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Investigation of Storage Stability of Gas Oils Containing Waste Originated Biodiesel

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One of the pillars of sustainable development is the mobility, which has significant energy demand. Nowadays in Europe the demand for diesel fuel continuously growing, while the demand for gasoline decreases slightly. Currently, the biodiesel is the biofuel which is blended into the gas oil with the highest amount in case of Diesel engines, which can be produced from different, even waste-derived triglycerides (with transesterification with alcohol). Due to the adverse properties of biodiesel the storage stability of biodiesel/diesel blends have to be examined in detail.
In our experimental work we studied the changes in the qualities of biodiesels produced from vegetable oil which contained various waste cooking oil (waste-derived component) share (10, 30, 50 %), and its 7 and 10 % blends with gas oil in case of long-term (more than 150 weeks) storage.
We found that with the increasing the proportion of used cooking oil in the vegetable oil used as raw material for biodiesel the oxidation reactions took place in greater amount during the storage of the biodiesel product. Biodiesel made from vegetable oils containing 10 % used cooking oil was the most applicable for blending; in case of using higher proportion it is very necessary to use further amount of antioxidant additives to minimize the degradation. The test results suggest that without the addition of additives the biodiesels are not allowed to store longer than six months, and the diesel-biodiesel blends are not allowed to store longer than 1 year. We established mathematical relationships which describe well the relationship between the Rancimat induction period and the kinematic viscosity and the acid number in case of the investigated biodiesels.

1. Introduction

One of the pillars of sustainable development is mobility, which has very significant energy demand. For the air, water and land transport engine fuels are required. The use of traditional, crude oil based blending components leads to the depletion of oil reserves in long term. In Europe, the dependence on crude oil is a problem, because in the area of the European Union a smaller amount of economically recoverable crude oil is located than the demand, so there is significant dependence on imports. To reduce its energy dependence the EU not only tried to provide a higher amount of electricity from renewable sources, but also engine fuel blending components (Srivastava, 2014).
The EU Directives (2003/30/EC, 2009/28/EC) prescribe the increase of the share of alternative engine fuel blending components in order to reduce energy dependence, partly for environmental reasons, and due to the growing use. These guidelines proposed the use of biofuels earlier to 5.75 % (related to energy content) in 2010, and currently to 10 % in 2020 for the Member States.
The biodiesels are currently produced mainly by using vegetable oils. The great advantage (Silitonga, 2013) of the use of plant oils, used cooking oils, animal fats as feedstock is that engine fuels are gained from renewable and/or waste derived energy sources, but their disadvantage can be the inadequate storage stability because of the olefinic double bonds and the hydrolysis sensitivity of the ester bond. Biofuels blended into the diesel gas oils with suitable carbon atomic number and boiling range affect the fuel properties (Hancsók, 2011) and further more information in (Solymosi, 2013).

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In Asia from palm oil, the United States from soybean oil, and the European Union countries mainly from rapeseed oil produce the biodiesel (Farahani, 2011). An important aspect from the point of the environmental impact is the contribution to greenhouse gas emission reduction associated with the climate change and to the improvement of air quality in cities. But recently this advantage has been partly questioned due to the negative impact of indirect land use.
The oxidation stability of biodiesels and biodiesel/diesel gas oil blends is basically determined by the amount of fatty acid chains containing unsaturated bond(s) and their structure, by the ester bonds and also by the quality of the used cooking oil possibly applied to produce biodiesels. In addition, the storage stability may deteriorate in improper storage conditions, such as light and air (oxygen) exposure, high temperature or the presence of a variety of pollutants or water, which catalyze harmful reactions. The continuous change of these circumstances can have a significant impact on the stored material. The quality of biodiesels and its mixtures with gas oil, like all organic matters, change during storage with progress of time. The rate of this change depends on the quality of the stored material and storage conditions (Dunn, 2008). When using an incorrect storage or manufacturing technology precursors can appear, the precursors resulting insoluble materials (Tang, 2008). The rate of adverse reactions is affected by many other conditions, such as the amount and type of the present inhibitors and promoters, the solubility of the used gas oil, the added dispersant additives, metal deactivators added to the product and other additives, the effect of the refinery technologies, etc. (Siddharth, 2010) and further more information in (Aricetti, 2012). So our objective was to investigate the storage stability of waste-originated biodiesels and their blends, and the effects of the additivation before storage.

2. Experimental

2.1 Objectives

The main objective of our experimental work was to study the changes in the quality of biodiesels produced from plant oil containing various amount (10, 30, 50 %) used cooking oil (waste derived component), and the mixtures of these biodiesels (7 and 10 %) and an ultra low sulphur (<10 mg/kg) gas oil during the long-term (more than 150 weeks) storage. In the frame of this work furthermore we investigated if it is possible to find such mathematical correlations to estimate other important analytical properties based on the measurement only of Rancimat induction periods.

2.2 Feedstocks

The gas oil was ultra low sulfur ("sulphur-free") gas oil, its properties are shown in Table 1. The data clearly show that the gas oil meets the current EU standard, with the exception of the winter CFPP quality standards. The main quality characteristics and fatty acid composition of biodiesels produced from vegetable oils containing 10, 30 and 50 % used cooking oil used in the experiments can be seen in Table 2.

2.3 Production and storage of experimental samples

Through the preparation of the samples from the previously described raw materials mixtures containing 7 and 10 % of biodiesel were produced, which were stored at ambient temperature in metal cans, which were not accessible to sunlight and moisture. Signs and the compositions of the samples produced are shown in Table 3. The samples were prepared using five different additivation methods, in case of every blending ratio (Table 4). Experimental sampling and analysis of the samples were carried out every two weeks.

2.4 Analytical methods

For the analytical testing of the samples the test methods listed in Table 5 were used, which are prescribed in the current standards, with the compilance of the precision required by the methods.

Table 1: Properties of the applied gas oil

Properties	A3	EN 590:2009+A1:2010
Density, 15.6 °C, kg/m^3	835.4	820-845
Sulphur content, mg/kg	4	max. 10
Nitrogen content, mg/kg	54	-
Kinematical viscosity, 40 °C, mm^2/s	2.814	2.0-4.5
CFPP, °C	-15	max. -20 (winter); max. +5 (summer)
Flash point (Pensky-Martens), °C	64	minimum 55

Table 2: Properties of the used biodiesels

Properties		TO-2	TO-3	TO-4
Density, 15.6 °C, kg/m^3		878.9	879.2	879.2
Sulphur content, mg/kg		3	5	6
Nitrogen content, mg/kg		39	72	95
Kinematic viscosity 40 °C, mm^2/s		4.483	4.500	4.517
Acid number, mgKOH/g		0.11	0.19	0.33
Fatty acid composition, %				
palmitic acid	C16:0	6.6	9.5	13
palmitic oleic acid	C16:1	0.3	0.4	0.6
stearic acid	C18:0	2.2	2.9	3.6
oleic acid	C18:1	60.4	57.5	53.6
linoleic acid	C18:2	20.1	20.6	21.3
linolenic acid	C18:3	8.1	6.9	5.7
arachidic acid	C20:0	0.6	0.5	0.5
eicosenic acid	C20:1	1.2	1	0.9
behenic acid	C22:0	0.3	0.3	0.3

Table 3: Sample names and compositions of the samples produced for storage stability experiments

Sample names	Used biodiesel	Used gas oil	Blending ratio
TO5- TO9	TO-2	A3	B7
TO10- TO14	TO-2	A3	B10
TO15-TO19	TO-3	A3	B7
TO20-TO24	TO-3	A3	B10
TO25-TO29	TO-4	A3	B7
TO30-TO34	TO-4	A3	B10

Table 4: Materials used for additivation

1. Performance package (225 mg/kg)
2. Commercial additive 1 (500 mg/kg)
3. Commercial additive 2 (500 mg/kg)
4. Performance package + Commercial additive 1
5. Performance package + Commercial additive 2

Table 5: Applied analytical methods

Properties	Methods
Oxidation stability (biodiesel, Rancimat method)	EN 14112:2004; EN 15751:2009
Kinematic viscosity 40 °C	EN ISO 3104:1996
Acid number	MSZ 11723
CFPP (cold filter plugging point)	EN 116:1999
Water content (Karl-Fischer titration)	EN ISO 12937:2001
Density 15.6 °C	EN ISO 12185:1998

3. Results and discussion

3.1 Long-term storage

We have investigated in the current long-term storage experiments since 2010 the effects of the real storage conditions on the aging process, and on the physical and chemical properties of the samples

containing various amounts (proportion) of biodiesel. Due to the extremely large number of experimental results only the most characteristics are presented in graphical form.

For the investigation of oxidation stability the Rancimat method was used. Since the value of the oxidation stability according to the biodiesel standard is minimum 8 h, and in case of gas oils the recommended value by the WWFC (World Wide Fuel Charter – contains the expectations of the car manufacturers) is minimum 35 h, so its examination is very important. The Rancimat method - due to its sensitivity - reflects the progress of the quality degradation processes well. In the case of the biodiesel samples the oxidation stability is decreasing as time goes by. This is reflected well by Figure 1. Figure 2 illustrates the effect of different additivation methods, for samples containing 10 % of biodiesel TO-3. The sudden increase in the induction period at the 52th week can be explained by the change of Rancimat method prescribed by the standard at that point. The modified Rancimat method increased the amount of the sample for biodiesel/gas oil blends from 3.0 g to 7.5 g. It can be seen that from the viewpoint of preservation the oxidation stability the 2nd (sample TO-21) and the 4th (sample TO-23) were the most effective additivation methods.

It is clearly established that the biodiesels used as a raw material did not fulfill the requirements of the standard (≥ 8 h) at the beginning of the storage. None of the samples containing any proportion of TO-3 biodiesel in 10 % or TO-4 biodiesel met the specifications after such a long period of storage. We found that regardless of the feedstock composition of the samples on the basis of the induction periods the 2nd and 4th additivation methods seem to be the best for the preservation of the storage stability. Their common feature is that both contain “Commercial additive 1” additive, so it may have a key role in the long-term preservation of storage stability.

The change in the acid number of the biodiesel is characteristic to their quality changes, since the forming acidic components provide information about the extent of hydrolysis or oxidation reactions. We observed that the acid number increased continuously. All three biodiesels stepped over the limits prescribed in the standard (0.5 mg KOH/g). However, in case of the mixtures, the acid number increase was slighter. The cause of this was that the acid number of the crude originated gas oil part changes narrowly during the storage.

Water in biodiesel can cause hydrolysis reactions, with its effect there is an increased risk of microbial contamination and emulsion formation. The maximum value requirement of the water content is necessary not only because the presence of water accelerates the oxidation process, but also because in addition to the contribution to the growth of microorganisms it can cause corrosion problems. The acidic compounds formed with the hydrolysis of ester bonds of monoglycerides contribute to corrosion too; the presence of water is required for the process to occur. So the hydrolysis contributes to the increase in acid number and decrease in the flash point, thus to the decrease of storage stability. It was observed that the water content of the samples slightly increased, but the mixtures did not reach a maximum limit (not higher than 200 mg/kg) prescribed in the standard. Contrary, after more than one year of storage this property of the biodiesel samples exceeded the prescribed standard value (500 mg/kg). It is apparent that the water content of the biodiesels remained within the standard value until week 80, and then showed a slighter increase than before. It is because with the progressing of the time the samples were less capable of binding water.

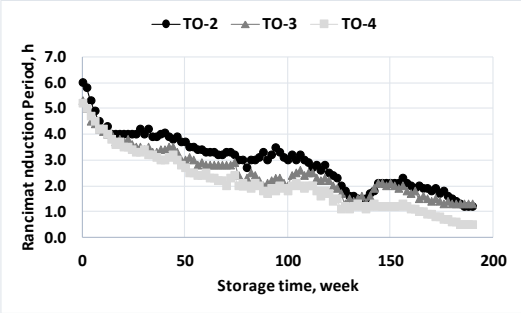

Figure 1: Changes in oxidation stability of biodiesels

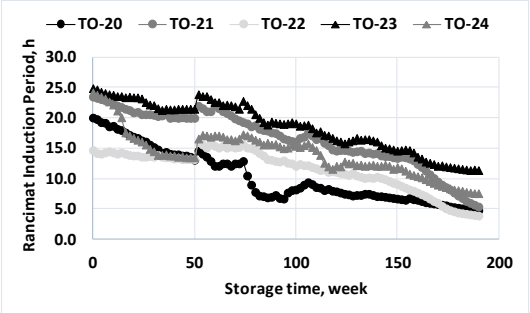

Figure 2: Changes in oxidation stability of mixtures containing 10 % TO-3 biodiesel

When investigating the other properties we found that in terms of densities for each sample a slight increase was observed, but the density limits set in the standard were not exceeded by the samples. The density growth rate decreased with the time. It seems that the density is not suitable to follow the oxidation

reactions, but the measurement of density is important because of the compliance with the standards. We also observed that in the current storage a slight increase was observed in the case of kinematic viscosities. The viscosity data of the mixtures and raw materials met the standard limits. In case of the iodine numbers of the samples we observed slight, steady decrease. In case of gas oils the standard cold filter plugging point for the summer quality is +5 °C maximum and in case of winter quality -20 °C. This measurement has a reproducibility of ± 2-3 °C. Since the values of all samples varied within this value, there can not be seen clear trends about the changes of this parameter. So the CFPP is not applicable to signal the progress of fuel quality decrease.

3.2 Correlation between the different properties of biodiesels

We also investigated the possible relationships between the properties of various biodiesels during storage. As the Rancimat induction period proved to be the most sensitive quality characteristic, we studied the changes of kinematic viscosity and acid number in function of this property (Figure 3-6).

Figure 4 shows the changes in kinematical viscosity of TO-3 biodiesel (produced from 30 % used cooking oil containing plant oil) in the function of oxidation stability. Lower kinematical viscosity values belong to the higher oxidation stability values. Figure 5 shows the changes in kinematical viscosity of TO-4 biodiesel (produced from 50% used cooking oil containing plant oil) in the function of oxidation stability. In this case lower kinematical viscosity values belong to the higher oxidation stability values, too. With the knowing of the oxidation stability value the value of kinematic viscosity can be estimated very well using the correlations.

Figures 3-5 show the changes in acid number of TO-3 biodiesel (produced from 30 % used cooking oil containing plant oil) in the function of oxidation stability. Lower acid number values belong to the higher oxidation stability values. Figure 6 shows the changes in acid number of TO-4 biodiesel (produced from 50 % used cooking oil containing plant oil) in the function of oxidation stability. In this case lower acid numbers values belong to the higher oxidation stability values, too. But in case of this property the accuracy of the estimation is lower.

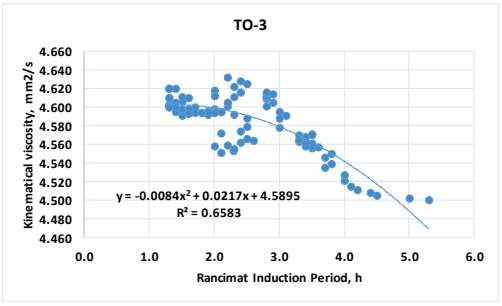

Figure 3: Changes in kinematic viscosity of TO-3 biodiesel in the function of oxidation stability

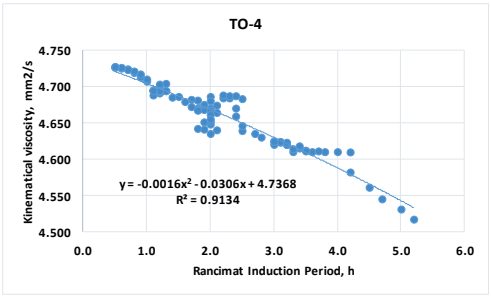

Figure 4: Changes in kinematic viscosity of TO-4 biodiesel in the function of oxidation stability

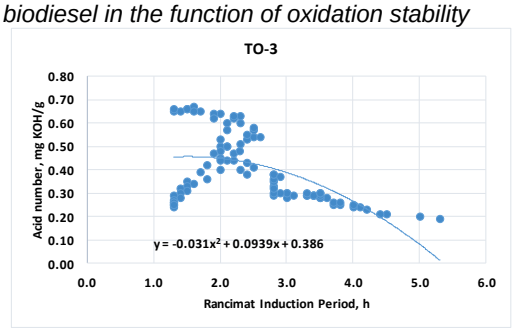

Figure 5: Changes in acid number of TO-3 biodiesel in the function of oxidation stability

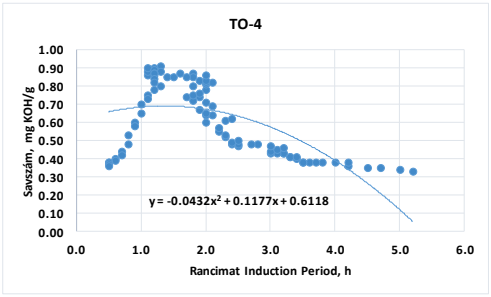

Figure 6: Changes in acid number of TO-4 biodiesel in the function of oxidation stability

4. Summary and conclusions

In our experimental work we studied the changes in the qualities of biodiesels produced from vegetable oil which contained various waste cooking oil (waste-derived component) share (10, 30, 50 %), and its 7 and 10 % blends with gas oil in case of long-term (more than 150 weeks) storage.

The changes in the Rancimat induction period indicated properly the quality degradation processes taking place during the experiments. The induction period of samples strongly decreased. Increase of the blending ratio of biodiesel has adversely affected the induction period. In the samples oxidation reactions

(in varying degrees) took place over time, which was reflected in the increase of acid number as well. Changes in the values of the kinematic viscosity were less significant.

Investigating the relationships between the properties of biodiesels it was found that in the case of biodiesels with the decrease in Rancimat induction period simultaneuously acid number increase occurs, with progress of the oxidation. With the mathematical correlations presented in case of a similar fatty acid composition biodiesels, the kinematic viscosity and the acid number of the samples can be estimated by measuring the value of Rancimat induction period – with good approximation. This can reduce the time needed to measure the samples, and the cost of the tests.

Based on the experimental results described above, we conclude that with the increased proportion of used cooking oil blended into vegetable oil used as raw material for biodiesel the oxidation processes occurred with a higher rate. The cause of this is the presence of a part of the unstable compounds of used cooking oil in the final biodiesel product. From the tested biodiesels the biodiesel produced from vegetable oil containing 10 % used cooking oil was the most applicable to blend into gas oil; in case of increased share a further antioxidant additive is needed to minimize the quality decrease. The used cooking oil/vegetable oil mixtures can be good feedstocks for biodiesel production in case of proper additivation.

Acknowledgement

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