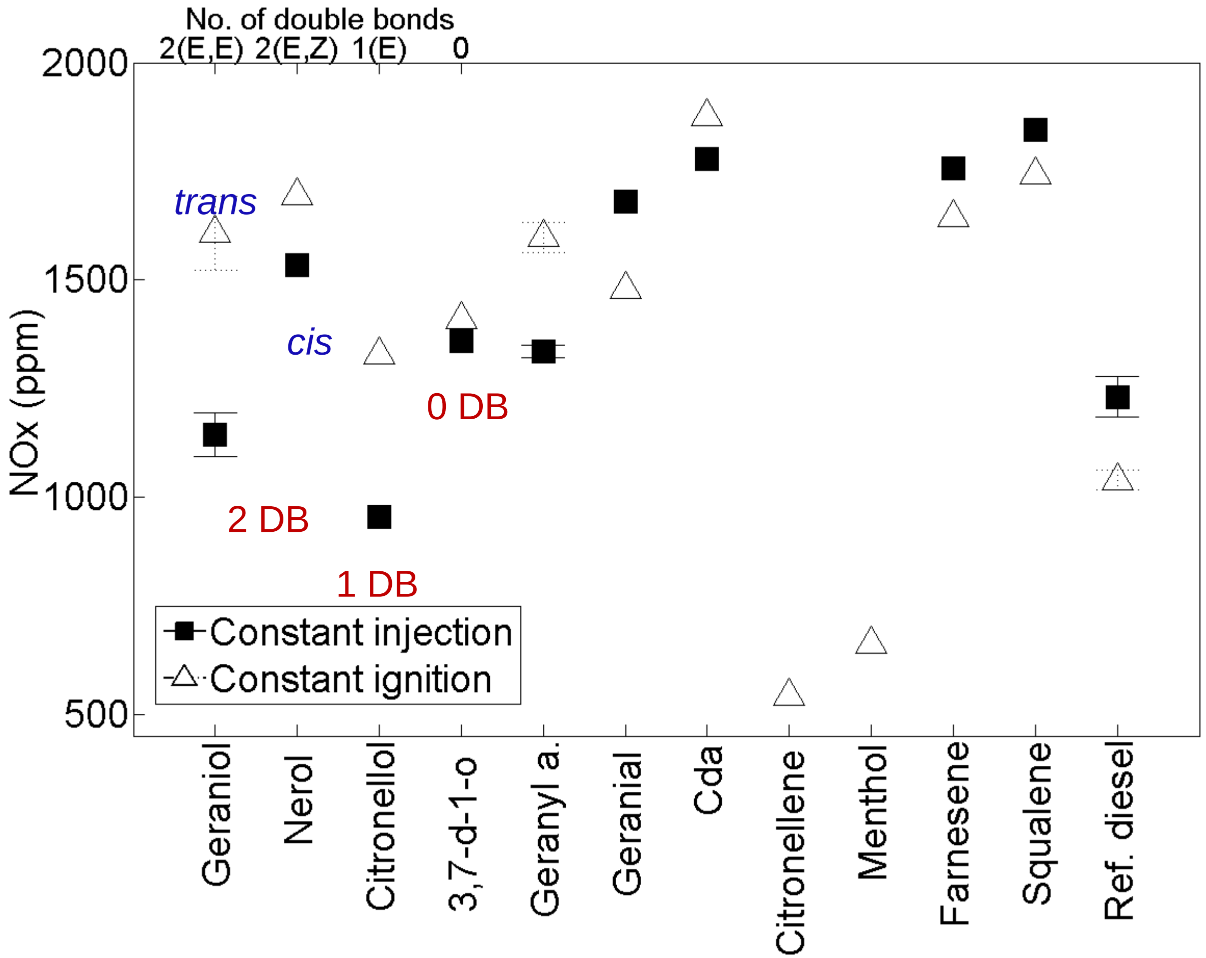
-OH→=O

P. Hellier, L. Al-Haj, M. Talib, S. Purton and N. Ladommatos, "Combustion and emissions characterisation of terpenes as biofuels produced by the micro-algae Synechocystis", Fuel, Volume 111, September 2013, Pages 670-688

Ignition delay

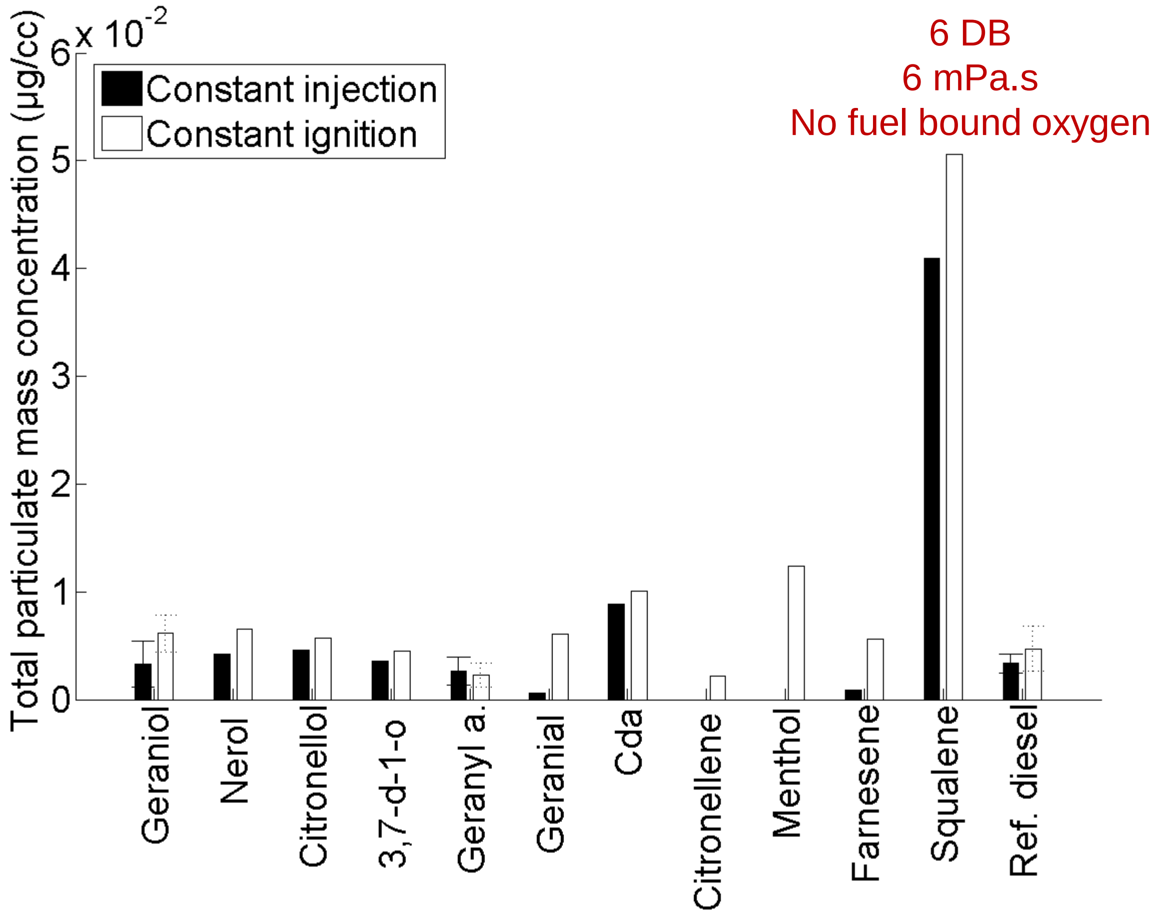


NOx emissions



Ignition delay → Max. T; Time at T → Long I.D. reduces both → NOx

Total particulate mass

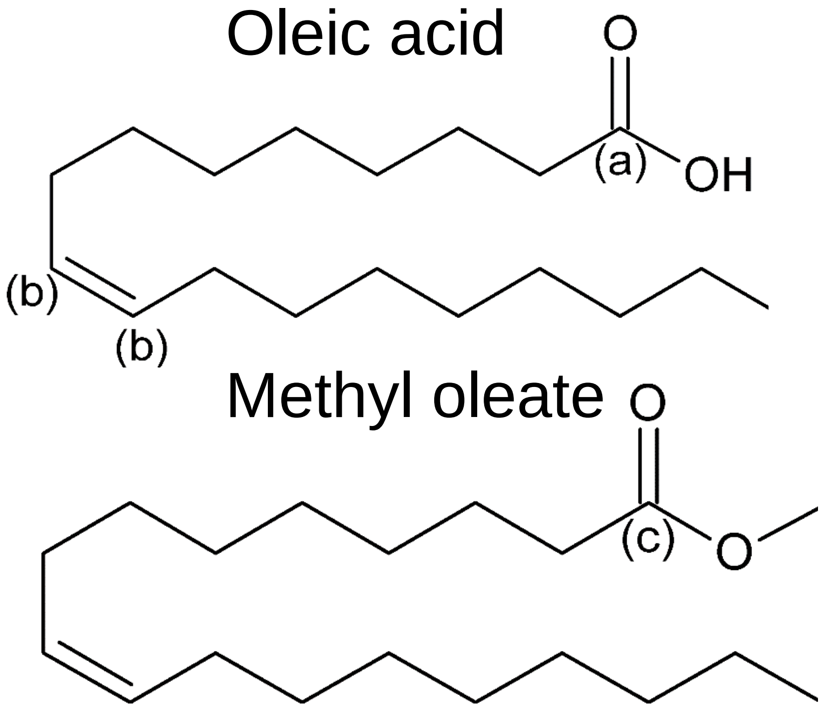


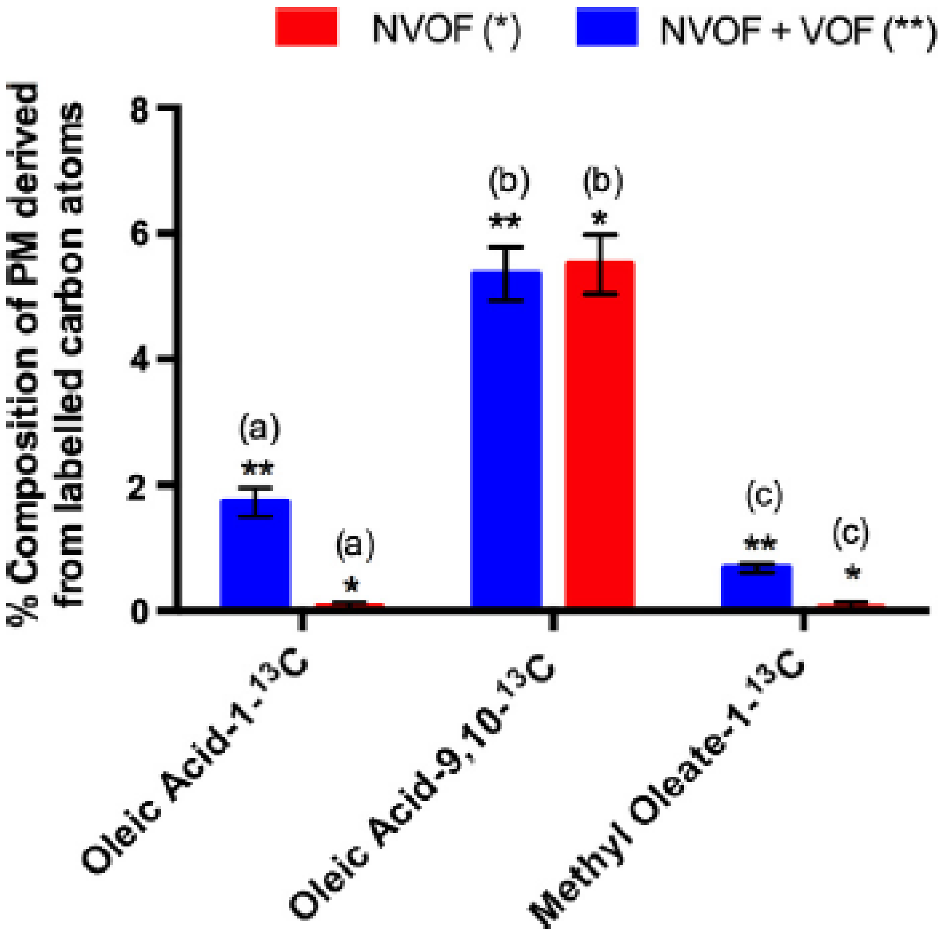
Alkyl chain length → viscosity → fuel air mixing → fuel pyrolysis

Alkyl chain saturation → soot precursors → soot formation

Individual carbon contribution to PM

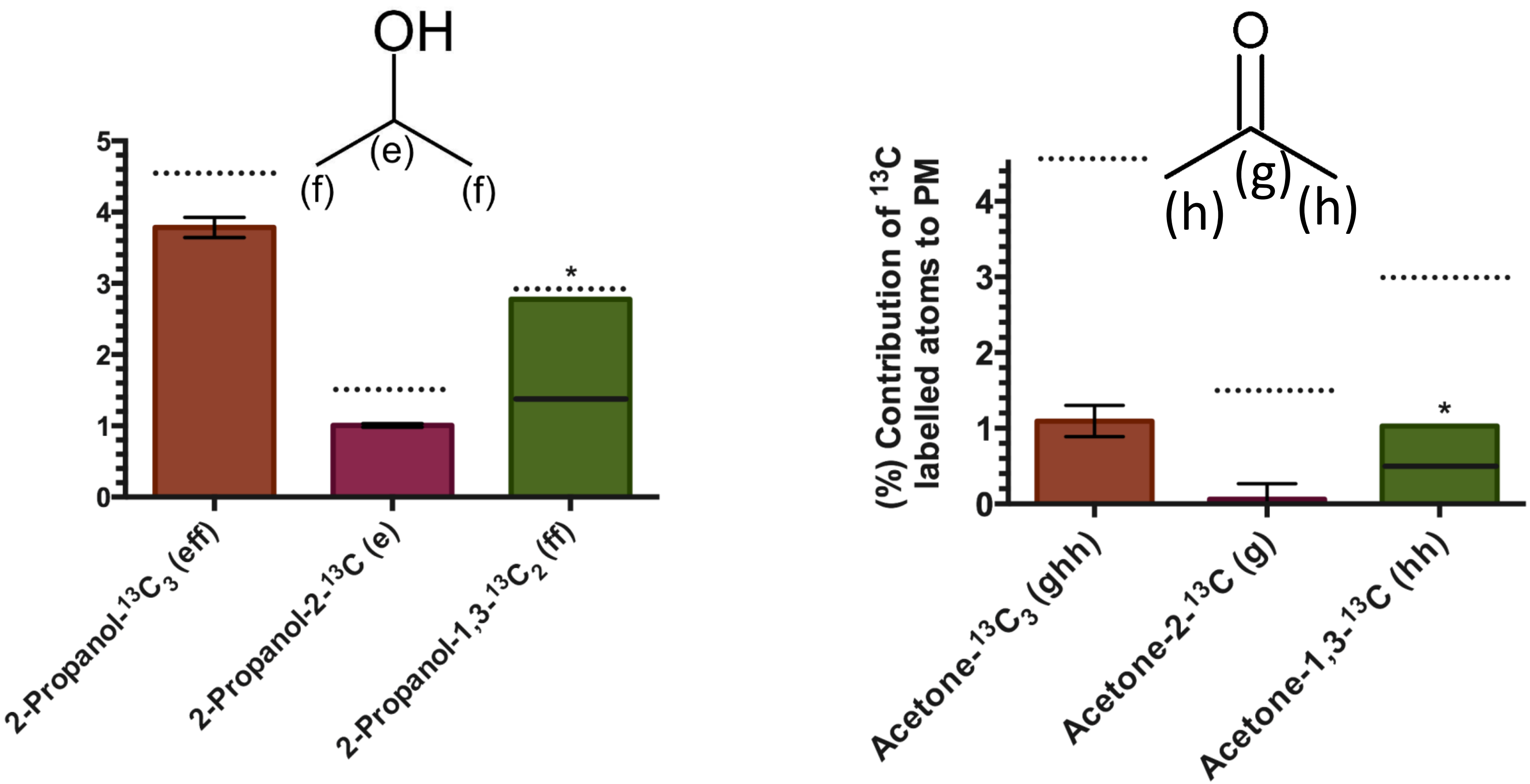
^{13}C labelled fuel carbon in measured engine exhaust PM.





Eveleigh A, Ladommatos N, Hellier P, Jourdan A-L. An investigation into the conversion of specific carbon atoms in oleic acid and methyl oleate to particulate matter in a diesel engine and tube reactor. Fuel. 2015 Aug;153:604–611.

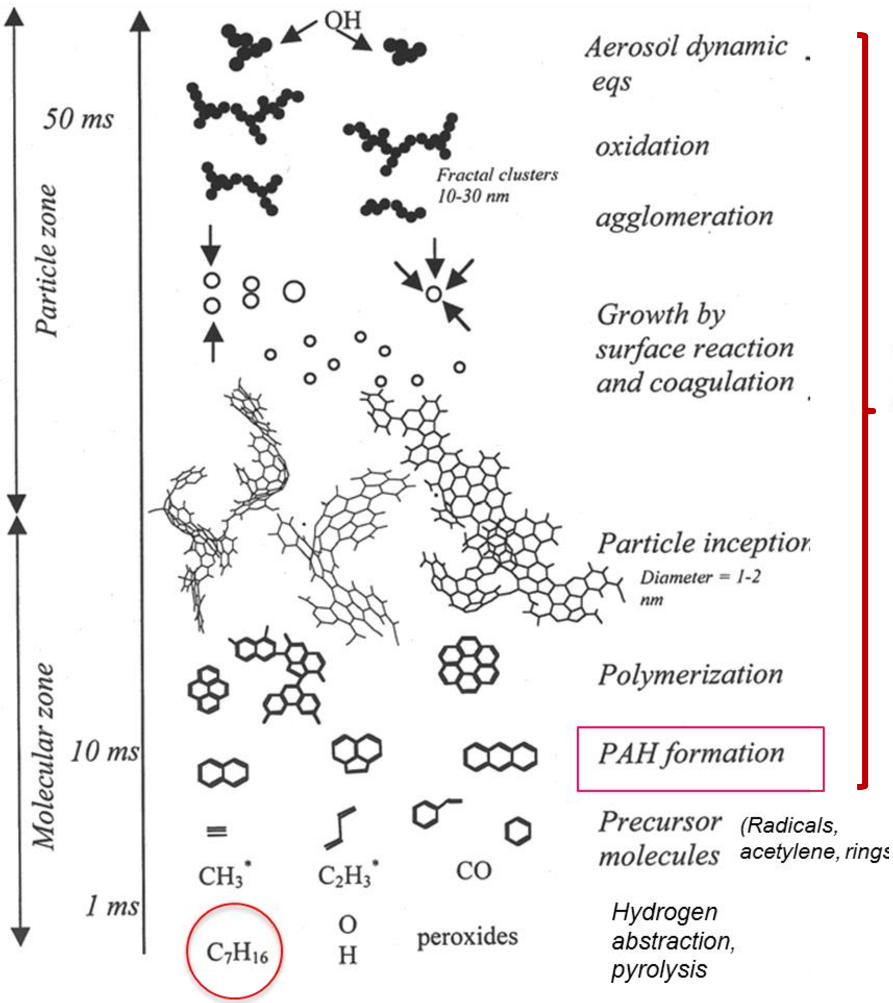
Oxygen bond type



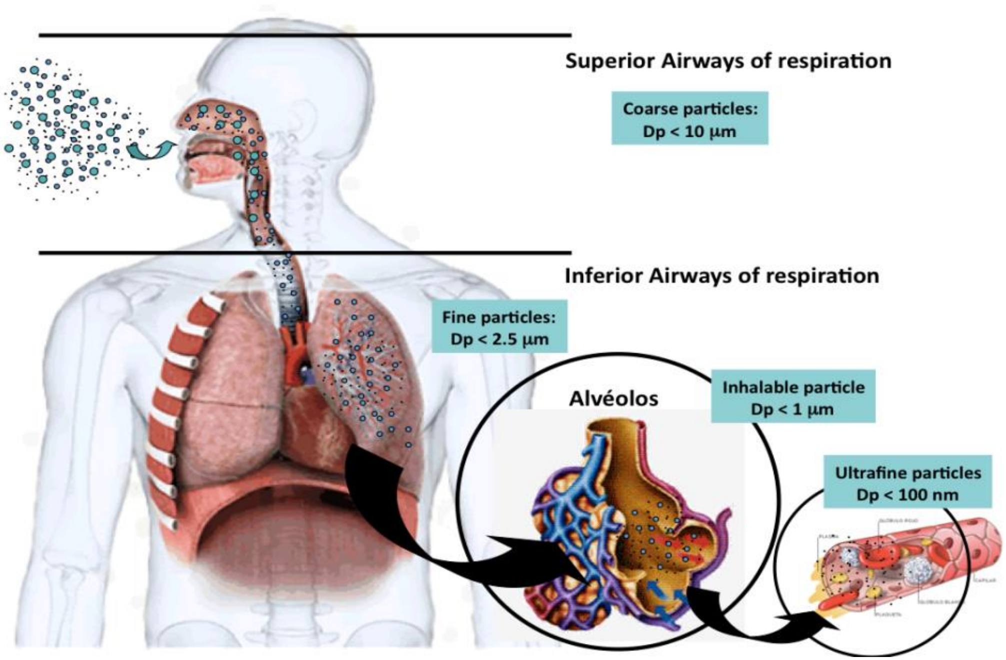
- Oxygenates blended at 10 % mol / mol in *n*-heptane.
- Oxygen double bond reduces C contribution to soot relative to oxygen single bond.

Eveleigh A, Ladommatos N, Hellier P, Jourdan A-L. Quantification of the Fraction of Particulate Matter Derived from a Range of 13 C-Labeled Fuels Blended into Heptane, Studied in a Diesel Engine and Tube Reactor. Energy & Fuels. 2016 Sep 15;30(9):7678–7690.

Polycyclic aromatic hydrocarbons

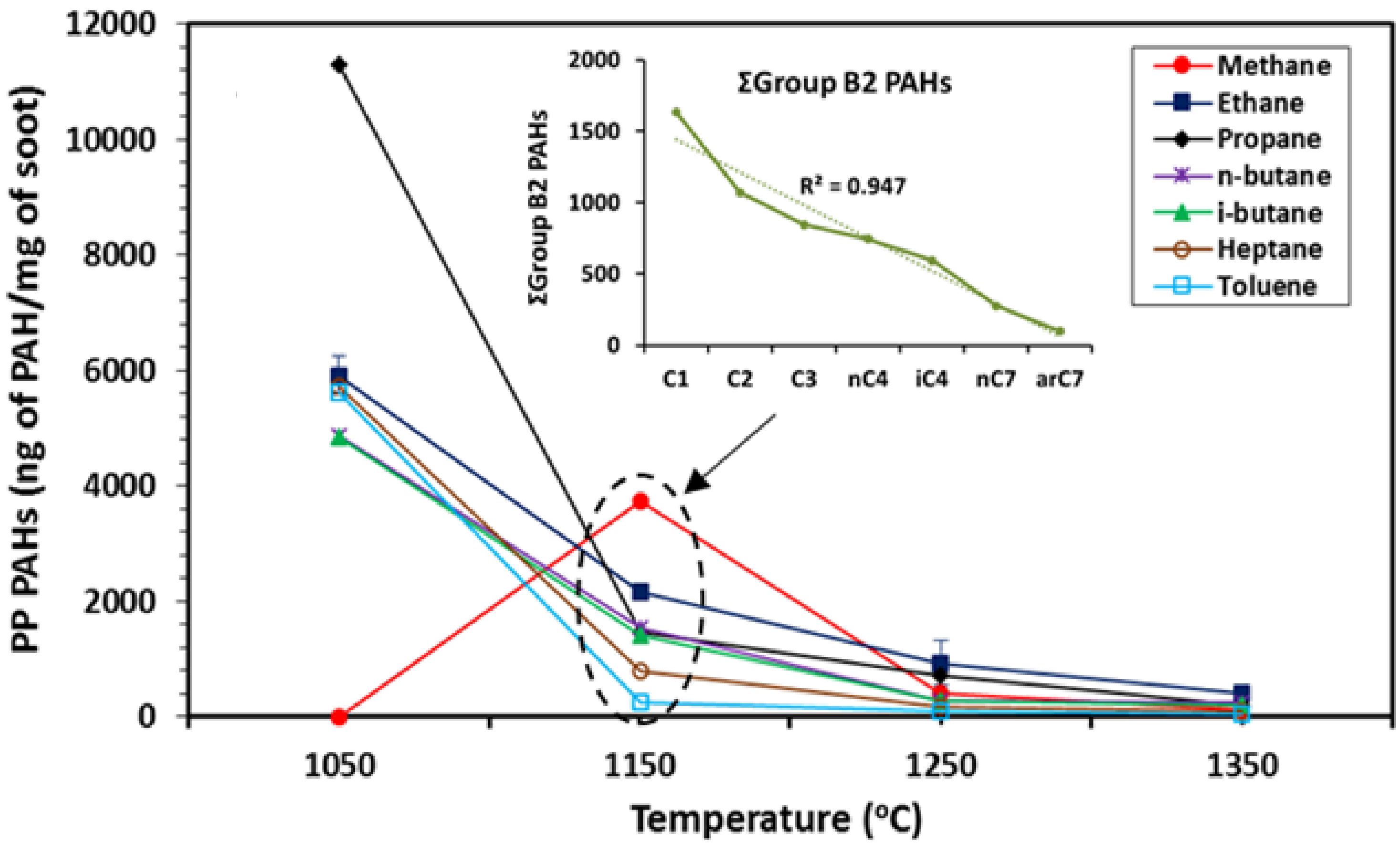


- PAHs adsorbed on particle surface.
- Ultrafine particles (<100 nm) penetrate lungs.



(a) Pugmire, R. J., Yan, S., Ma, Z., Solum, M. S., Jiang, Y. J., Eddings, E. G., et al. (n.d.). Soot Formation Process. Department of Chemical & Fuels Engineering, Department of Chemistry, University of Utah , http://acerc.byu.edu/News/Conference/2003/Presentations/Pugmire.pdf (retrieved 2-04-2015), (b) Health effect of PAHs (http://www.cleanairegypt.org/air-pollution-and-aerosols/: retrieved 20-11-2015)

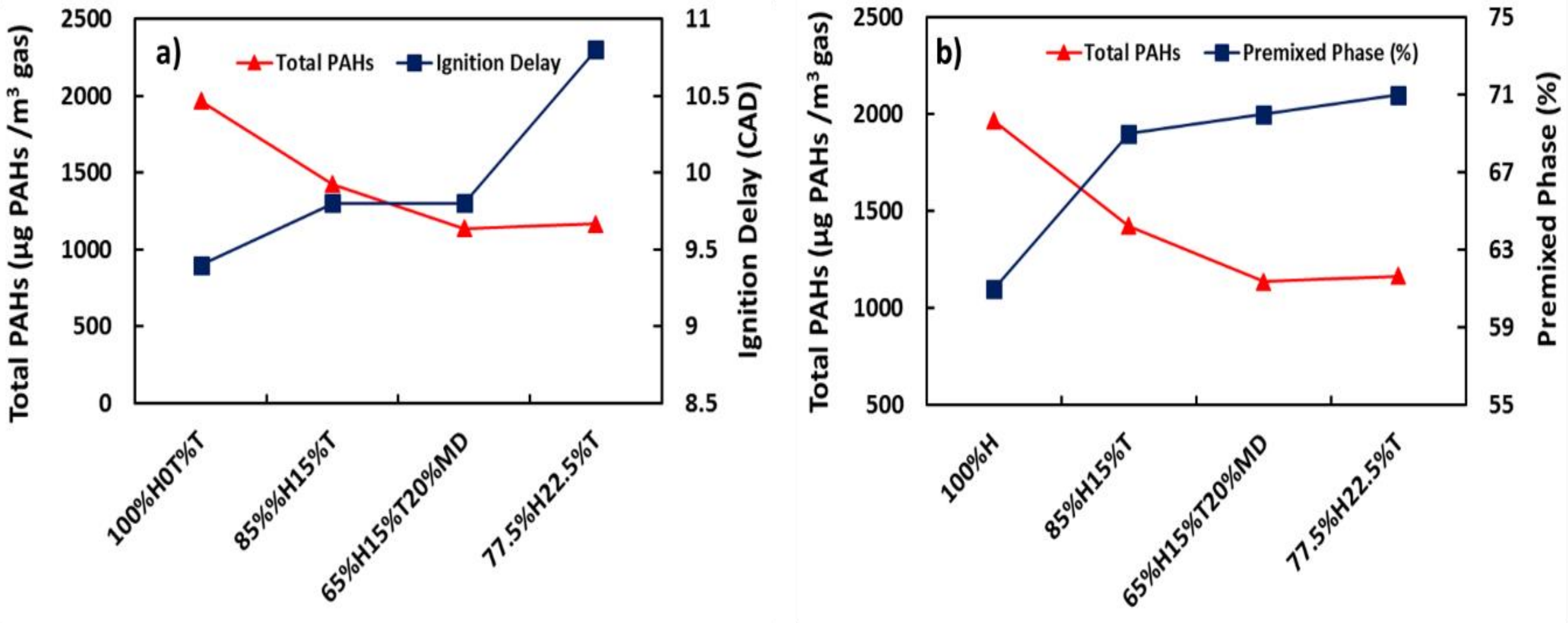
Fuel effects on PAH



- Increased temperature reduces PAH (pyrolysis furnace)
- Increasing carbon chain length decreases carcinogenicity

Dandajeh, H. A., Ladommatos, N., Hellier, P., & Eveleigh, A. (2018). Influence of carbon number of C 1 –C 7 hydrocarbons on PAH formation. Fuel, 228, 140–151. https://doi.org/10.1016/j.fuel.2018.04.133

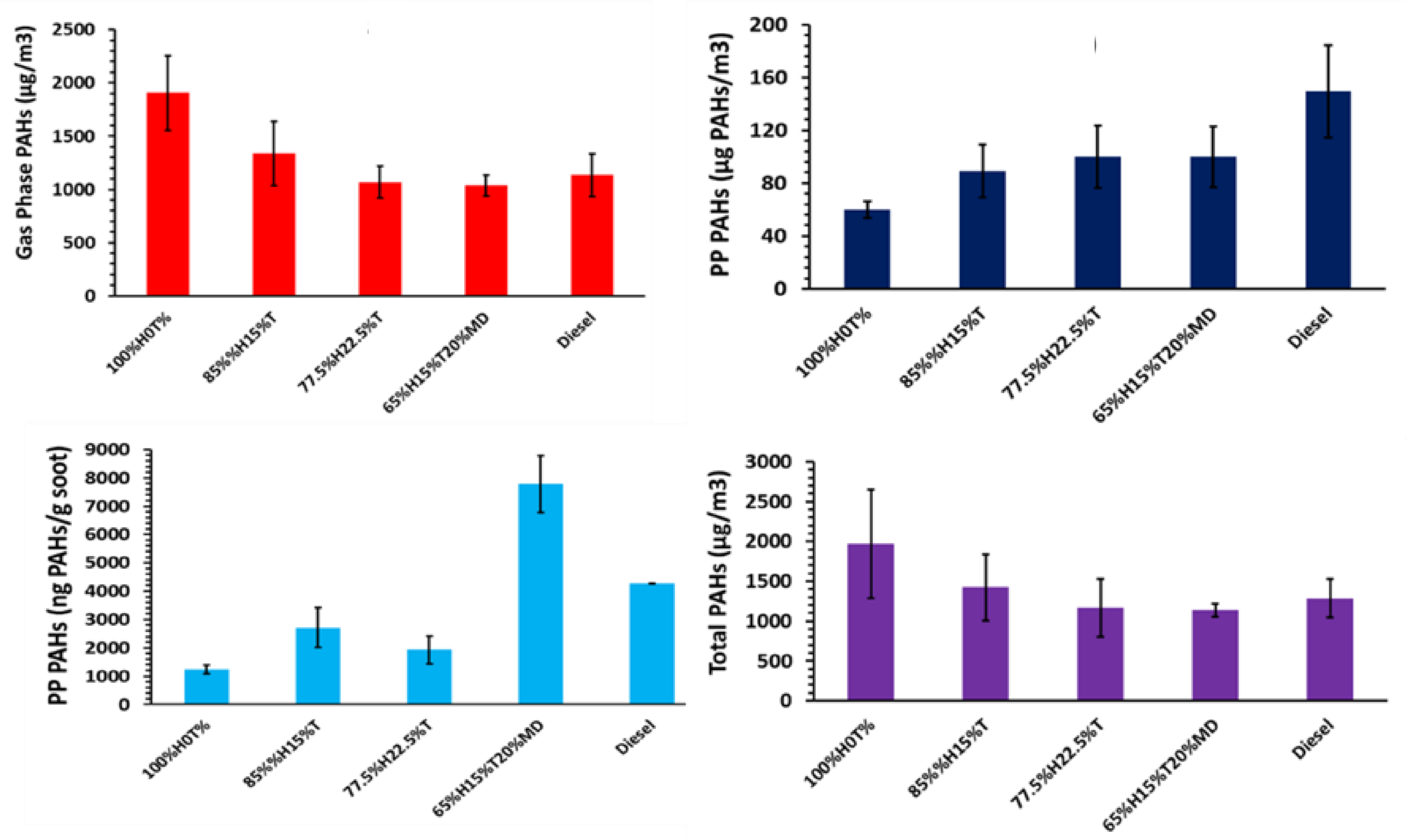
Engine exhaust PAH



- *n*-heptane (H), toluene (T) and methyl decanoate (MD) blends
- Total PAH decreases with increasing toluene

Increasing toluene → Increasing ignition delay, premixed and temperatures

Total PM or PM toxicity?



Conclusions

- Renewable fuels provide opportunity for molecular design.
- Degree of biomass processing and resultant molecular structure corresponds to SI and CI ignition quality.
- NOx is primarily influenced by molecular structure via ignition delay and combustion phasing.
- Oxygen bond type impacts significantly on:
  - Ignition delay (e.g. GM algae fuels)
  - Individual carbon atom PM (^{13}C labelling)
- Total exhaust PAH shows strong temperature dependence.
- PAH per mass of PM shows fuel structure influence.

Thank you

Questions?

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EP/M009424/1 and EP/M007960/1
BP Global Fuels

Contact:- **Dr Paul Hellier,** Lecturer in Engines and Fuels

Department of Mechanical Engineering, University College London

p.hellier@ucl.ac.uk

References

Hellier, P., Ladommatos, N., Allan, R., Payne, M., & Rogerson, J. (2011). The Impact of Saturated and Unsaturated Fuel Molecules on Diesel Combustion and Exhaust Emissions. SAE International Journal of Fuels and Lubricants, 5(1), 106–122. https://doi.org/10.4271/2011-01-1922

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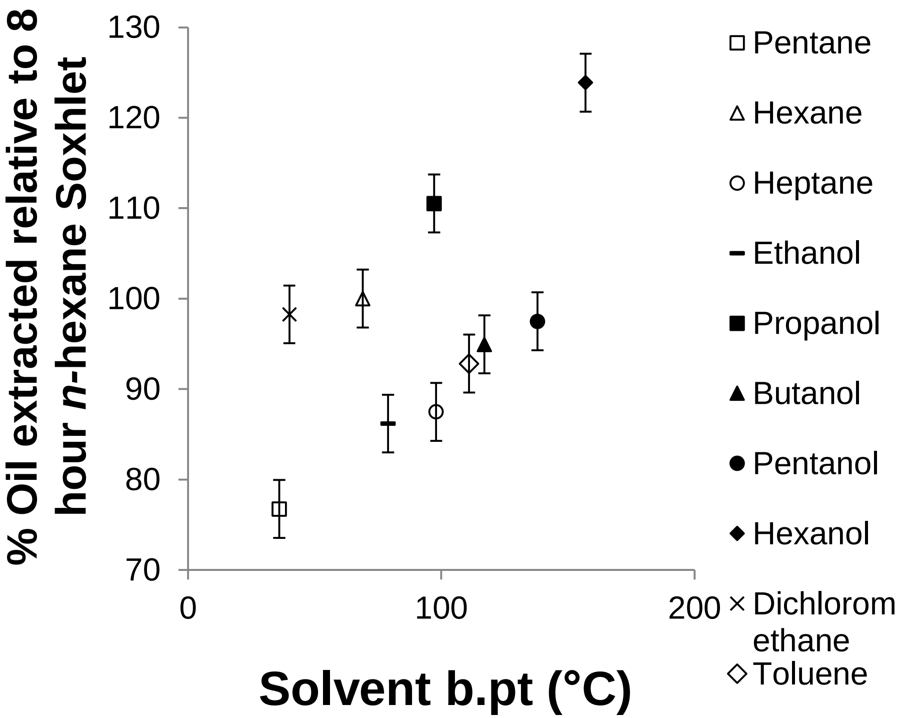
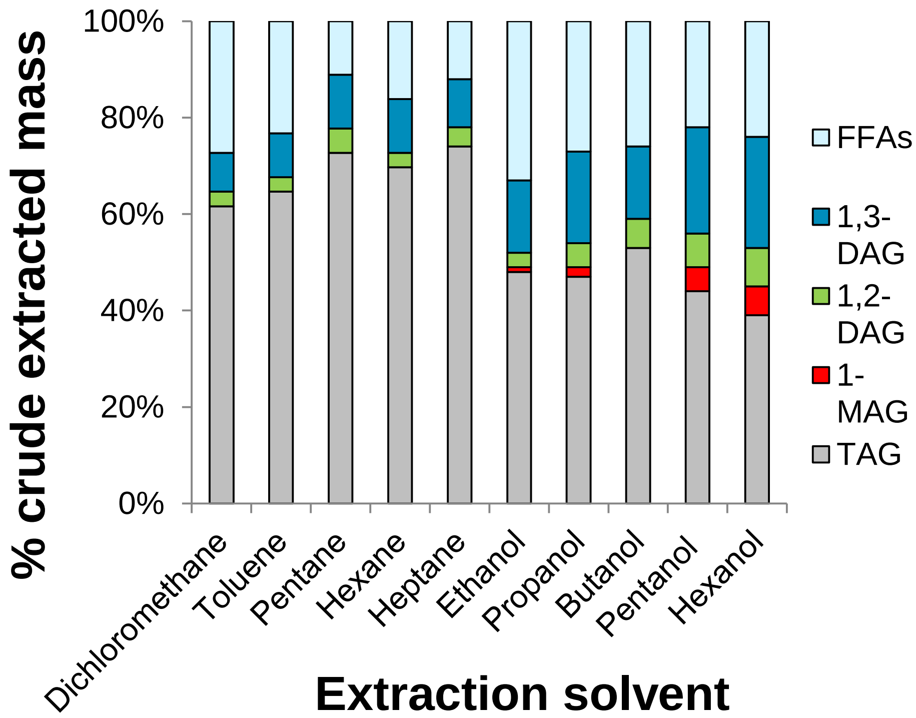
Food waste to fuels

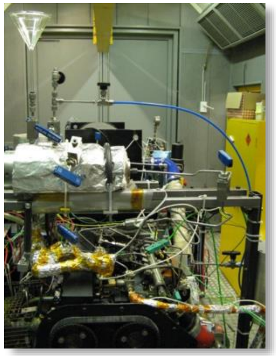
- e.g. Spent coffee grounds contain ~ 15 % lipids
- Recovery process impacts on crude composition.

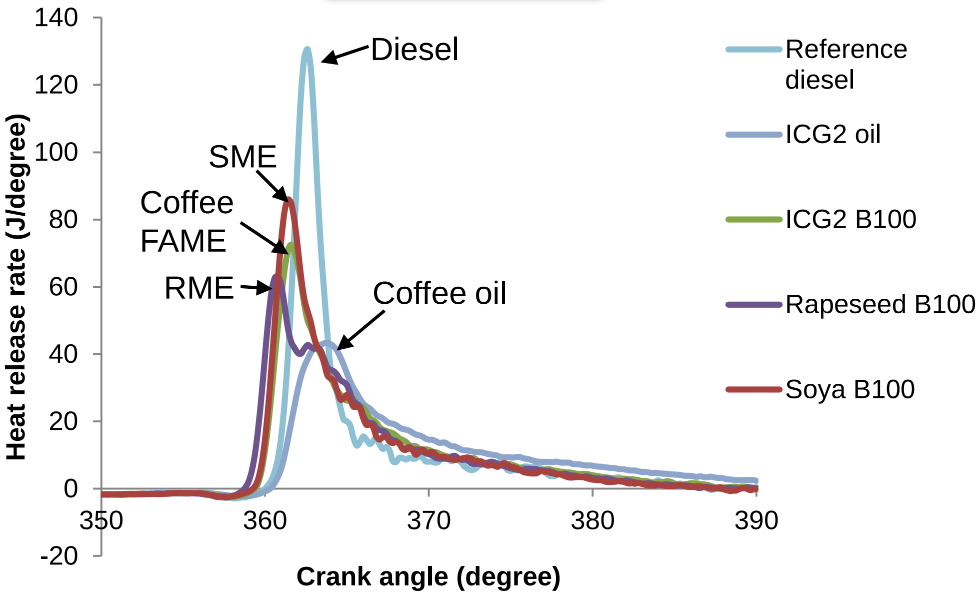


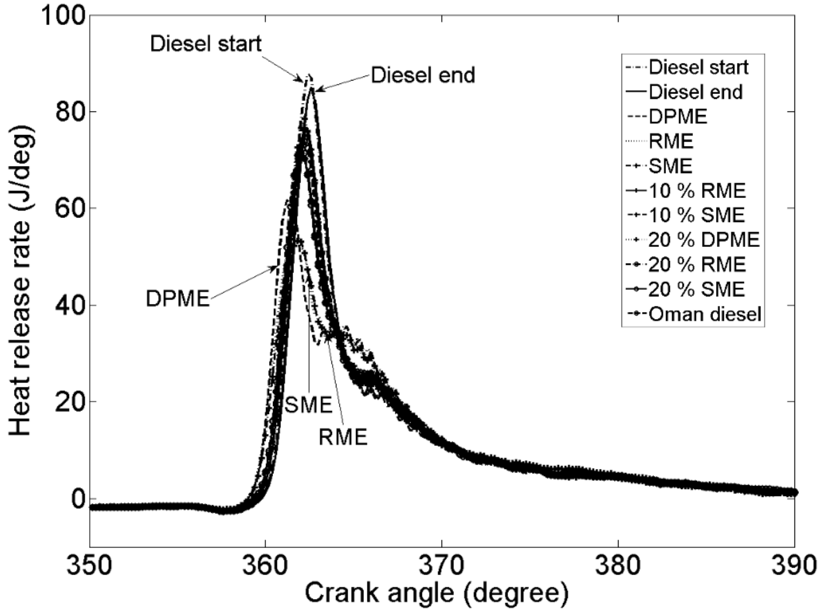


Efthymiopoulos, I., Hellier, P., Ladommatos, N., Russo-Profili, A., Eveleigh, A., Aliev, A., … Mills-Lamptey, B. (2018). Influence of solvent selection and extraction temperature on yield and composition of lipids extracted from spent coffee grounds. Industrial Crops and Products, 119, 49–56.

Coffee and Dates (in an engine)

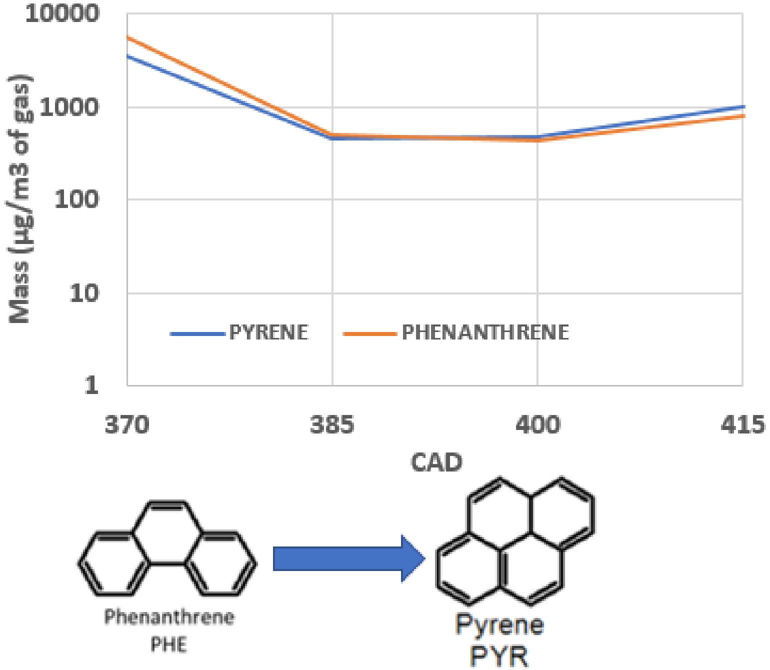


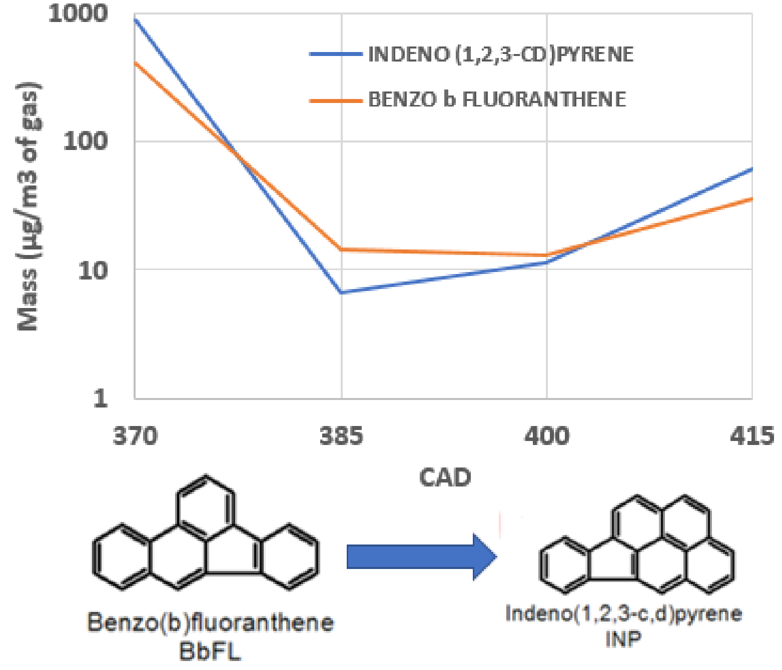




– Coffee and date pit methyl esters – conventional alternatives, but sustainable feedstocks?

PAH formation





- In-cylinder sampling during diesel combustion and quantification of individual PAH
- Evidence of PAH formation, consumption and oxidation rates varying with species