ISSN 1407-7353

MATERIAL SCIENCE AND APPLIED CHEMISTRY

MATERIĀLZINĀTNE UN LIETIŠĶĀ ĶĪMIJA

2008-7353

IMPROVEMENT OF COLD FLOW PROPERTIES AND STABILITY OF BIODIESEL FUEL PRODUCED FROM FATTY WASTE

NO ATKRITUMTAUKVIELĀM IEGŪTU BIODĪZEĻU ZEMO TEMPERATŪRU ĪPAŠĪBU UN STABILITĀTES UZLABOŠANA

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Key words: biodiesel, oxidative stability, cold flow properties

Introduction

The reduction of pollution by gases that cause greenhouse effect is one of the most topical contemporary environmental problems; there are undertaken a lot of different measures for its solution. Having in mind that the main sources of air pollution are motor transport and energetic units, which use the non-renewable resources of fossil diesel fuel, the fuel used in motor transport is gradually replaced by renewable biofuel, the leader of which is evidently biodiesel – fatty acids methyl esters (FAME) used as fuel in diesel engines.

Biodiesel is an alternative, environment friendly, biodegradable, renewable and local source of energy.

The most important quality problems are connected with the oxidative stability and poor cold flow properties of biodiesel that depends on the amount of monoalkyl esters of unsaturated fatty acids.

Nevertheless the cost price of biodiesel fuel produced from edible vegetable oil is relatively high, so it is difficult for such biofuel to compete with fossil diesel fuel [1]. Therefore alternative ways are investigated to reduce the cost price through application of more effective production technologies and usage of cheaper and unsuitable for food (due to contained harmful substances) vegetable oils for the production of FAME – castor oil, physic nut oil, etc. [2, 3].

The costs of biodiesel could be minimized both rationally using cheaper raw materials – such as oils pressed from spoiled rapeseed, linseed oil contaminated with plant protection chemicals and hence unsuitable for food, used frying oil, animal fat obtained in the process of meat and milk processing, dead animals and slaughterhouse waste (fat meat bone mass) and free fatty acids generated during edible oil and biodiesel fuel production; and finding out possibilities to apply the by-product of biodiesel production – glycerol that is obtained at very large amounts (about 10% from products). Smart glycerol revenue could reduce the final manufacturing costs of the process up to 6.5% [4] or even 12–36% [5].

Materials and methods

The oxidative stability of variable biodiesels was improved by two different phenol type antioxidants – butylated hydroxytoluene (BHT) and butylated hydroxyanisole (BHA). The impact of commercially available antifreezes – *Chimec 6635* (produced at *Chimec*, Italy), *Clarinat Sosi Flow* (from *Clariant*, Republic of South Africa), *Viscoplex 10-35* (from *Degussa*, Japan), *Grotamar 71* (from *Schülke & Mayr GmbH*, Germany), *Wintron XC-30* (from *Biofuel Systems Group Limited*, Great Britain) and *Infineum R-442* (from *Infenium*, Great Britain) to the cold flow properties of methyl esters was studied.

Cold flow properties and oxidative stability (Table 1) of fatty acids methyl esters were analyzed according to the requirements of LVS EN 14214 *Automotive fuels. Fatty acid methyl esters (FAME) for diesel engines. Requirements and test methods.*

Table 1

Parameters that were used to characterize oxidative stability and cold flow properties

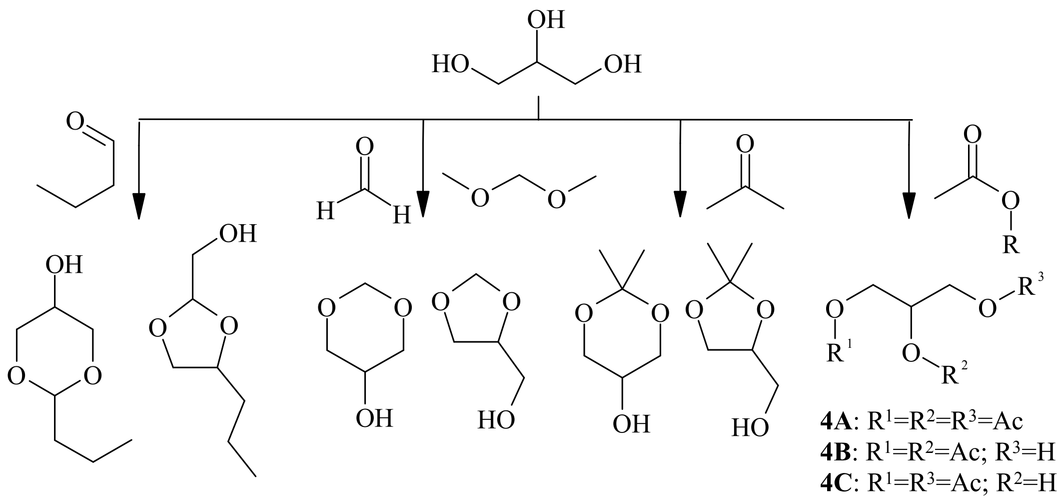
Quality parameter	Unit	Test method
Rancimat induction period (RIP)	hrs	EN 14112
Cloud point (CP)	^oC	EN 23015
Pour point (PP)	^oC	EN 3016
Cold filter plugging point (CFPP)	^oC	ISO 116

Preparation of fatty acids methyl esters from fatty waste

Used frying oil may be successfully applied for biodiesel production, but initial separation of solid particles by filtering as well as separation of moisture by heating at 115°C temperature should be carried out previously. Fatty waste of animal origin before usage for production of biodiesel has to be purified by separation of meat bone mass and moisture. Comparative quality analysis of fatty waste showed that the biggest problems may be caused by high content of free fatty acids (more than 2%) and high amount of saturated fatty acids in fatty waste of animal origin. Investigation of biodiesel synthesis from prepared fatty waste showed that if fatty waste contains high amount of free fatty acids mineral acid catalyzed esterification should be carried out before alkali catalyzed transesterification is used for production of biodiesel.

Synthesis of acetals and ketals from crude glycerol

Purification of crude glycerol was carried out by the traditional method, which includes several stages: at first crude glycerol was acidified and methanol was distilled off. Then fatty acids and glycerides were separated from the mixture and solution of glycerol was neutralized with sodium hydroxide. Water was distilled of in vacuum and sodium phosphates were separated by decantation and filtration. The purity of obtained technical glycerol was 89.6%.
Pure and technical glycerol was used for synthesis (Scheme 1) of several acetals (**1A**, **1B**, **2A**, **and 2B**), ketals (**3A**, **3B**) and acetyl derivatives (**4A**, **4B**) of glycerol as potential PP and CFPP depressants. Cyclic acetals and ketals were obtained as mixtures of isomers: 1,3-dioxane and 1,3-dioxolane derivatives. The yields of these reactions varied from 9% to 82%. The lowest yield was observed in reaction with dimethoxymethane – 9.0%; the highest yield was obtained when glycerol reacted with n-butyraldehyde – 82%. Acetates of glycerol were synthesized by simultaneous transesterification of rapeseed oil and *in situ* treatment of liberated glycerol with methyl (or ethyl) ester of acetic acid – solution of different isomers of acetylated glycerol in biodiesel has been obtained by this one-pot method.



1A **1B** **2A** **2B** **3A** **3B**

4A: $R^1=R^2=R^3=Ac$
4B: $R^1=R^2=Ac$; $R^3=H$
4C: $R^1=R^3=Ac$; $R^2=H$
4D: $R^1=R^2=H$; $R^3=Ac$
4E: $R^1=R^3=H$; $R^2=Ac$

Scheme 1

Results and discussion

Comparative analysis of the quality of fatty acids methyl esters synthesized in laboratory conditions from animal and vegetable fatty waste showed (Table 2) that pure methyl esters could not be used directly in diesel engine.

Table 2

Quality parameters of methyl esters

Parameter	Unit	Standard limits		Methyl esters			
		min	max	RME	LME	TME	PME
Ester content	% (m/m)	96.5	-	98.7	98.1	97.8	97.2
Density at 15°C	g/cm^3	0.860	0.900	0.888	0.896	0.867	0.866
Viscosity at 40°C	mm^2/s	3.50	5.00	4.6	4.77	5.14	5.47
Water content	mg/kg	-	500	400	380	430	450

Oxidation stability (110°C)	hrs	6.00	-	6.32	0.38	0.44	0.18
Acid value	mg KOH/g	-	0.50	0.40	0.50	0.40	0.45
Iodine value	g I_2/100g	-	120.0	116.3	176.2	51.5	64.9
Linolenic acid methyl ester	% (m/m)	-	12.0	9.5	48.0	ND	0.8
Methanol content	% (m/m)	-	0.20	0.15	0.1	0.18	0.17
Alkaline metals	mg/kg	-	5.0	3.5	4.0	4.2	4.3
Phosphorus content	mg/kg	-	10.0	9.0	9.5	9.8	9.4
Cold filter plugging point (CFPP)	°C	-	-5* -32**	-5	-8	+18	+19

* summer period, ** winter period; ND – not detected

The most relevant problems may be caused by low oxidation stability and high CFPP of methyl esters of animal origin – tallow methyl esters (TME) and pork lard methyl esters (PME), respectively; as well as high content of linolenic acid methyl ester, high iodine value and low oxidative stability of linseed oil methyl esters (LME).

It was found out (Fig. 1) that oxidative stability of fatty acids methyl esters of animal and vegetable origin could be increased by adding 400 ppm of synthetic antioxidants: BHA and BHT with synergist citric acid (20% of antioxidant quantity) added.

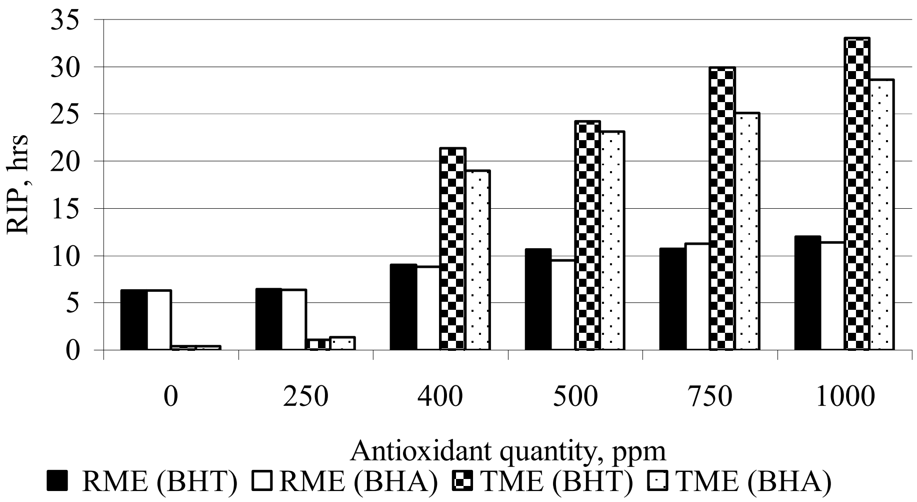


Fig. 1. *Dependence of induction period (IP) upon quantity of antioxidant*

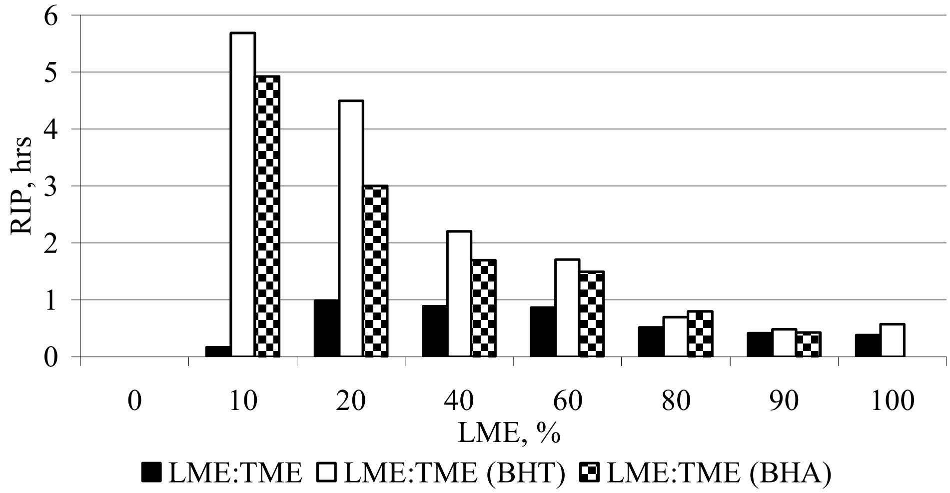


Fig. 2. *Dependence of induction period (IP) upon composition of LME:TME mixture*

In parallel the oxidative stability of mixtures containing methyl esters of low oxidative stability such as LME, tallow fatty acids methyl esters (TME) and lard fatty acid methyl esters (PME) was examined. It was found that mixtures containing 10 to 20% of LME and 80 to 90% of TME (Fig. 2) or PME, were characterized by higher oxidative stability in both cases: with and without antioxidant additives.

Significant problems were encountered regarding CFPP of methyl esters produced from fatty waste. It is evident (Table 2) that vegetable oil biodiesels, like rapeseed oil methyl esters (RME) and LME, apparently, due to high amount of unsaturated fatty acids, have comparatively low CFPP, while the CFPP temperature of TME and PME is already positive.

Possible way to improve the cold flow properties of the biodiesel is the usage of special additives (depressants). The influence of the type and amount of the commercially available depressants - *Wintron XC-30*, *Viscoplex 10-35*, *Chimec 6635*, *Clarinat Sosi Flow* - to CFPP of RME (CFPP = -5^{o}C without any antifreezes) was evaluated. It was found that the optimal concentration of all analyzed depressants in RME is 1000 ppm. *Chimec 6635* can be distinguished as the most effective; its dose of 1000 ppm decreased CFPP of RME even by four times from – 5^{o}C up to -19^{o}C. Further increase of the amount of depressants in RME (over 1000 ppm) had no positive effect on the RME cold flow properties.

Table 3 presents the data on the dependence of CFPP of methyl esters mixtures, containing 80% RME, 16% PME and 4% LME, on the type and quantity of the depressant used. According to the presented data, it is possible to state that the optimal concentration of all analyzed depressants is 5000 ppm in this case. The best results were received using *Viscoplex 10-35*, but the minimal reached CFPP temperature was -10^{o}C.

Table 3

Effectiveness of depressants to CFPP of mixture RME:PME:LME=20:4:1

Depressant	Concentration, ppm									
	1000	2000	3000	4000	5000	6000	7000	8000	9000	10000
Chimec 6635	-3	-4	-5	-6	-5	-5	-5	-5	-4	-4
Clarinat Sosi Flow	-3	-7	-7	-5	-4	-4	-4	-5	-5	-5
Viscoplex 10-35	-6	-8	-7	-9	-10	-10	-7	-7	-8	-8

Grotamar 71	-3	-5	-4	-5	-4	-4	-4	-5	-5	-5
Wintron XC-30	-4	-4	-4	-5	-5	-5	-5	-5	-5	-5
Infineum R-442	-4	-5	-4	-5	-5	-5	-5-	-5	-5	-5

It is well known that acetylglycerols can improve cold flow properties of petrol fuel [6], so ketales, acetales and acetylglycerols, synthesized from technical and pure glycerol, were tested for their impact on the cold flow properties of RME. The influence of obtained glycerol acetals and acetates on CP, PP and CFPP was tested – 1% (m/m) of corresponding glycerol acetals were added to RME; the content of glycerol acetates obtained *in situ* together with RME was about 10% (m/m) from mixture. Values of CP, PP and CFPP of the analyzed biodiesel samples are provided in Table 3. Nearly all synthesized additives decrease the CFPP value about 2 to 3 times in comparison with RME without any additives of antifreezes.

Table 4

Influence of glycerol acetals, ketals and acetates on low temperature properties of RME, 1% (m/m) additive

Nr.	Reagents	Additive	CFPP, ^{o}C	CP, ^{o}C	PP, ^{o}C
1.	Formaldehyde, pure glycerol	**2A&2B**	-14	-3	-25
2.	Formaldehyde, technical glycerol	**2A&2B**	-11	-2	-24
3.	Acetone, pure glycerol	**3A&3B**	-14	-3	-23
4.	Acetone, technical glycerol	**3A&3B**	-13	-2	-23
5.	n-Butyraldehyde, technical glycerol	**1A&1B**	-10	-3	-24
6.	Methyl acetate, technical glycerol*	**4A&4B&4C&4D**	0	-6	-31
7.	Ethyl acetate, technical glycerol*	**4A&4B&4C&4D**	0	-3	-26
8.	Dimethoxymethane, pure glycerol	**2A&2B**	-	-1	-26
9.	RME		-6	-2	-14

* ~ 10% (m/m) glycerol acetates obtained *in situ* together with RME

Conclusions

1. Oxidative stability of fatty acids methyl esters can be improved with addition of synthetic antioxidants. Effectiveness of synthetic antioxidants BHA and BHT was nearly the same; it was established that optimal antioxidant concentration for stabilization of rapeseed oil and tallow methyl esters is 400 ppm (also using synergist – citric acid, 20% of antioxidant quantity).

2. Mixtures of methyl esters of fatty acids of animal and vegetable origin with antioxidants added were more stable against oxidation than individual products. The maximum of oxidative stability was observed in mixtures containing 90% of fatty acids methyl esters of animal origin and 10% of fatty acids methyl esters of vegetable origin.
3. The most appropriate industrial depressant for improvement of cold flow properties of pure RME appeared *Chimec 6635*; its optimal dose of 1000 mg/kg decreases the CFPP from -5^{o}C to -19^{o}C. Depressant *Viscoplex 10-35* was found to be the most effective (with optimal dose of 5000 mg/kg) for improvement of above mentioned properties of the RME mixture with PME and LME (in proportion 20:4:1).
4. Ketals, acetals and acylglycerols can be synthesized from technical glycerol (with 89.6% glycerol content) with the yield up to 82%. All synthesized additives (used in quantity 1% (m/m)) improved CFPP about 2-3 times in comparison with pure RME.
5. Glycerol acetates can be obtained *in situ* together with RME in transesterification of rapeseed oil with methyl- or ethyl acetates; such mixture can be used as additive to improve biodiesel cold flow properties.

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V. Makarevičiene, E. Sendzikiene, M. Gumbite, I. Sartakova, M. Jure, M. Strēle, R. Seržane, A. Smirnovs, I. Mieriņa, T. Paeglis. No atkritumtaukvielām iegūtu biodīzeļu zemo temperatūru īpašību un stabilitātes uzlabošana.

Pēdējos gados arvien lielāku nozīmi tautsaimniecībā iegūst no atjaunojamiem dabas resursiem iegūstamās alternatīvās degvielas, tai skaitā arī biodīzelis. Tomēr tā veiksmīgu izmantošanu ierobežo taukskābju monoalkilesteru nepietiekamā oksidatīvā stabilitāte, kā arī neapmierinošās zemo temperatūru īpašības. Tā kā abi šie faktori lielā mērā ir saistīti tieši ar taukskābju piesātinātības pakāpi, tad pētījumiem izmantoti biodīzeļi, kas sintezēti no ļoti atšķirīgām taukvielām – stipri nepiesātinātās linu eļļas, dzīvnieku taukiem, kas pamatā veidoti no piesātinātām taukskābēm, kā arī rapšu eļļas. Biodīzeļu oksidatīvās stabilitātes izmaiņas BHA un BHT klātbūtnē tika vērtētas izmantojot Rancimāta indukcijas periodu. Pētīta dažādu komerciāli pieejamo temperatūras depresantu un no biodīzeļa ražošanas blakusprodukta – jēlglicerīna – sintezētu acetālu un ketālu ietekme uz taukskābju metilesteru auksta filtra nosprostošanās punktu, sastingšanas un saduļķošanās punktiem.

Makareviciene V., Sendzikiene E., Gumbyte M., Sartakova, I., Jure M., Strele M., Serzane R., Smirnovs A., Mierina I., Paeglis T. Improvement of cold flow properties and stability of biodiesel fuel produced from fatty waste.

The use of alternative fuels made from renewable natural resources has considerably increased during the last years, as well as the importance of biodiesel. Nevertheless, insufficient oxidative stability and unsatisfactory cold flow properties of monoalkyl esters of fatty acids limit their successful application. As both of these parameters are largely related to unsaturation degree of fatty acids, we investigated biodiesels obtained from very different fats – strongly unsaturated linseed oil, animal fat mostly based on saturated fatty acids, as well as rapeseed oil. The influence of BHA and BHT additives on oxidative stability of biodiesels was evaluated by Rancimat induction period. The impact of different commercially available antifreezes, as well as acetals and ketals (synthesized from crude glycerol obtained as by-product of biodiesel production) on cold filter plugging point, pour and cloud points of methyl esters of fatty acids was studied.

Макаревичиене В., Сендзикиене Э., Гумбите М., Сартакова И., Юре М., Стреле М., Сержане Р., Смирнов А., Миериня И., Паэглис Т. Улучщение низкотемпературных свойств и стабильности биодизелей полученных из жировых отходов.

В последние годы альтернативные топлива получаемые из возобновляемых природных ресурсов, в том числе биодизель, приобретают всё большее значение в народном хозяйстве. Однако, успешное использование биодизеля ограниченно недостаточной окислительной стабильностью и неудовлетворительными низкотемпературными свойствами моноалкильных эфиров жирных кислот. Поскольку оба эти факторы в значительной мере связаны именно со степенью ненасыщенности жирных кислот, для исследованний мы использовали биодизели синтезированые из различных жиров - сильно ненасыщенного льняного масла, животных жиров, в основе которых насыщенные жирные кислоты, а также рапсового масла. Изменения окислительной стабильности биодизелей в присутствии BHA и BHT оценивались тестом индукционного периода на приборе Ранцимат. Изучалось влияние разных коммерчески доступных антифризов, а также ацеталей и кеталей (синтезированных из сырого глицерина, полученного при производстве биодизеля) на температуру закупорки фильтра на холоде и температуры застывания и помутнения метиловых эфиров жирных кислот.