Additives for Rapeseed Oil Fuel

J. Kastl[1], E. Remmele[1]
[1]Technology and Support Centre in the Centre of Excellence for Renewable Resources, Biogenic Fuels, Lubricants and Process Materials, Straubing, Germany

Keywords: rapeseed oil fuel, quality, additive, ignitability, ignition delay, constant volume combustion chamber

Introduction

Rapeseed oil fuel is used as an alternative to diesel fuel, mainly in the agricultural sector and in stationary CHP plants. It is non-hazardous to waters, nontoxic, easy to handle and has a lower carbon footprint compared to fossil diesel fuel. Due to the differences between rapeseed oil fuel and fossil diesel, a technical adaption of the engine system is required.
The specifications of rapeseed oil for the use as fuel in engines capable of running on vegetable oils are defined in the German standard DIN 51605 (2010) [1]. The use of additives to improve properties of rapeseed oil fuel is explicitly allowed if there are no negative effects on the operating performance or the effectiveness of the exhaust gas treatment. Also the water hazardousness of the mixture must still be classified as "non-hazardous to water" according to the German administrative regulation VwVwS (2005) [2]. In contrast to fossil diesel fuels, the use of additives is not common with rapeseed oil fuel.
Rapeseed oil fuel differs from fossil diesel fuel amongst others in regard to the ignitability, the low temperature flow behaviour and the deposit formation, which have been researched in a project financed by the Agency for Renewable Resources (FNR). The results of the works concerning the use of additives to improve the low temperature flow behaviour of rapeseed oil fuel have been described in Kastl and Remmele (2010)[5] (2011)[6] [7].

Problems and Objective

The ignitability is usually described by measuring the ignition delay, which is defined as the time between injection of the fuel and the start of the combustion. For the proper function of a diesel engine, the ignition delay has to be within a defined range, to avoid disturbances of the combustion process. Especially during cold start or at lower load conditions the ignitability of the fuel has a strong impact on the operating performance and the emissions of the engine. Compared to fossil diesel fuel, rapeseed oil shows a different chemical structure and composition. The ignitability of rapeseed oil fuel is lower than of diesel fuel, the ignition delay is longer.
In fossil diesel fuels it is common to improve the ignitability by the use of additives. In works aiming at the optimization of rapeseed oil fuel it has not been thoroughly researched whether the ignitability of rapeseed oil fuel can be improved by additives. Goal of the works was therefore to investigate the effectiveness of additives, which are commercially available for the use in fossil diesel fuel, fatty acid methyl esters (FAME, "biodiesel") or vegetable oils, in regard to improving the ignitability of rapeseed oil fuel.

State of knowledge

The ignitability of rapeseed oil fuel is mostly measured by using a measuring principle called 'constant volume combustion chamber'. In the measurement device the fuel is injected into a combustion chamber. Unlike with combustion engines, this chamber has no moving parts, e. g. piston, and therefore has a constant volume. Due to the high temperature and high pressure in the chamber, the injected fuel self-ignites and the combustion starts. By measuring the temperature and pressure inside the chamber the ignition delay can be determined.
Attenberger and Remmele (2003) [3] [4] used a measurement device called 'fuel ignition tester', which is based on this measurement principle, to investigate the ignition delay of rapeseed oil fuel. The authors were able to show that this measurement device is suitable for rapeseed oil fuel.

Approach

In this work the 'fuel ignition tester' is used, the approach is based on the procedure used by Attenberger and Remmele (2003) [3] [4]. 13 additives or additive packages from nine different suppliers, labelled as Z01 to Z13, were chosen. Each one was tested in five different concentrations, beginning with the dosage recommended by the supplier. The values for the recommended dosage were mostly given for the use in fossil diesel fuel, as only little was known about the application in rapeseed oil fuel. The recommended dosage ranged from 0.05 Vol.-% to 3.2 Vol.-%.

Each sample was done in triplicates. To rate the effectiveness of the additives in regard to the ignitability of rapeseed oil fuel, measurements of the base fuel without additives were used as reference (blank sample). By statistically comparing the values for the ignition delay of the five mixtures per additive with each other and the blank sample, the significance of differences could be investigated. The comparison was carried out with the SAS software package using a multiple t-test with a significance level of $\alpha=0.05$.

Besides the effectiveness of the additives, further influences on fuel-related properties have to be taken into account. This includes the fulfilment of the limit values required by the DIN 51605 as well as water hazardousness or the influence on exhaust gas after-treatment systems. Compliance with the fuel standard DIN 51605 was researched by laboratory analyses. The influence on after-treatment systems was judged by analyzing the additives in regard to the concentration of elements known as ash formers or catalyst poisons. The water hazardousness was rated by using the mixing rule given in the VwVwS [2].

Results

The ignition delays for the mixtures in the recommended dosage are shown in Fig. 1 as mean value of the three measurements with the standard deviation. As can be seen, four of the tested additives (Z05, Z09, Z11 and Z13) in this concentration show a significantly shorter ignition delay than the reference. Additionally, mixtures in twice and threefold of the base concentration were tested. Fig. 2 depicts the ignition delays for the samples in threefold base concentration compared to the reference. Significantly different ignition delays compared to the reference could be seen in the mixtures of the four additives already effective in the recommended dosage. The ignition delays of the mixtures of each of these additives in simple and threefold base concentration are not significantly different from each other, which means that the recommended dosage is sufficient to reach the lower ignition delay.

To minimize negative side effects on other fuel-related properties the dosage of these additives should be as low as possible, while still showing a positive influence on the ignition delay. Therefore, mixtures in half the base concentration were examined. It could be shown that only Z11 has a significantly lower ignition delay compared to the blank sample without additives, when used in half of the recommended dosage.

Apart from the effectiveness in regard to the target property ignitability, the effects of additivation on other fuel-related properties were researched. Analysis showed that the additives Z09 and Z13 can be used in rapeseed oil fuel in the recommended dosage without negative effects on fuel quality, water hazardousness and exhaust gas after-treatment systems.

However, none of the mixtures of additive Z05 with a significantly lower ignition delay than the reference fulfils the requirements of the DIN 51605 in terms of water hazardousness. Same holds true for the mixtures of additive Z11, where a significantly lower ignition delay goes along with higher water hazardousness.

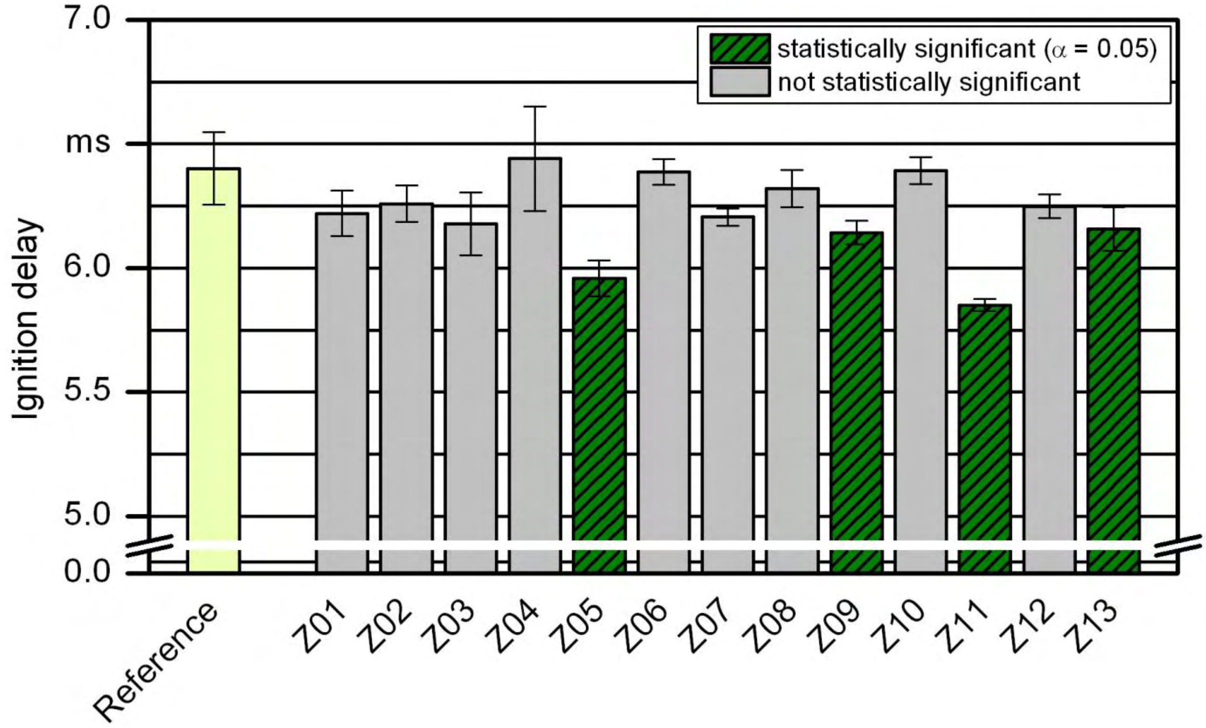

Figure 1: Ignition delays of 13 additive-rapeseed oil fuel-mixtures in the recommended dosage and the reference — mean value with standard deviation

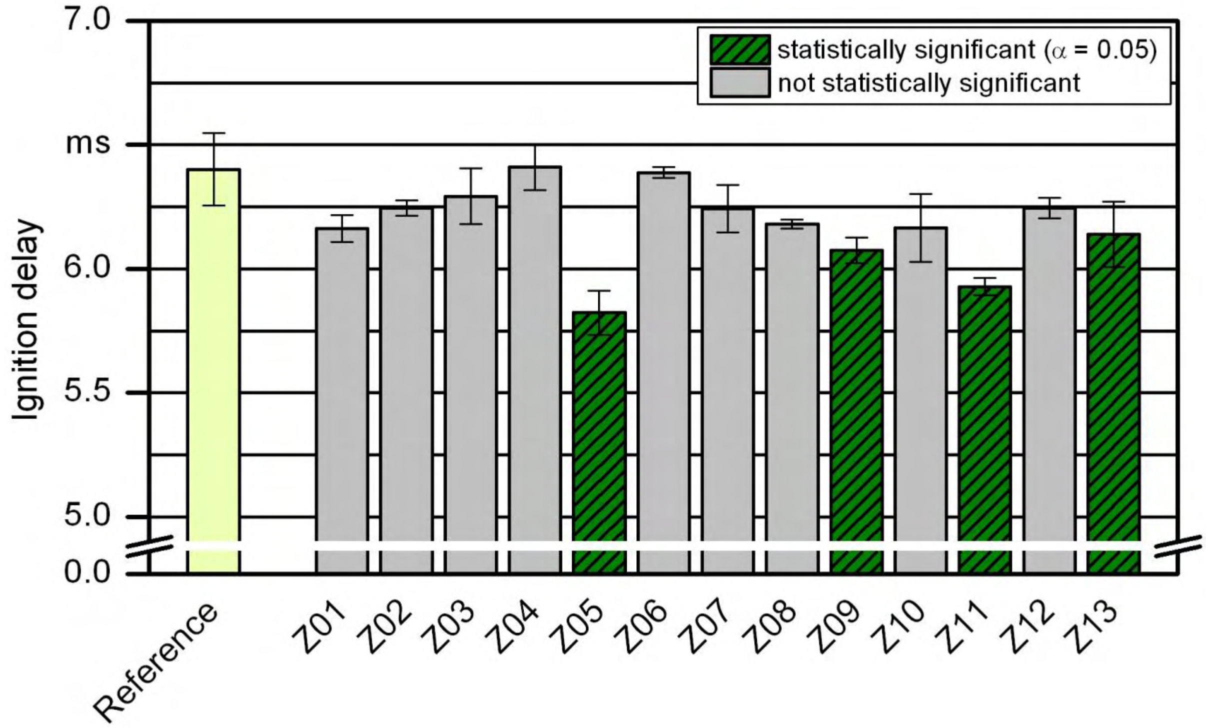

Figure 2: Ignition delays of 13 additive-rapeseed oil fuel-mixtures in threefold recommended dosage and the reference — mean value with standard deviation

The four additives, whose mixtures with rapeseed oil fuel show significantly shorter ignition delays than the reference, contain the same active substance, 2-ethyl-hexyl-nitrate, in different concentrations. This substance is the ignition improver most often used in fossil diesel fuels. Apparently, the different concentration of the active substance in the additives has an influence on the effectiveness measured in the ‘fuel ignition tester’.

Additives for Rapeseed Oil Fuel

J. Kastl[1], E. Remmele[1]
[1]Technology and Support Centre in the Centre of Excellence for Renewable Resources, Biogenic Fuels, Lubricants and Process Materials, Straubing, Germany

Keywords: rapeseed oil fuel, quality, additive, ignitability, ignition delay, constant volume combustion chamber

Introduction

Rapeseed oil fuel is used as an alternative to diesel fuel, mainly in the agricultural sector and in stationary CHP plants. It is non-hazardous to waters, nontoxic, easy to handle and has a lower carbon footprint compared to fossil diesel fuel. Due to the differences between rapeseed oil fuel and fossil diesel, a technical adaption of the engine system is required.
The specifications of rapeseed oil for the use as fuel in engines capable of running on vegetable oils are defined in the German standard DIN 51605 (2010) [1]. The use of additives to improve properties of rapeseed oil fuel is explicitly allowed if there are no negative effects on the operating performance or the effectiveness of the exhaust gas treatment. Also the water hazardousness of the mixture must still be classified as “non-hazardous to water” according to the German administrative regulation VwVwS (2005) [2]. In contrast to fossil diesel fuels, the use of additives is not common with rapeseed oil fuel.
Rapeseed oil fuel differs from fossil diesel fuel amongst others in regard to the ignitability, the low temperature flow behaviour and the deposit formation, which have been researched in a project financed by the Agency for Renewable Resources (FNR). The results of the works concerning the use of additives to improve the low temperature flow behaviour of rapeseed oil fuel have been described in Kastl and Remmele (2010)[5] (2011)[6] [7].

Problems and Objective

The ignitability is usually described by measuring the ignition delay, which is defined as the time between injection of the fuel and the start of the combustion. For the proper function of a diesel engine, the ignition delay has to be within a defined range, to avoid disturbances of the combustion process. Especially during cold start or at lower load conditions the ignitability of the fuel has a strong impact on the operating performance and the emissions of the engine. Compared to fossil diesel fuel, rapeseed oil shows a different chemical structure and composition. The ignitability of rapeseed oil fuel is lower than of diesel fuel, the ignition delay is longer.
In fossil diesel fuels it is common to improve the ignitability by the use of additives. In works aiming at the optimization of rapeseed oil fuel it has not been thoroughly researched whether the ignitability of rapeseed oil fuel can be improved by additives. Goal of the works was therefore to investigate the effectiveness of additives, which are commercially available for the use in fossil diesel fuel, fatty acid methyl esters (FAME, “biodiesel”) or vegetable oils, in regard to improving the ignitability of rapeseed oil fuel.

State of knowledge

The ignitability of rapeseed oil fuel is mostly measured by using a measuring principle called ‘constant volume combustion chamber’. In the measurement device the fuel is injected into a combustion chamber. Unlike with combustion engines, this chamber has no moving parts, e. g. piston, and therefore has a constant volume. Due to the high temperature and high pressure in the chamber, the injected fuel self-ignites and the combustion starts. By measuring the temperature and pressure inside the chamber the ignition delay can be determined.
Attenberger and Remmele (2003) [3] [4] used a measurement device called ‘fuel ignition tester’, which is based on this measurement principle, to investigate the ignition delay of rapeseed oil fuel. The authors were able to show that this measurement device is suitable for rapeseed oil fuel.

Approach

In this work the 'fuel ignition tester' is used, the approach is based on the procedure used by Attenberger and Remmele (2003) [3] [4]. 13 additives or additive packages from nine different suppliers, labelled as Z01 to Z13, were chosen. Each one was tested in five different concentrations, beginning with the dosage recommended by the supplier. The values for the recommended dosage were mostly given for the use in fossil diesel fuel, as only little was known about the application in rapeseed oil fuel. The recommended dosage ranged from 0.05 Vol.-% to 3.2 Vol.-%.

Each sample was done in triplicates. To rate the effectiveness of the additives in regard to the ignitability of rapeseed oil fuel, measurements of the base fuel without additives were used as reference (blank sample). By statistically comparing the values for the ignition delay of the five mixtures per additive with each other and the blank sample, the significance of differences could be investigated. The comparison was carried out with the SAS software package using a multiple t-test with a significance level of $\alpha=0.05$.

Besides the effectiveness of the additives, further influences on fuel-related properties have to be taken into account. This includes the fulfilment of the limit values required by the DIN 51605 as well as water hazardousness or the influence on exhaust gas after-treatment systems. Compliance with the fuel standard DIN 51605 was researched by laboratory analyses. The influence on after-treatment systems was judged by analyzing the additives in regard to the concentration of elements known as ash formers or catalyst poisons. The water hazardousness was rated by using the mixing rule given in the VwVwS [2].

Results

The ignition delays for the mixtures in the recommended dosage are shown in Fig. 1 as mean value of the three measurements with the standard deviation. As can be seen, four of the tested additives (Z05, Z09, Z11 and Z13) in this concentration show a significantly shorter ignition delay than the reference. Additionally, mixtures in twice and threefold of the base concentration were tested. Fig. 2 depicts the ignition delays for the samples in threefold base concentration compared to the reference. Significantly different ignition delays compared to the reference could be seen in the mixtures of the four additives already effective in the recommended dosage. The ignition delays of the mixtures of each of these additives in simple and threefold base concentration are not significantly different from each other, which means that the recommended dosage is sufficient to reach the lower ignition delay.

To minimize negative side effects on other fuel-related properties the dosage of these additives should be as low as possible, while still showing a positive influence on the ignition delay. Therefore, mixtures in half the base concentration were examined. It could be shown that only Z11 has a significantly lower ignition delay compared to the blank sample without additives, when used in half of the recommended dosage.

Apart from the effectiveness in regard to the target property ignitability, the effects of additivation on other fuel-related properties were researched. Analysis showed that the additives Z09 and Z13 can be used in rapeseed oil fuel in the recommended dosage without negative effects on fuel quality, water hazardousness and exhaust gas after-treatment systems.

However, none of the mixtures of additive Z05 with a significantly lower ignition delay than the reference fulfils the requirements of the DIN 51605 in terms of water hazardousness. Same holds true for the mixtures of additive Z11, where a significantly lower ignition delay goes along with higher water hazardousness.

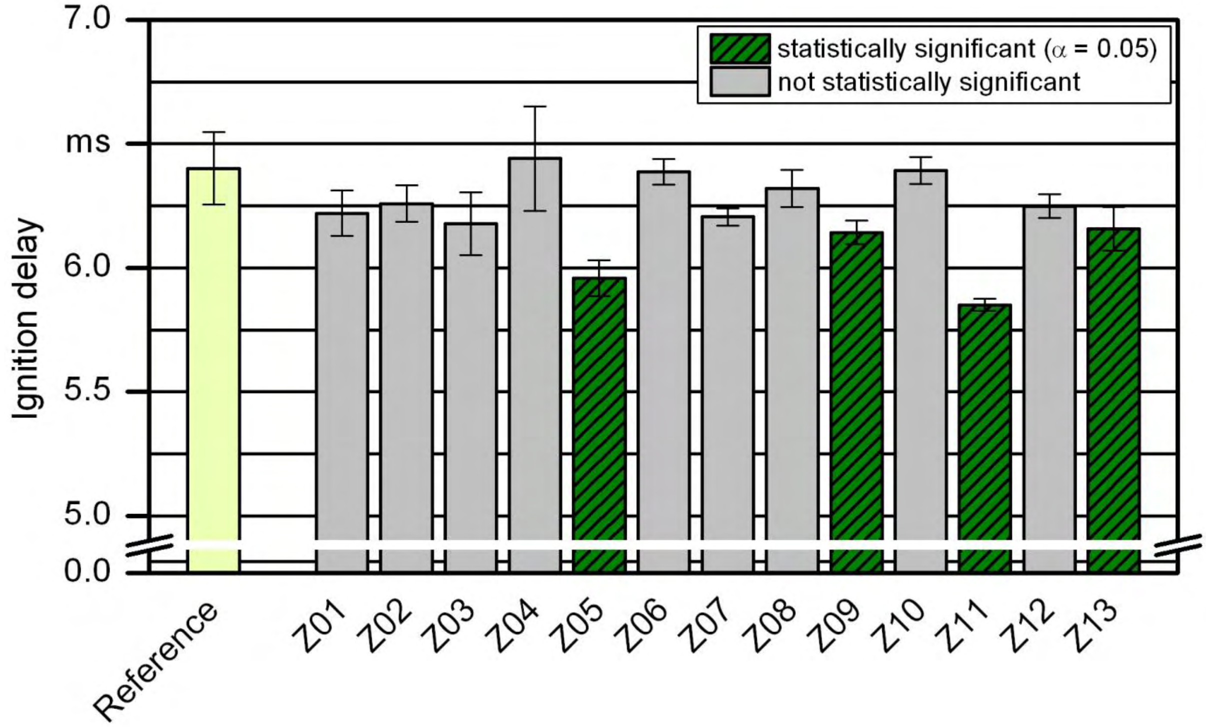

Figure 1: Ignition delays of 13 additive-rapeseed oil fuel-mixtures in the recommended dosage and the reference — mean value with standard deviation

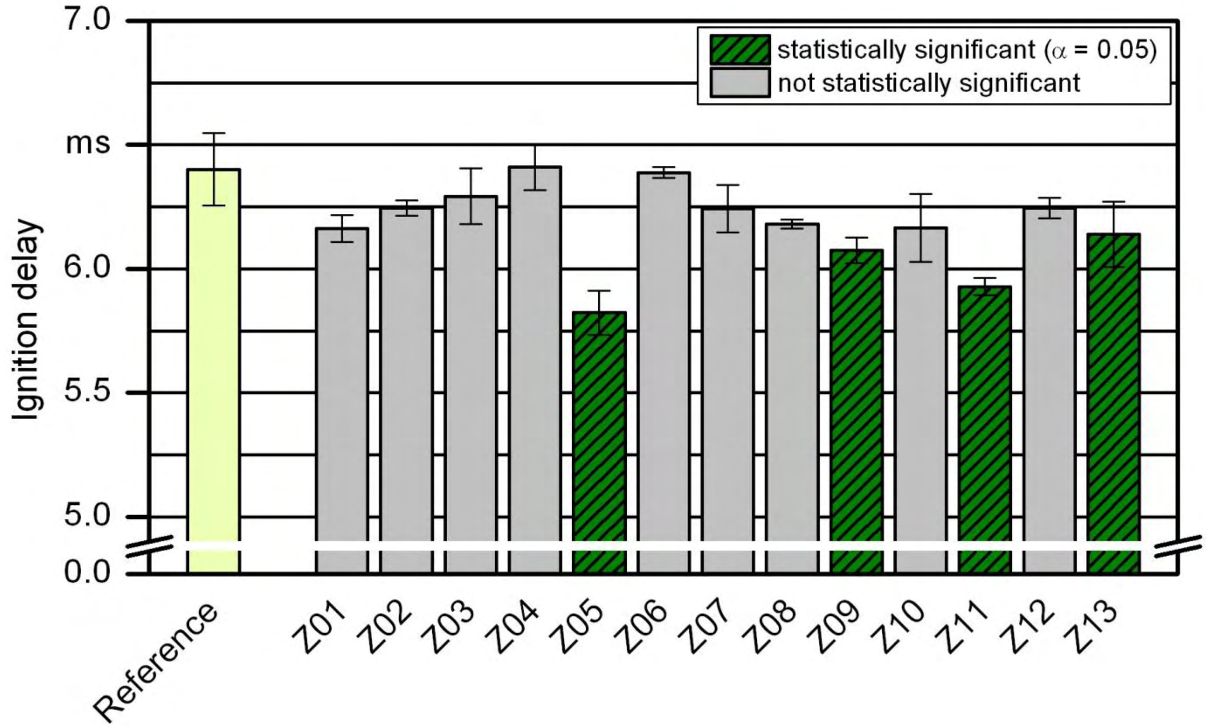

Figure 2: Ignition delays of 13 additive-rapeseed oil fuel-mixtures in threefold recommended dosage and the reference — mean value with standard deviation

The four additives, whose mixtures with rapeseed oil fuel show significantly shorter ignition delays than the reference, contain the same active substance, 2-ethyl-hexyl-nitrate, in different concentrations. This substance is the ignition improver most often used in fossil diesel fuels. Apparently, the different concentration of the active substance in the additives has an influence on the effectiveness measured in the ‘fuel ignition tester’.

Conclusions and Outlook

During the investigation of the effectiveness of the additives, four additives with positive influence on the ignition delay could be identified. In the measurements with the 'fuel ignition tester', increasing the concentration did not decrease the ignition delay further. When reducing the concentration to half the recommended dosage only one of the additives had a significantly lower ignition delay.

Besides the effectiveness to reduce the ignition delay further influences on fuel-related properties have been researched. Taking into account the influence on parameters required in the German standard DIN 51605, the water hazardousness of the mixtures and possible effects on exhaust gas after-treatment systems, only two of the tested additives can be recommended for further research.

At this time nothing can be said about the applicability for practical use. Several other aspects have to be examined in upcoming experiments, e. g. the influence on the operating performance, the emission characteristics and the effectiveness of the exhaust gas treatment. The mixtures have to be monitored over a longer period of time, to ensure that the addition of additives does not impair the storage stability of the fuel. Last but not least the influence of the additives on the long-term use has to be researched.

Acknowledgment

The authors would like to thank the Agency for Renewable Resources (FNR, Fachagentur Nachwachsende Rohstoffe e.V.) for financing the work. The complete research report [7] will be available at www.tfz.bayern.de.

Literature

[1] Deutsches Institut für Normung e. V. (2010): DIN 51605 - Fuels for vegetable oil compatible combustion engines - Fuel from rapeseed oil - Requirements and test methods. Berlin: Beuth

[2] Bundesministerium für Umwelt, Naturschutz und Reaktorsicherheit (1999): Allgemeine Verwaltungsvorschrift zum Wasserhaushaltsgesetz über die Einstufung wasser- gefährdender Stoffe in Wassergefährdungsklassen vom 17. Mai 1999. Bekanntmachung der Auskunfts- und Dokumentationsstelle nach Nummer 3 der Verwaltungsvorschrift wassergefährdender Stoffe (VwVwS) vom 17. Mai 1999. Bundesanzeiger, Jg. 51, Nr. 98a vom 29. Mai 1999, 31 Seiten

[3] Attenberger, A.; Remmele, E. (2003): Entwicklung einer Prüfmethode zur Bestimmung der Cetanzahl von Rapsölkraftstoff. Berichte aus dem TFZ, Nr. 6. Straubing: Technologie- und Förderzentrum im Kompetenzzentrum für Nachwachsende Rohstoffe, 82 Seiten

[4] Attenberger, A.; Remmele, E. (2004): Development of a Test Method for a Cetane Number Determination of Rapeseed Oil Fuel. In: Swaaij, W. P. M. van; Fjällström, T.; Helm, P.; Grassi, A. (Hrsg.): Proceedings of the Second World Conference on Biomass for Energy, Industry and Climate Protection, Rome, Italy, 10 - 14 May 2004. Florence: ETA-Florence, S. 1529-1531

[5] Kastl, J.; Remmele, E. (2010): Influence of additives on the cold flow behaviour of rapeseed oil fuel. Landtechnik, Jg. 65, Nr. 6, S. 453-455

[6] Kastl, J.; Remmele, E. (2011): Additives for Rapeseed Oil Fuel. In: Bartz, W. J. (Hrsg.): Fuels 2011 - Conventional and Future Energy for Automobiles. 8th International Colloquium, January 19-20, 2011, Technische Akademie Esslingen, Proceedings. Ostfildern: Technische Akademie Esslingen, S. 213-218, ISBN 3-924813-86-8

[7] Kastl, J.; Remmele, E. (2011): Additivierung von Rapsölkraftstoff: Auswahl der Additive und Überprüfung der Wirksamkeit. Berichte aus dem TFZ. Straubing: Technologie- und Förderzentrum im Kompetenzzentrum für Nachwachsende Rohstoffe (in preparation)