HUNGARIAN JOURNAL
OF INDUSTRIAL CHEMISTRY
VESZPRÉM
Vol. 39(3) pp. 369-373 (2011)

INVESTIGATION OF STORAGE STABILITY OF BIODIESELS

S. KOVÁCS✉, GY. PÖLCZMANN, J. HANCSÓK

University of Pannonia, Institute of Chemical and Process Engineering
MOL Department of Hydrocarbon and Coal Processing, Veszprém, H-8201, P.O.Box: 158, HUNGARY,
✉E-mail: kovacss@almos.uni-pannon.hu

The production and application of fuels from agricultural origin have emerged into focus in the last couple of years. A number of environmental, political and economical factors has confirmed and strengthened this process. The main reason of this tendency is the energy policy of the European Union, namely to reduce the green house gas emission of fuels, to decrease the significant dependence of EU on import energy and crude oil and to support rural development. To achieve these objectives, the European Union created the 2003/30/EC and 2009/28/EC directives, which regulate the application of biomass derived fuels. The main purpose is to promote the use of biofuels in transportation by recommending and specifying the share of the bio-components. This proposed value (10 energy % share of biofuels in the transport sector by 2020 in the EU) can be reached by the conversion of different triglyceride-containing biofeedstocks (e.g. vegetable oils, used frying oils, animal fats, algae oils, brown grease, etc.) to different biofuels or blending components. Nowadays FAME (Fatty Acid Methyl Esters), called as first generation biofuel, is mostly used as diesel bio blending component. But this biofuels due to its chemical structure the presence of the double bond in the molecule have a high reactivity with the oxygen, especially when it placed contacting air. That is why the long term storage stability of biodiesel is an important issue. The aim of our research work was to investigate the long term storage stability of biodiesel samples originated from different feedstock. The effects of the real storage conditions on the properties (induction period, acid value, iodine value, density, water content and kinematic viscosity) of the different biodiesels were investigated. Results showed that the acid number and the water content increased, while the induction period and the iodine number decreased with increasing storage time of biodiesel samples.

Keywords: biodiesel, storage stability, oxidation stability, Rancimat method

Introduction

The production and application of the agricultural origin fuels have emerged into focus in the last couple of years. A number of factors which affect the whole mankind has confirmed and strengthened this process, which are of environmental, political and economic nature [1].

The main reason of this tendency is the energy policy of the European Union, namely to reduce the green house gas emission of fuels, to decrease the significant dependence of EU on import energy and crude oil and to support rural development. To achieve these objectives, the European Union created the 2003/30/EC and 2009/28/EC directives, which regulate the application of biomass derived fuels. The main purpose is to promote the use of biofuels in transportation by recommending and specifying the share of the bio-components [2, 3].

This proposed value (10 energy % share of biofuels in the transport sector by 2020 in the EU) can be reached by the conversion of different triglyceride-containing biofeedstocks (e.g. vegetable oils, used frying oils, animal fats, algae oils, brown grease, etc.) to different biofuels or blending components. Nowadays FAME (Fatty Acid Methyl Esters), called as first generation biofuel, is mostly used as diesel bio blending component.

The chemical structure of these alternative fuels and the applied feeds determined its quality and performance properties. Due to the presence of significant amount of unsaturated fatty acids, the oxidation stability has high importance during long term storage. The amount and structure of the fatty acids and ester bonds are major factors influencing these properties outside the storage conditions [4-9].

The storage stability can be worsen due to storage conditions, such as light and air exposure, high temperature, different pollutants and the presence of water, which are catalyzing the harmful reactions. Hydroperoxides are formed during these oxidation reactions and they react with other free radicals. Insoluble deposits and gums are formed in these reactions too. These degradation products in engine causing operational problems; like fuel filter plugging, injector fouling and deposit formation in engine combustion chamber. This increase the kinematic viscosity of the degraded fatty acid methyl ester samples. The products of the primary oxidation reaction they can be further oxidised to form aldehydes, ketones and shorter chain fatty acids. These compounds cause corrosions in the injection system *(Fig. 1)*.

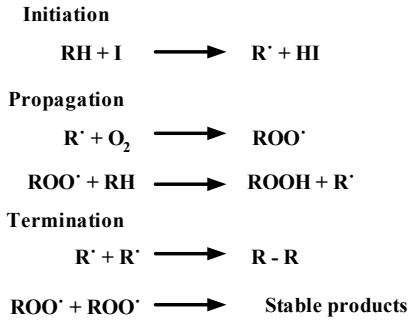

Figure 1: Mechanism of the biodiesel oxidation process

However, the natural antioxidants can prevent or delay these reactions [4, 5].

Storage stability of biodiesel is its ability to resist degradation in contact with environment and storage conditions. The preservation of this during storage is an important issue for the viability and sustainability of the biodiesels [5, 10, 11].

Experimental

As previously mentioned the aim of our research work was to investigate the long term storage stability of biodiesel samples originated from different feedstock. The effects of the real storage conditions on the physical and chemical properties of the different biodiesels were investigated.

Materials

The applied biodiesels main properties and fatty acid composition is summarized in *Table 1*. The raw material of "A" and "C" biodiesels were rapeseed oil with different fatty acid composition. In case of sample "B" the raw material was sunflower oil with high oleic acid content.

Table 1: The main properties and the fatty acid composition of the biodiesel samples

Property		A	B	C	EN 14214
Density, 15 °C, kg/m^3		883.2	884.9	883.7	860–900
Sulfur content, mg/kg		3	5	7	max. 10
Kinematic viscosity, 40°C, mm^2/s		4.523	4.473	4.400	3.5–5.0
Acid value, mgKOH/g		0.09	0.08	0.35	max. 0.5
Iodine value, gI_2/100g		112	83	101	max. 120
Water content, mg/kg		101	256	420	max. 500
Fatty acid composition, %					
palmitic acid	C16:0	4.9	2.4	4.0	-
palmitoleic acid	C16:1	0.2	0.1	0.2	-
stearic acid	C18:0	1.5	2.5	1.7	-
oleic acid	C18:1	61.5	91.8	75.5	-
linoleic acid	C18:2	21.2	1.2	12.3	-
linolenic acid	C18:3	8.1	0.6	5.2	-
arachidic acid	C20:0	0.6	0.8	0.3	-
gondoic acid	C20:1	1.3	0.5	0.7	-
behenic acid	C22:0	0.3	0.1	0.1	-
erucic acid	C22:1	0.3	0.0	0.0	-
lignoceric acid	C24:0	0.1	0.0	0.0	-

Test methods

The oxidation stability of biodiesel samples was evaluated according to the Rancimat method EN 14112 *(Fig. 2)*. During the measurements of the oxidation is induced by constant air flow of 10 l/h through 3 g of biodiesel 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.

During the storage other analytical and performance properties of the samples were determined by standard test methods specified, complying with the specified precision data *(Table 2)*.

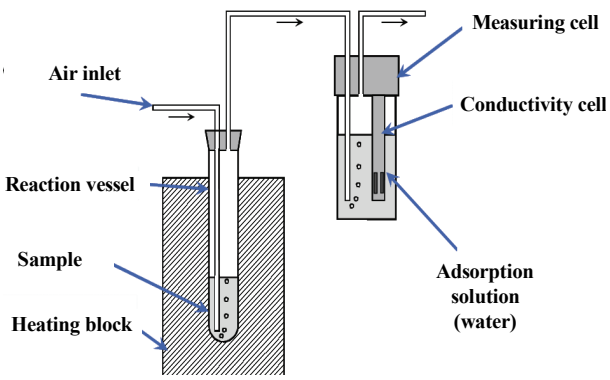

Figure 2: Schematic of Rancimat test

Table 2: Test methods

Properties	Test methods
Density, 15 °C	EN ISO 12185:1996
Sulfur content	EN ISO 20846:2004
Viscosity, 40 °C	EN ISO 3104:1996
Acid value	EN 14104:2003
Iodine value	EN 14111:2003
Water content	EN ISO 12937:2000
Oxidation stability, 110 °C	EN 14112:2003
Fatty acid composition	EN ISO 5509:2000; EN 14103:2003

Results and discussion

During our experimental work the effect of real storage conditions on the physical and chemical properties of the different biodiesels were investigated. The ambient temperature fluctuations and the contact with the air in case of sampling had effect to the samples. The analytical measurements were carried out in every second week.

Oxidation stability – induction period

The biodiesel samples originated from different sources showed different induction periods, but always decreased. The difference in the measurement results is due to the different fatty acid compositions (the different raw material). The sample A was found below the minimum induction period (6 h) after 25 weeks. The other two samples (B and C) satisfied the oxidation stability requirements of the valid standard after 30 weeks *(Fig. 3)*.

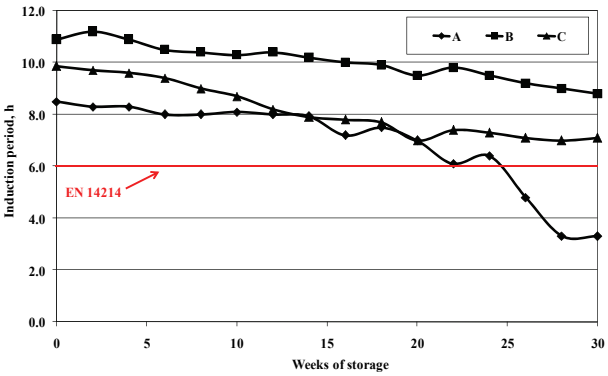

Figure 3: Changes in the induction period of the biodiesel samples

Based on the results the induction period of the biodiesel samples decreased in the order "B", "C", "A". The reason of this the decreasing oleic acid content and the increasing linoleic and linolenic acid content of the biodiesels. The lower amount of polyunsaturated C18 fatty acids methyl esters (C18:2, C18:3) in the biodiesel is favourable to the oxidation stability, because its relative oxidation rate is approx. 1200 or 2500 times higher than that of C18:0 stearic acid methyl ester *(Table 3)* [12].

Table 3: The induction periods and relative oxidation rates of several fatty acid methyl esters (25 °C)

Fatty acid methyl ester Symbol	Induction period, h	Relative oxidation rate
C18:0	-	1
C18:1	82	100
C18:2	19	1200
C18:3	1.34	2500

Acid value

As expected, the experimental results showed an increasing trend in case of all samples but none of the samples exceeded the requirement of the standard 0.5 mg KOH/ g *(Fig. 4)*.

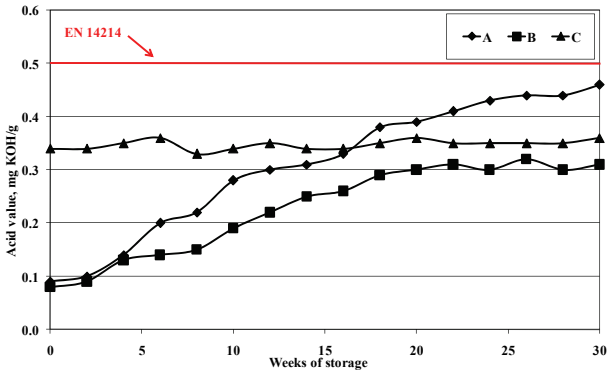

Figure 4: Changes on the acid value of the biodiesel samples

The acid value increasing due to the oxidation of the primary oxidation products of the esters. During these reactions aldehydes, ketone and shorter chain fatty acids are formed. The hydrolysis of the fatty acid esters are resulted the increasing acid value. The products of this reaction are the different alcohols and acids. The higher water content of biodiesel "C" is the reason of the high initial acid value (Table 1). Based on the experimental results it can be concluded the change of this parameter correlates well with the degradation of the biodiesel samples.

Iodine value

The iodine value is in context with the number of the double bonds of the hydrocarbons. In case of biodiesels shows how the material is prone to polymerization and form deposits in the storage vessels and in the engines. The iodine value of the samples decreased gradually *(Fig. 5)*. This indicates the decrease of the number of double bonds and the progress of the deterioration (the polymerization reaction). The reason of the iodine value differences was the different fatty acid composition. The observed slight decrease of iodine number in the case of biodiesel "B" due to the lower amount of poly-unsaturated fatty acids (1.8%) (Table 1).

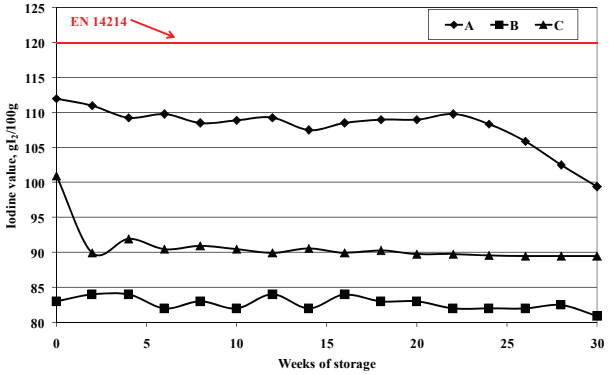

Figure 5: Changes on the iodine value of the biodiesel samples

Water content

Water in biodiesel can initiate hydrolysis reactions, could increase the microbial contamination and the risk of emulsification. Based on the water content of the biodiesel samples it can be concluded that it showed increasing trend in all cases *(Fig. 6)*.

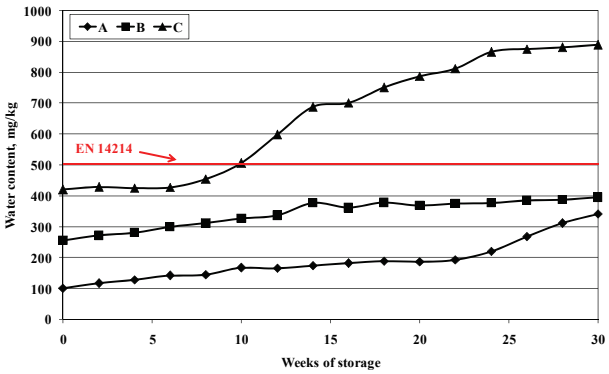

Figure 6: Changes on the water content of the biodiesel samples

Based on the experimental results it can be concluded that the water content of biodiesel C on week 10 exceeded the requirements (500 mg/kg) of the valid standard. The biodiesel is hygroscopic and absorbs the water content of the air. The difference in the results caused by the different initial water content. The systematic study of this property is important because of the standard set values and the microbial contamination.

Density

According to the literature the change of the density correlates well the changes during the storage. Based on the measurement results we did not find a clear trend. However in case of all sample the measured density satisfied the valid standard (*Fig. 7*).

The change of the density does not reflect the results of the Rancimat method. This measurement is not suitable for tracking the biodiesel degradation. But this is a standard property and it is important to do the test periodically.

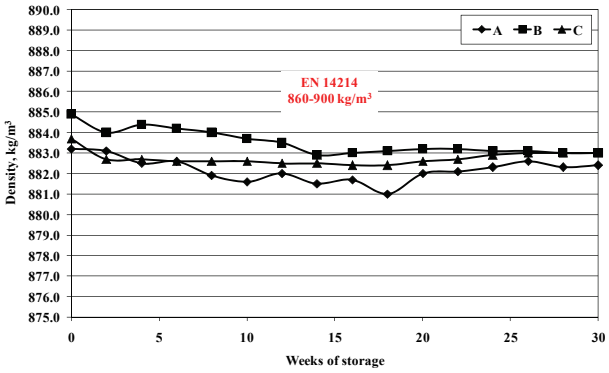

Figure 7: Changes on the density of the biodiesel samples

Kinematic viscosity

Based on the results of the viscosity measurement we did not find clear tendency *(Fig. 8)*. The values are satisfied the requirements of the valid standard in all cases. The change of the viscosity does not reflect the results of the Rancimat method. But this is a standard property and it is important to do the test periodically.

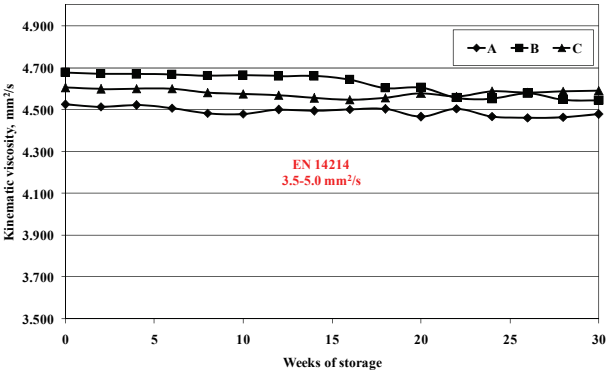

Figure 8: Changes on the kinematic viscosity of the biodiesel samples

Summary

The main objections of our biodiesel long term storage stability experiments are the followings:

- The biodiesel samples originated from different sources showed different induction periods, but in every case it decreased. Based on the experimental results we concluded that the storage stability of the biodiesel samples largely dependent of the initial storage stability of the samples. It is no coincidence that the EN 14214 standard is recommended the addition of stabilizers to improve the oxidation stability of FAME immediately after production or before blending to fossil gas oils.

- The storage stability of samples the better their polyunsaturated fatty acids content are smaller.
- The acid value is an excellent feature of the biodiesel quality change because the formed acidic components gave information about the rate of hydrolysis and oxidation reaction. The experimental results are correlating with will the results of Rancimat test.
- The water content of the biodiesel samples showed increasing trend in all cases.
- In case of density and viscosity the measurement results did not show clear trends. The change of these properties does not reflect the results of the Rancimat method.

In case of the investigation of long term storage stability of biodiesel the history of the samples can be a important information.

ACKNOWLEDGMENTS

"This work was supported by the European Union and co-financed by the European Social Fund in the frame of the TAMOP-4.2.1/B-09/1/KONV-2010-0003 and TAMOP-4.2.2/B-10/1-2010-0025 projects."

REFERENCES

1. A. DEMIRBAS: Biorefineries: Current activities and future developments, Energy Conversion and Management, 50 (2009) 2782–2801
2. Directive 2003/30/EC of the European Parliament and of the Council, (2003)
3. Directive 2009/28/EC of the European Parliament and of the Council, (2009)
4. G. KNOTHE: Some aspects of biodiesel oxidative stability, Fuel Processing Technology, 88 (2007) 669–677
5. S. JAIN, M. P. SHARMA: Stability of biodiesel and its blends, Renewable and Sustainable Energy Reviews, 14(2) (2010) 667–678
6. D. BAKER: BioDiesel – A role for SAE. SAE Motor Vehicle Council, March 31, (2006)
7. J. HANCSÓK, M. KRÁR, SZ. MAGYAR, L. BODA, A. HOLLÓ, D. KALLÓ: Investigation of the production of high cetane number bio gas oil from pre-hydrogenated vegetable oils over Pt/HZSM-22/Al_2O_3, Microporous and Mesoporous Materials, 101 (2007) 148–152
8. G. KNOTHE: Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters, Fuel Processing Technology, 86 (2005) 1059–1070
9. J. HANCSÓK, M. KRÁR, SZ. MAGYAR, L. BODA, A. HOLLÓ, D. KALLÓ: Investigation of the production of high quality bio gas oil from pre-hydrogenated vegetable oils over Pt/SAPO-11/Al_2O_3, Studies in Surface Science and Catalysis, 170 B (2007) 1605–1610
10. G. KARAVALAKIS, S. STOURNAS, D. KARONIS: Evaluation of the oxidation stability of diesel/biodiesel blends, Fuel, 89 (2010) 2483–2489
11. A. BOUAID, M. MARTINEZ, J. ARACIL: Long storage stability of biodiesel from vegetable and used frying oils, Fuel, 86 (2007) 2596–2602
12. H. P. SCHMIEDEL: FAME im Mineralölprodukten insbesondere HEL. Deutsche Wissenschaftliche Gesellschaft für Erdöl, Erdgas und Kohle e.V., 2001