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Development of a Low-Emission Fuel with High Biogenic Content and High Oxidation Stability

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Low-emission Fuel with High Biogenic Content and High Oxidation Stability

Compared to fossil diesel fuel, biodiesel has significantly lower carbon monoxide, particulate mass and hydrocarbon emissions. In contrast, however, there are higher nitrogen oxide emissions and a reduced aging stability. In a joint research project, the Transfer Center for Automotive Technology at Coburg University (TAC) and the University of Applied Sciences and Arts in Lemgo (Germany) have analyzed how the oxidation stabilization of biodiesel by hydrazides can be further improved.

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1 MOTIVATION

The discussion about statutory limits on NO_x emissions and the demand for technical solutions to keep diesel engine emissions within these limits show the importance of researching and further developing technologies aimed at reducing emissions from combustion engines. In this regard, the focus is usually placed on solutions for an engine's interior (such as exhaust gas recirculation or targeted adjustment of fuel injection), solutions for other parts of a vehicle (in the form of exhaust gas treatment), or replacement of combustion engines with electric motors. Until now, less attention has been given to low-emission fuels, even though research in this area has already produced many promising results.

Many studies have shown that biodiesel produces significantly less carbon monoxide, particulate matter and hydrocarbons than petrodiesel during combustion, thereby contributing to emissions reduction [1]. However, using biodiesel in engines not optimized for the fuel may increase NO_x emissions. Furthermore, biodiesel is more prone to oxidative aging, which causes the fuel to have decreased storage stability and necessitates the use of additives to counteract the problem. To allow fuels to have a high biodiesel content despite these issues, additives had been developed to reduce NO_x emissions as well as to increase the fuel's storage stability. The promising results are a milestone in the development of fuels with low NO_x emissions suitable for use in cities.

The lower storage stability of biodiesel via-à-vis petrodiesel is due to the unsaturated hydrocarbon compounds that make biodiesel more susceptible to oxidation reactions. Allylic and bis-allylic C-H bonds are especially prone to oxidation [2]. Biodiesel contains a high level of fatty acid methyl esters with such C-H bonds (approximately 90 % in Rapeseed oil Methyl Esters, RME). Radical abstraction of hydrogen atoms at these sites can initiate autoxidation chain reactions, which lead to the formation of organic acids, short-chain by-products, and long-chain molecules. This can negatively affect a fuel's corrosiveness, cetane number, viscosity and ability to pass through filters. In addition, the reaction between fatty acid methyl esters and oxygen causes a fuel's polarity to increase, which may result in phase separation in mixtures of non-polar paraffinic diesel and aged biodiesel [3]. For typical storage durations, this oxidative ageing of fuel can be alleviated by adding antioxidants. Antioxidants can donate hydrogen radicals, which can form stable products with radicals resulting from autoxidation. The remaining antioxidant radicals are stabilized through steric or mesomeric effects, allowing them to stop the autoxidation chain reactions.

However, additional measures, such as increasing the concentration of antioxidants, must be taken if a fuel containing biodiesel is expected to remain unused for long periods. For example, this may happen in plug-in hybrid vehicles whose batteries are regularly charged on the power grid, which means that the combustion engine is rarely used and the fuel may stay in its tank for a long time. As the number of new plug-in hybrid vehicles registered in the past years [4] continues to grow, this issue will become increasingly relevant.

Why NO_x emissions increase slightly when biodiesel is burned is not yet fully understood in the current state of research. It is known, however, that introducing additives to diesel fuel can reduce NO_x emissions. For example, Varatharajan et al. (2011) [5] showed that at a concentration of 0.025 % (m/m), aminic antioxidants such as p-phenylenediamine can reduce NO_x emissions by up to 43 %. Using the antioxidant N,N'-diphenyl-1,4-phenylendiamine (DPPD) at concentrations of 0.2 % (m/m), Varatharajan and Cheralathan (2013) [6] were able to achieve a reduction in NO_x emissions of about 26 %. Palash et al. (2014) [7] demonstrated that a 16.54 % reduction in NO_x emissions could be achieved using 0.15 % (m/m) DPPD in a mixture of 80 % diesel and 20 % jatropha oil methyl ester. In 2013, Von İleri and Koçar [8] published a study involving engine tests that investigated the effect of the phenolic antioxidants butylhydroxyanisole (BHA), butylhydroxytoluene (BHT) and tert-butylhydroquinone (TBHQ) as well as of the nitrogen-containing substance 2-ethylhexyl nitrate (EHN) on emissions. In the study, a 4.63 % reduction in NO_x emissions could be achieved using EHN. The study also showed that the phenolic antioxidants were able to reduce NO_x emissions. The reduction in NO_x emissions is explained by the antioxidants' radical-scavenging properties. The stabilization of radicals can, as a result,

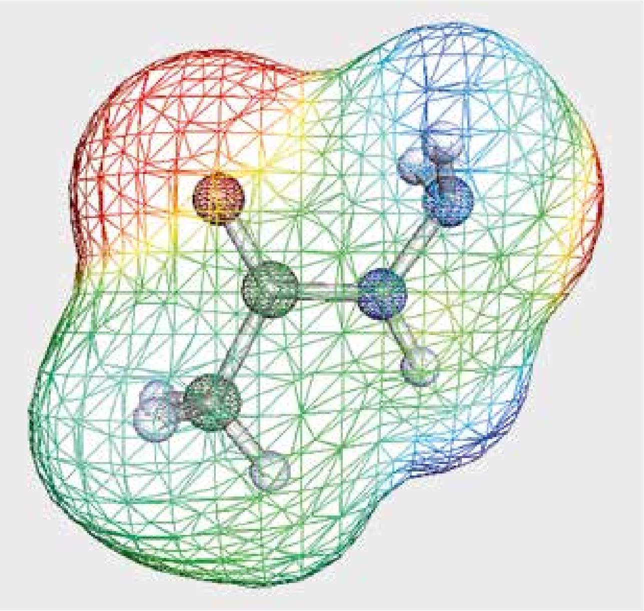

FIGURE 1 Surface charge density of acethydrazide: red areas depict negative partial charges, blue areas positive partial charges (© TAC)

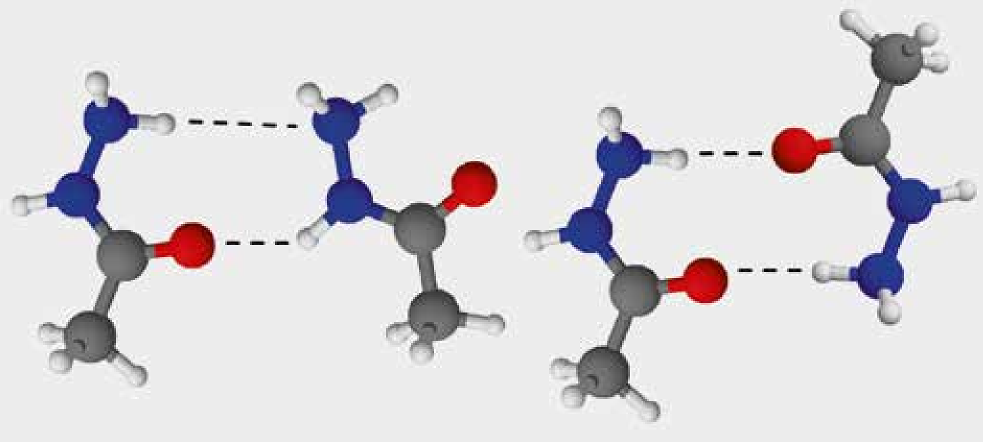

FIGURE 2 Possible modifications for formation of hydrogen bridge bonds between acethydrazide molecules (© TAC)

not only occur during oxidation reactions, but also interfere with the chemistry of combustion and inhibit the formation of NO_x.

2 HYDRAZIDES AS FUEL ADDITIVES

The studies presented here are based on experiments by Krahl et al. (2010) [9], which showed that NO_x emissions can be cut by up to 45 % in combustion chamber tests by adding stearic acid hydrazide at a concentration of 2 % (m/m). The reduction in NO_x emissions is the result of hydrazide decomposing during combustion into hydrazine, which then breaks down into NH_2, which reacts with NO_x to form N_2 and H_2O. It should be noted that NO_x reduction according to this mechanism can only take place stoichiometrically. Each hydrazide group deployed can reduce at most two NO_x molecules.

However, the stearic acid hydrazide used by Krahl et al. (2010) [9] is very poorly soluble in non-polar or partially polar solvents such as petrodiesel or biodiesel. This poor solubility of hydrazides is due to their quadrupole nature, **FIGURE 1**, which causes them to have a high potential to form strong hydrogen bridge bonds, **FIGURE 2**. Krahl et al. (2010) [9] overcame this problem by adding high concentrations of solubilizers. And because these solubilizers had to be used at concentrations of up to 2 % (m/m), they constituted a rather significant component in the fuel. As such, it seemed worthwhile to further develop hydrazides in terms of their solubility. In this study, the chemical structure of hydrazides was altered, and the effectiveness of the modified hydrazides were tested.

The hydrazides presented here have a solubility of at least 7.26 mmol/kg in the biodiesel fuels tested. Depending on the molar mass of the additives, this corresponds to an adjusted concentration of around 1000 ppm. Improvement in solubility was achieved by surrounding the hydrazide group with sterically demanding molecular groups to prevent the formation of hydrogen bridge bonds, **FIGURE 3** [10].

3 USE OF HYDRAZIDES TO REDUCE NITROGEN OXIDE EMISSIONS

Hydrazides that do not require solubilizers to dissolve in biodiesel were tested using an AFIDA (Advanced Fuel Ignition Delay Analyzer) combustion chamber manufactured by ASG Analytik-Service GmbH. This chamber simulates combustion inside a diesel engine under isometric conditions and without intake air swirl during the loading and injection process. The use of the AFIDA combustion chamber for testing NO_x emissions can be traced back to Tanugula (2010) [11], who was the first to perform tests on stearic acid hydrazide for the purpose of NO_x reduction.

One particular advantage of the combustion chamber tests is that only a small amount of fuel is required for measurements. The amount of fuel required is at most around 40 to 50 ml; this is over 1000 times lower than the amount required for performing similar tests using complete engines. Therefore, the hydrazides only had to be synthesized in small batches; this is advantageous as the synthesis processes can sometimes be

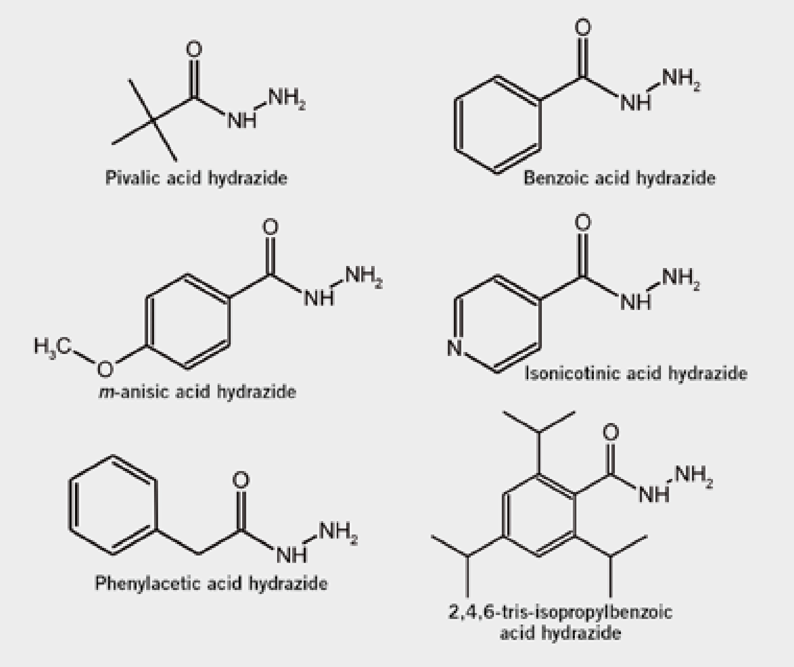

FIGURE 3 Hydrazides with a solubility of at least 7.26 mmol/kg in biodiesel (© TAC)

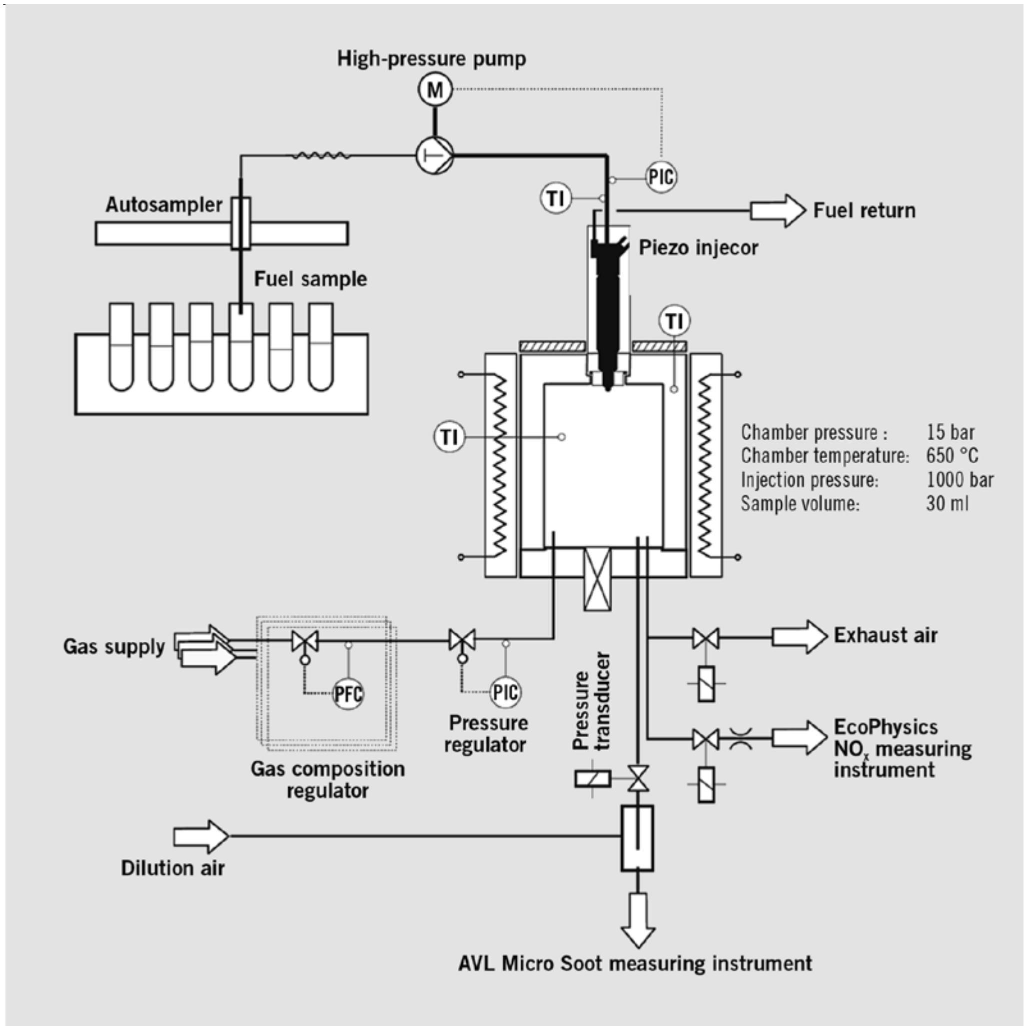

FIGURE 4 Schematic diagram of the AFIDA combustion chamber (© H. Stein, Analytik Service Gesellschaft)

time-consuming. **FIGURE 4** shows the schematic diagram of the combustion chamber.

The combustion chamber tests showed that adding hydrazides to RME at a concentration far below the 2 % (m/m) used by Krahl et al. (2010) could reduce NO_x emissions, **FIGURE 5** and **FIGURE 6**.

NO_x emissions were reduced by approximately 10 % by adding 0.1 % (m/m) benzoic acid hydrazide or 0.1 % (m/m) phenylacetic acid hydrazide. However, after the injection system on the combustion chamber was modified to significantly increase the ignition delay, these results could not be reproduced; likewise, the addition of the phenolic antioxidants used in the abovementioned studies (such as BHT) yielded no reduction in NO_x emissions. The results obtained before the modification suggest that the mechanism proposed by Krahl et al. (2010) seemed implausible. This is because the results cannot be explained by a mass balance of the reduced NO_x and by the number of hydrazide molecules used in a stoichiometric reaction. In view of this, it is proposed that another mechanism is responsible for the effect of antioxidants in the reduction of NO_x. The approach to explaining the mechanism is based on the fact that, as with antioxidants, hydrazides too have radical-scavenging properties, which interferes with the combustion chemistry. After the combustion chamber was modified there was no NO_x reduction, because the NO_x-reducing species must be present during NO_x formation for them to effectively reduce NO_x molecules. Owing to the longer ignition delay, these species may already have decomposed or been oxidized themselves before they could interfere with the combustion chemistry.

4 USE OF HYDRAZIDES TO STABILIZE OXIDATION

To demonstrate any possible radical-scavenging properties they may have, the hydrazides were tested, analogously to antioxidants, for their oxidation-stabilizing characteristics. These experiments were carried out using the Rancimat test as specified in DIN EN 15751 and the PetroOxy test as specified in DIN EN 16091. These techniques thermo-oxidatively accelerate the aging of fuels, yielding what is known an induction period, which is an indicator of a fuel's storage stability.

It was shown that hydrazides at a concentration of 7.26 mmol/kg (≙ 1000 ppm) significantly increased the oxidation stability of the RME tested and that its effectiveness is comparable to commercially available antioxidants such as butylhydroxytoluene, **FIGURE 7**. The antioxidative effect of hydrazides can be explained by the fact that hydrogen radicals can split from the hydrazide group and that these radicals, as with aminic antioxidants, are then able to interfere with oxidation chain reactions.

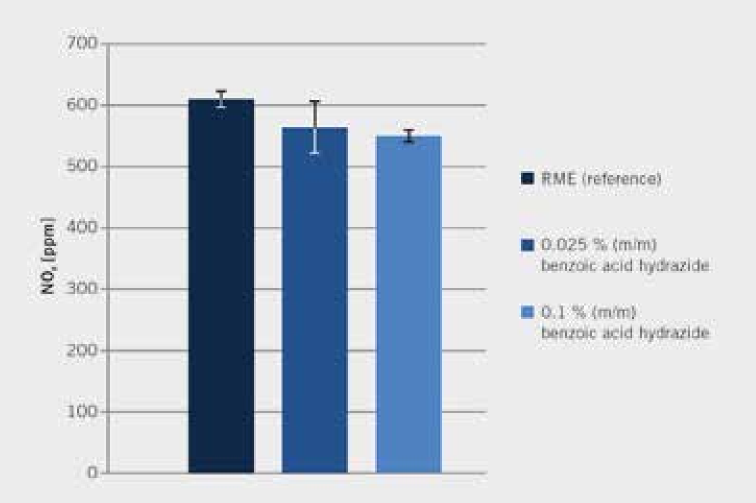

FIGURE 5 AFIDA combustion chamber measurements with benzoic acid hydrazide in RME (© TAC)

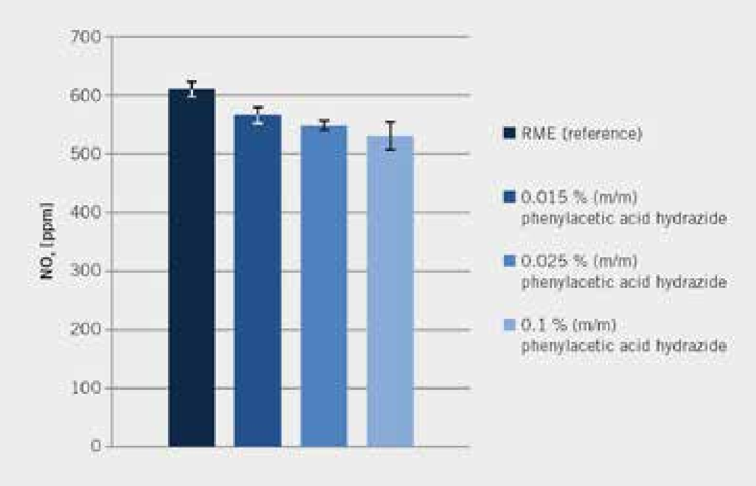

FIGURE 6 AFIDA combustion chamber measurements with phenylacetic acid hydrazide in RME (© TAC)

To rule out any interactions with antioxidants that naturally occur in biodiesel, such as tocopherols, oxidation stability experiments were also performed with distilled RME. Because of the absence of naturally occurring antioxidants, the distilled RME showed no oxidation stability in the Rancimat test and only very low oxidation stability in the PetroOxy test. These tests were also performed on 2,4,6-tris-isopropylbenzoic acid hydrazide; this substance was synthesized for this purpose using a complex method and was especially optimized for good solubility and oxidation stability [12]. The hydrazide groups are shielded by the sterically demanding isopropyl groups located close to them, which hinders the formation of hydrogen bridge bonds and significantly improves the solubility. The isopropyl groups also stabilize the radical hydrazide group after the hydrazide group has donated a hydrogen radical, thereby also increasing the antioxidation potential, **FIGURE 8**.

5 SUMMARY

In summary, the lower oxidation stability of biodiesel compared with petrodiesel can be considerably improved by using hydrazides. Furthermore, other results suggest that hydrazides can also reduce NO$_x$ emissions in the presence of conditions that are optimal for the release of the active species. Future research in the field of hydrazides must concentrate on further improving their antioxidation potential and on studying their NO$_x$-reducing properties using engine tests. The study showed that oxidation stability can be further improved by designing hydrazides for this specific purpose, e.g. steric shielding of the hydrazide group. This will also improve the solubility of the hydrazides in question, enabling them to be used at higher concentrations or in fuel mixtures with a low or even no biodiesel content. For example, this is beneficial for applications where hydrazides are used to reduce NO$_x$ emissions of paraffinic biofuels, such as Hydrogenated Vegetable Oils (HVO).

The results of this study show that there still remains potential for reducing emissions through goal-driven fuel design and that further research may be able to make a promising contribution to creating low-emission fuels suitable for use in cities.

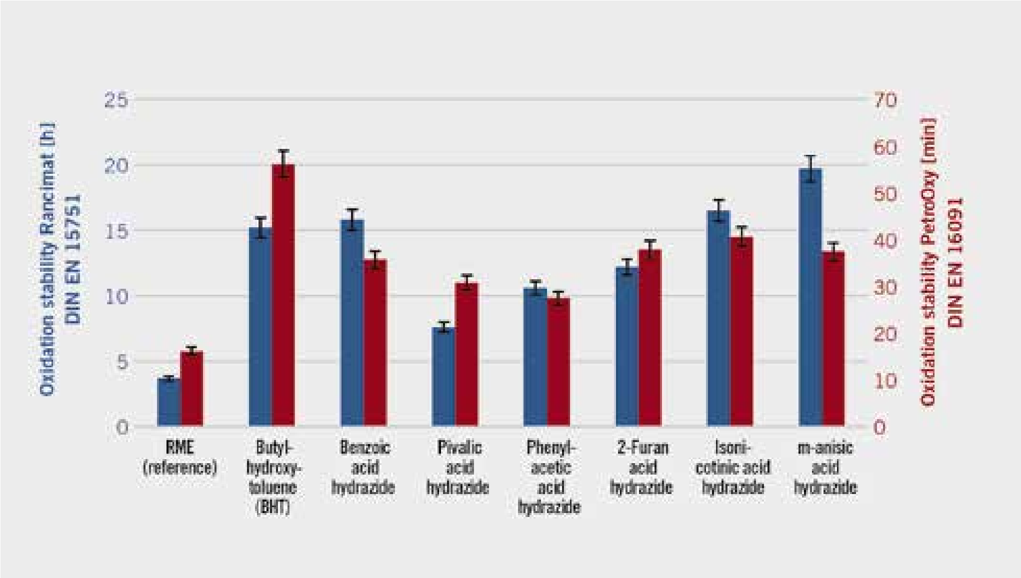

FIGURE 7 Rancimat and PetroOxy measurements with an additive concentration of 7.26 mmol/kg in RME (© TAC)

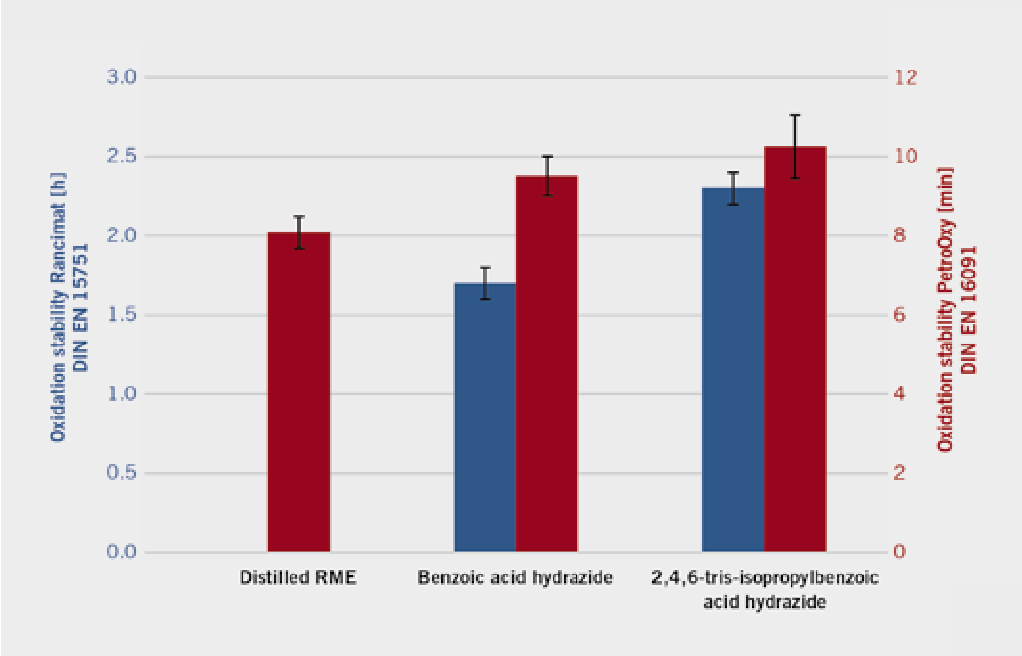

FIGURE 8 Rancimat and PetroOxy measurements with an additive concentration of 7.26 mmol/kg in RME (© TAC)

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