Applications

Stability and Quality of Biodiesel

Highly reliable characterization of the oxidation behavior of fatty acid methyl ester and biodiesel to test quality and stability in production, research and development.

Biodiesel is produced chemically through the transesterification 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).

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 neighboring electrons, creating new radicals. The radical concentration multiplies exponentially within a short space of time thanks to this mechanism (simplified illustration Fig. 1).

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 of biodiesel and the stabilizing effects of additives.

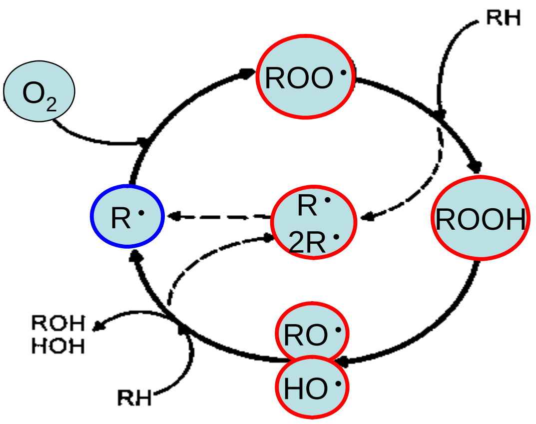

Fig. 1: Simplified oxidation cycle of organic substances.

Stability tests

Tests can in principle be carried out on fatty acids and their derivatives at both isothermic (static) and dynamic temperature profiles. Based on the standard EN 14112 to test the oxidation stability of biodiesel at 110°C, the following measurement results are produced:

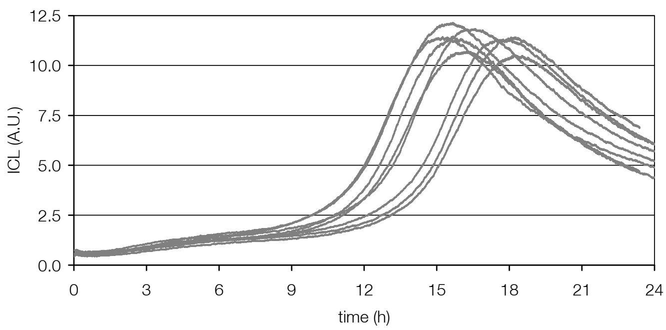

Fig. 2: Time curve of the chemiluminescence of commercial biodiesel B7. Series consisting of 8 experiments under identical conditions (T = 110°C isothermal, t = 24h, Gas = 30ml/min Air, sample weights 98,9..102,3 mg)

The curves of the experiments show a so-called oxidation induction phase – hydroperoxides (ROOH) accumulate in the sample owing to the thermo-oxidative stress of the measurement conditions.

Upon reaching a critical ROOH concentration, the oxidation begins to accelerate auto-catalytically (the intensity of the chemiluminescence emission (I_{CL}) increases significantly). The calculation of the oxidation induction time OIT with the tangential method produces values of 11:16..14:05 (hh:mm, mean value = 12:32, n=8, 99% confidence = 1:30). The CL experiments on biodiesel are easily reproducible and very reliable.

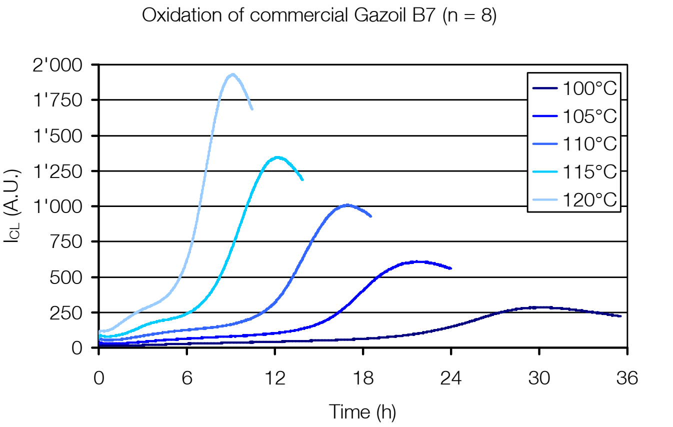

Fig. 3: Oxidation behavior of biodiesel B7 at different static temperature conditions (120..100°C; ΔT = 5°C) with synthetic air.

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

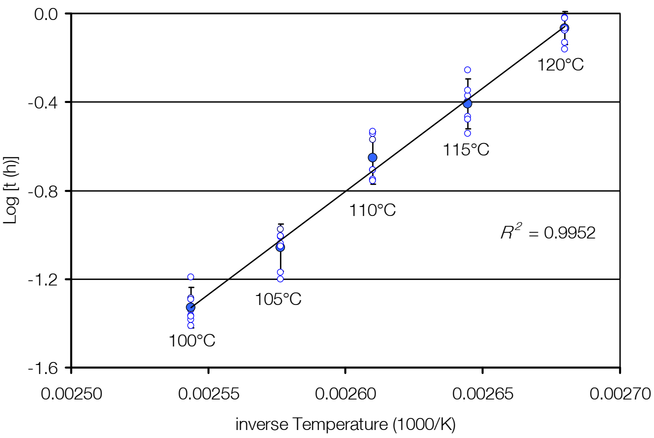

Fig. 4: Arrhenius diagram of the OIT of Biodiesel B7 under different static temperature conditions (n = 8 for each T profile). The regression analysis of the trend increase shows activation energy of 71,5 kJ/mol for the OIT.

Peroxide concentration

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. This procedure is particularly well suited to testing raw materials and production batches.

The hydroperoxide decay can be quantitatively measured through the characterization of samples in a non-oxidizing atmosphere (inert, e.g. nitrogen or argon); the total emission TLI (Total Luminescence Intensity = integral of the CL curve) is directly proportional to the hydroperoxide concentration and provides information on the quality and aging history of the sample analyzed.

Catalysis thanks to transition metals

The oxidation stability of fatty acid methyl ester is strongly influenced by the presence of transition metal ions. Through the presence of even a low concentration of the elements Cu, Fe, Mn, Va, Co, Cr etc. the activation energy of the hydroperoxide decay is so strongly reduced (catalyzed), that the reaction takes place spontaneously at room temperature. The Chemiluminescence method enables these catalytic effects and the consequences of metal deactivation through suitable additives to be characterized efficiently and the activation energy level to be quantified.

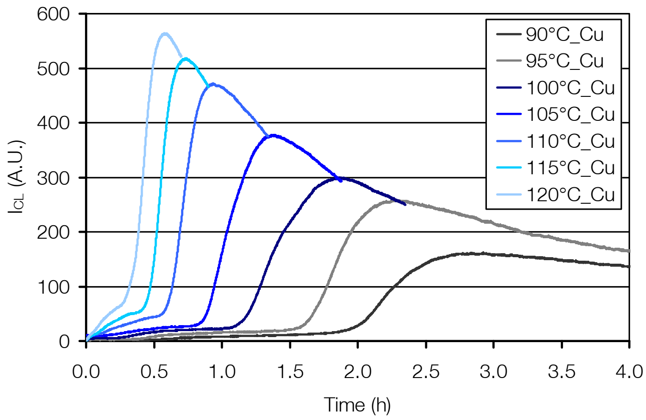

Fig. 5: Oxidation behavior of biodiesel B7 at different static temperature conditions (120..90°C; ΔT = 5°C) with synthetic air in direct contact to metallic copper.