Verfahren zur Modifikation von FAME

Überblick über neuere Entwicklungen

Processes to modify FAME – Survey on recent developments

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Johann Heinrich von Thünen-Institut

Modifications of FAME

- Collection of some problems with neat biodiesel and blends
  - Opportunities to solve the problems with blends
    - Opportunities to solve the problems with neat biodiesel

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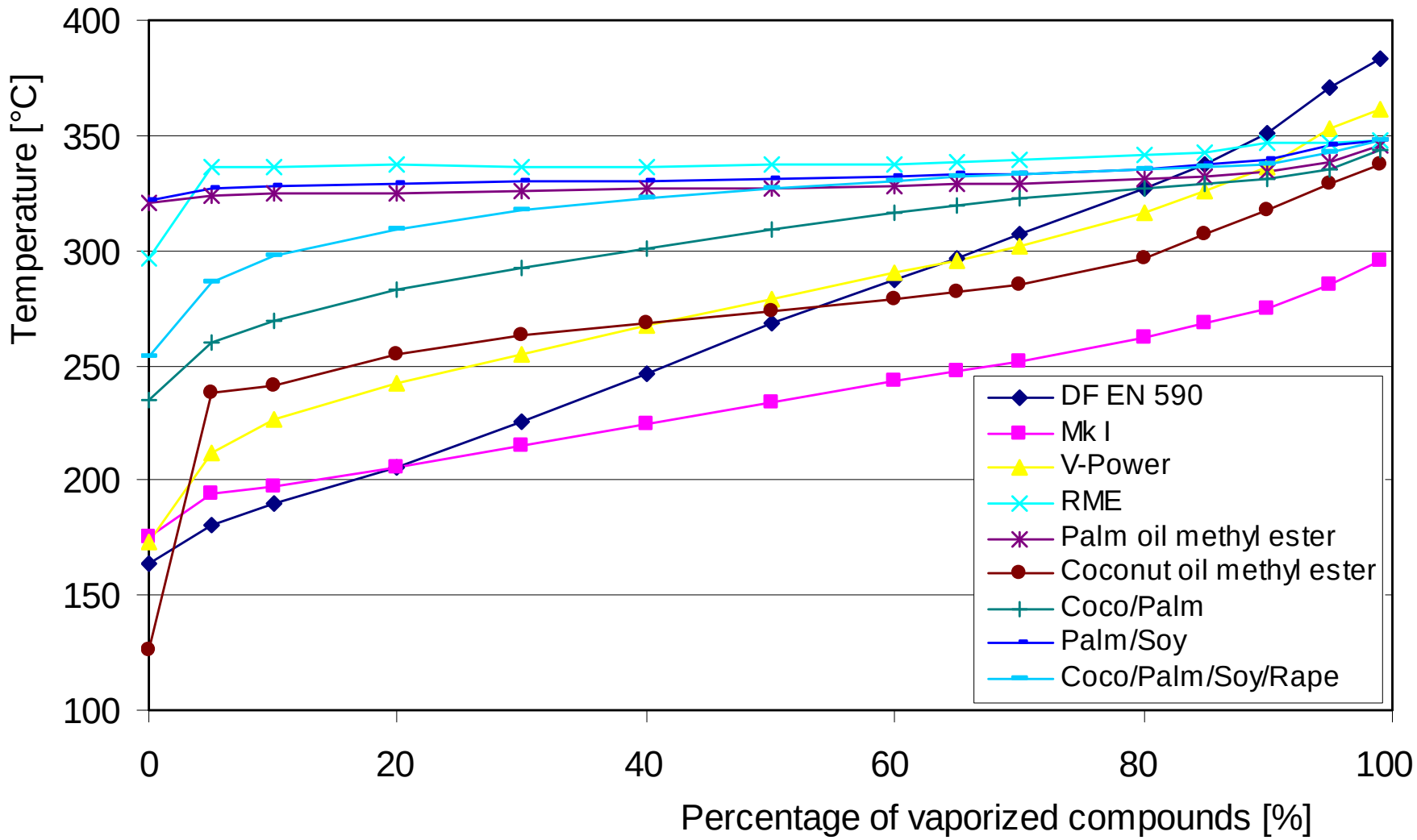
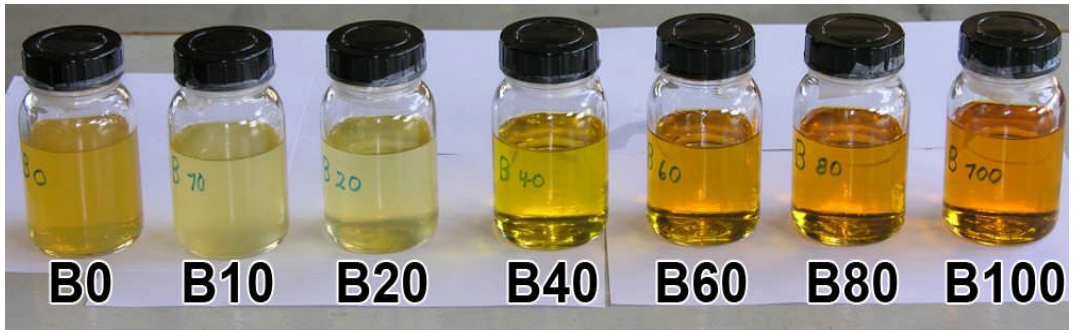
Boiling Curves for Different Diesel Fuels



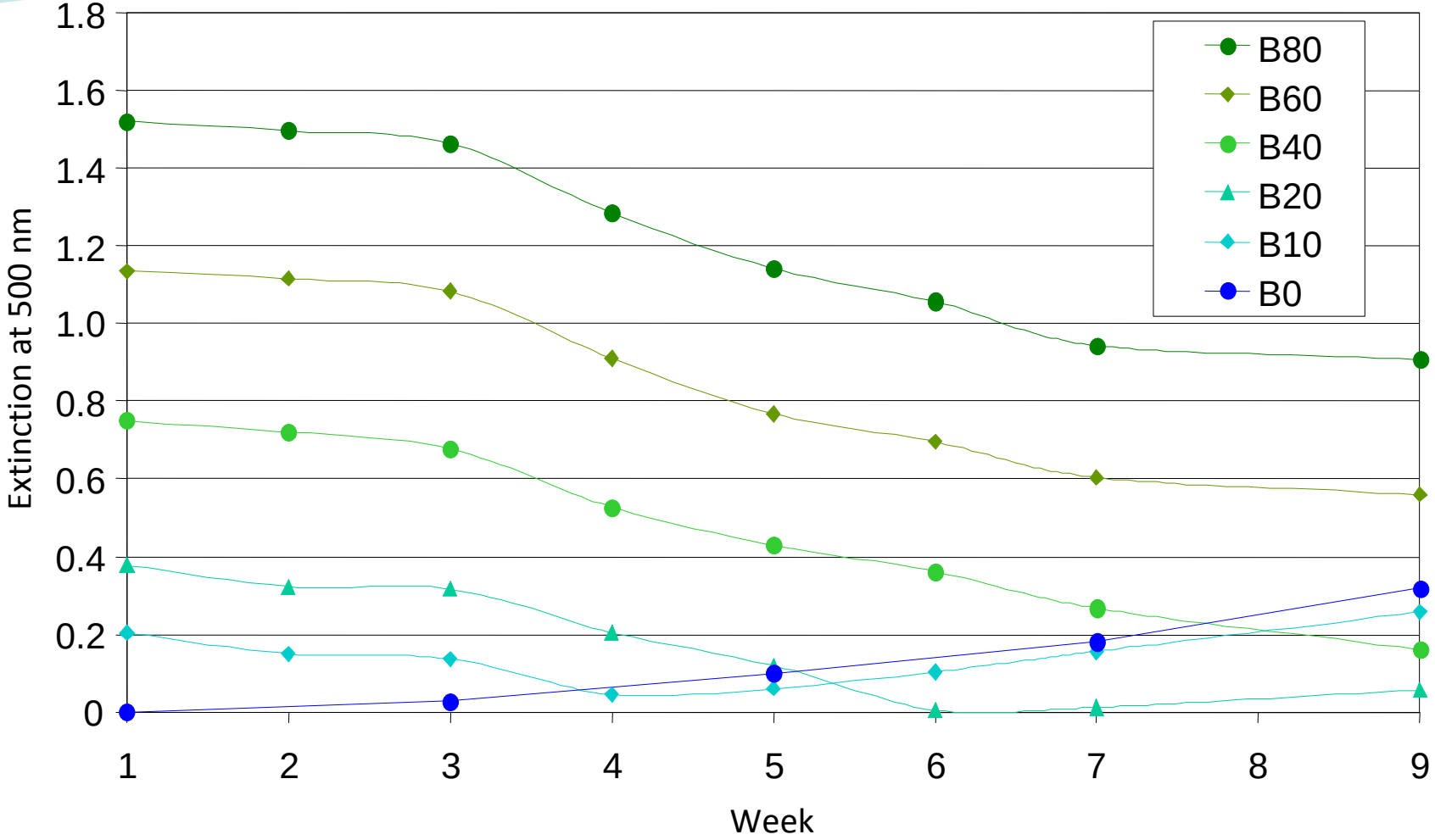
Ageing of RME



- Ageing experiments
- B0 … B100

- B20, aged through 2 years

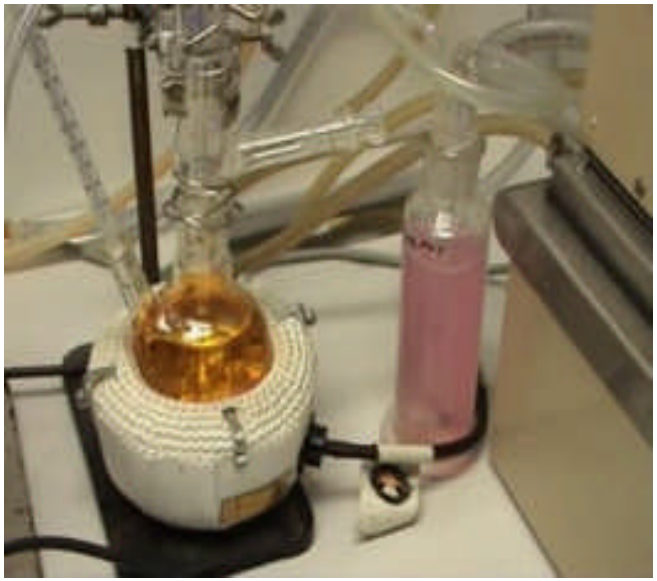
Spectroscopic Monitoring of Aging in the Sunlight



Artificial Ageing by Thermo-Oxidation or UV Irradiation

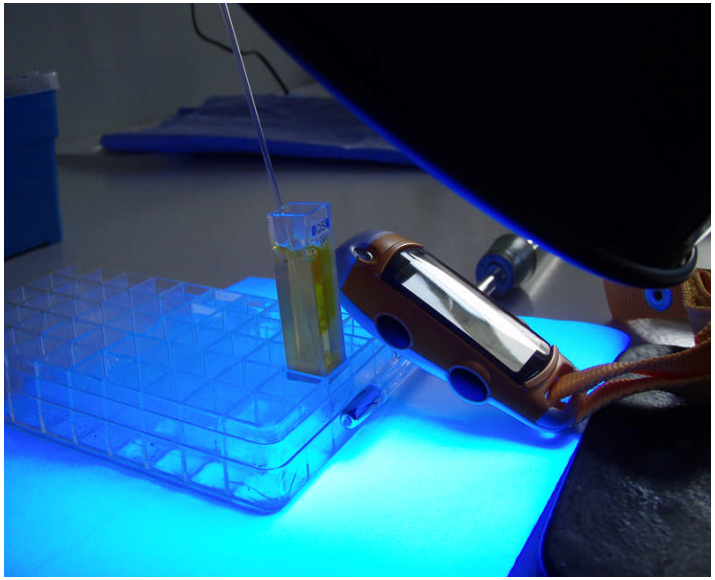
Thermo-oxidation

- T = 110 °C
- Aeration

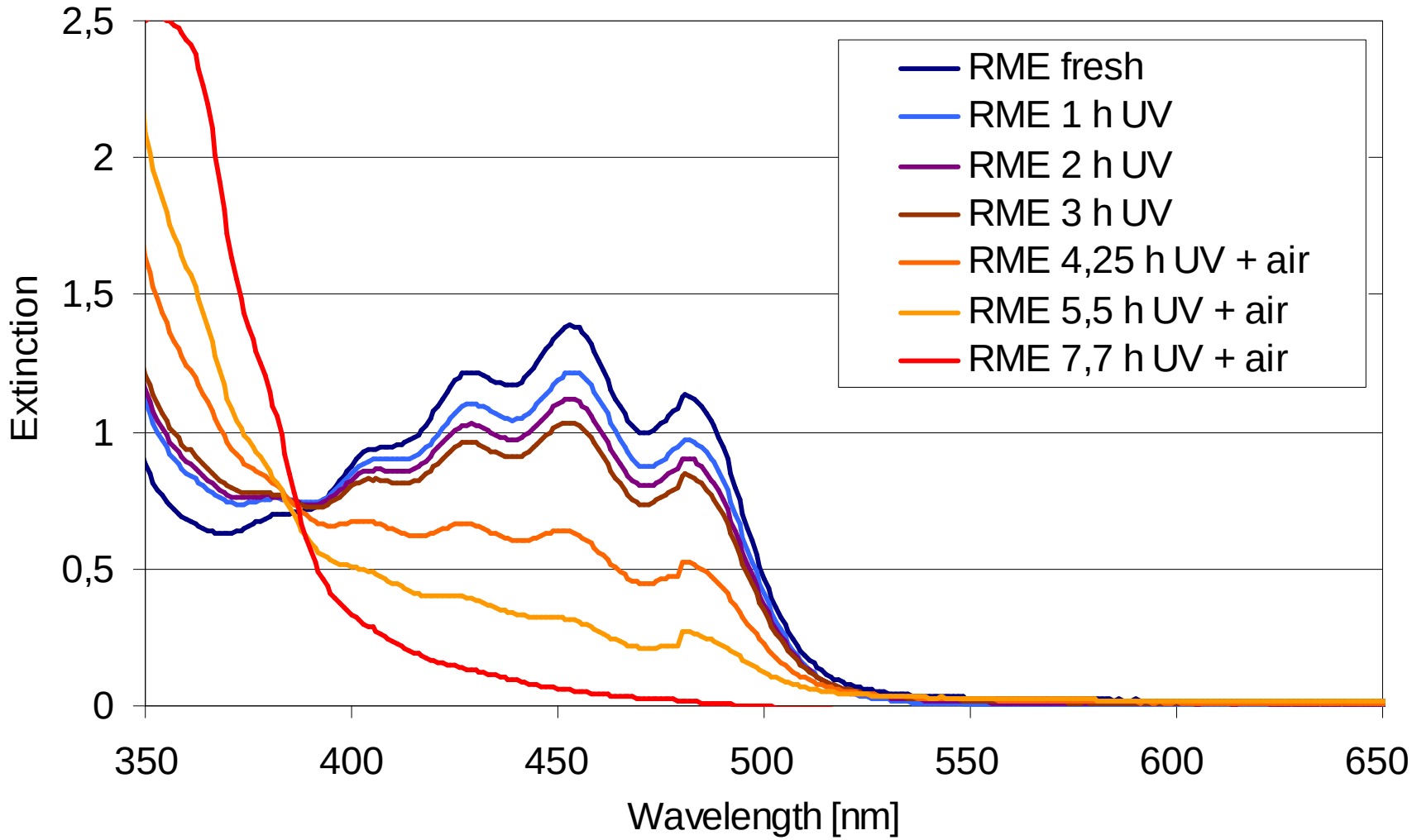


Oxidation by UV irradiation

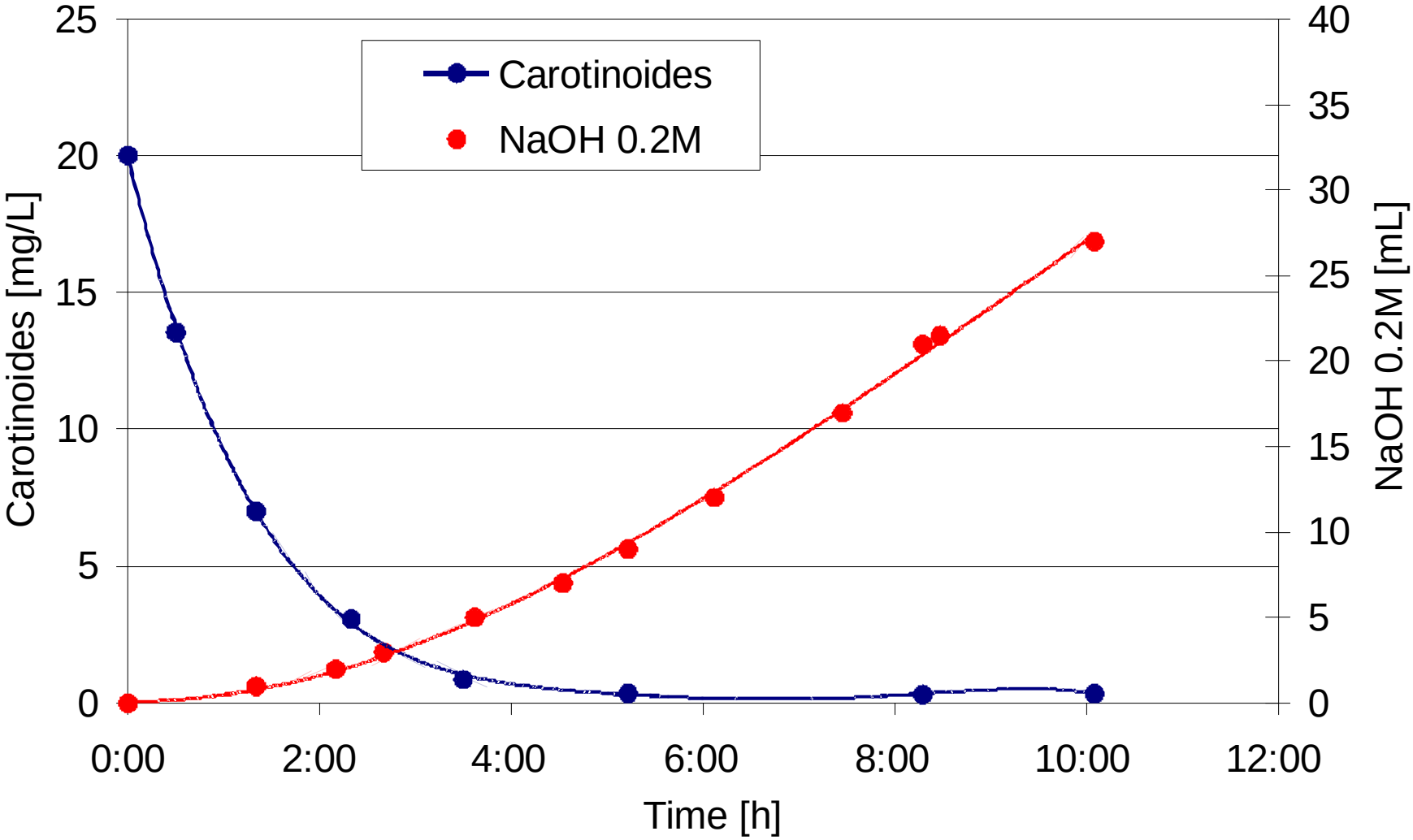
- Aeration
- λ = 256 nm



Ageing through Oxidation by UV Irradiation

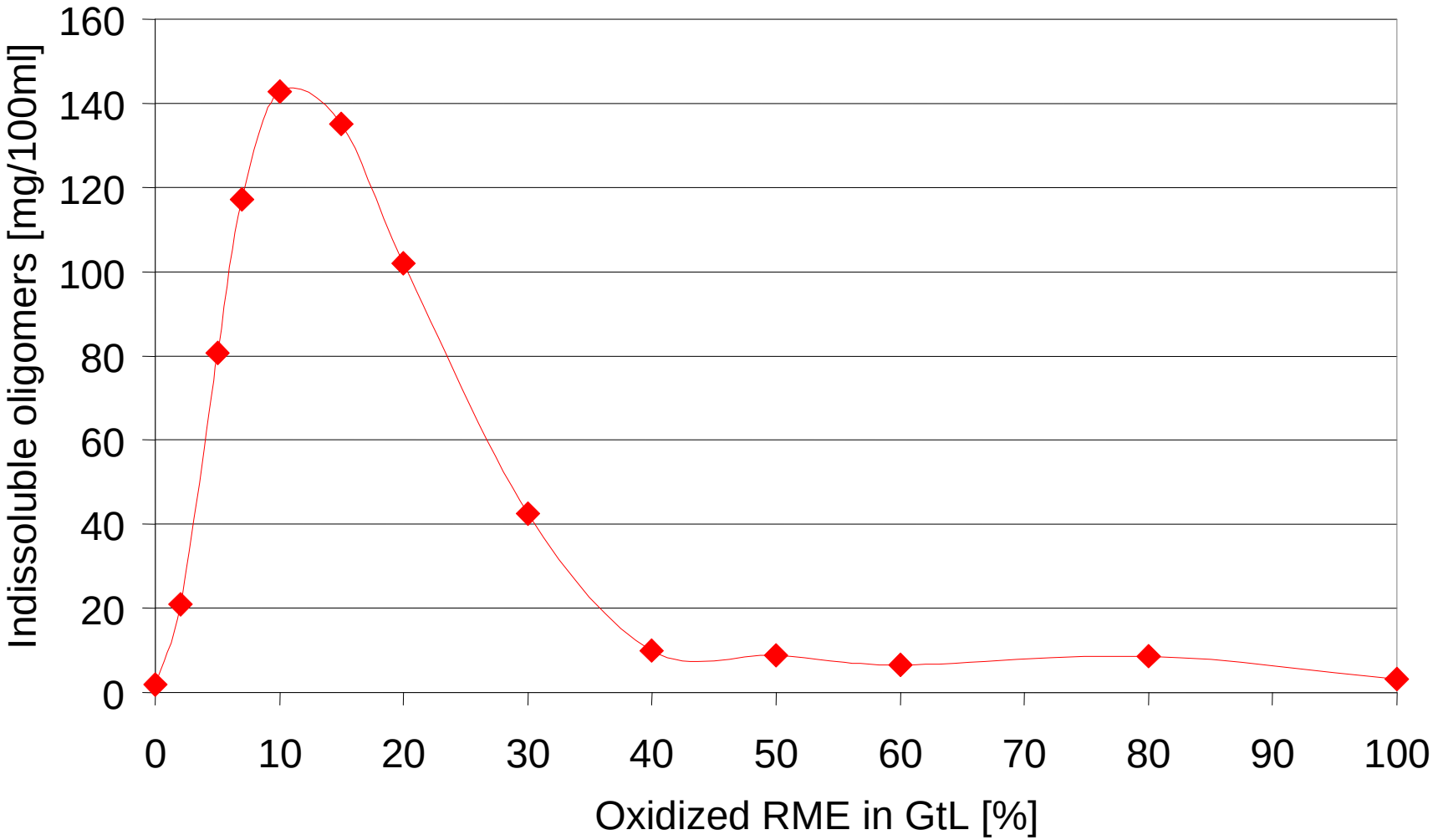


Thermo-Oxidation of RME Exposed to 140 °C in Air – Trends of Antioxidants and Acid Number

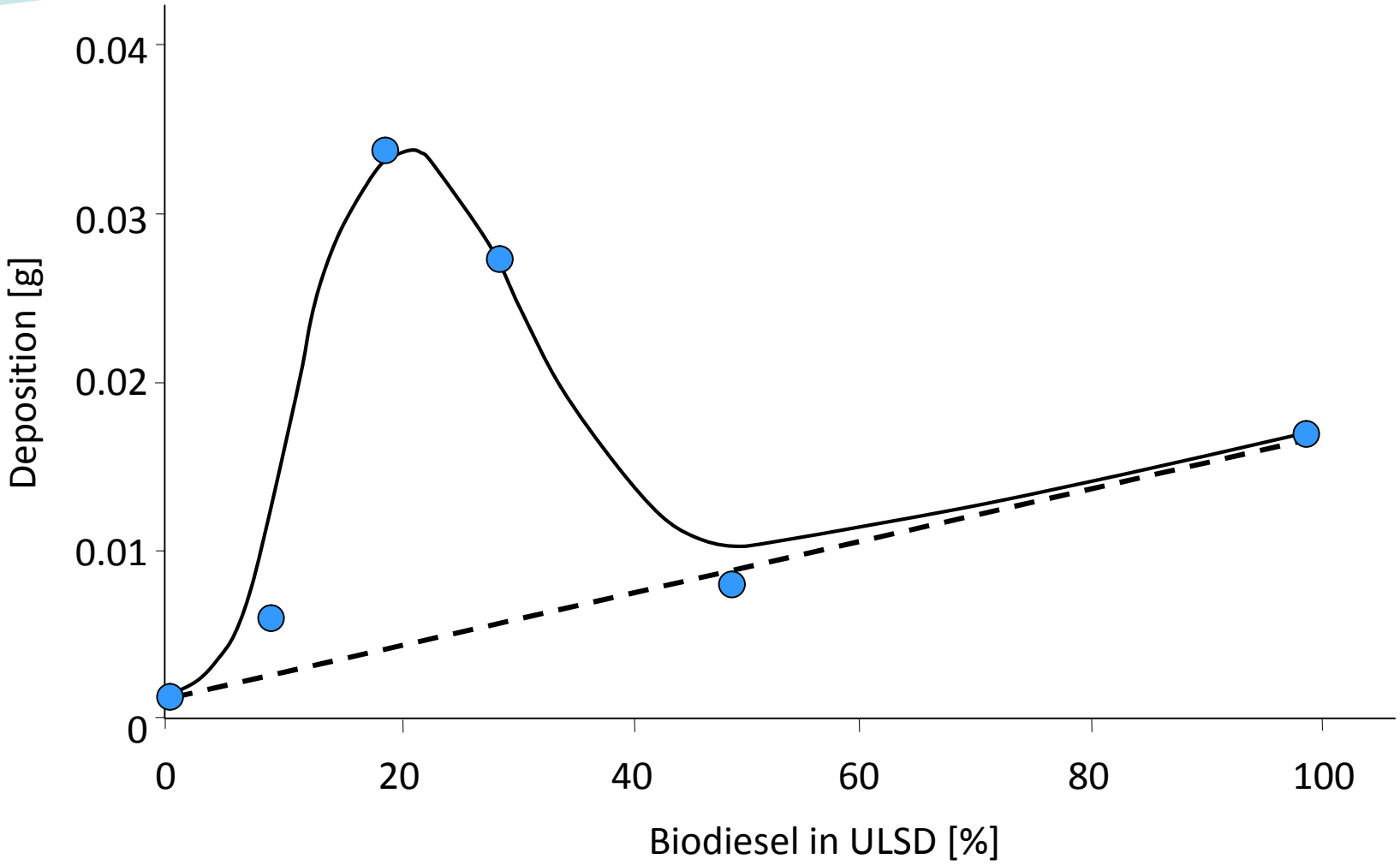


Sedimentation Occurs when Oxidized RME is Mixed with GTL

Indissoluble Oligomers in Blends of GtL and Oxidized RME

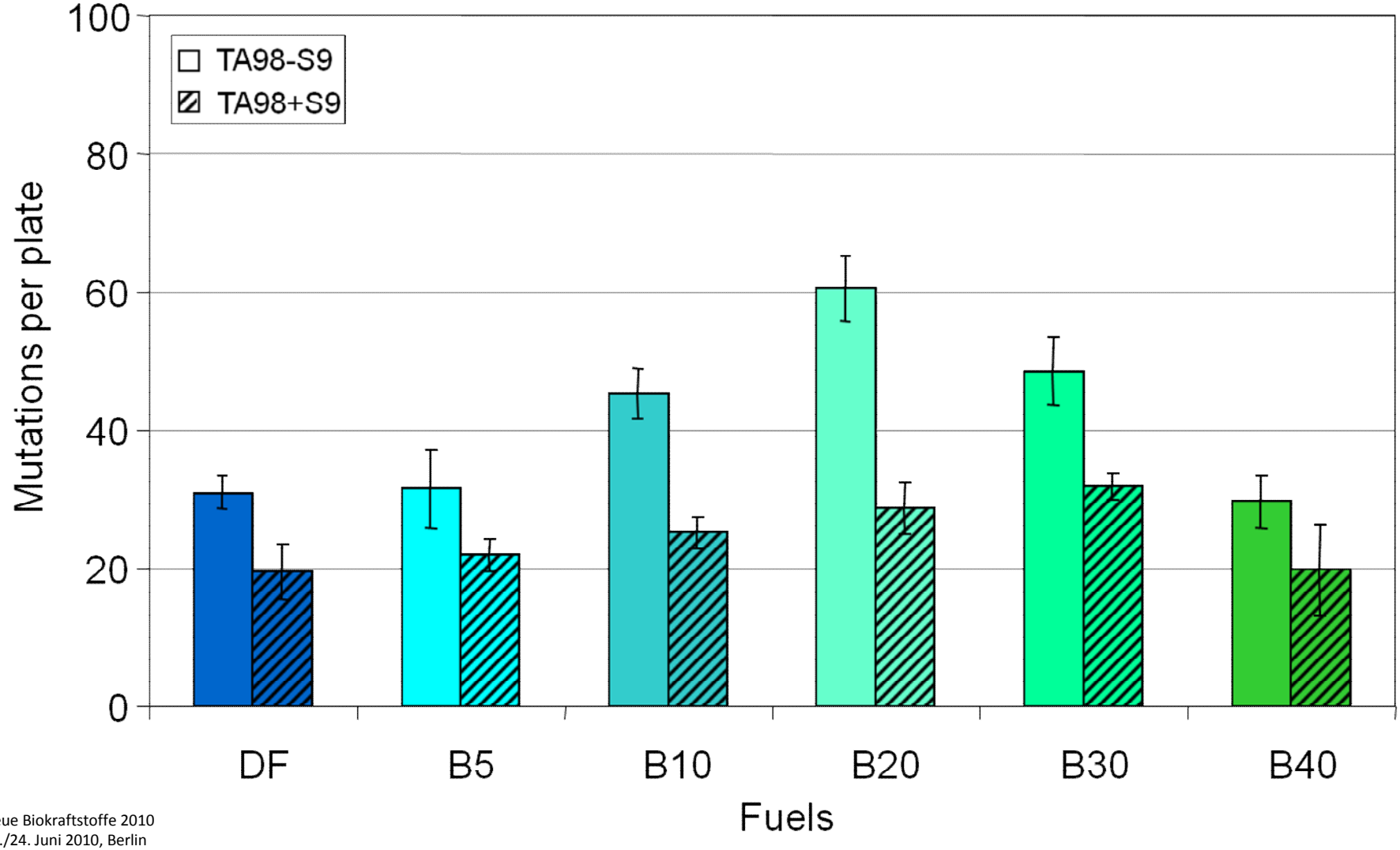


Sediment Formation in DF-Biodiesel Blends



Source: Fang and McCormick, 2006
SAE Paper 2006-01-3300

Mutagenicity of Particulate Extracts in the AMES Test; MAN D08, ETC Test

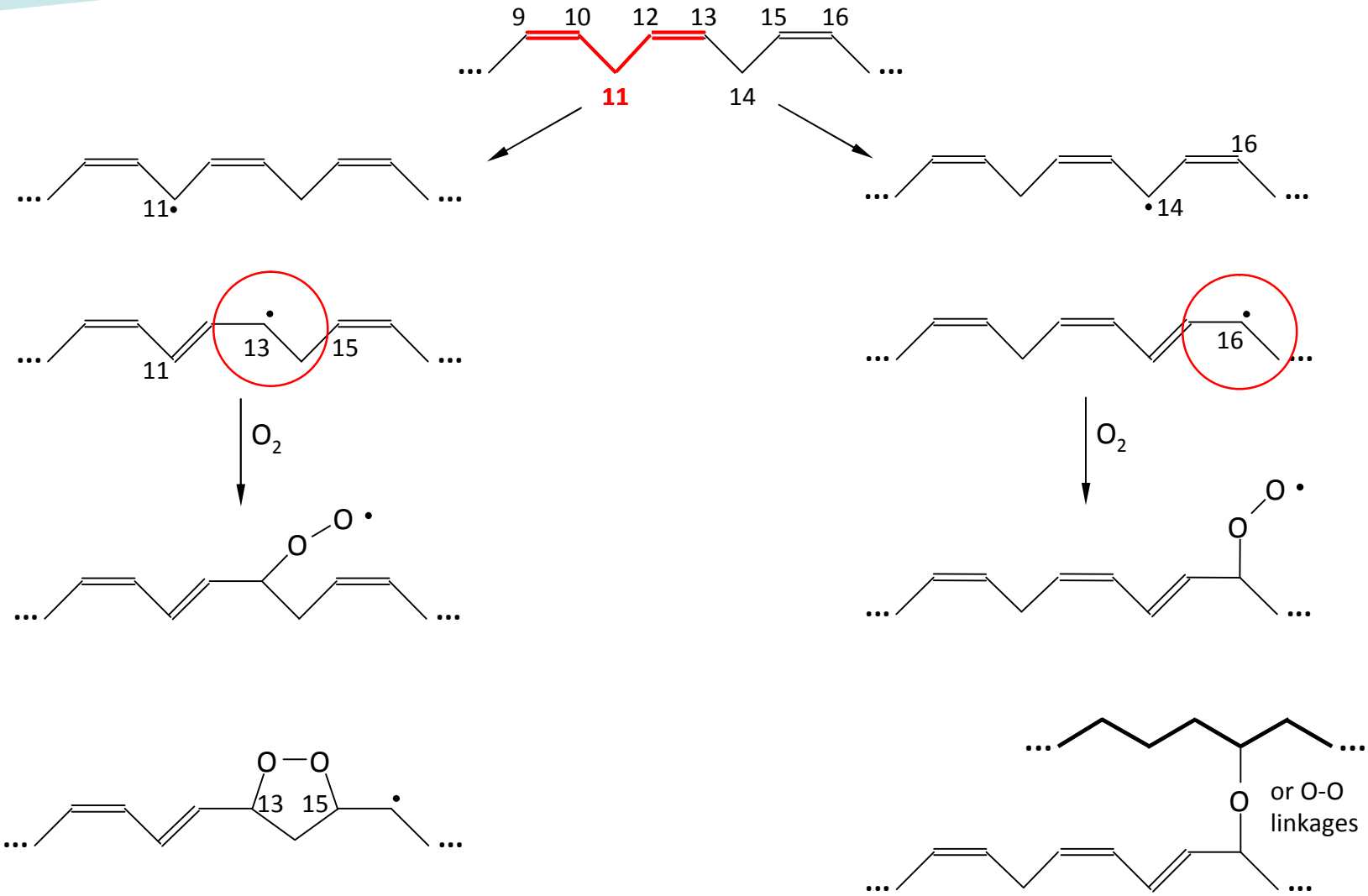


Elementary Analyses

	Oligomers [% wt]	**Biodiesel*** [% wt]
Carbon	65.6	76.99
Hydrogen	9.6	12.27
Nitrogen	0.1	0
Oxygen	24.8	10.6
Sulphur	0	0

*Source: Matthias, C., Melin, T., Beyer, H., Heinzel, A. (2008). Entwicklung eines Biodieselreformers mit Metallmembran für den APU- Einsatz in Nutzfahrzeugen in Kombination mit einer PEM-Brennstoffzelle. AiF-Schlussbericht

Possible Mechanism: Oligomerization



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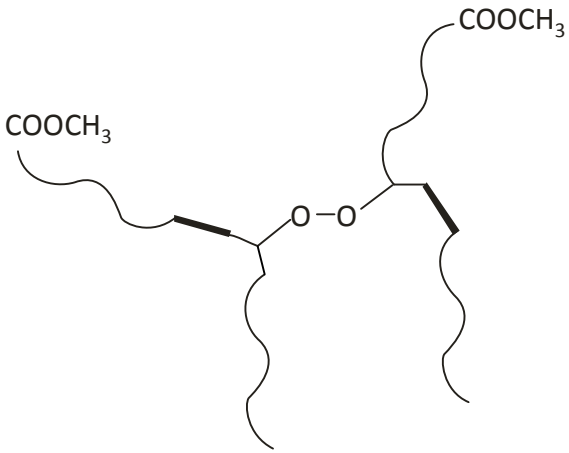
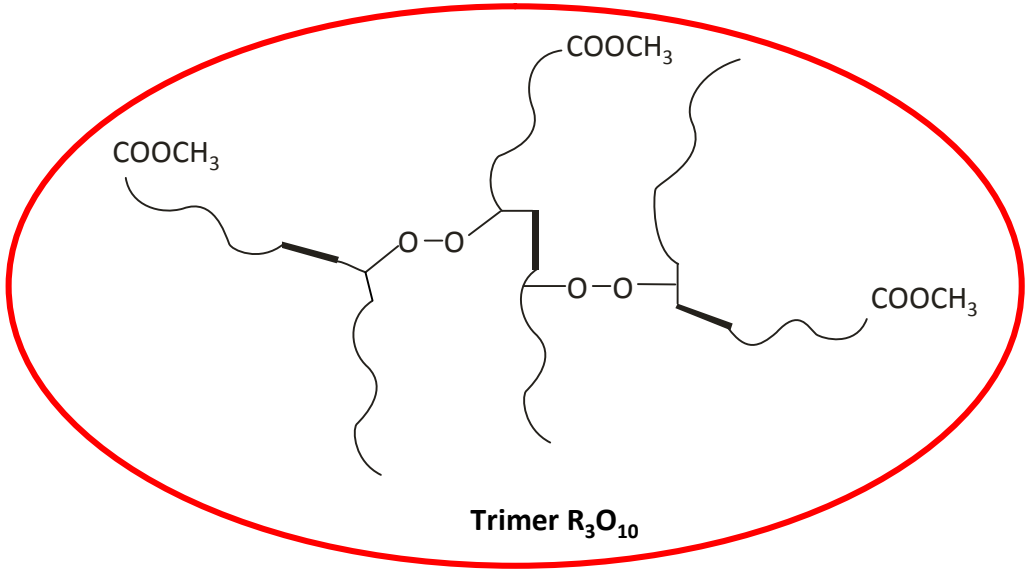
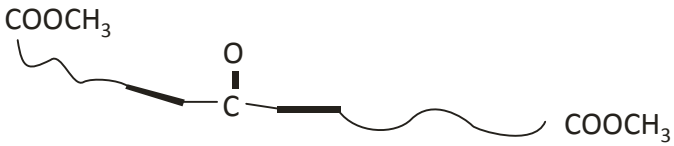
Possible Oligomers



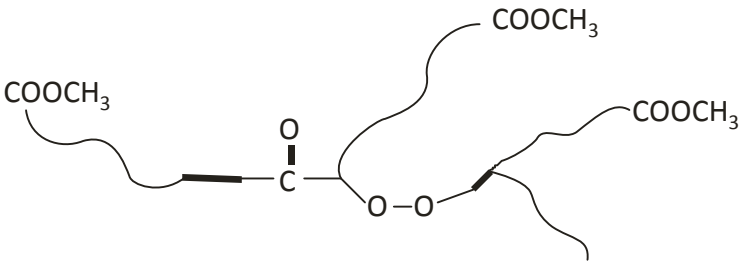
Dimer R_2O_6



Trimer R_3O_{10}



Aldol Dimer R'_2O_5 (R' < R)



Aldol Oligomer R'_2RO_9

Source: Fang and McCormick, 2006
SAE Paper 2006-01-3300

Further Results from the Literature

Precipitate gels were detected by Peyton, McGinnis and Bureman (NALCO), too. These occurred in soy oil methyl ester and mixed FAME in the case of B5 and B20 – not in case of B100.
No sedimentation was found for palm oil methyl ester in every blend (B5 … B100).

For soy oil methyl ester and mixed FAME the precipitate forming compounds were also found in B100; however, in the neat fuels they stayed dissolved and did not precipitate.

The compounds were identified as azelaic acid monomethyl ester (formed by oxidative degradation of methyl oleate) and hexanoic acid (formed by the oxidative degradation of methyl linoleate).

Source: Peyton, K., McGinnis, T., Bureman, P.: Preventing Sediment Formation In Stored Biodiesel Fuel Blends. Biodiesel Magazine, December 2008

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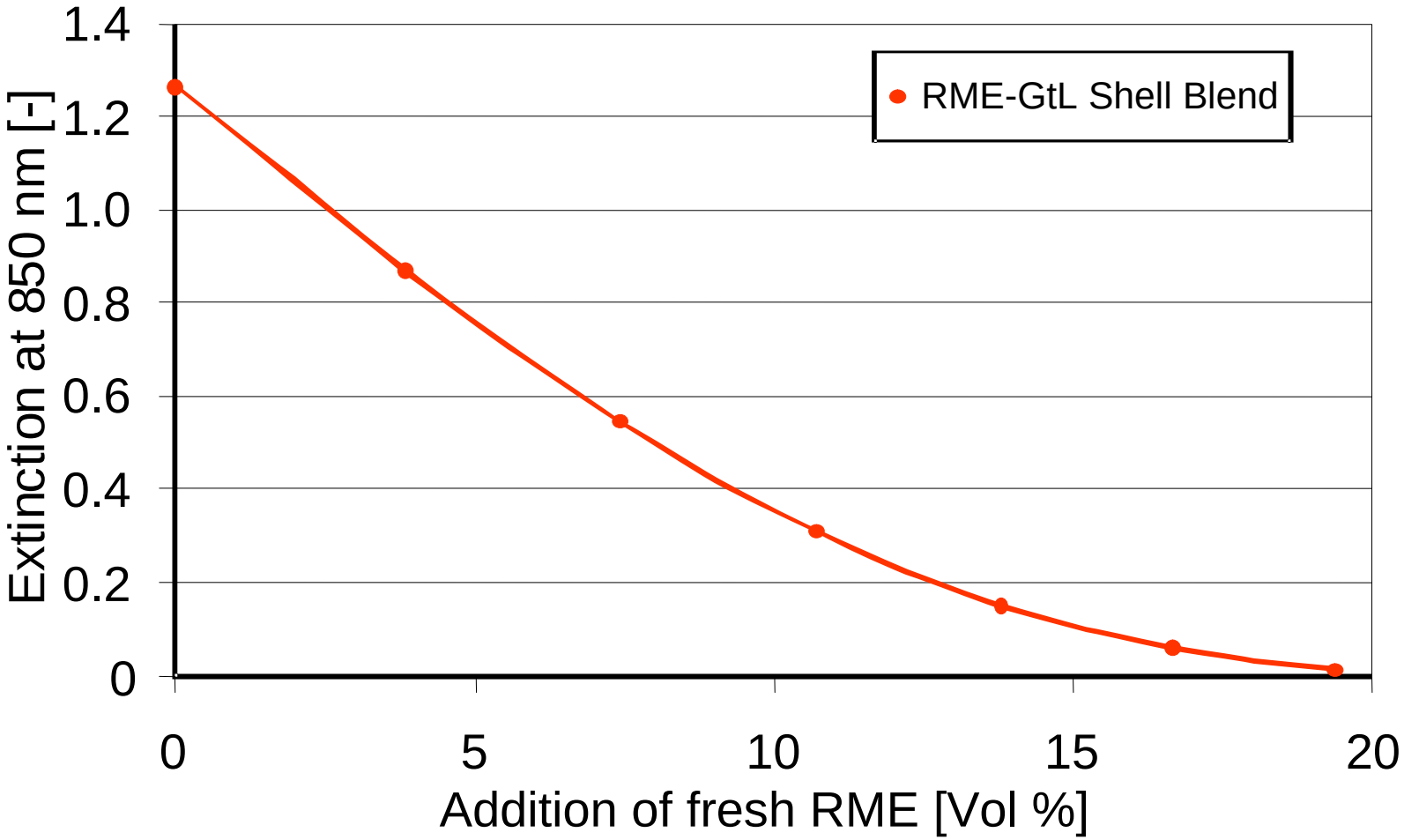
Dissolution of the Sediments

Dissolution of Sediments in B10GTL via Addition of Fresh RME (UV/VIS)



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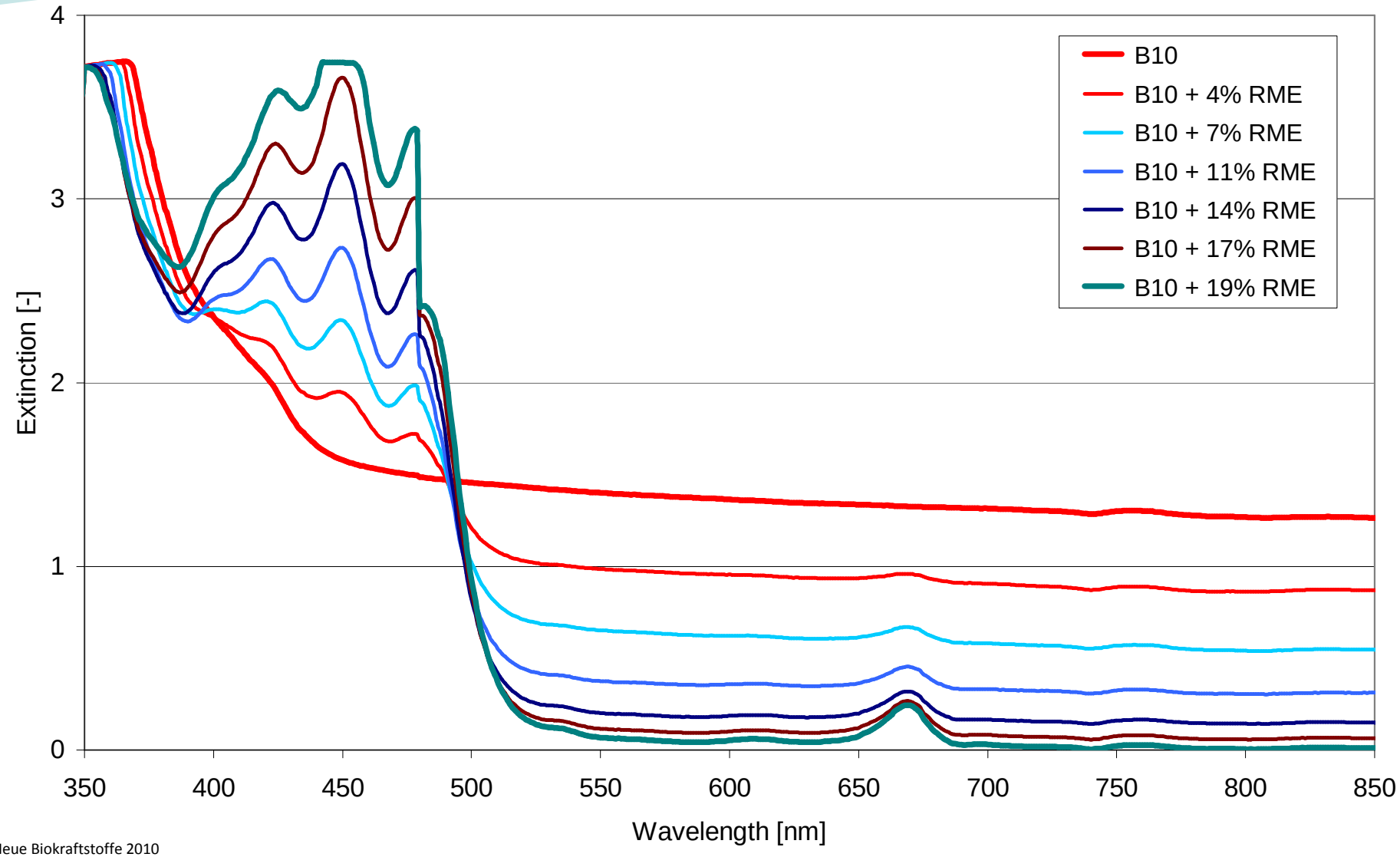
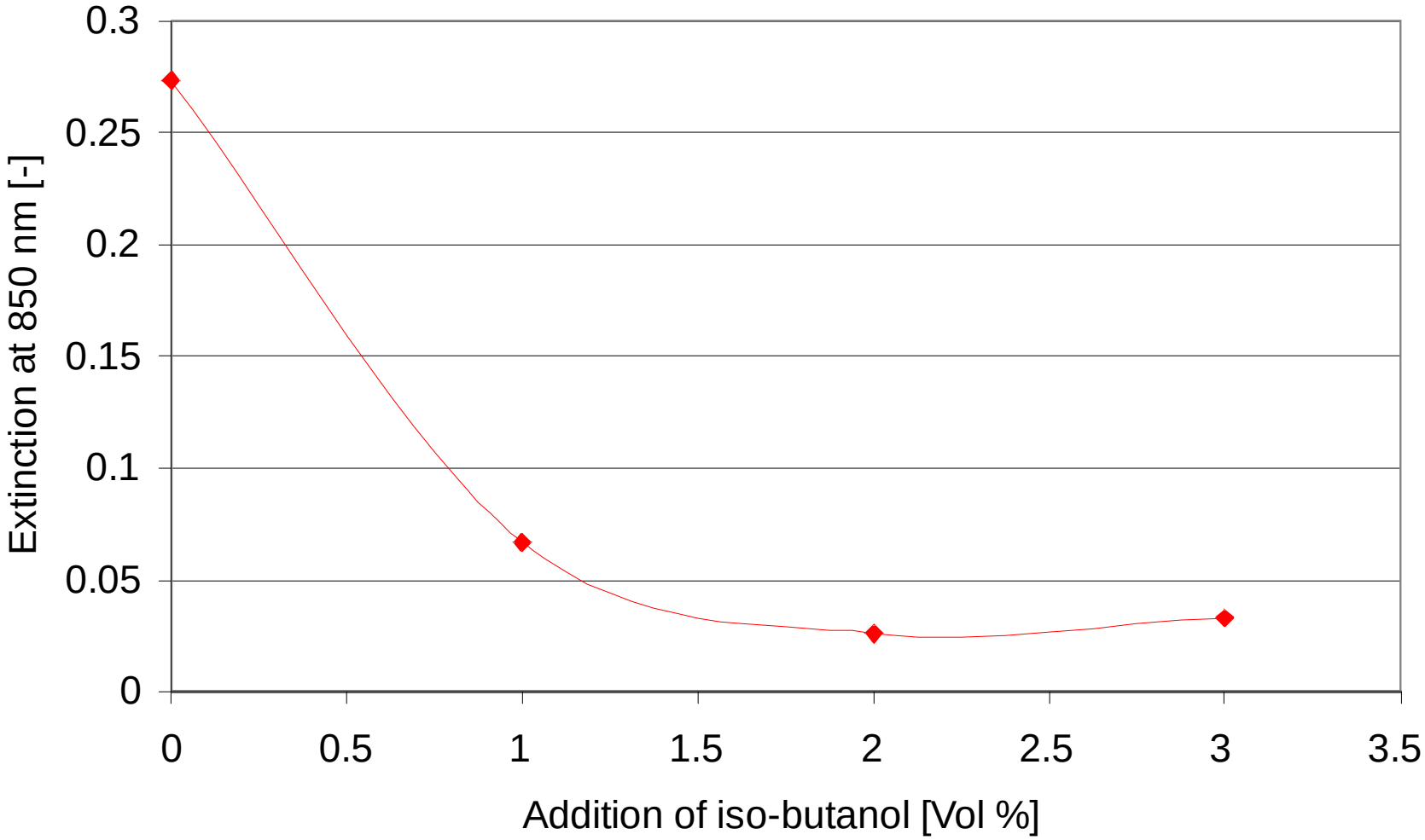


Dissolution of Sediments via Addition of Alcohols



Dissolving the Sediments

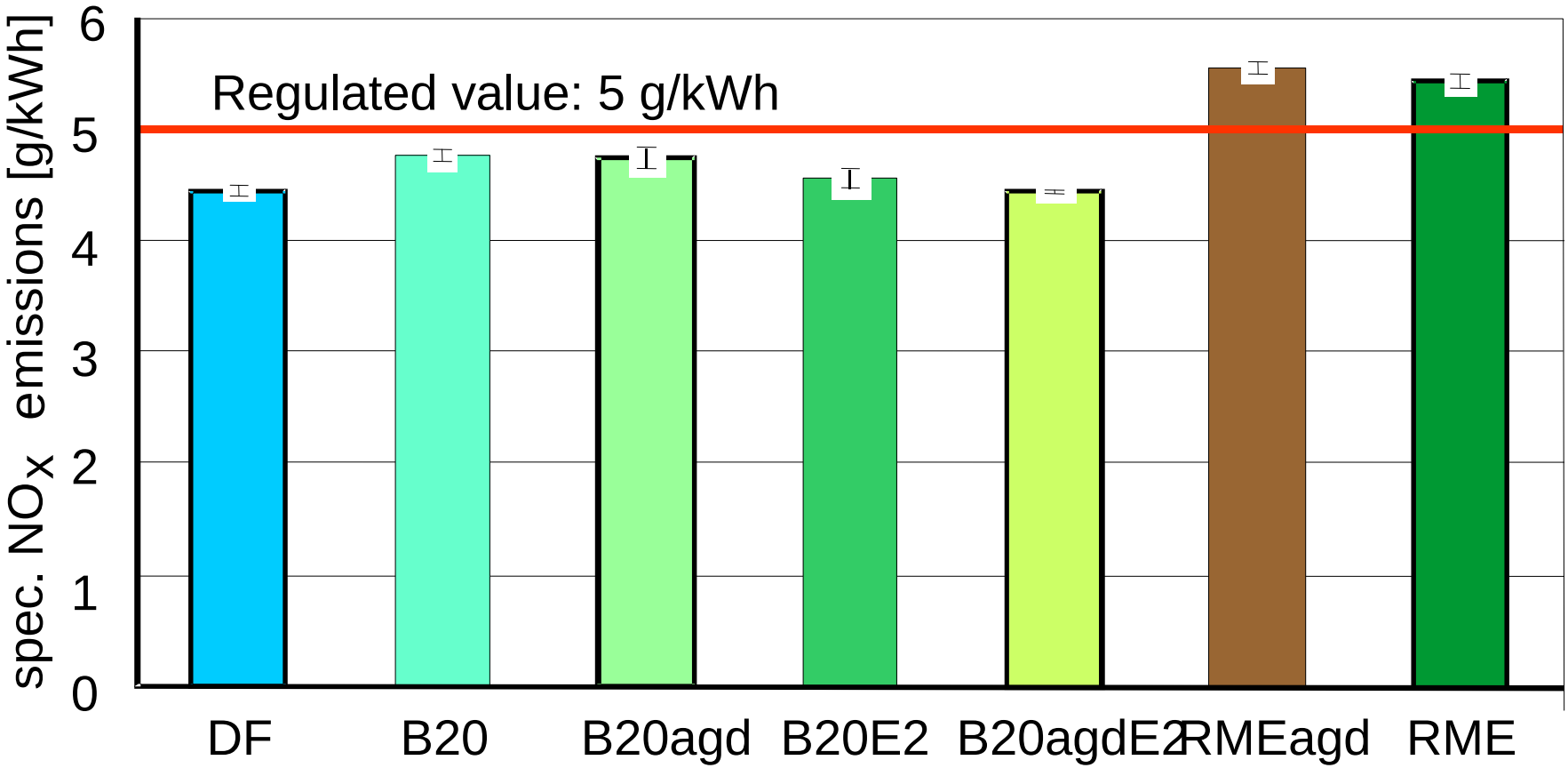
A dissolution of the sediments is achievable via addition of

- ethanol
- butanol
- octanol

This can also be observed when carrying out the filter blocking tendency test IP 387.

An addition of n-butanol to an existing B10 blend proved to be more efficient than an addition of n-butanol to the FAME before the preparation of the B10 blend.

Dissolution of Sediments via Addition of Ethanol – Effects on the Emission of NO_x; OM906, ESC Test



More Results from the Literature

Peyton, McGinnis und Bureman propose to add antioxidants in order to prevent sediment formation.

Source: Peyton, K., McGinnis, T., Bureman, P.: Preventing Sediment Formation In Stored Biodiesel Fuel Blends. Biodiesel Magazine, December 2008

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Biodiesel: Demands of engine manufacturers, fuel producers, consumers, and the society, which may lead to changes in oil composition, processing, and utilization

Results of the Biodiesel Workshop, Wuhan, 2007

Plant oil composition

- Boiling (start) temperature must be brought down ⇨ chain lengths 12…16
- Melting point (resp.: CFPP) should be low enough ⇨ non-saturated fatty acids
- No polymerization ⇨ 1 or 2, not 3 double bonds

⇨ C12:1 … C16:2

Processing

- Low phosphorus content

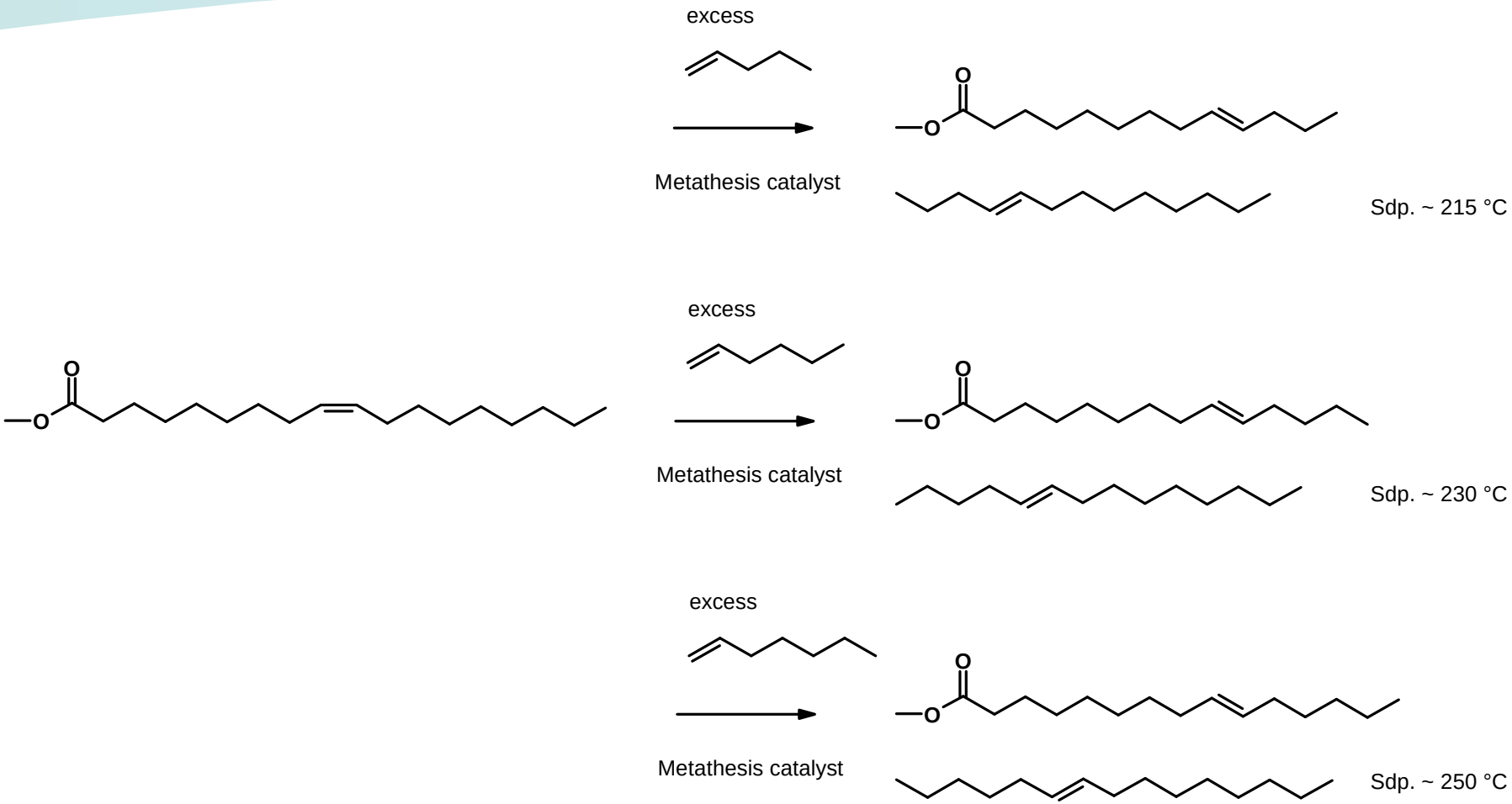
Environment and health

- Low summer smog formation potential
- Low mutagenic potency
- Low cytotoxic effects

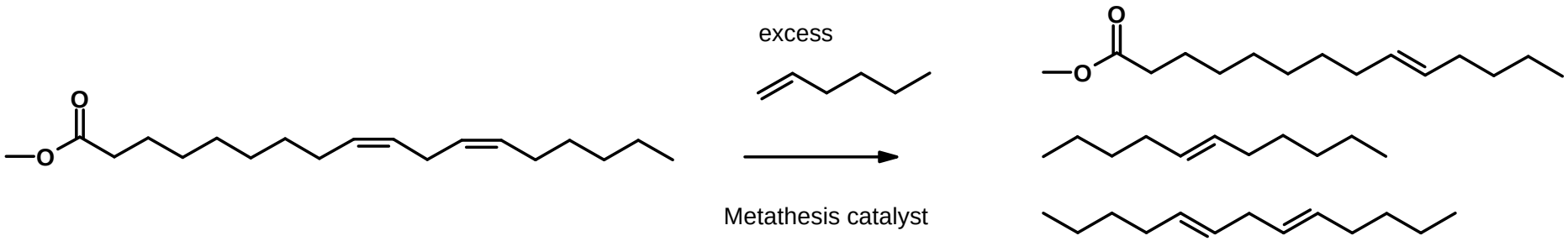
Further demands

- Biotechnical methods for transesterification?
- Alternative pathways for utilization of glycerol?

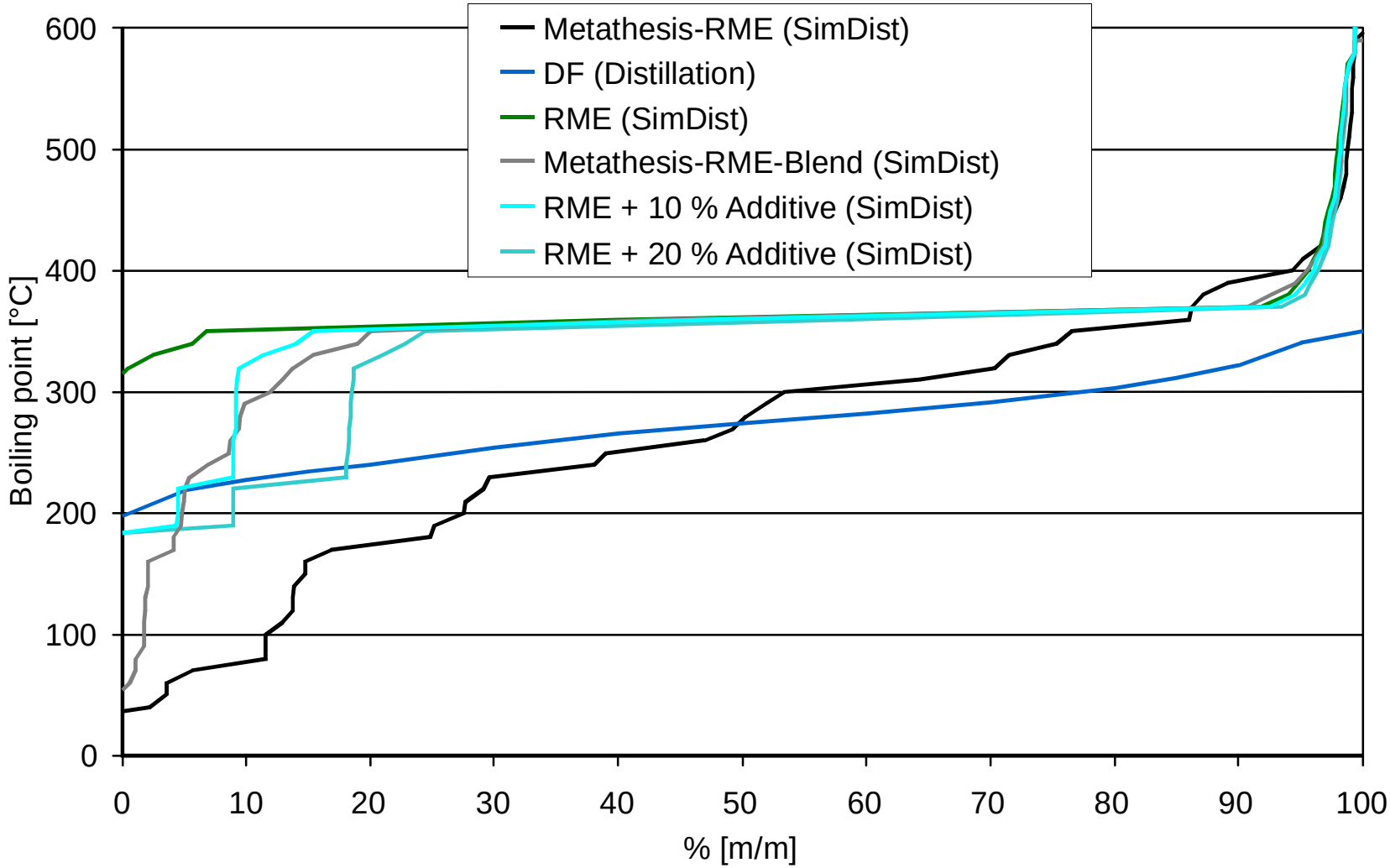
Schematic of the Cross-Metathesis of Oleic Acid Methyl Ester for the Formation of New Biodiesel Blends



Schematic of the Cross-Metathesis of Methyl Linoleate for the Formation of Biodiesel Compounds with Very Low Boiling Point



Influence of Metathesis Products and Additives on the Boiling Behaviour of Diesel Fuels



Thank you very much for your kind attention!

Acknowledgement:
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