

6. Internationaler Fachkongress für Biokraftstoffe
01./02.11.2008 in Berlin

Qualitätssicherungsmaßnahmen zur Oxidationsstabilität von Biodiesel (B7)

Das No-Harm-Projekt der AGQM

- Hintergrund
- Die No-Harm-Kriterien
- Prüfergebnisse
- Weiterführung: „Relative Wirksamkeit“

Arbeitsgemeinschaft Qualitätsmanagement Biodiesel e.V.



Description of the Situation

- Reasons of product safety require that the mineral oil industry submit proof that any additive to mineral oil Diesel meets the no-harm criteria. **This not only covers additives which are added to the mineral oil product directly but also additives in the blending component.**
- The addition of flow improvers as blending component in Biodiesel is completely excluded in Germany at present, and only BHT has been approved as oxidation stabiliser by the oil industry.
- France has enacted a regulation which expressly requires the addition of 1000 mg BHT/kg (other additives can be used, if the same effect is obtained).
- Mineral oil companies fear the by the use of high dosages of stabilisers unsuitable FAME could be “brightened”.
- Requirements for FAME as blend component are described as a strongly recommendation in DIN 51628:
 - Stabilisation is recommended in general (minimum dosage defined)
 - Target: 8 h oxidation stability of the FAME
 - The permissible maximum of oxidation stabilizers is limited.
 - The additive has to comply no-harm criteria.
 - (Min.) dosage of stabilisers should be calculated based on relative efficiency (against BHT).

Arbeitsgemeinschaft Qualitätsmanagement Biodiesel e.V.

Background

DIN 51628:2008-00

(General Requirements and Test Methods)

Tabelle 1 — Allgemein anwendbare Anforderungen und Prüfverfahren

Eigenschaften (Properties)	Einheit (Unit)	Grenzwerte (Limits)		Prüfverfahren ^a (Test Methods)
		Minimum	Maximum	
Aussehen		Klar und trübungsfrei bei Temperatur		Visuelle Begutachtung
Oxidationsstabilität	g/m ³		25	DIN EN ISO 12205:1996-11
Oxidationsstabilität ^j	h	20,0		DIN 51627-2:2008-08

Literaturhinweise (References)

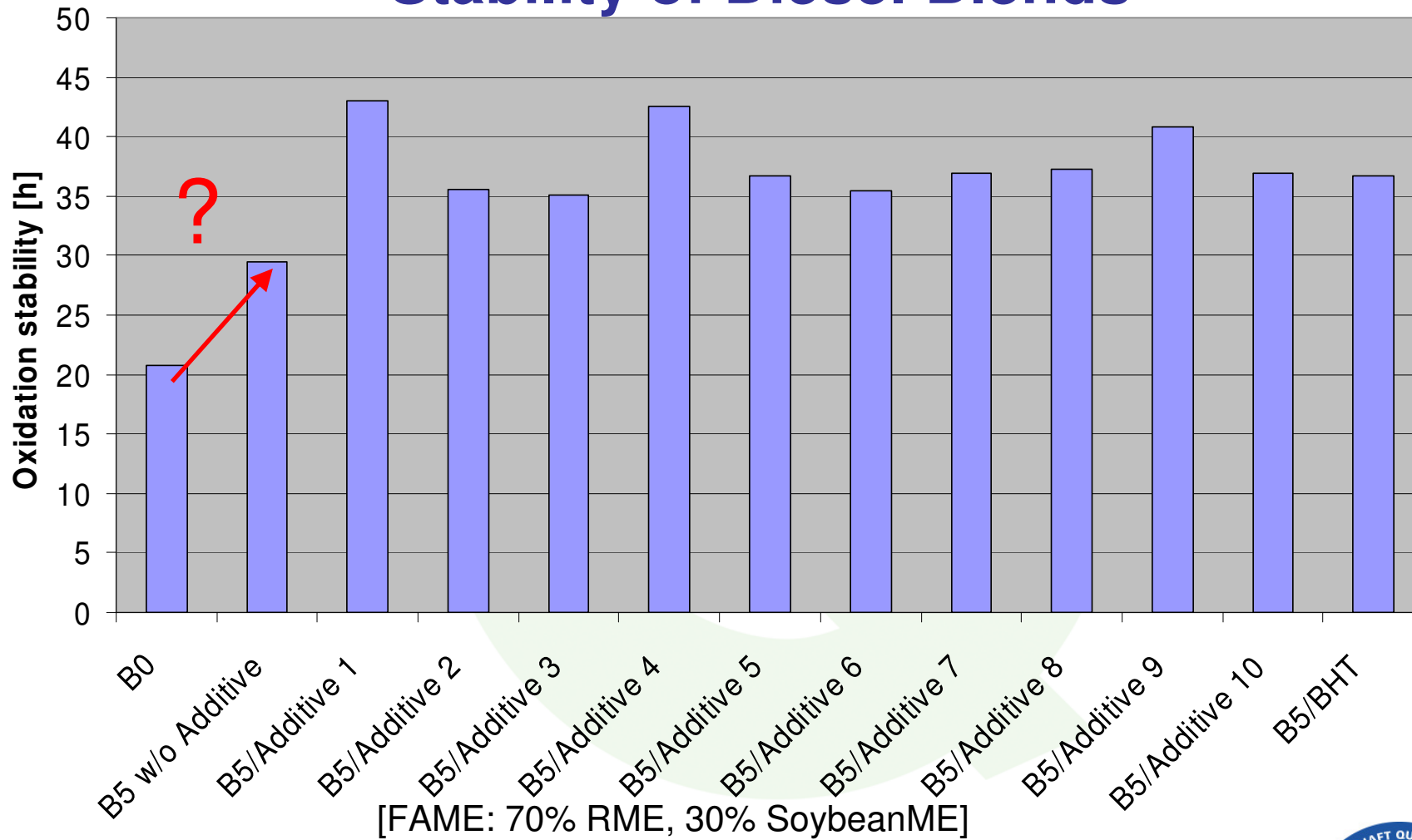
...

- [8] AG QM Fachbericht, *Bestimmung der No-Harm Eigenschaften und relativen Wirksamkeit von Oxidationsstabilisatoren für Fettsäuremethylester als Kraftstoffkomponente*, herausgegeben 2008 durch und zu beziehen bei der Arbeitsgemeinschaft Qualitätsmanagement Biodiesel e.V. (AGQM), Claire-Waldorf-Straße 7, 10117 Berlin, Tel (030) 31904-433, Fax (030) 31904-435, email: info@agqm-biodiesel.de, ISBN 978-3-00-024859-7

Arbeitsgemeinschaft Qualitätsmanagement Biodiesel e.V.



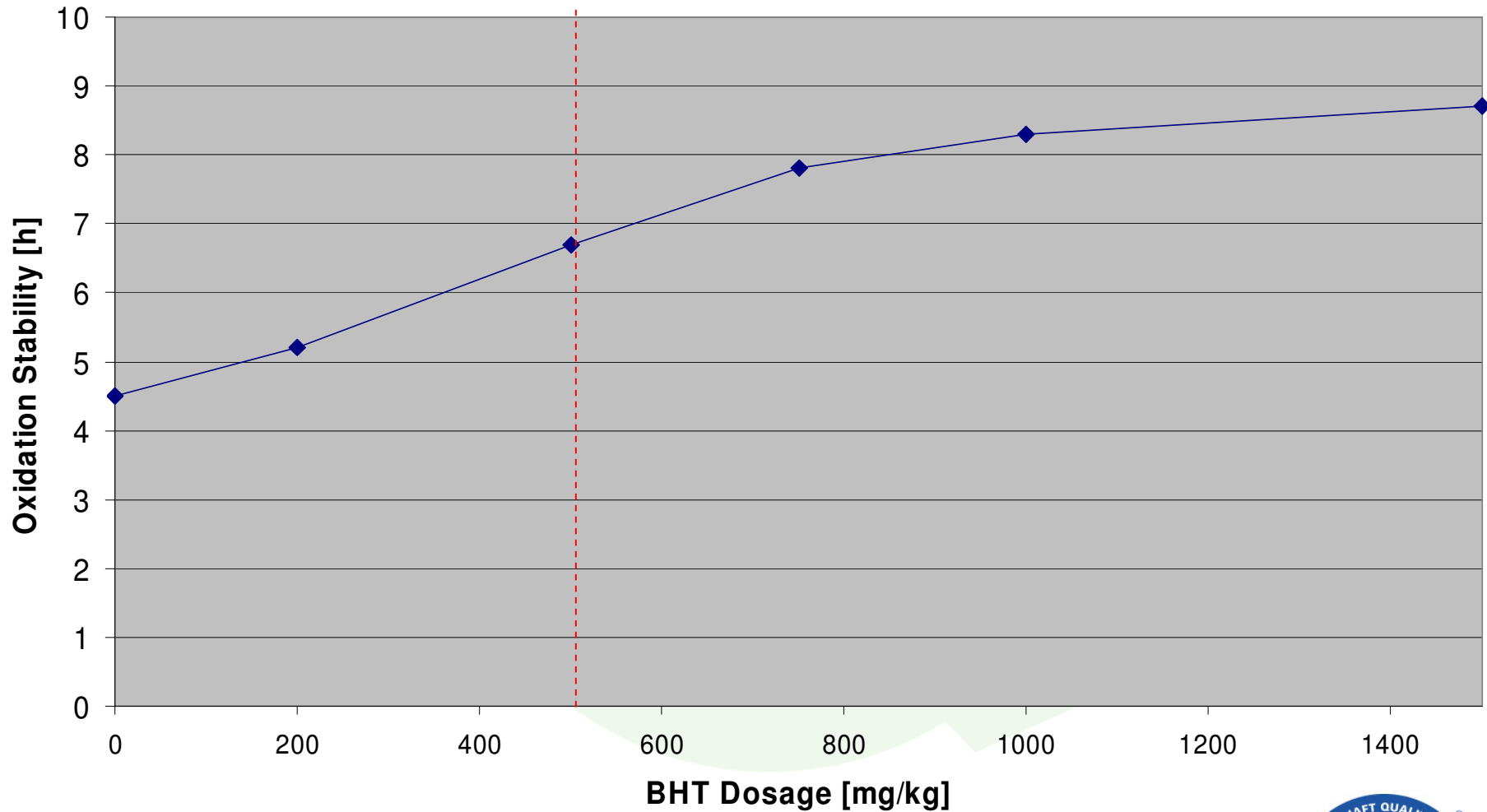
Impact of FAME and Stabilisers on Oxidation Stability of Diesel Blends



Arbeitsgemeinschaft Qualitätsmanagement Biodiesel e.V.



Behaviour of SoybeanME using BHT as Additive



Arbeitsgemeinschaft Qualitätsmanagement Biodiesel e.V.

02/12/2008

Haupt: Das No-Harm-Projekt der AGQM (Oxidationsstabilisatoren, FAME für B7)



AGQM Projects on Oxidation Stabilisers

<p>May 2007 to November 2007</p>	<p>Evaluation of Oxidation Stabilisers for Biodiesel <i>(B100)</i></p>	<ul style="list-style-type: none"> • Test for minimum requirements • Comparative studies in different Biodiesel matrices • Partly in presence of oxidation accelerating traces of copper • Interaction tests (different stabilisers) • Effect of stabilisers in FAME on the oxidation stability of the mineral oil Diesel fuel blends (small part)
<p>2008 (will be repeated on demand)</p>	<p>Evaluation of Oxidations Stabilisers for FAME for Compliance with No Harm Criteria when used as Blending Component in Diesel Fuel</p>	<ul style="list-style-type: none"> • Compliance with predefined minimum requirements • XUD9 test according to CEC F-23-1-01 • DGMK Filtration test 663 • Test for engine oil compatibility (based on DGMK 531-1)
<p>2008 (will be repeated on demand)</p>	<p>Evaluation of the Relative Efficiency ...</p>	<ul style="list-style-type: none"> • Makes it possible to determine a relative value for the efficiency in case of the use of FAME as blend component compared to that of 3,5-di-tert-butyl-4-hydroxy-toluene (BHT)

Arbeitsgemeinschaft Qualitätsmanagement Biodiesel e.V.



Basic Fuels for the Tests

- Diesel fuel without FAME according to DIN EN 590 with summer specification. In order to ensure that this requirement is fulfilled, certified reference Diesel fuel is used on principle.
- The FAME component is a mixture of 70 % rapeseed oil methyl ester and 30 % soybean methyl ester according to DIN EN 14214 (without consideration of oxidation stability); fatty acid composition as follows:

Fatty Acid	Minimum (m/m)	Maximum (m/m)
< C16		1%
C16:0 / Palmitic acid		7%
C18:0 / Stearic acid		3%
C18:1 / Oleic acid	47%	52%
C18:2 / Linolic acid	28%	32%
C18:3 / Linolenic acid	8%	9%
> C18		3%

Arbeitsgemeinschaft Qualitätsmanagement Biodiesel e.V.



Minimum Criteria

- A **detailed application directive** is available which describes all relevant technological requirements to ensure safe application.
- If the application-specific rate of addition is maintained, the product does **not change to another water pollution hazard category or other labelling requirement features of the Biodiesel**.
- The required oxidation stability of the FAME composition according to the project is obtained with **rates of addition not higher than 1200 mg/kg FAME**. At the applicable concentration, the Biodiesel, at 20 °C, remains **clear and without precipitation**.
- The **ash content of the additive** is not more than 2 mg/kg FAME related to the rate to be applied.
- The **flash point of the FAME** composition with stabiliser added shall not be lower than 100 °C (as when measured according to Pensky-Martens).
- There are no obvious **unfavourable interactions with the other tested oxidation stabilisers** or the interactions have clearly been specified and can therefore be avoided by suitable action or restriction of action.

Arbeitsgemeinschaft Qualitätsmanagement Biodiesel e.V.



XUD9-Test according to CEC F-23-1-01

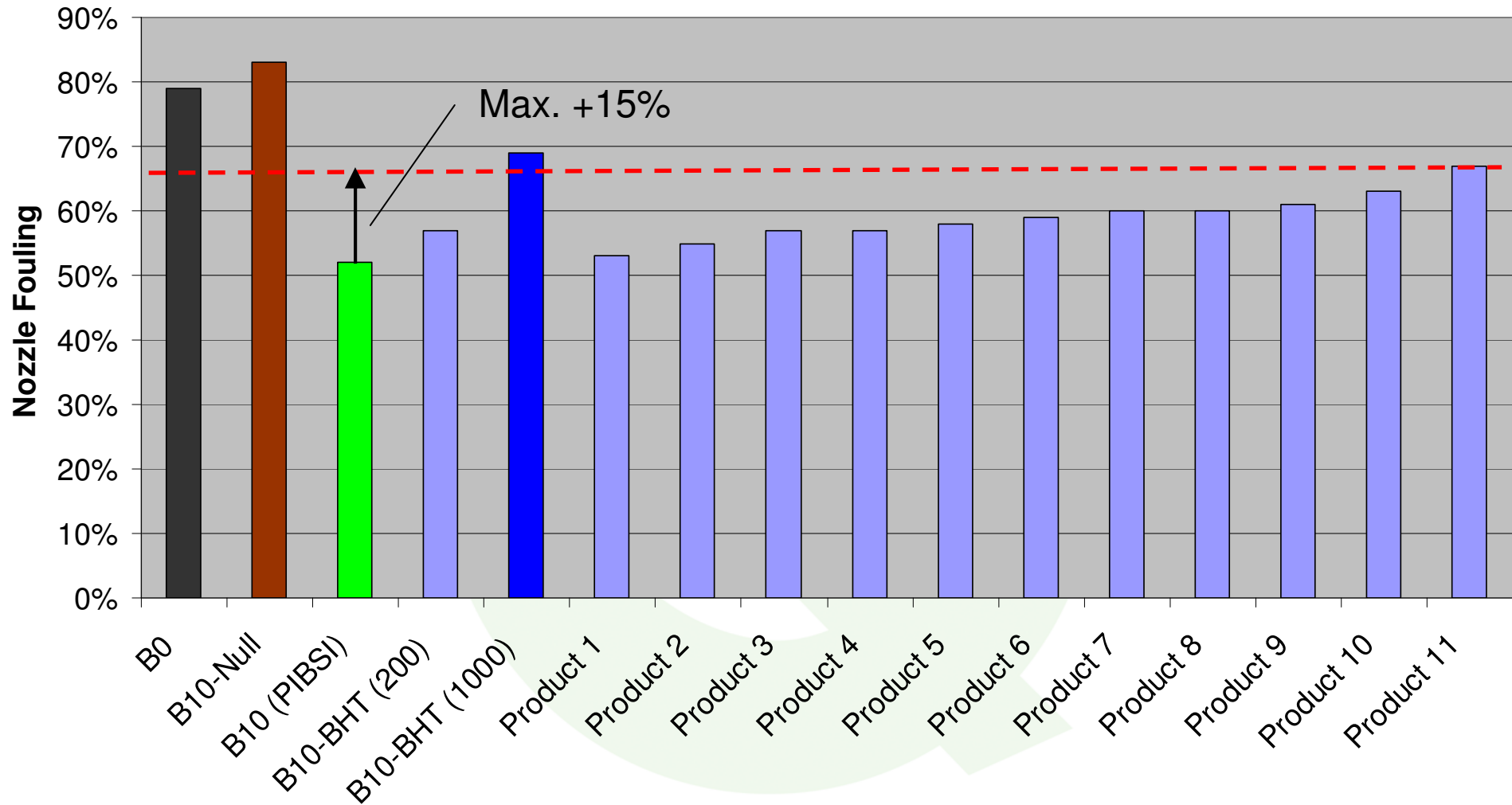
- This test method is designed to evaluate the **capability of a Diesel fuel to control the formation of deposits on the injector nozzles** of an Indirect Injection Diesel engine (airflow rig complying with ISO 4010). Results of tests run to this method are expressed in terms of the percentage **airflow loss** at various injector needle lift points.

$$\eta = 100\% \bullet \frac{(F_{clean} - F_{dirty})}{F_{clean}}$$

- It is known from tests of FAME-containing Diesel fuel that about 80% nozzle fouling occurs if no action is taken. **Even if this is not considered to be critical, no correct evaluation of change due to the use of additive can be made.**
- The core component of a revised concept is the use of a reference fuel to which additional detergents have been added to obtain a state in which nozzle fouling of ca. 60 % is obtained with a B10 blend (without stabilizer).

Arbeitsgemeinschaft Qualitätsmanagement Biodiesel e.V.

XUD9-Test according to CEC F-23-1-01:Results



Arbeitsgemeinschaft Qualitätsmanagement Biodiesel e.V.

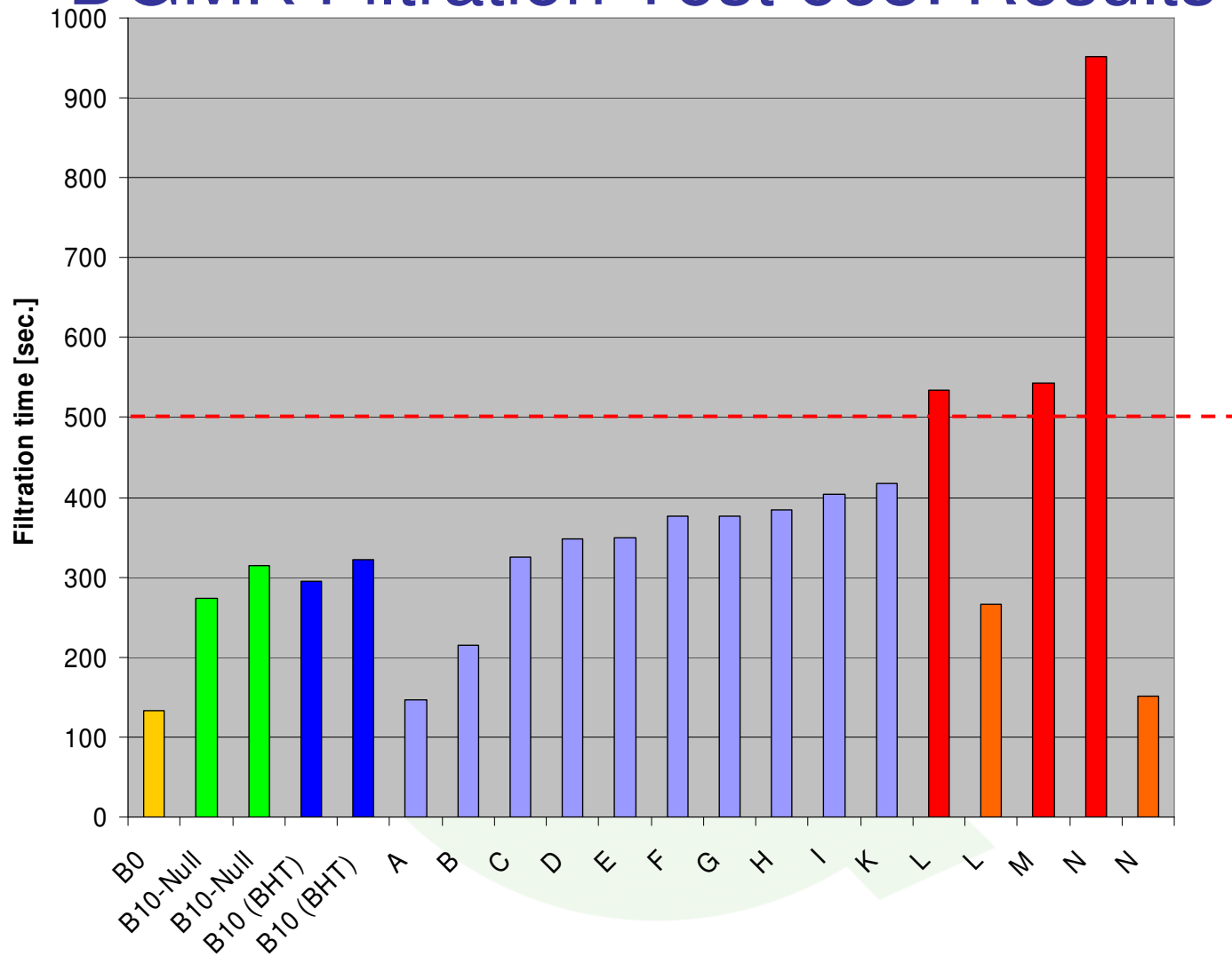
DGMK Filtration Test 663

- The DGMK filtration test 663 is generally applied in the mineral oil industry especially for evaluating the impact of additives. The purpose of the test is to exclude that precipitation caused by additives can block the fuel filter.
- The method is neither standardised in Europe nor on country level and has been modified repeatedly in recent years to reflect improvements of the accuracy of data resulting from the work of DGMK (DGMK project No. 663). The latest revision of the method is used.
- Principle:
A pre-treated sample of 500 ml maintained at 7 °C for 24 h is filtered at a pressure of 200 mbar (absolute) using a prescribed vacuum filtration device and prescribed filter media.

Arbeitsgemeinschaft Qualitätsmanagement Biodiesel e.V.



DGMK Filtration Test 663: Results



Arbeitsgemeinschaft Qualitätsmanagement Biodiesel e.V.

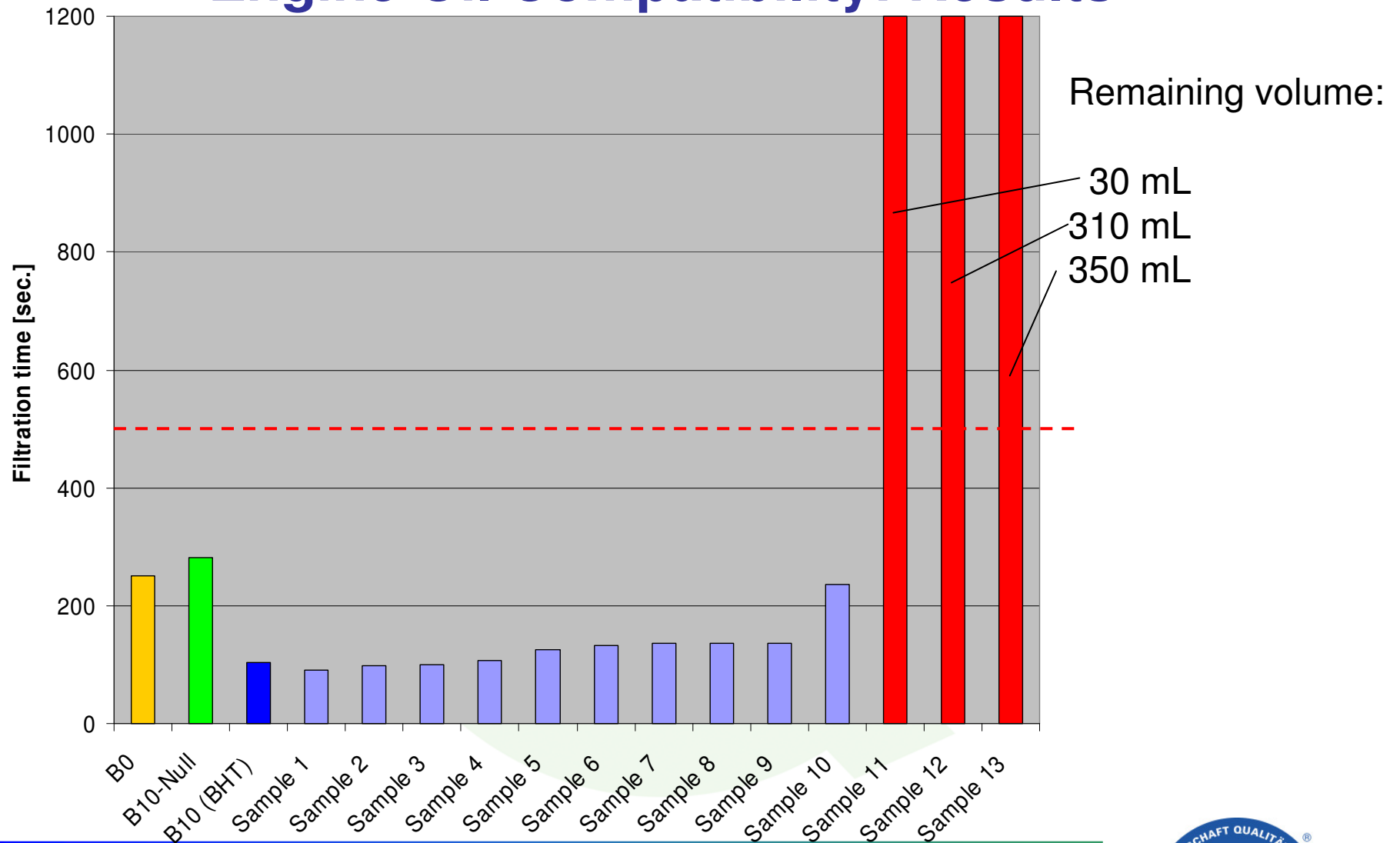


Engine Oil Compatibility on the Basis of DGMK 531-1

- The fuel system of Diesel vehicles is such that small amounts of engine oil enter the Diesel fuel system. In some cases it has been observed that reactions occurred between mineral oil components and the additives contained in the Diesel fuel, which caused clogging of fuel filters and consequent failure of the vehicle.
- The test method according to DGMK531-1 should detect and help evaluate reactions between engine oil and Diesel fuel additives which can cause clogging of filters. The method was developed for testing lubricity additives and will now be applied (in a modified way) to the engine oil compatibility of stabilisers in blends containing FAME
- **Principle:**
The reference engine oil is heated to 40° C and then mixed with the test additive in a ratio of 10 parts engine oil : 1 part stabiliser. After cooling to room temperature, Diesel fuel is added to the additive/oil mixture, and this mixture conditioned at 90° C for 3 days. After subsequent cooling to room temperature, the mixture is evaluated visually and with the DGMK Filtration Test 663.

Arbeitsgemeinschaft Qualitätsmanagement Biodiesel e.V.

Engine Oil Compatibility: Results



Arbeitsgemeinschaft Qualitätsmanagement Biodiesel e.V.

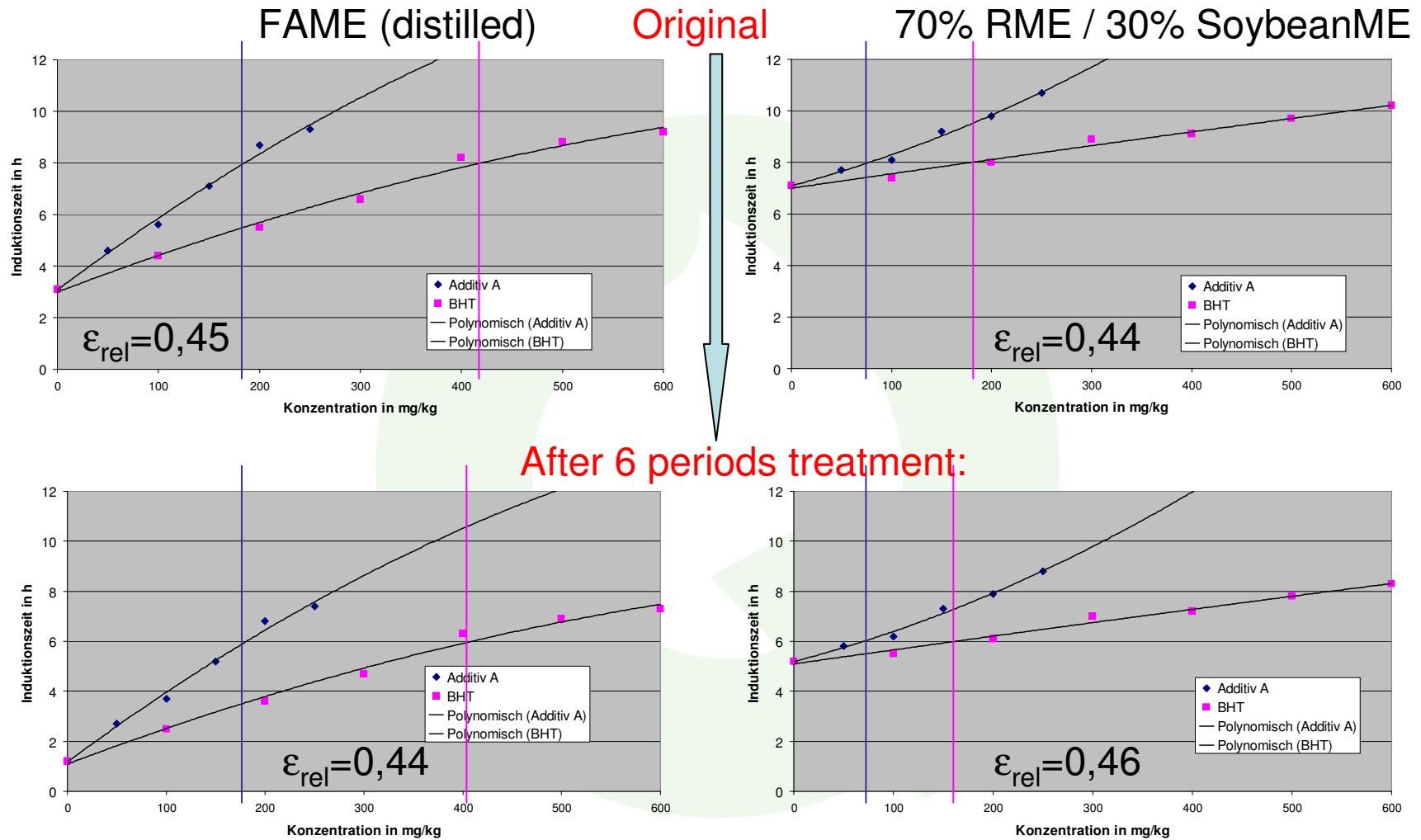


Continuation: Relative Efficiency, Test Scenarios

	FAME 70% RME/30% SoyME (v/v)	FAME 70% RME/30% SoyME (v/v), distilled
Without Ageing	Scenario a (Intersection with 8 h-line)	Scenario c (Intersection with 8 h-line)
After 6 weeks' Ageing	Scenario b (Intersection with 6 h-line)	Scenario d (Intersection with 6 h-line)

Arbeitsgemeinschaft Qualitätsmanagement Biodiesel e.V.

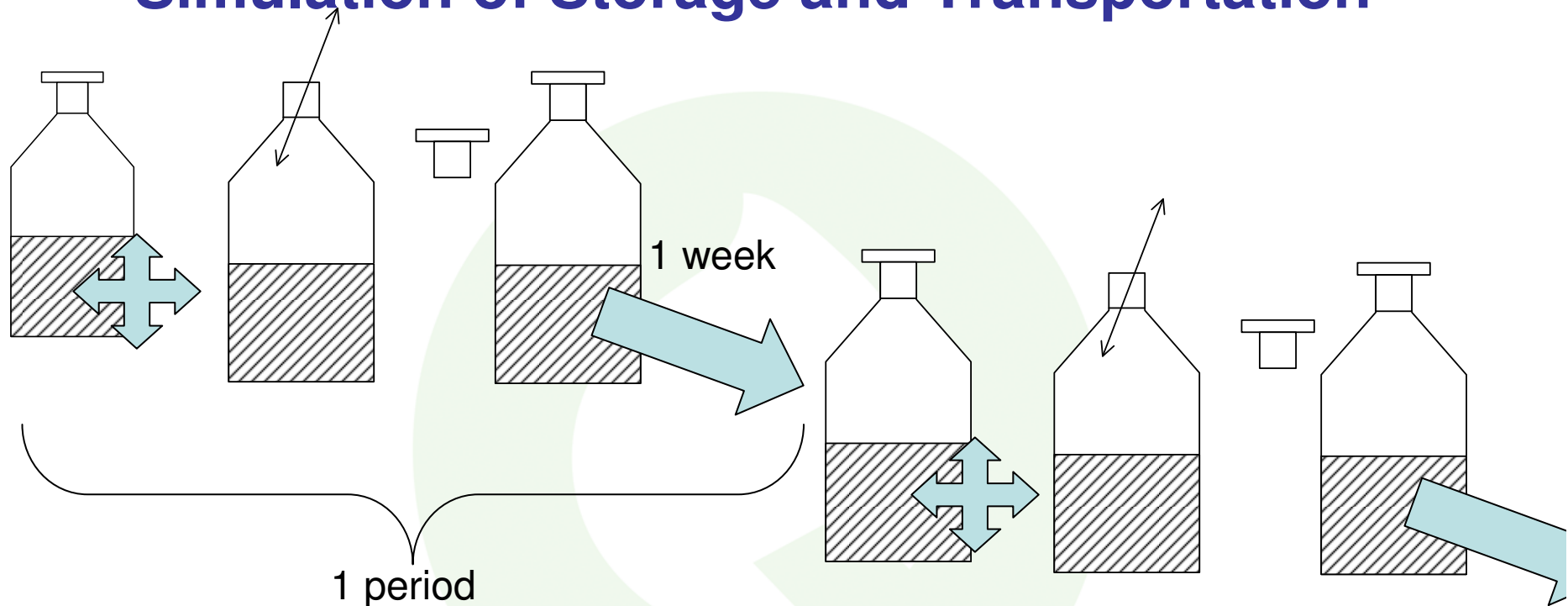
How to Evaluate the Relative Efficiency



Arbeitsgemeinschaft Qualitätsmanagement Biodiesel e.V.



Lab Treatment: Simulation of Storage and Transportation

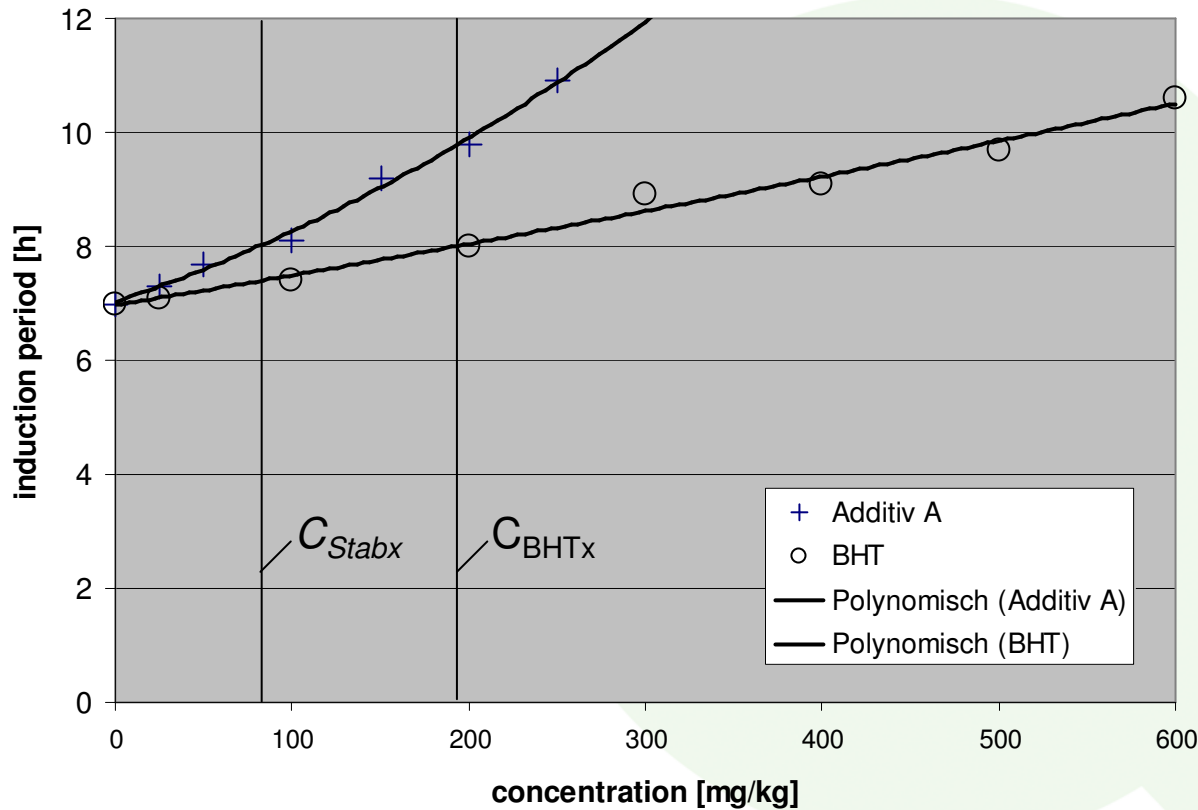


Experience:

6 periods (= 6 weeks) reduce the oxidation stability of a „usual“ FAME by 2 hours

Arbeitsgemeinschaft Qualitätsmanagement Biodiesel e.V.

Relative Efficiency: Calculation (I)



Based on the measuring data, a smoothing function $t_{ind} = f(c_{stab})$ with a polynomial of the second degree is calculated for the tested additive as well as for BHT with

t_{ind} being the induction time h and

c_{stab} being the dosage of the oxidation stabiliser in mg/kg.

Relative Efficiency: Calculation (II)

Relevant for the evaluation of the relative efficiency are x-coordinates of the intersection points of the (linear) smoothing functions with the 8-h-line (scenarios a and c) and/or the 6-h-line (scenarios b and d). The value is considered valid if

- there are at least two measuring points above as well as below the intersection point and
- overall per additive there is one measuring point at the most outside the monotony.
- The relative efficiency ε_{relx} is the relation

$$\varepsilon_{relx} = \frac{C_{stabx}}{C_{BHTx}}$$

with

- C_{stabx} being the concentration of the proband at the intersection point and
- C_{BHTx} being the concentration of BHT at the intersection point.
- The arithmetic mean is calculated from the four values ε_{rela} , ε_{relb} , ε_{relc} und ε_{reld} of the four scenarios.

Arbeitsgemeinschaft Qualitätsmanagement Biodiesel e.V.

Filing of Test Results

No-harm test:

- Non-ambiguous consecutive registration number
- Name of product
- Producer or importer (if the latter places the product on the market)
- Date of entry in the list
- Level of classification (no-harm criteria fulfilled for B10 or no-harm criteria fulfilled B7)
- *List will be published 05/12/2008*

Relative efficiency:

- Non-ambiguous consecutive registration number
- Name of product
- Producer or importer (if the latter places the product on the market)
- Date of entry in the list
- Value ε_{rel} of the necessary dosage of BHT
(on application of the producer/importer the value ε_{rel} can be retained and the public list contains only "value available")
- *Final statements will be published 15/12/2008*

AGQM confirms on request the corresponding registration number.

Arbeitsgemeinschaft Qualitätsmanagement Biodiesel e.V.



Summary

- The No-Harm test program provides security for the use of additives for users, additive producers and the mineral oil companies.
- Critical behaviour of additives can be detected by the defined tests.
- In the most cases the reason for critical filterability are not the active components but solvents or anti-settling components.
- The determination of the relative efficiency makes the use of oxidation stabilisers more reliable and helps to secure a „right“ level of oxidation stability in the final blend.

Contact:

AGQM
Arbeitsgemeinschaft Qualitätsmanagement Biodiesel e.V.
(Association Quality Management Biodiesel reg. Ass.)

Claire-Waldoff-Str. 7
10117 Berlin

Tel.: +49 (30) 31 90 44 33
Fax: +49 (30) 31 90 44 35
e-Mail: j.haupt@agqm-biodiesel.de

Thank you for your attention!

Arbeitsgemeinschaft Qualitätsmanagement Biodiesel e.V.

