Extremely rapid and facile method to predict the oxidation stability of mineral oil based products

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PHOTOCHEM method for quality control in petro industry

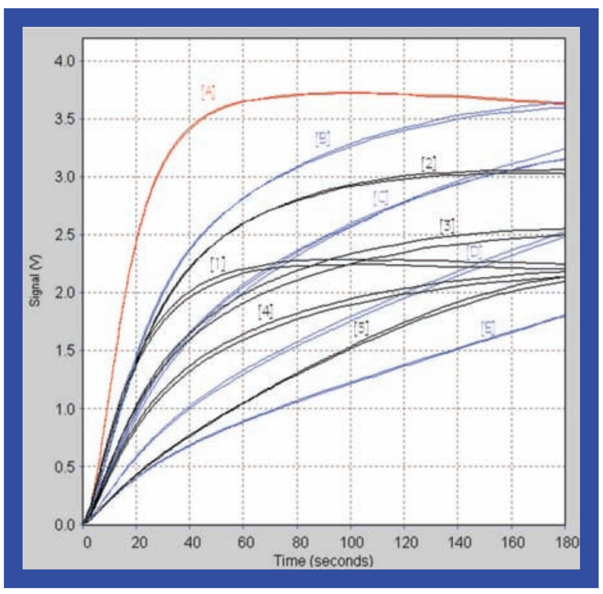

Figure 1: Measuring curves of the blanks, standards and the sample for the determination of the antioxidative capacity of the lipid soluble compounds. Voltage proportional to the generated luminescence as a function of measuring time. The inhibition (reduction) of luminescence through antioxidants in the standards [B]-[E] (0,5 1,0 2,0 und 3 nmol) (the blue lines) and the samples [1] – [5] (the black lines) compared to the blank [A] (the red lines) is to be observed.

Diesel fuel injection equipment manufacturers support the development of alternative sources of fuel. In Europe and in the United States of America, as well as in other countries, fuel resources such as rapeseed methyl ester (RME) and soybean methyl ester (SOME), together known as fatty acid methyl esters (FAME), are being used as alternatives and extenders for mineral oil derived fuels. There is great interest for significant variation in product quality and specification for products basically described as biodiesel. Biodiesel is defined as the mono alkyl esters of long chain fatty acids derived from vegetable oils or animal fats. There are some standards including a number of parameters in biodiesel specifications that the biodiesel fuel must fulfill in order to be sold in several countries.

Basically, there are 3 standards for diesel and biodiesel fuel:

- EN 590
- DIN 51606
- EN14214

EN590:2000 describes the physical properties that all diesel fuel must fulfill if it is to be sold in all EU countries, Switzerland, Norway, Czech Republic and Iceland. It allows the blending of up to 5% biodiesel with normal DERV (95/5 mix).

DIN 51606 is a German standard for biodiesel. It is regarded to be the currently existing strictest standard and is used as evidence of compliance by almost all manufacturers.

EN14214 is the standard for biodiesel at present which is finalized by the European Committee for Standardization (CEN). It is briefly based on DIN 51606.

EN14214 provides the minimum requirements for FAME quality whether used as pure FAME or as a blend component. FAME may be blended in quantities of up to 5% in European diesel fuel according to the EN590 specification.

The standard EN14214 ensure that the following important factors in the fuel production process are satisfied:

- free methanol
- water
- free glycerin
- mono, di- and tri-glycerides
- free fatty acids
- total solid impurity level
- alkali/alkaline earth metals
- oxidation stability

Among the all other general requirements, the oxidation stability is an important point, which will be focused in this study. The outstanding necessity of high oxidation and thermal stability of mineral oil based products is:

- Longer oil life
- Improved filter life
- Lower maintenance costs, etc.

Therefore, there is a significant increase in understanding the factors that influence the aging phenomenon of mineral oil based products, mostly biodiesel and biodiesel blends. Briefly, the major factors influencing stability are:

- Presence of partially reacted or un-reacted oils
- Level and type of unsaturation, 18:2 and18:3
- Presence of additives, either natural or added

Additives are commonly used not only to increase the stability but also to increase the lubricity and to enhance existing fuel quality.

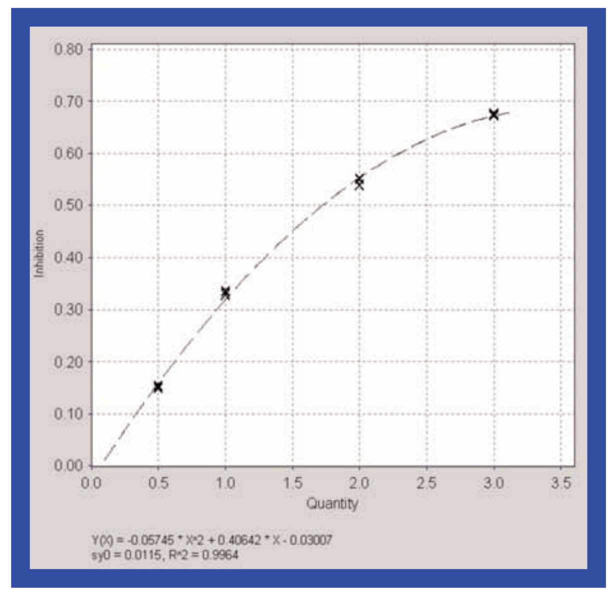

Figure 2: Calibration curve with 0,5 1,0 2,0 and 3,0 nmol Trolox® (see the corresponding measuring curves in Fig. 1)

Diesel fuel that includes biodiesel additives is referred to as a premium biodiesel. Additives can be classified in different groups such as;

- Antioxidants
- Antirust
- Viscosity index improvers
- Extreme pressure (EP)
- Metal passivators

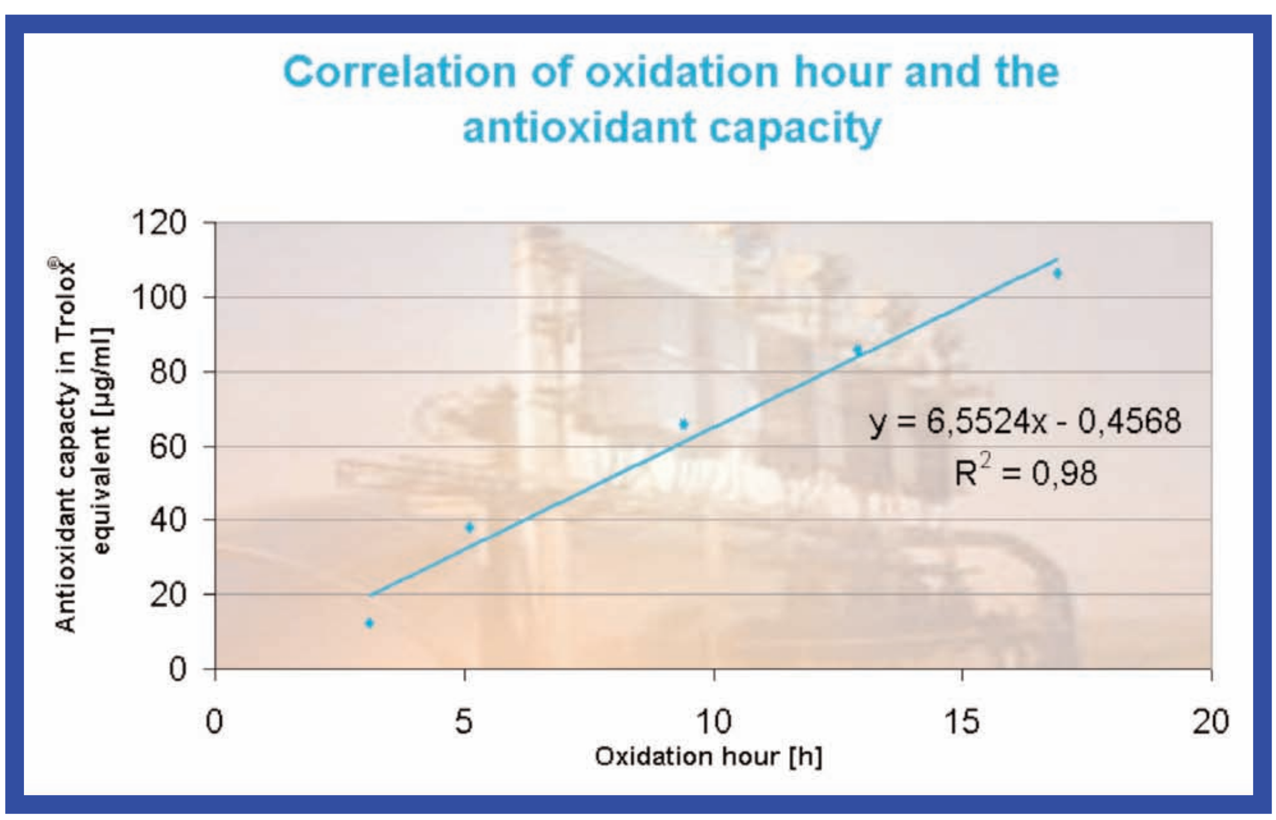

Figure 3: Correlation of oxidation hour and the antioxidant capacity in biodiesel

Figure 4: PHOTOCHEM

- Friction modifiers
- Solid lubricants and etc.

There are methods existing in market for determining the oxidation and thermal stability of mineral oil based products. One of the methods for instance measures volatile acids after aging and produces induction period value. This induction time is mostly used for defining the oxidation stability. It is preferred mostly by European FIE and some automobile manufacturers. However, this method has some disadvantages like;

- Volatile acid formation is not representative of deposit formation
- Certain deposit formation pathways are not oxidation dependent
- Deposit formation may be preferred

Because of this, there is a great interest for predicting the oxidation stability using an another method. With the PHOTOCHEM® , Analytik Jena offers the first system for the quantification of antioxidants in water-soluble and lipid-soluble substances separately on a single system. PHOTOCHEM® analyzes by using of photochemiluminescence detection method. The key feature of this method is the speed of oxidative reactions that is up to 100 times higher compared to normal conditions. This increase is achieved by photochemical stimulation of the reacting molecules, which makes very fast measuring times possible.

Measuring principle

The working principle of the photochemiluminescence method is based on the multiple acceleration of a natural reaction leading to the generation of a superoxide anion radical. This is achieved by optical excitation of a photosensitive substance and subsequent formation of the measuring free radicals (superoxide anion radicals). These radicals are partially eliminated from the sample by reaction with the antioxidants present in the sample. In the measuring cell the remaining radicals cause the detector substance to luminescence. Thereby the antioxidant capacity of the sample is exactly determined in a separate cell by means of a photomultiplier tube. The antioxidative capacity of the sample is quantified by comparison with the standard (constructing a calibration curve with Trolox® for determination of total lipid soluble antioxidants) and is given in equivalent units of standard.

Table 1: Oxidation hour and the equivalent concentration units of Trolox® for lipid-soluble substances in biodiesel samples

Probe	Oxidation hour (h)	Trolox® equivalent [µg/ml]
FAME [1]	3,1	12,52 ± 0,04
FAME + 50 ppm BHT [2]	5,1	38,12 ± 0,01
FAME + 250 ppm BHT [3]	9,4	65,63 ± 0,04
FAME + 500 ppm BHT [4]	12,9	85,73 ± 0,04
FAME + 50 ppm Crompton [5]	16,9	106,30 ± 0,30

Sample preparation

Biodiesel samples are stored under exclusion of air to prevent the loss of antioxidants. As diluent n-hexane has been used. 1 ml sample is diluted with 1ml n-hexane. Depending on the sample, further dilutions have been performed. Before measuring with PHOTOCHEM® each sample has been placed on a vortex.

Performance of the measurement and calibration

ACL calibration and measurements are carried out according to the standard kit protocol. At the beginning a blank analysis (the red measuring curves) is performed, where no antioxidants were present. Afterwards, with different amounts of Trolox® (the standard antioxidant substance) a calibration curve has been created (the blue measuring curves). A very important point that has be cleared here is that the instrument does not measure only Trolox® but also all lipid soluble antioxidants present in the sample. After the calibration curve is created, one can perform the analysis of samples (the black measuring curves). The measuring curve of the blanks, standards and samples for the determination of the antioxidative capacity of the lipid soluble compounds is given in Fig. 1. The calibration curve is constructed by measuring a series of standard solutions, namely, 0,5 1,0 2,0 and 3,0 nmol Trolox® (Fig. 2).

Results

The results given in Table 1 are presented in equivalent concentration units of Trolox® for lipid soluble substances in biodiesel measured with PHOTOCHEM® . The oxidation hours are also given in the table for each biodiesel sample.

A direct proportionality between the oxidation hour and the antioxidant capacity of the biodiesel samples can be noticed (Fig. 3). The samples with high oxidation hours have also high antioxidant capacity. The results show that PHOTOCHEM® can be utilized very well for the determination of antioxidant capacity in bio fuels.

Conclusion

The advantage of this method lies in its high sensitivity, high reproducibility and its short measuring times. The time that is required to perform a one single measurement of a sample is about 3 min. This time is compared to the other methods available on the market, which is above 6 hours, is very short. Not only the measuring times, but also the sample preparation is profitable. It does not require complicated and time-consuming sample preparation. Moreover, the measurement is independent on a particular pH value or temperature. Hence, it opens up the possibility to predict the oxidation stability of mineral oil based products not only in research institutes but also in routine analysis.