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RESEARCH ARTICLE

Storage Stability of Gas Oils Containing Waste Originated Biocomponent

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Abstract

Nowadays in Europe the demand for diesel fuel is 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 has to be examined in detail.

In our experimental work we investigated 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 130 weeks) storage. We found that with increasing the proportion of used cooking oil in the vegetable oil used as raw material for biodiesel, the oxidation reactions took place in a greater degree. 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 a further amount of antioxidant additives to minimize the degradation.

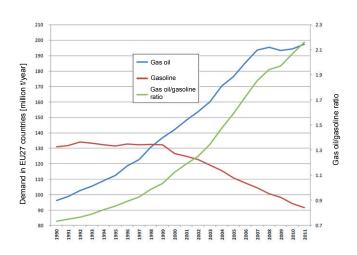
Keywords

biodiesel • used cooking oil • storage stability

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 [1].

In Europe the demand for diesel gas oil continues to grow, while the demand for gasoline shows slight decrease. This is shown in Figure 1 [2]. The reasons for this are the spread of Diesel engines and the increase in volumes of delivered industrial products. The figure clearly shows that the slight increase of the demand for diesel gas oils was typical in the last 20 years. This will further enhance the established gas oil deficit and the excess of gasoline in Europe, and further increase the energy dependence of the EU. In order to ensure sustainable development the deficit resulting from the growing use has to be replaced with alternative energy sources.



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Fig. 1. Changes of motor fuel demand in the European Union

The EU Directives [2003/30/EC, COM (2006) 848, COM (2006) 34, 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 [3-6]. 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 [7] of the use of plant oils, used cooking oils, animal fats as feedstock is that we gain engine fuels from renewed 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 [8].

In Asia from palm oil, the United States from soybean oil, and the European Union countries mainly from rapeseed oil produce the biodiesel [9]. 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 [10]. When using an incorrect storage or manufacturing technology precursors can appear, the precursors resulting insoluble materials [11]. 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. [16,17]

During the oxidation high molecular weight molecules are formed, insoluble sediments and resinous compounds as a result of the polymerization reactions. This can lead to deposits formed on the engine parts and also to filterability problems [12]. The compounds derived from these reactions result in an increase in kinematic viscosity and lead to fouling. Such polymers can be formed which are soluble in biodiesel, but in diesel gas oil mixtures not, so they can secede after blending [13]. The separation of biodiesel and gas oil into two phases can also occur at high level of oxidation, which causes pumping and injection problems.

The oxidation products affect negatively the performance of fuel system. These deposits cause problems especially in case of the injectors and the fuel pump parts [14]. If chemical reactions occur in biodiesel, short-chain acids and aldehydes are formed. These acidic compounds can cause corrosion in the fuel supply system, and this may cause increased wear. The corrosion process also starts in the presence of water, which is accelerated by the presence of acids and hydroperoxides formed during the oxidation [15].

2 Experimental

2.1 Objectives

The main objective of our experimental work was to study the changes in the quality of biodiesels produced from vegetable oil containing various amount (10, 30, 50%) used cooking oil (waste-derived component), and the mixtures of these biodiesels (7 and 10%) and gas oil from the MOL Danube refinery during the long-term (136 weeks) storage. Our further aim was to determine the effect of the various additives used for blending, and to determine the follow-up quality improvement options in case of not proper quality mixtures which suffered quality decrease by the storage.

2.2 Feedstocks

The gas oil was ultra low sulfur ("sulfur-free") gas oil made available by MOL Plc to the Department, 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.

Tab. 1. Properties of the gas oil used for blending

Drepartica		EN 500-2000 - 41-2010
Properties	UT gas oli	EN 590:2009+A1:2010
Density, 15.6°C, kg/m³	835.4	820-845
Sulphur content, mg/kg	4	max. 10
Nitrogen content, mg/kg	54	-
Kinematic viscosity 40°C, mm ² /s	2.814	2.0-4.5
CFPP, °C	-15	max20 (winter) max. +5 (summer)
Flash point (Pensky-Martens), °C	64	min. 55
Engler-distillation, °C		
initial boiling point	191	-
10 v/v%	220	-
30 v/v%	250	-
50 v/v%	274	-
70 v/v%	304	-
90 v/v%	340	-
end boiling point	361	-

Tab. 2. Properties of the used biodiesels

Properties		C2	C3	C4	
		biodiesel	biodiesel	biodiesel	
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,	mm²/s	4.483	4.500	4.517	
Acid number, mgKOH/g		0.11	0.19	0.33	
lodine number, gl ₂ /100g		160	166	171	
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	
erucic acid	C22:1	-	-	-	
lignoceric acid	C24:0	-	-	-	

 Tab. 3. Signs and composition of the storage stability samples

Sample name	Used biodiesel	Used gas oil	Blending ratio
C5-C9	C2	C1	B7
C10-C14	C2	C1	B10
C15-C19	C3	C1	B7
C20-C24	C3	C1	B10
C25-C29	C4	C1	B7
C30-C34	C4	C1	B10

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). All the additives are commercially available. The most important from them is the Biostable 403 which is a biodiesel stabilizing additive. Experimental sampling and analysis of the samples were carried out every two weeks.

Tab. 4. Materials used for additivation

1. Performance package (225 mg/kg)	
2. Biostable 403 (500 mg/kg)	
3. Lubco3022 (500 mg/kg)	
4. Performance package +Biostable 403	
5. Performance package +Lubco3022	

Tab. 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

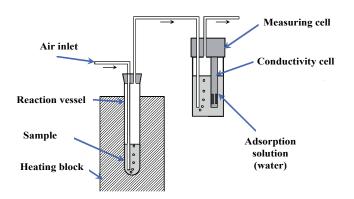


Fig. 2. Scheme of Rancimat test method

2.4 Analytical method

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.

The oxidation stability of biodiesel samples was evaluated according to the Rancimat method (Figure 2). During the measurements of the oxidation is induced by constant air flow of 10 l/h through 3g of biodiesel and 7.5g biodiesel containing gas oil sample kept at 110°C. The vapors released during the oxidation process together with the air are passed into a flask containing distilled water and fitted with an electrode for measuring the conductivity. The formation of volatile carboxylic acids (mainly formic and acetic) in the sample and its absorption in the water increase the conductivity in the measuring vessel. The time that elapses until the secondary oxidation products are detected, is known as the induction period.

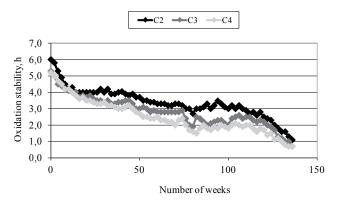


Fig. 3. Changes in oxidation stability of biodiesels

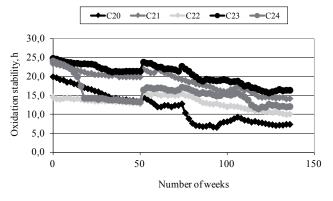


Fig. 4. Changes in oxidation stability of gas oil containing 10% C3 biodiesel

3 Results and discussion

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) 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 3.

Figure 4 illustrates the effect of different additivation methods, for samples containing 10% of biodiesel C3. 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 three grams to 7.5 grams. It can be seen that from the viewpoint of preservation the oxidation stability the 2nd (sample C21) and the 4th (sample C23) were the most effective additivation methods.

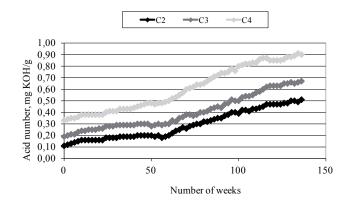


Fig. 5. Changes in acid number in case of biodiesels

It is clearly established that the biodiesels used as a raw material did not fulfill the requirements of the standard (\geq 8h) at the beginning of the storage. None of the samples containing any proportion of C3 biodiesel in 10% or C4 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 Biostable 403 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. The results obtained in case of biodiesel samples are shown in Figure 5. 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.

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 (Figure 6) 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.

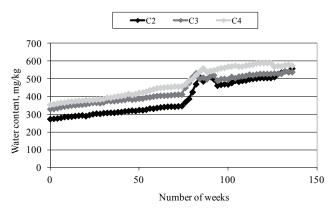


Fig. 6. Changes in water content in case of biodiesels

It is because with the progressing of the time the samples were less capable of binding water.

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 \pm 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.

Based on the results of the experiments presented above, we concluded that from our measured properties primarily the Rancimat induction period exceeded the values specified in the standard. Therefore, we made experiment to improve this property. We used physical methods first (eg. filtering with different adsorbents), which were able to make some quality improvements, but the product yield was inadequate, so these methods in case of biodiesel-diesel blends are not industrially applicable. Then we investigated the effects of post-additivation. We focused on the two best additives based on the results of our pre-experiments. For the tests biodiesels (C2, C3 and C4) with significantly reduced induction period (RIP = 2.0, 1.5, 1.0), and their mixtures were used. To the samples the following additives were added: biodiesel stabilizing additive (Biostable 403) or antioxidant additives (BHT: butylated hydroxy toluene). The additives were applied in 250, 500, 750, 1000 mg/kg concentration and even a concentration of 2000 mg/kg was used for pure biodiesel.

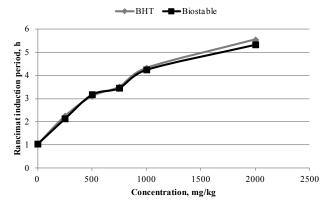


Fig. 7. Oxidation stability of C2 biodiesel after post-additivation

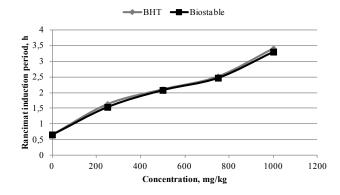


Fig. 8. Oxidation stability of C3 biodiesel after post-additivation

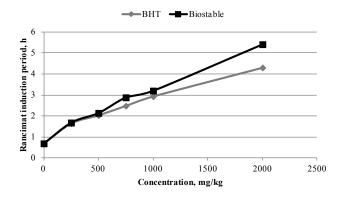


Fig. 9. Oxidation stability of C4 biodiesel after post-additivation

In case of additivated biodiesels (Figures 7-9) we concluded based on the results that in case of both additives with increased concentration the induction periods of the three biodiesels increased. When applying 2000 mg/kg the standard value of the oxidation stability (8h) was approximated in case of biodiesel from vegetable oil containing a minimum of used cooking oil. In case of the other biodiesel samples the improvement was significant, but the standard value was not approached.

We additivated the C5, C10 (containing C2 biodiesel) and the C25, C30 samples (containing C4 biodiesel) with the tested additives (Figures 10-13). It can be seen that the additivation even in case of the lowest concentration significantly improved the induction period over 20 h, regardless of the sample composition.

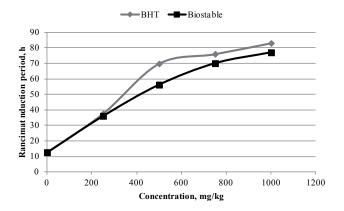


Fig. 10. Effect of post-additivation on the induction period of C5 sample

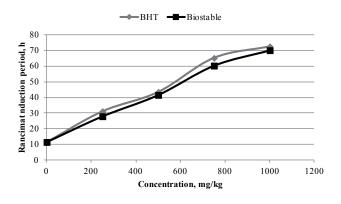


Fig. 11. Effect of post-additivation on the induction period of C10 sample

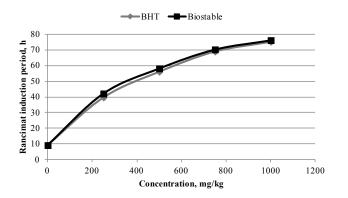


Fig. 12. Effect of post-additivation on the induction period of C25 sample

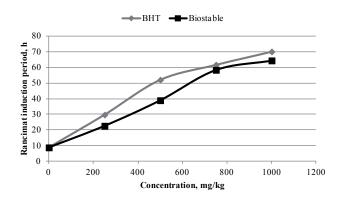


Fig. 13. Effect of post-additivation on the induction period of C30 sample

In summary we found that the additivation results were positive, improving the quality of the biodiesels, as well as the quality of the mixtures. However, more increased size experiments are needed to verify the blending possibility of the improved quality biodiesel into gas oil. The other properties were only slightly changed by the effect of post-additivation. The results – with the support of pilot scale experiments – can form a basis for an industrial quality improvement technology.

4 Summary, conclusions

Based on the assessment of the changes during 136 weeks of storage of biodiesels produced from rapeseed oil and partly used cooking oil (10, 30, 50%) and gas oils containing biodiesel 7.0 and 10.0% we made the following observations:

- The application properties did not exceed the limits prescribed by the standard, except for the Rancimat induction period (oxidation stability). We point out that biodiesels used as raw materials (without additivation) did not fulfill the requirements of the standard ($\geq 8h$) at the beginning of the storage. We found that regardless of the material composition of the sample on the basis of the induction period data the 2nd and 4th additive packages seem to be the best for the preservation of the storage stability. Their common feature is that both contain Biostable 403, so it may have a key role in long-term preservation of the storage stability. So there is a good additivation method. By using this additive we can still produce stable blends with relatively short time stored biodiesels. The test results, however, suggest that without the addition of additives it is not practical to store the biodiesels longer than six months, and the biodiesel - diesel blends longer than 1 year.
- It was not possible to establish a clear and distinctive trend in case of density changes (we experienced usually a slight increase), changes in the values do not follow the trends of oxidation stability measured by the Rancimat apparatus. Therefore, the measuring of density - although a relatively easy and fast method – seems not applicable alone for the unequivocal following of the quality decrease.
- The kinematic viscosity values in most cases showed a slightly increasing trend. The experimental data fulfilled the values prescribed by the current standards in every case. Changes in the kinematic viscosities do not reflect the quality decrease so well as the oxidation stability measurements with Rancimat apparatus, but due to the need to meet the requirements of the standards it is important to carry out the measurements.
- The acid numbers of samples showed a slightly increasing trend, too. Acid numbers of all three biodiesels reached the maximum levels specified in the standard. The experimental results approximated the trends of the Rancimat results. In the case of blends with increasing the proportion

of biodiesel in the gas oil the acid numbers increased more.

- The trend observed in the case of iodine numbers was a slight decrease, suggesting polymerization, oxidation.
- The water content of the stored samples increased slightly, but the mixtures did not reach the maximum allowable standard limit. On the contrary, this property of the biodiesel samples after more than a year of storage already exceeded the standard value. Based on these results, the biodiesels and diesel fuels containing biodiesel should be stored in floating roof tanks, away from contact with air, because the water absorption capacity of the biodiesel/ diesel fuel blends significantly increased with blending 5 v/v% biodiesel. However, not only because of the standards, but also because of the microbial contamination and the corrosion it is especially important to pay attention to the water content also.

In summary we found that the additivation results were positive, improving the quality of the biodiesels, as well as

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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. 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.

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