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Original Research

Oxidation Stability of Biodiesel Fuel Produced from Fatty Wastes

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Abstract

The aim of this work was to examine possibilities to use wastes of animal fat and vegetable oil for the production of biodiesel fuel, evaluating the conformity of the product obtained to the oxidation stability requirements. The oxidation stability of rapeseed oil, linseed oil, tallow and lard fatty acid methyl esters samples and their mixtures was measured by commercial equipment Rancimat 743 applying accelerated oxidation test (Rancimat test) specified in EN 14112.

It was found that fatty acid methyl esters of vegetable origin are more stable for oxidation comparing with methyl esters of animal origin. The optimal level of synthetic antioxidants such as butylated hydroxyanizole (BHA) and butylated hydroxytoluene (BHA) for stabilization of fatty acid methyl esters was determined to be 400 ppm (also using synergist – citric acid, 20% of the antioxidant quantity). Mixtures of methyl esters of animal and vegetable origin with antioxidants were more stable compared with pure products. The highest oxidation stability showed mixtures containing 80-90% of fatty acid methyl esters of animal fat and 10-20% of fatty acid methyl esters of vegetable oil with synthetic antioxidants added.

Keywords: oxidation stability, induction period, fatty wastes, fatty acid methyl esters, antioxidants

Introduction

Increasing environmental pollution by wastes as well as atmospheric pollution by greenhouse gases is forcing us to take measures to solve these environmental problems. A whole range of international agreement has been signed including EU regulations and directives have been adopted to regulate emissions of greenhouse gases to the atmosphere, to promote usage of renewable energy sources, and to assure effective management and utilization of waste of all kinds. Taking into account that the main source of atmospheric pollution is road transport, European Union member states are promoting the production and use of biofuel.

Currently the most often-used type of biodiesel fuel is vegetable oil fatty acid methyl esters produced by transesterification of high quality vegetable oil by methanol [1]. However, even applying the latest and the most modern technology, the cost of biodiesel fuel is rather high. Thus there is a need to look for new ways to make the production of biodiesel fuel more economically attractive. One such alternative could be utilization of animal and vegetable fatty wastes for biofuel production. Animal waste, which is generated in Lithuania and which might be used for the production of biodiesel fuel includes beef tallow, lard and fibre linseed oil which is unsuitable for use in the food industry due to high levels of plant protection chemicals. Processing these wastes is problematic due to a wide variety in terms of their composition and physico-chemical properties and requires the search for new technological solutions. Furthermore, it is necessary to evaluate conformity of the products obtained to the strict quality requirements of standard EN 14214 for biodiesel fuel [2].

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Oxidation stability is an important biodiesel fuel quality parameter. It is expressed by the induction period (IP) which, according to the requirements of the standard, should be at least 6 hours when measured by a standardized Rancimat method [3].

The autooxidation process takes place during the storage of fatty acid methyl esters. In the primary stage of oxidation process peroxides and hydroperoxides are formed. Later, aldehydes and ketones are formed and finally during the polymerization process resins are produced [4]. This makes fuel unsuitable for use in an engine.

The rate of oxidation of fatty acid methyl esters depends on the nature of fatty acids, temperature, oxidation reaction catalysts and inhibitors contained in fats, light, radiation intensity, etc. Oxidation stability of fatty acid methyl esters could be increased using natural and synthetic antioxidants [5]. These substances bind free radicals and stop chain reactions. Thus, fatty peroxyradicals are stabilized and oxidation chain reaction is broken. The effect of antioxidants on the behaviour of edible vegetable oils is widely investigated, but very little is known on the effectiveness of antioxidants on the stabilization of fatty acid methyl esters (FAME). The first FAME stability studies were carried out by measuring different physical and chemical parameters during FAME storage under different conditions [6, 7]. For measurement of the oxidative stability of vegetable oil and fatty acid methyl esters the newly developed Rancimat method was used successfully [8, 9]. The effect of various antioxidants on the induction period of rapeseed oil methyl esters at different temperatures was studied by several authors, but no significant improvement was noticed [10]. Other authors tested the effect of antioxidants based on tert-butylhydroquinone and found good stability improvement of soybean oil methyl esters [11, 12].

The aim of this work was to examine possibilities to use waste products of animal fat and vegetable oil for the production of biodiesel fuel, evaluating the conformity of the product obtained to the oxidation stability requirements of the biodiesel fuel standard.

Experimental Procedures

Edible grade refined rapeseed oil, linseed oil, beef tallow and pork lard for production of fatty acid methyl esters were purchased from the market. Oils and fats were stored at 4°C.

Rapeseed oil methyl esters (RME), linseed oil methyl esters (LME), lard methyl esters (PME) and tallow methyl esters (TME) were prepared following a standard procedure of two-step transesterification by methanol using catalyst sodium hydroxide. All above-mentioned biodiesel samples were analyzed according to the requirements of European standard EN 14214 [13] to check their quality. Prepared samples were stored in closed bottles in a dark place at 18 ± 2 °C.

Fatty acid composition of biodiesel samples was determined according to the requirements of European standard EN 14103 [14]. Content of natural antioxidants in samples were analyzed according to the requirements of international standard ISO 9936 [15].

Synthetic antioxidants butylated hydroxyanizole (BHA) and butylated hydroxytoluene (BHA) as well as synergist citric acid were purchased from Sigma, Vienna. For stabilization of esters and their mixtures, ethanol solutions containing 10% of separate antioxidants as well as citric acid were used. The ratio of antioxidant and citric acid in all experiments was 4:1. Antioxidants were added to ester samples at the beginning of storage tests.

Oxidation stability of samples was evaluated with commercial appliance Rancimat 743 applying accelerated oxidation test (Rancimat test) specified in EN 14112 [16]. The end of the induction period (IP) was determined by the formation of volatile acids measured by a sudden increase of conductivity during a forced oxidation of ester sample at 110°C with an airflow of 10 l/h passing through the sample.

All experiments were carried out in two series. As a final result the arithmetic mean of the two determinations provided that repeatability requirements indicated in the appropriate standard were taken. If the repeatability requirements were not met results were disregarded and two mew determinations on test portions taken from the same test sample were carried out.

Results and Discussions

Seeking to compare oxidation stability of animal fat fatty acid methyl esters and vegetable oil fatty acid methyl esters under conditions of the prolonged storage effect of storage duration on TME, PME, LME and RME induction period was studied (Fig. 1).

It was determined that stored for 1 day TME and PME had low oxidation stability. IP did not confirm to the requirements of the standard and was only 0.4 h for TME and 0.3 h for PME. After 7 days of storage, oxidation stability of the TME and PME was significantly

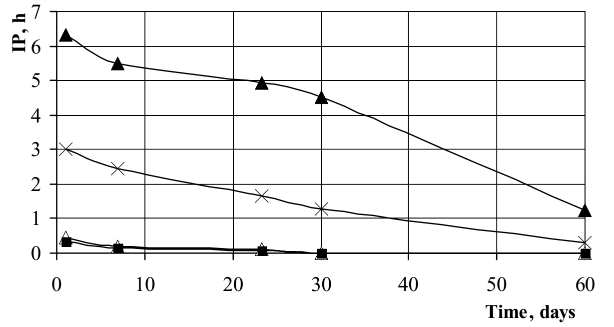

Fig. 1. Dependence of induction period (IP) upon storage time: ■ – PME, Δ - TME, × - LME, ▲ – RME.

Table 1. Fatty acid composition and content of natural antioxidants in different kinds of fatty acid methyl esters.

Kind of methyl esters	Fatty acids			Content of natural antioxidants	
	Saturated	Unsaturated	Polyunsaturated	Carotenoids, mg/kg	Tocopherols and tocotrianols, mg/kg
RME	4.7	61.2	34.1	70	583
PME	33	50.6	16.4	-	-
TME	40.7	57	2.3	-	-
LME	4.4	25.1	70.5	-	694

reduced, while after 60 days esters were oxidized completely as IP was equal to zero. Oxidation stability of LME decreased more slowly. After 60 days of storage IP of LME was 0.3 h. At the same time, freshly produced RME conformed to the oxidation stability requirement of EN 12412 - the IP was higher than 6 h. However, after the first 7 days of storage the IP decreased to 5.5 h, while after 30 days the IP started falling quickly, i.e. the process of autooxidation began. However, even after 30 days of storage IP was longer than 1 h. Difference of oxidation stability of methyl esters of vegetable and animal origin may be explained by the presence of natural antioxidants such as tocopherols, tocotrianols in vegetable oil fatty acid methyl esters (Table. 1). Larger amounts of polyunsaturated fatty acids in esters of vegetable origin (LME and RME) did not play a significant role for oxidation stability of fatty acid methyl esters of vegetable origin in comparison with that of fatty acid methyl esters of animal origin (PME and TME).

To increase the oxidation stability of fatty acid methyl esters, the effectiveness of synthetic antioxidants, commonly used for stabilization of edible vegetable oil, was tested. The antioxidant BHT and BHA mixtures with synergist citric acid (20% of antioxidant quantity) were added to the ester samples in a concentration range between 200 and 1000 ppm. The goal of this experiment was to find the optimum antioxidant concentration for each feedstock and to compare antioxidant effectiveness on oxidation stability of RME and TME.

It was determined (Fig. 2) that the effectiveness of BHA and BHT was nearly the same and optimal antioxidant concentration for RME and TME stabilization was 400 ppm. Furthermore, both antioxidants showed much better effect on TME.

Oxidation stability of unstable TME also can be improved by mixing with more stable RME. For this reason TME was mixed with RME at various rates and oxidation stability of these mixtures was evaluated. It was found that oxidation stability of TME-RME mixture increased with the amount of RME in the mixture.

However, without antioxidants, IP of these mixtures did not reach 6 h (Fig. 3). This could be explained by the fact that 30-day-old RME and 7-day-old TME was used for the production of mixtures. When antioxidants were used, not only mixtures, but also pure products confirmed the oxidation stability requirement of EN 14214. Surprisingly, the highest IP was found in mixtures which contained 10% of RME and 400 ppm of antioxidants BHT and BHA. Comparing the two antioxidants, BHT was more effective than BHA. IP of mixture containing 10% of RME with BHA increased to 22.1 h. In case BHT was used for stabilization of the same mixture, IP was increased to 23.2 h.

In parallel, the oxidation stability of mixtures containing methyl esters of low oxidation stability such as linseed oil fatty acid methyl esters (LME), tallow fatty acid methyl esters (TME) and lard fatty acid methyl esters (PME) was examined. This experiment was carried out

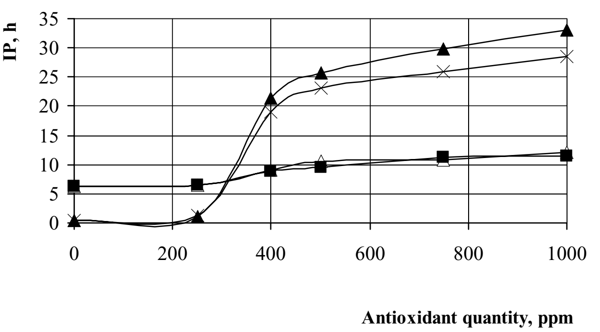

Fig. 2. Dependence of induction period (IP) on antioxidant quantity: ▲ – TME + BHT, × – TME + BHA, ■ – RME + BHA, Δ - RME + BHT.

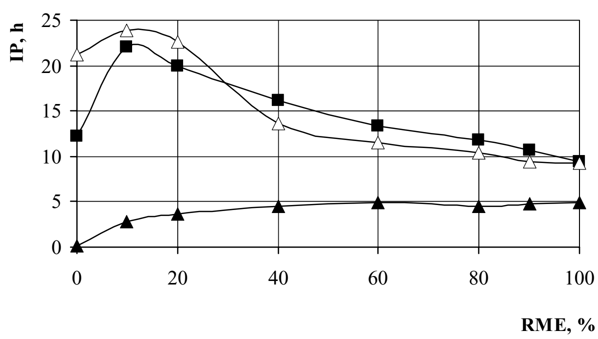

Fig. 3. Dependence of induction period (IP) on composition of RME-TME mixture: ▲ – RME-TME , Δ - RME-TME + BHT (400 ppm), ■ – RME-TME +BHA (400 ppm).

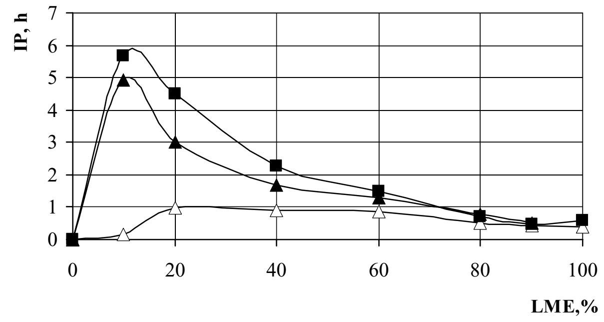

Fig. 4. Dependence of induction period (IP) upon composition of LME-TME mixture: Δ – LME-TME, ▲- LME-TME + BHA (400 ppm), ■ – LME-TME +BHT (400 ppm).

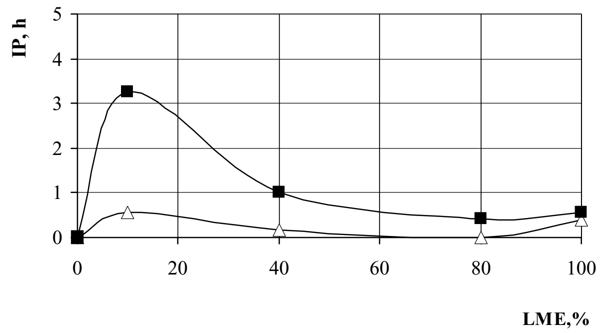

Fig. 5. Dependence of induction period (IP) upon composition of LME-PME mixture: Δ – LME-PME , ■ – LME-PME +BHT (400 ppm).

after 2 months of storage period when TME, PME and LME were substantially oxidized, e.g. IP of pure esters was very low even when antioxidants were added before the experiment. The dependence of IP upon composition of mixtures containing LME and TME is demonstrated in Fig. 4.

It was observed that when LME and TME were mixed at the ratio of 1:4, the oxidation stability of the mixtures in relation to the pure products increased but nevertheless IP of this mixture was very low – only 0.9 h (Fig. 4). These results showed the same tendency as was observed in the case of TME-RME mixtures. The greatest increase in oxidation stability was observed in the mixture containing 10% of LME with antioxidants added. The IP of such a mixture was 4.8 h when BHA (400 ppm) was used. In a case of BHT (400 ppm), IP of 5.7 h was determined. IP of this mixture without antioxidants was equal to 0.3 h.

The dependence of induction period upon composition of LME and PME mixture is demonstrated in Fig. 5. The results show that oxidation stability of these mixtures was lower compared to that of LME and TME mixtures in all ranges of concentrations, even when BHT was added. LME-PME mixtures similarly to the case of LME-TME mixtures with antioxidants added were most oxidation stable, when mixed at the ratio of 1:9. The IP of the above--mentioned mixture was 0.5 h without antioxidant and 3.3 h when BHT was used for stabilization purposes.

Storage studies of pure RME clearly showed that oxidation stability of the esters depends on time. Methyl esters with antioxidants could be stored for longer times. IP of fresh RME was 6.3 h and increased to 10.7 h when 400 ppm of BHT was added and to 9.5 h when 400 ppm of BHA was added. After 23 days of storage, IP of pure RME decreased by 23% and was equal to 4.9 h. The IP of samples stabilized with BHT decreased insignificantly (to 9.9 h) while IP of samples stabilized by adding BHA remained almost the same and was equal to 9.4 h.

Taking into account that the effectiveness of antioxidants is higher when they are used for TME stabilization compared with other esters, it is probable that oxidation stability of RME-TME mixtures will be sufficiently high to ensure satisfactory quality throughout the established period. This hypothesis is being tested in current research.

Conclusions

1. Fatty acid methyl esters of animal origin are less stable for oxidation than fatty acid methyl esters of vegetable origin. This difference may be explained by the absence of natural antioxidants in fatty acid methyl esters of animal fat.
2. Oxidation stability of fatty acid methyl esters can be improved by using synthetic antioxidants. The effectiveness of synthetic antioxidants BHA and BHT was nearly the same and optimal antioxidant concentration for rapeseed oil and tallow fatty acid methyl esters stabilization was established to be 400 ppm (also using synergist – citric acid, 20% of antioxidant quantity).
3. Mixtures of fatty acid methyl esters of animal and vegetable origin with antioxidants added were more stable for oxidation than individual products. Oxidation stability maximum was observed in mixtures containing 90% of fatty acid methyl esters of animal origin and 10% of fatty acid methyl esters of vegetable origin.

Acknowledgements

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