Stability and Quality Assessment of Biodiesel using the Chemiluminescence Approach.

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INTRODUCTION: Biodiesel is produced chemically through the trans-esterification of vegetable oils with methanol. The general acronym for all methyl ester based on vegetable and animal oil is FAME (fatty acid methyl ester according to DIN EN 14214). In times of increasing fuel prices, more and more private and commercial diesel vehicle owners are switching to biodiesel.

Biodiesel can be used in its pure form – known as B100 – in suitable engines or as a blend with mineral diesel in any mixing ratio (e.g. B7 with 7% FAME).

PROBLEM OXIDATION: A major disadvantage of biodiesel is poor aging resistance owing to the easy oxidizability of unsaturated fatty acids by atmospheric oxygen (such as all natural vegetable oils). The consequences of oxidation are, on one hand, a breakdown of the biodiesel into short-chained fatty acids, and the formation of indissoluble polymers (gums) on the other. This may result in engine damage. The oxidation of oils and fats by atmospheric oxygen is known as rancidity. Rancid oils and fats are unfit for use.

The fatty acid methyl ester is attacked by radicals (if possible directly next to the double bond) owing to heat, light and other stress factors. The radicals react quickly with the atmospheric oxygen and peroxy radicals are formed. Now the autocatalytic oxidation process (also known as auto-oxidation) can begin. The peroxy radicals are extremely reactive and abstract weakly bonded neighbouring electrons, creating new radicals. The radical concentration multiplies exponentially within a short space of time thanks to this mechanism.

CL-METHOD: The stability of biodiesel can be significantly improved with anti-oxidant additives. These are expensive and should therefore be used as sparingly as possible. ACL Instruments' products enable precise and extremely sensitive characterization of the stability and quality of biodiesel and the stabilizing effects of additives.

The major advantages of the CL-method compared to other commonly applied methods (e.g. Rancimat®, calorimetric methods, PetroOxy®) is the monitoring of a signal directly related to the oxidation reaction and its kinetics; the much higher sensitivity enables to perform experiments even at moderate temperature conditions (far below 110°C); beside stability testing, the CL-method is also well-suited to analyse the quality of oils (e.g. if the tested oils and its ingredients are already damaged by oxidation reactions).

STABILITY TESTING: Tests can in principle be carried out on fatty acids and their derivatives at both isothermal (static) and dynamic temperature profiles. Among other testing conditions (Fig. 2), the testing of the biodiesel oxidation stability at 110°C was performed (Fig. 3).

If oxidation stability is also measured under additional isothermal temperature conditions, OIT can easily be analyzed kinetically (e.g. through the quantification of OIT activation energy and the forecast for static temperature conditions).

QUALITY TESTING: In addition to actual oxidation stability, the quality and oxidation condition of biodiesel products can also be analyzed simply and quantitatively with the Chemiluminescence method by determining the hydro-peroxide concentration with simple short-experiments in inert atmosphere. This procedure is particularly well suited to testing raw materials and production batches.

Fig. 1: Oxidized fatty acid methyl ester (fame) in polyolefin bottles. The distortion of the bottles is due to the oxygen consumption in the bottle volume by the preceding oxidation (results of sub-pressure).

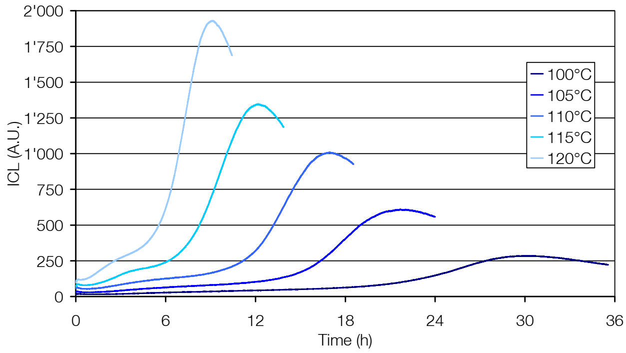

Fig. 2: Testing the stability of biodiesel B7 formulation against oxidation at different isothermal conditions (100..120°C, ΔT = 5°C) in synthetic air.

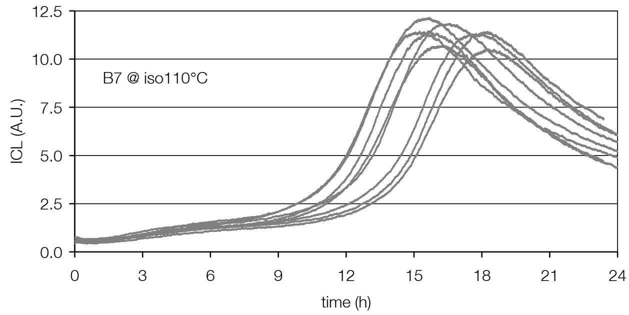

Fig. 3: Set of 8 experiments at iso110°C to test the stability of biodiesel B7 formulation against oxidation in synthetic air.

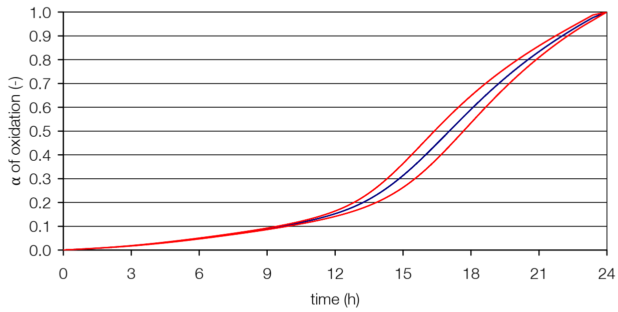

Fig. 4: Reaction progress α_x (n=8, blue curve) of oxidation with confidence intervall (96% confidence, limits are represented by the red curves): commercial biodiesel B7 @ 110°C.

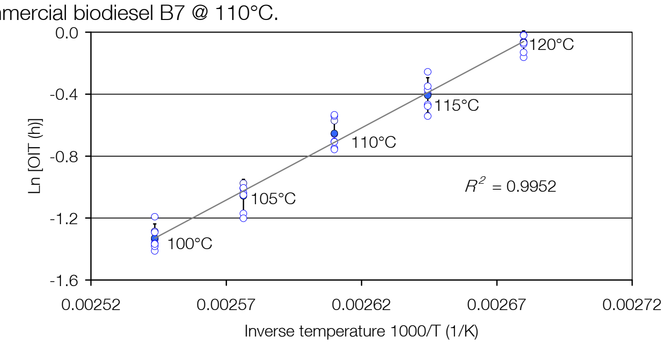

Fig. 5: Arrhenius-diagram of biodiesel B7 OIT's (Oxidation Induction Time) measured with Chemiluminescence at different isothermal conditions in air (n=8 for each temperature condition, white circles). The mean values, the confidence intervals (confidence level 96%) and the trend (linear regression of the mean values) of the OIT data were calculated: there is a very high correlation of the CL-data (R^2 = 0.995), the resulting activation energy of the oxidation onset event is 71.5kJ/mol.

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