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Title: Impact of Biomass-Derived Fuels on Soot Oxidation Kinetics and DPF Regeneration Behaviour

SUMMARY

To comply with the new regulations on particulate matter emissions, the manufacturers of light duty as well as heavy duty vehicles more commonly use diesel particulate filters (DPF). The regeneration of DPF depends to a significant extent on the properties of the soot stored. Earlier studies have suggested that composition of engine fuels, due to their ability to influence the in-cylinder formation conditions, can impact the microstructure and reactivity of diesel particulate matter.

Concurrently, with the focus of research shifting towards the usage of bio-fuels as alternatives for fossil fuels, it is of vital importance to understand the effects of these bio-fuels on physical and chemical characteristics of particulate matter.

Led by the Chair for Combustion Engines (VKA) at RWTH Aachen University, a Cluster of Excellence named “Tailor-Made Fuels from Biomass” was established in 2007 that aims to develop new biofuels in an integrated process, combining chemistry, process engineering and combustion science. In this cluster, new processes have been developed that allow the production of biofuels that can directly be derived from glucose by new catalyst. One of the fuels developed in this Cluster is 2-methyltetrahydrofurane (2-MTHF). This molecule forms a ring structure and contains oxygen that directly originates from the glucose, the fuel was derived from. Due to its very low self-ignitability (Cetane Number 15) it was blended with 30 vol% of di-n-buthyl ether (DBE, Cetane Number 100) to improve its ignition behaviour.

To help better understand the influence of these new fuels on the DPF behaviour, the primary focus of this work was to analyse the important factors such as particulate matter reactivity and kinetics of soot oxidation, to enable a better control of after-treatment systems.

The experiments for particulate measurements and sampling were conducted with three different fuels (1) petroleum based diesel fuel (without FAME, in particular without oxygen), (2) 100% RME i.e. today's biofuel and (3) a blend of 70 % v./v. 2-MTHF + 30 % v./v. DBE, designated as 2-MTHF/DBE in this study. To ensure that the findings are relevant for future automotive business, the testing program was carried out on a EURO 6 compliant High Efficiency Combustion System (HECS) designed for future passenger car applications.

A number of tools have been employed to investigate the size, concentration, composition, volatility, micro-structure and soot combustion behaviour. The test methodology of TGA was optimized to get a better approximation of the soot oxidation behaviour from a charged particulate filter. Further to it, a Laboratory Gas Test Bench (LGTB) method was developed to analyse the kinetics of soot oxidation using a temperature programmed oxidation (TPO). Soot samples were collected on uncatalyzed DPF to avoid the influence of catalyst coatings on the oxidation kinetics. The activation energy of soot samples from different fuels was calculated with the help of an Arrhenius plot with using the oxidants such as O_2 (to cover thermal filter regeneration) and NO_2 (passive regeneration) independent to each other. The boundary conditions for these measurements were maintained comparable to real engine operation with taking into account the influence of exhaust gas concentrations, residence time of exhaust gases in DPF and temperatures etc. In contrast to an engine test bench, an independent control of these critical exhaust gas parameters (i.e. space velocity, temperature etc.) was possible during measurements. Use of real soot loaded DPF samples on LGTB, enabled a similar diffusion and gas transport phenomenon, comparable to real DPF engine applications. In order to understand the relationship of soot oxidation behavior with its microstructure, a high resolution transmission electron microscopy (TEM) was conducted on soot samples collected thermophoretically on cupper grids. The elemental composition (C:H:O) of soot samples extracted from loaded filters was determined with using DIN 51732 standard. The results suggests following conclusions:

- Elemental analysis results show that soot samples from 2-MTHF/DBE fuel contains maximum oxygen concentration (~ 16 % m/m basis and ~11 % % atom basis) followed by petroleum based diesel soot. It is very interesting to see that RME soot contains minimum oxygen fraction (~ 3 % m/ m basis and 1.8 % atom basis).
- Oxidative reactivity measurements using improved TGA method indicated an early oxidation in case of soot from oxygenated fuels. The oxidation temperature at 90% relative mass loss in TGA (an indication of completion of regeneration event) for 2-MTHF/DBE soot was found ~ 110 °C lower than petroleum diesel.
- The kinetics of soot oxidation at LGTB revealed lowest activation energy (Ea) for 2-MTHF/DBE soot and results derived from Arrhenius plot show 75 °C lower temperatures for thermal / active regeneration and 60 °C less for passive regeneration.

- Qualitative analysis of TEM micro-graphics indicates a higher disorder in 2-MTHF/DBE soot as compared to other investigated soot samples.
- The results from all the investigation methods indicate a relatively higher reactivity of the soot from 2-MTHF/DBE fuel as compared to both RME (B100) and petroleum based diesel soot. This increase of reactivity could be explained as follows:
    - Elemental analysis (C:H:O) of soot samples confirm a higher oxygen concentrations in the soot from 2-MTHF/DBE. This fuel has higher oxygen content in the molecular structure. It is plausible that the increase is additional caused by the position of the oxygen as an ether in DBE respectively a furan oxygen in 2-MTHF. Probably the reason is that the ether/furan-oxygen is not able to separate as CO_2 in the first step like it is possible with the ester oxygen in RME. Similar observations were also reported by A.Williams and co-workers, his work demonstrated that the form of oxygen functional group proved to play a role in DPF performance. A long-chain alcohol provided a more effective form of oxygen than oxygen group in ester or FAME /1/.
    - An increase in reactivity in 2-MTHF/BDE soot is also supported by the indication of a high degree of disorder as seen in TEM micro-graphics. This result very well corresponds to the findings of Vander Wals et. al. where disorder in soot structure helps to attain enhanced oxidation rates /2/.

The potential future biofuel candidate used in this work, due to the favourable physico-chemical properties (i.e. Ignition characteristics, evaporation behaviour, aromatic content, oxygen content and oxygen functionality etc.) resulted a very low engine out particulate emissions. Together with higher observed PM reactivity and an increasing part of CRT effect on the oxidation of the remaining particles a significant decrease of the regeneration frequency probably close to zero could be expected in case of future biofuels.

REFERENCES

/1/ A. Williams, R. L. McCormick, S. Black; "Biodiesel Fuel Property Effects on Particulate Matter Reactivity" 6th International Exhaust Gas and Particulate Emissions Forum sponsored by AVL, Ludwigsburg, Germany, March 9-10, 2010

/2/ Randy L. Vander Wal, Aaron J. Tomasek; Soot oxidation: dependence upon initial nanostructure, Combustion and Flame, Volume 134, Issues 1–2, July 2003, Pages 1-9, ISSN 0010-2180, 10.1016/S0010-2180(03)00084-1.

CONTACT INFORMATION

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Impact of Biomass-Derived Fuels on Soot Oxidation and DPF Regeneration Behaviour

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Motivation

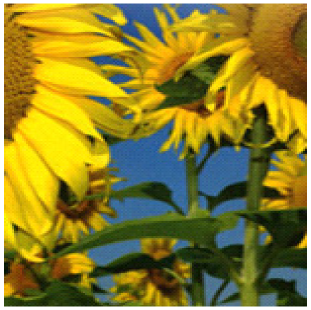
- » Regeneration of DPF is associated with fuel penality and additional CO_2 emissions
- » The regeneration behaviour of DPF depends to a significant extent on properties of stored soot
- » Composition of engine fuels, due to their ability to influence the in-cylinder formation conditions (<u>i.e thermal decomposition chemistry of fuels</u>), can impact the microstructure and reactivity of particulate matter
- » Focus of research is shifting towards development of new fuels from biomass (using low temperature processes) with entirely different properties & molecular structure
- » To gain a better control on after-treatment devices, it is vital to understand the PM reactivity and its combustion behaviour using new fuels
- » The present work focusses on the impact of „*<u>new engine fuels</u>*“ on „<u>PM reactivity</u>“ and „<u>DPF Regeneration Behaviour</u>“

Overview of the Production Processes of Biofuels

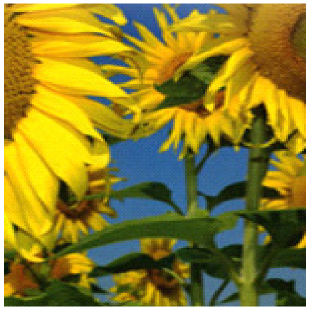
1. Generation of Biofuels:

Grains (Sugar Cane, corn, etc.) → Bioethanol

Rape, Sunflowers, Sojbeans, etc. → Biodiesel Fatty acid methyl ester (FAME)



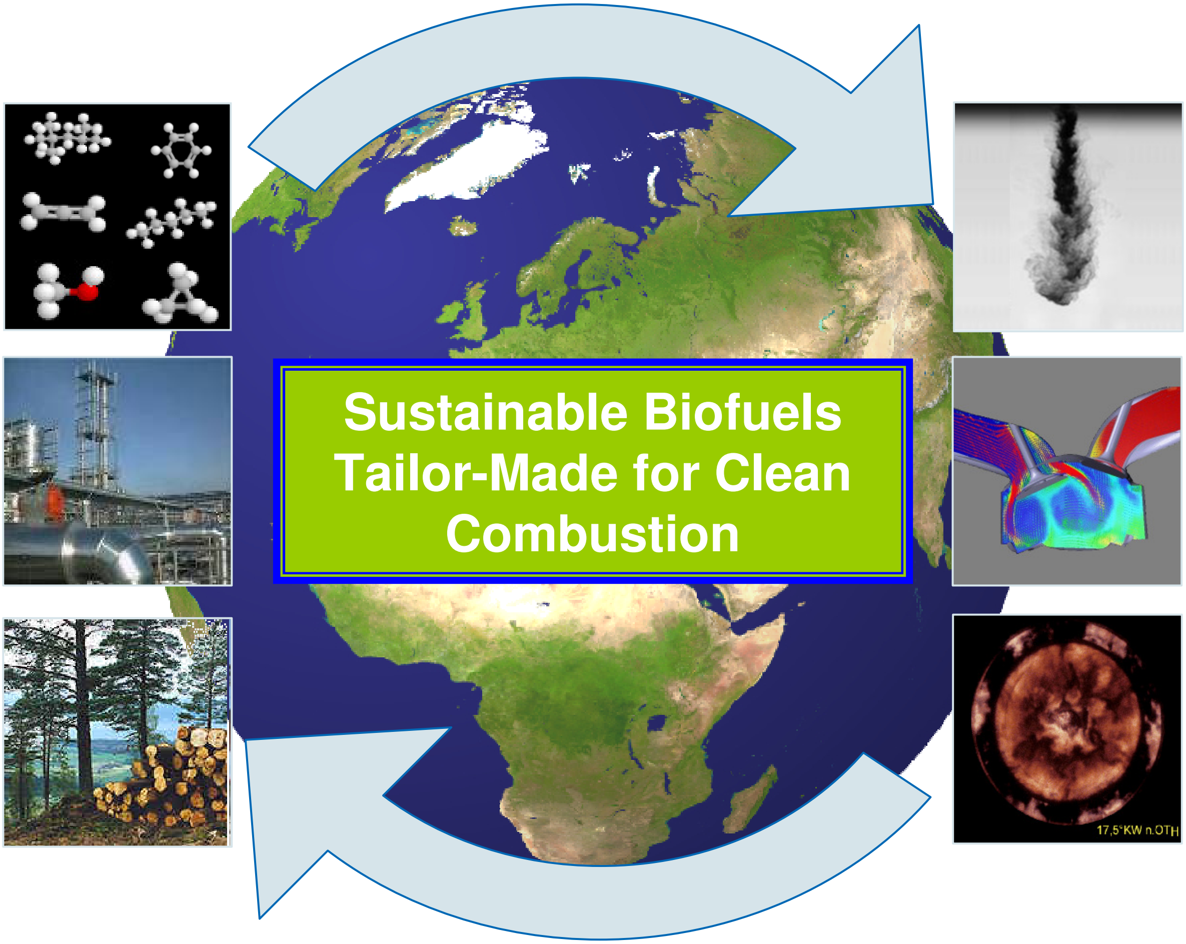
2. Generation of Biofuels:



Biomass (entire plant material) → Alcohols

Biomass (entire plant material) → Mixture of different Hydrocarbons (BTL)

The Vision: 3rd Generation of Biofuels



Novel Synthesis and Production Routes

Fuels
from Biomass

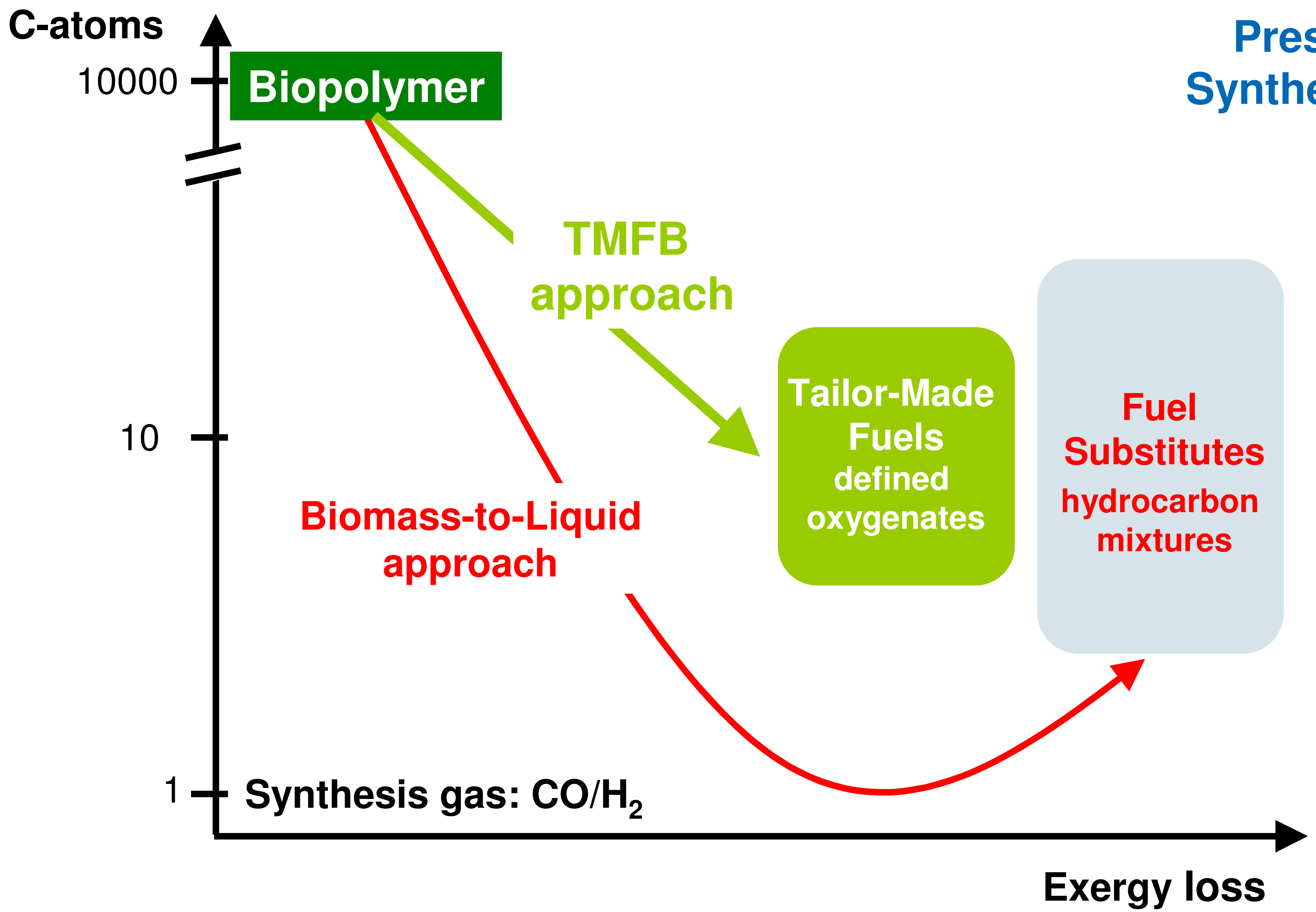
**Sustainable Biofuels
Tailor-Made for Clean
Combustion**

Combustion
Engine

Model-Based Specification of Combustion Characteristics

TMFB Vision: Biofuel Production

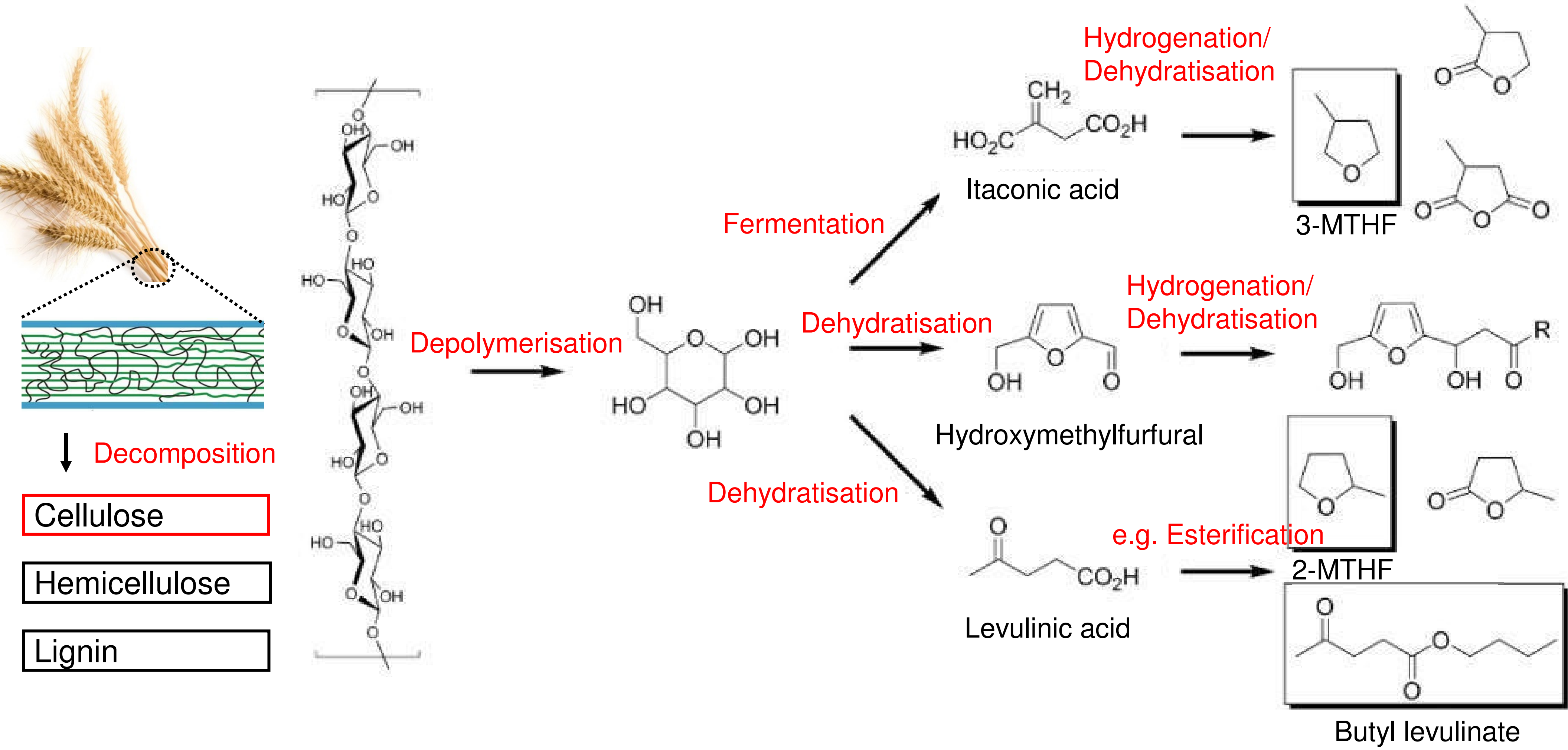
Preserving the Synthesis of Nature



Platform Chemicals and Resulting Fuel Components

TMFB Tailor-Made Fuels from Biomass

Biomass **Cellulose** **Glucose** **Platform chemicals** **Possible fuel components**



RWTH AACHEN

Methodology – Soot Reactivity & DPF Behaviour

Tailor-Made Fuels from Biomass

Soot from Biomass Derived Fuels

Engine Fuels

Petroleum based Diesel

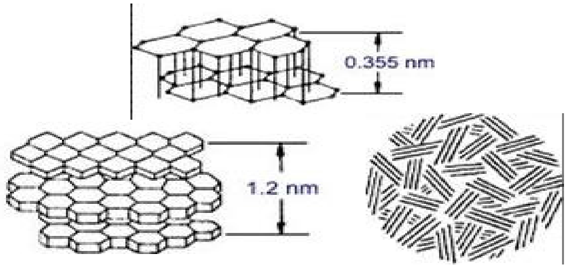
Today´s Biofuel

Future Biofuel

***H**igh **E**fficiency **C**ombustion **S**ystem*

FEV - H E C S

Particulate Emissions



Characterization Methods

- **Engine Out Emissions**
- **DPF Filling Behaviour**

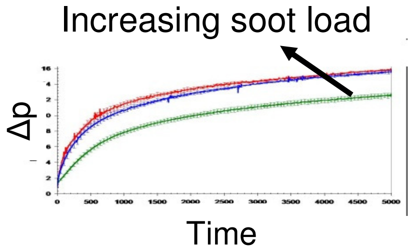
Morphology

- **Primary particle size**
- **Aggregate size**
- **Agglomerate**
- **Micro-structure**

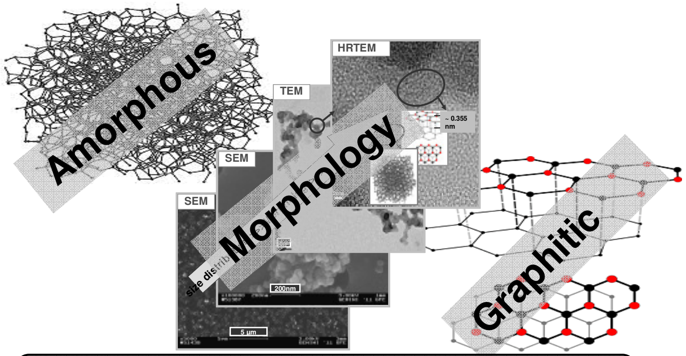
Soot Combustion

- **TGA Oxidative Reactivity**
- **TPO @ LGTB**
- **O_2 oxidative kinetics**
- **NO_2 oxidative kinetics**

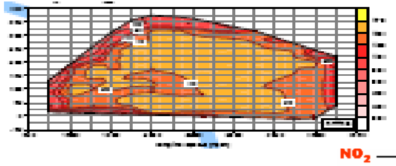
Soot Reactivity / DPF Behaviour

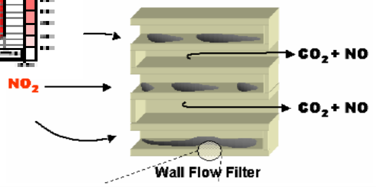


Soot Reactivity



DPF Regeneration





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Research Engine

Specifications	*HECS* Single Cylinder
Bore X Stroke	75x88.2 mm
Swept volume	390 cm³
Compression ratio	15
Valves per cylinder	4
Max. valve lift	8 mm
Maximum cylinder peak pressure	250 bar
Fuel injection equipment specifications:	Piezo Common Rail System
Max. injection pressure	2000 (2400 bar temporary) bar
HFR	310 cm³/60s@100bar
Max. boost pressure	3.75 bar (external device)
Charge air cooling level	Advanced
Variable swirl	Yes (with VVL)
Emission level	Euro 6+

***HECS*: High Efficiency Combustion System**

Test Fuels

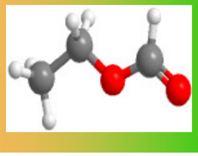
Tailor-Made Fuels from Biomass

Baseline petroleum based Diesel

- Consists of ~ 200 different types of hydrocarbons (incl. Paraffins/Olefin / Aromatics)
- No oxygen content

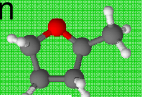
1^{st} Gen. Biofuels
• RME

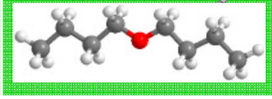
- Fatty Acid Methyl Esters
- Already in use as blends or pure component

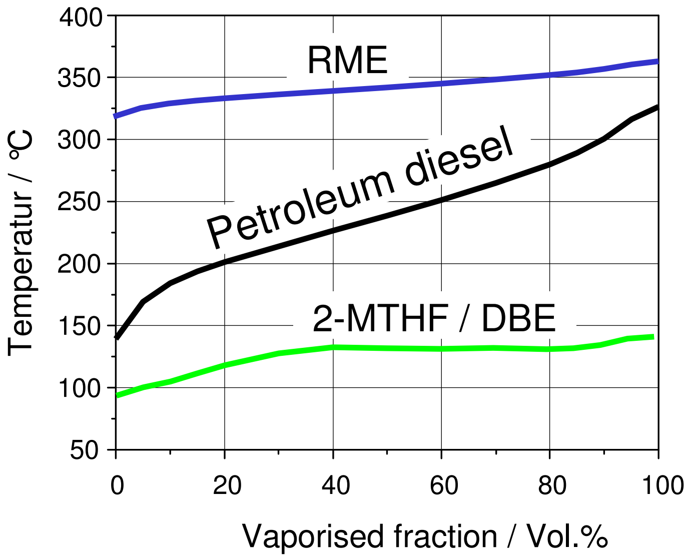


Future Biofuel Candidates

- Novel Fuel synthesis approach from Biomass
- Sustainable production process





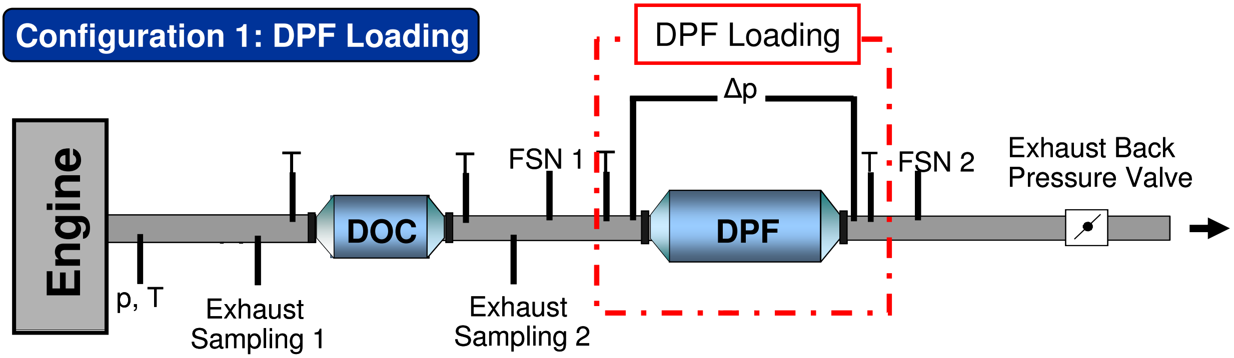


	Unit	ULSD-B0	RME (B100)	2-MTHF/ DBE *
Cetane Number	-	53	53.9	~ 30
Density (15°C)	kg/m³	832.9	883.1	824
Carbon content	w %	86.4	77.1	71.8
Hydrogen content	w %	13.5	12.1	12.7
Oxygen content	w %	0	10.8	15.5
Total Aromatics content	w %	27.1	0	0
Boiling Range	°C	202-333	352	84-147
Lower Heating value	MJ/kg	43	36	35.2

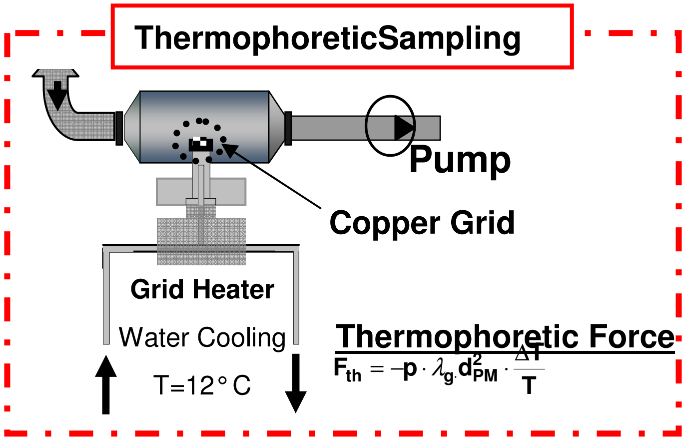
* 2-MTHF/DBE :70 % v./v. 2-Methyl-tetrahydrofuran (2-MTHF) + 30 % v./v. Di-n-butylether (DBE)

Engine Bench Set-up

Configuration 1: DPF Loading



Configuration 2: Thermophoresis Set up



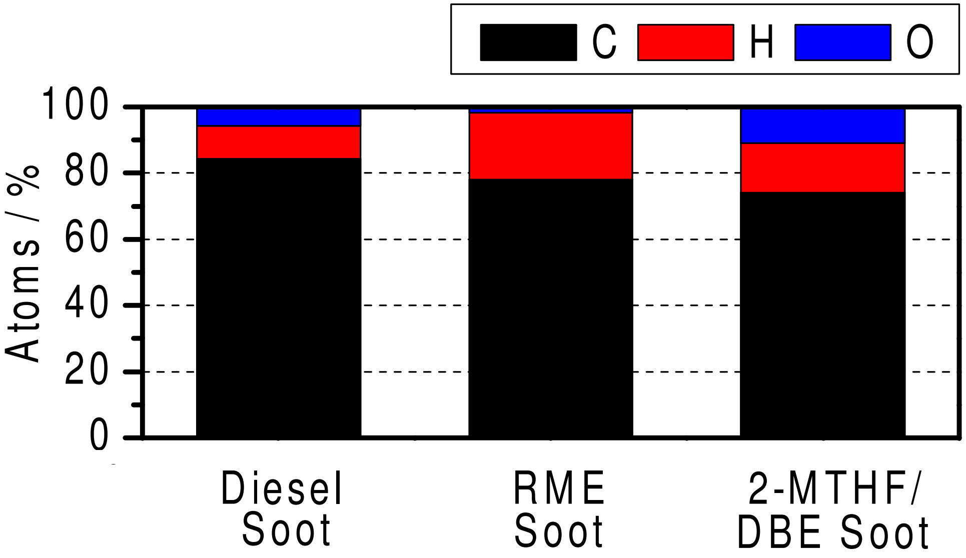
$$F_{th} = -p \cdot \lambda_g \cdot d_{PM}^2 \cdot \frac{\Delta T}{T}$$

Engine Operating Conditions	
Indicated Mean Effective Pressure (IMEP) / bar	14.8
Engine Speed / min^{-1}	2400
Boost Pressure / bar	2.6
Exhaust Gas Back Pressure / bar	2.8
Rail Pressure / bar	1800
Charged Air Temperature / °C	45
Estimated Euro 6 NO_x Emissions/ g/kWh	0.75

- Uncatalyzed aluminium-titanate DPF used for soot loading
- All the tests conducted under constant centre of combustion (CA_{50})

Elemental Composition of Soot

As per DIN 51732 Method



Engine Out ISNO$_x$ Emissions Euro 6 Level
n = 2400 min^{-1}; IMEP = 14.8 bar

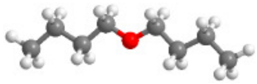
- ➢ Soot samples from 2-MTHF/DBE fuel contains maximum oxygen concentration
(~ 16 % m/m basis and ~11 % % atom basis)

- ➢ It is very interesting to see that RME soot contains minimum oxygen fraction (~ 3 % m/ m basis and 1.8 % atom basis)

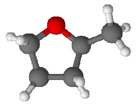
- ➢ Functionality of oxygen group make a big difference. (A oxygen atom in Furane respectively in Ether group is bonded to two oxygen atom, providing more effective form of oxygen)

- ➢ In FAME, two oxygen are bonded to one carbon atom, which is not effective

Ester

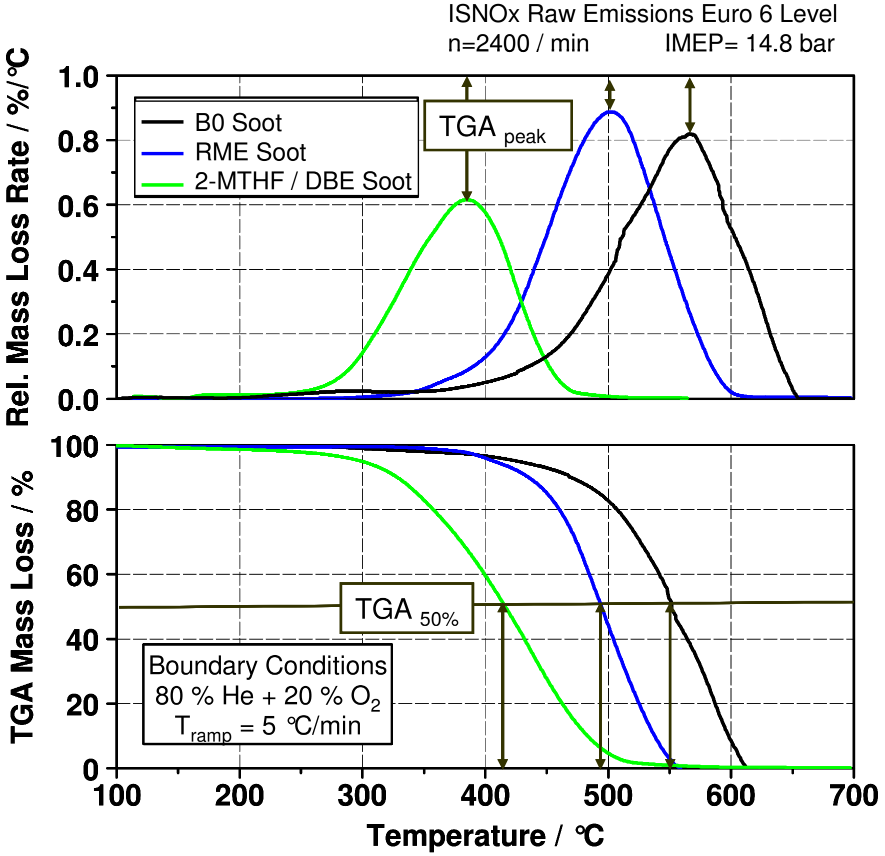


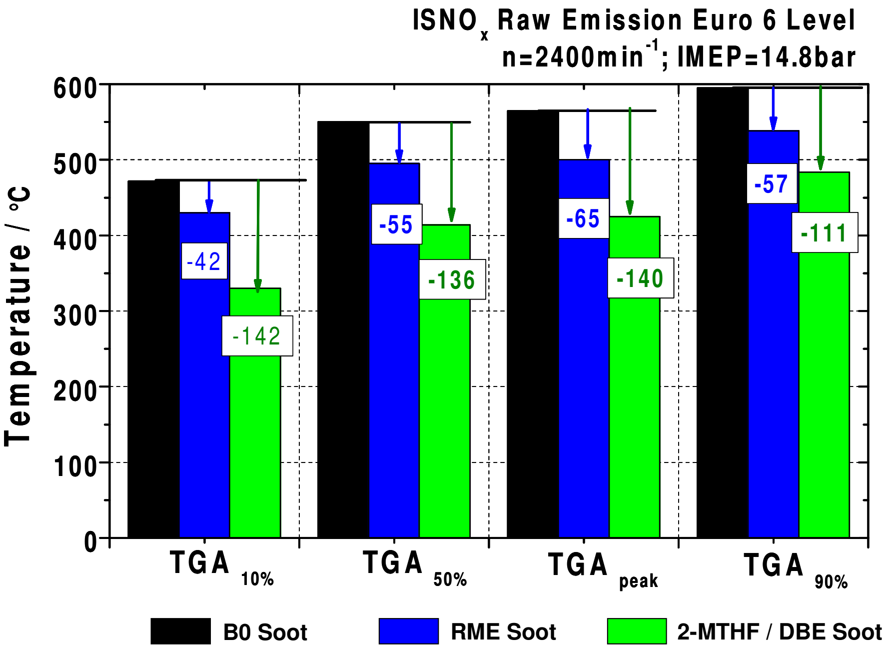
Ether



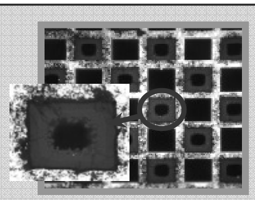
Furane

TGA Oxidative Reactivity





Soot loaded
DPF channels
used for the present TGA



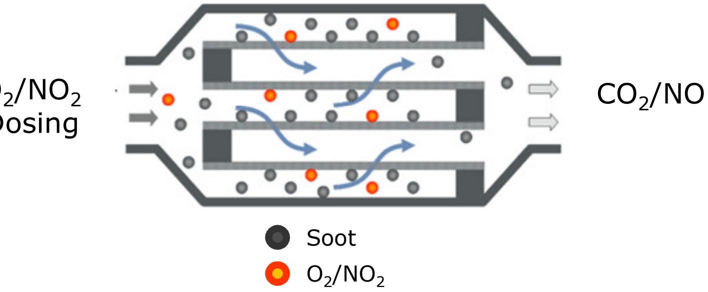
- ➢ Oxidative reactivity measurements using improved TGA method indicated an early oxidation in case of soot from oxygenated fuels
- ➢ 2-MTHF/DBE show lowest oxidation temperature i. highest oxidative reactivity

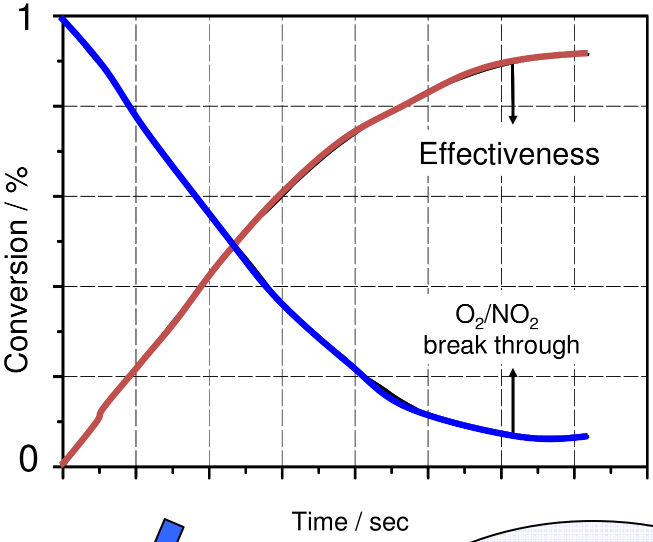
Soot Oxidation Kinetics
@ Laboratory Gas Test Bench

Derivation and Definetion of Arrhenius equation.

$$C + O_2 \rightarrow CO_2$$

$$C + 2NO_2 \rightarrow CO_2 + 2NO$$





$$k = A \cdot e^{\left(\frac{-Ea}{RT}\right)} \rightarrow \ln k = \ln A - \frac{Ea}{RT}$$

k- reaction rate constant
A- pre-exponential factor
Ea-Activation energy
R-Universal gas constant
T-Temperature of the reaction

$$1 - Eff = e^{(-kt)}$$

Eff- Effectiveness of soot mass conversion
t- Time of gas contact in the soot cake
k- reaction rate constant

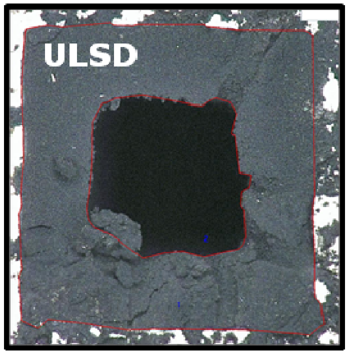
$$\ln k = -\ln\left[\frac{\ln(1 - Eff)}{t}\right] = \ln A - \frac{Ea}{RT}$$

Soot Oxidation Kinetics
@ Laboratory Gas Test Bench

Definition of Reaction Time.

Assumptions:

- Reaction time of gas was calculated as the time, the gas is present inside the soot cake
- Because of the high porosity of the soot cake this reaction time is proportional to ratio of soot volume to DPF volume
- Diffusion velocity is higher than reaction velocity

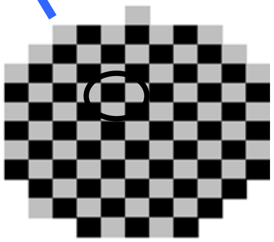


Quasi static state

$$\rho_{soot\ cake} = \frac{m_{weighed\ soot}}{V_{total\ soot}}$$

$$V_{total\ soot} = n \cdot V_{soot,channel}$$

$$V_{soot,channel} = l_{DPF} \cdot A_{soot,channel}$$

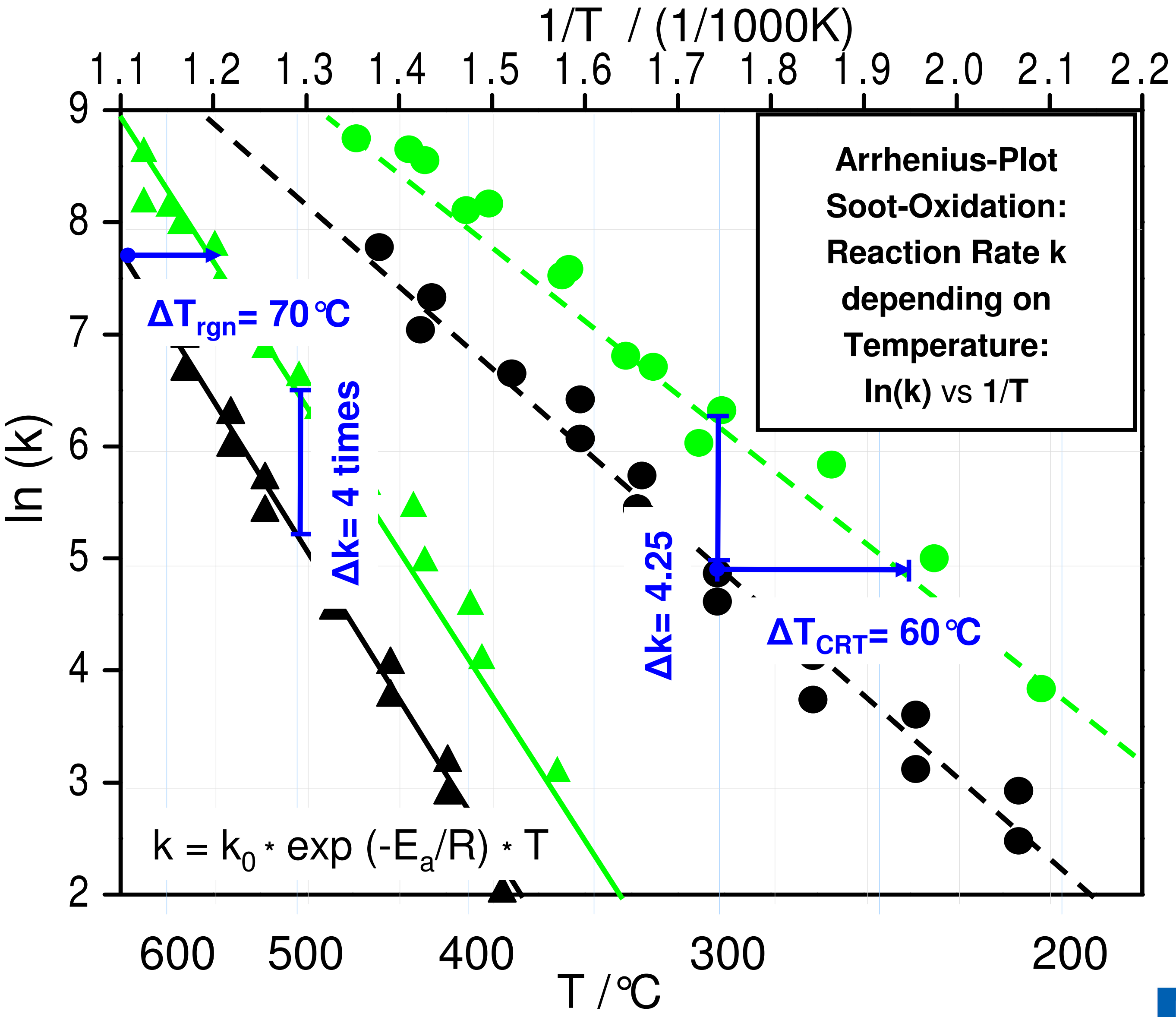


Soot Loaded DPF Channels

$$t = t_{filter} \cdot \frac{V_{soot}}{V_{filter}}$$

$$t_{filter} = \frac{1}{SV}$$

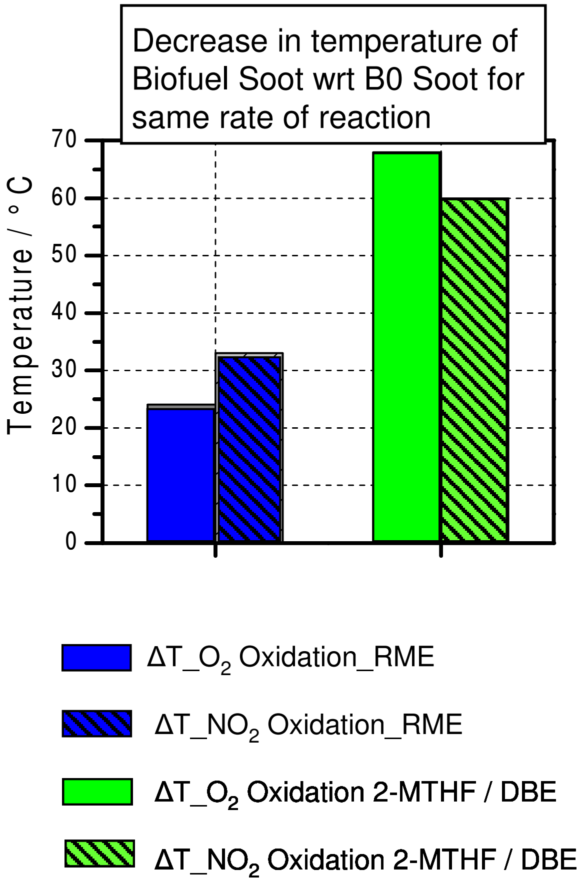
Arrhenius Plot

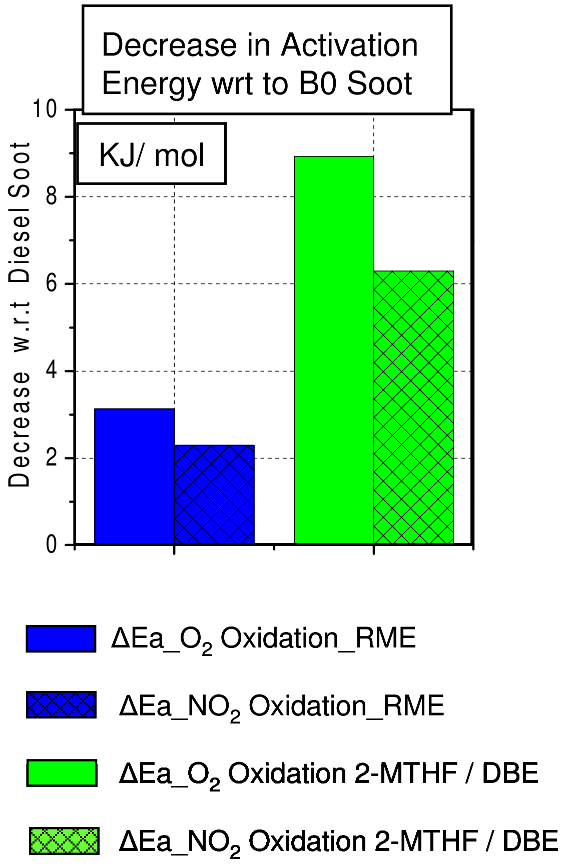


Arrhenius-Plot
Soot-Oxidation:
Reaction Rate k
depending on
Temperature:
ln(k) vs 1/T

$k = k_0 * \exp(-E_a/R) * T$

Soot Oxidation Kinetics





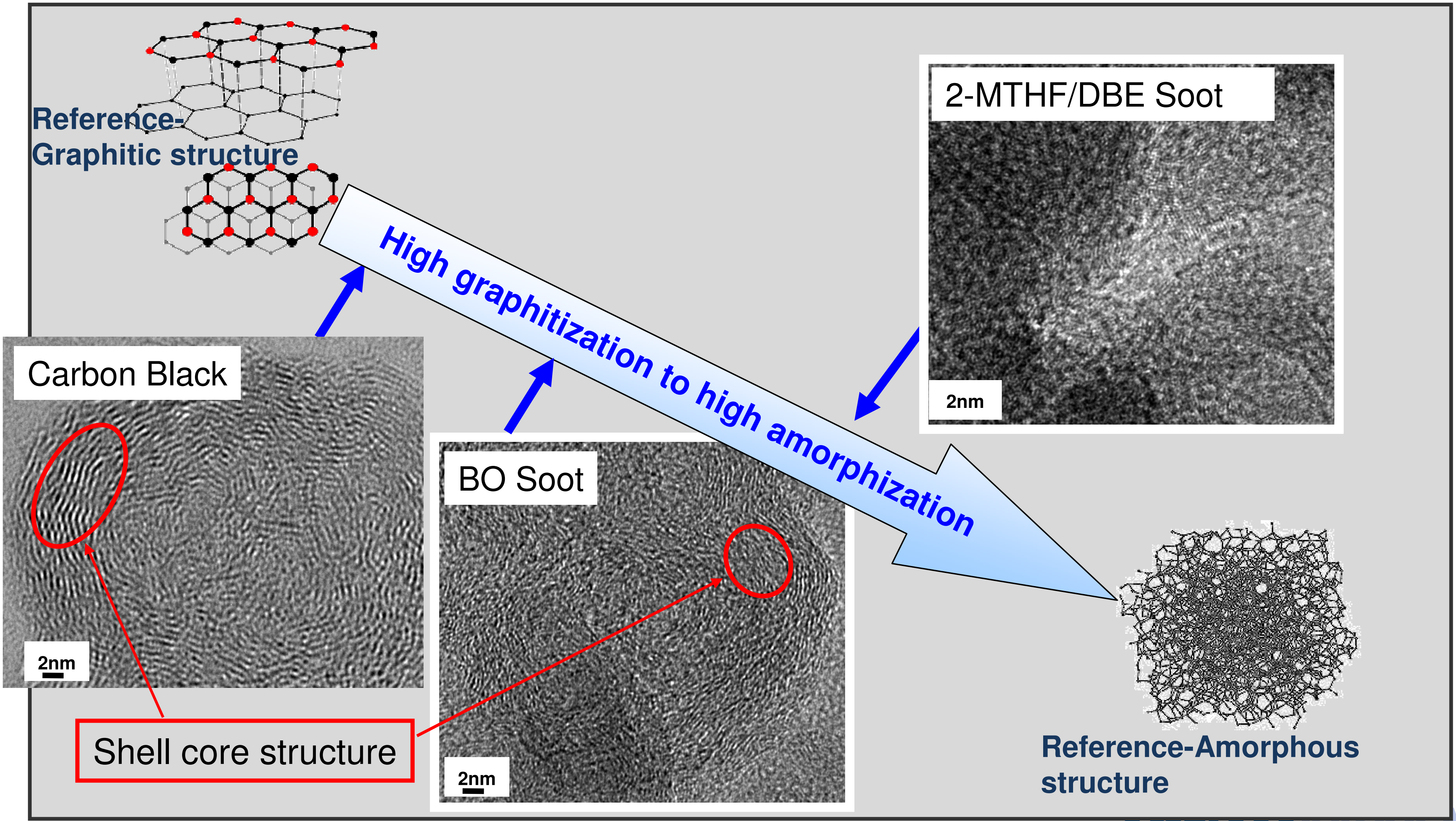
Main Inferences

Rate of raction for 2-MTHF/DBE soot oxidation is ~ 4 times faster than B0 soot

This results in the shifting of thermal regeneration temperature to 70℃ lower than B0 soot

Simlar obseravtions observed with NO_2 oxidation where passive regeneration temperature is shifted to 60℃ lower than B0 soot

High Resolution Transmission Electron Microscopy-Soot Microstructure



Reference-Graphitic structure

Carbon Black

BO Soot

2-MTHF/DBE Soot

High graphitization to high amorphization

Shell core structure

Reference-Amorphous structure

Key Conclusions

The experiments for particulate investigations were conducted with three different fuels, two of which contains oxygen in the fuel molecular structure. The samples were collected from a Euro 6 compliant High Efficiency Combustion System under const. engine operating conditions . The results suggest following:

- **All results show the relatively high reactivity of the soot from 2-MTHF/DBE as compared to the RME (B100) and ULSD soot, It could be explained by the additional oxygen amount. It is plausible that the increase is additional caused by the position of the oxygen as an ether respectively a furan oxygen. Probably the reason is, that the ether/furan-oxygen is not able to separate as CO_2 in the first step like it is possible with the ester oxygen in RME**

- **The oxidation rate of a soot samples were found to be related with its micro-structure, HRTEM micro-graphics hints a higher degree of disorder in the soot from 2-MTHF/DBE fuel.**

- **Due to its favorable properties, 2-MTHF / DBE produces drastically low PM emissions. Together with an increasing part of CRT® effect on the oxidation of the remaining particles a significant decrease of the regeneration frequency probably close to zero could be expected in case of potential future biofuel.**

Thank you for your attention!

DFG German Research Foundation

WR Wissenschaftsrat