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Investigation of storage stability of diesel fuels containing biodiesel produced from waste cooking oil

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ABSTRACT

Nowadays, the biodiesel is the biofuel which is blended into the diesel gas oil with the highest amount. Biodiesel can be produced from even waste-derived triglycerides (with the so-called transesterification process), but due to its adverse properties (even when produced from “clean” triglycerides like pure rapeseed oil) the storage stability of biodiesel/diesel blends containing biodiesel produced from waste have to be examined in detail. In our experimental work the changes in the quality of biodiesels produced from vegetable oil which contained various amount (10, 30, 50%) of used cooking oil (waste-derived component), and its 7 and 10% blends with gas oil in case of long-term (more than 150 weeks) storage were studied. It was 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 only 10% used cooking oil was the most applicable for blending; in case of the other biodiesels it is very necessary to use further amount of antioxidant additives to minimize the degradation. Furthermore, mathematical relationships were established which describe well the connection between the Rancimat induction period and the kinematic viscosity and acid number especially in case of the investigated BD-3 biodiesel. In the frame of further investigations post-additivation experiments were made with the stored biodiesels and its blends, and the results were positive: quality of the biodiesels improved, as well as the quality of the blends. However, more increased size experiments are needed to verify the blending possibility of this improved quality biodiesel into gas oil.

1. Introduction

One of the pillars of sustainable development is the 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 (Iqbal et al., 2015). In Europe, the import dependence on crude oil is a real problem. 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 and Hancsók, 2014). One of the main recommendations of the 2003/30/EC EU Directive is that the member countries should ensure a minimal blending share of biomass or other renewable originated fuel into the transportation fuels. The European Union targeted until 2010 an increase in the biofuel share (energy content) to 5.75 e% and until 2020 10 e% (Hancsók et al., 2012). One of the possible solution for that is the blending of biodiesels (transesterified vegetable oils) into diesel fuels.

In Europe the demand for diesel gas oil continues to grow, while after 1999 the demand for gasoline showed slight decrease, as it is shown in Fig. 1 (Mackenzie, 2012). The reasons for this are the spread of Diesel engines and the increase in volumes of the 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.

The biodiesels are currently produced mainly by using vegetable oils. The great advantage (Silitonga et al., 2013) of the use of vegetable oils, used cooking oils, animal fats and algaes as feedstock

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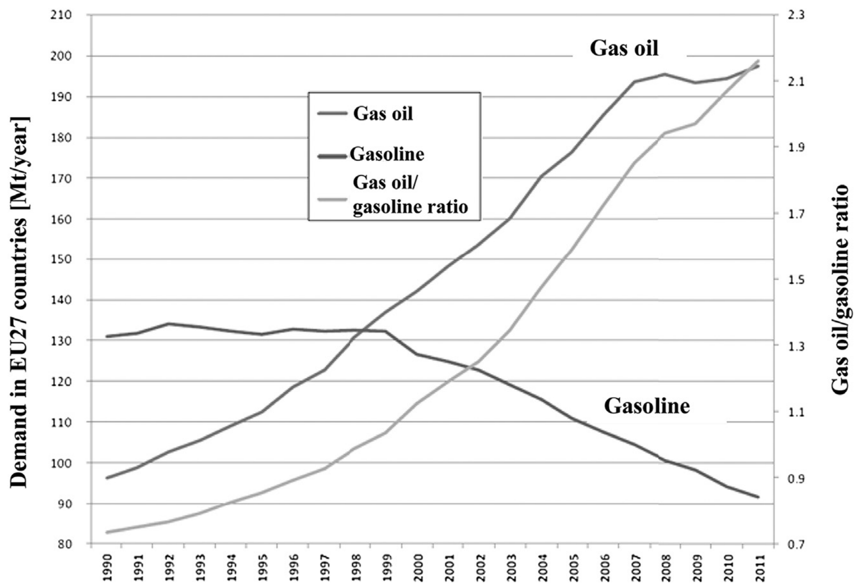

Fig. 1. Changes of engine fuel demand in the European Union.

is that engine fuels are gained from renewable and/or waste derived energy sources. Ten countries in the world (Malaysia, Indonesia, Argentina, USA, Brazil, The Netherlands, Germany, The Philippines, Belgium, Spain) account for more than 80% of the total biodiesel production potential (Bankovic-Ilic et al., 2014). In the European Union countries the biodiesel is produced (Farahani et al., 2011) mainly from rapeseed oil, in Asia from palm oil, and in the United States from soybean oil. 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 (Balat, 2011). Another important issue is the controversy of biofuels made from edible feedstocks. Furthermore, their disadvantage can be the inadequate **storage stability** because of the olefinic double bonds (Fig. 2) and the hydrolysis sensitivity of the ester bond (Kumar et al., 2010). Because of these disadvantages of the biodiesels, their blending share is limited in the current EU diesel fuel standards (Table 1) (Demirbas, 2008).

The storage stability of an engine fuel is the resistance against the deterioration processes which alter its properties and form undesirable compounds (Yang et al., 2014). The fuel is unstable, if these processes can proceed easily. 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 can catalyze harmful reactions. The continuous change of these circumstances can have a significant impact on the stored material. The quality of biodiesels and their 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 resulting insoluble materials formation (Tang et al., 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 dispersant additives, metal deactivators added to the product and other additives, the effect of the refinery technologies, etc. (Aricetti, 2012). If the properties of the fuels are changing too much there is the danger of becoming a non-standard product, which can not be sold in the market.

One of the main property which has to be monitorized during storage of biodiesel (especially if it is made from used cooking oil) is the oxidation stability. During the oxidation high molecular weight molecules, insoluble sediments and resinous compounds are formed as a result of the polymerization reactions. This can lead to deposits formed on the engine parts and such as to filterability problems (Monyem and Van Gerpen, 2001). 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 (Knothe, 2007). 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 (Waynick, 2005). 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 (Graboski and McCormick, 1998). The corrosion process also starts in the presence of water, which is accelerated by the presence of acids and hydroperoxides formed during the oxidation (Dantas et al., 2011).

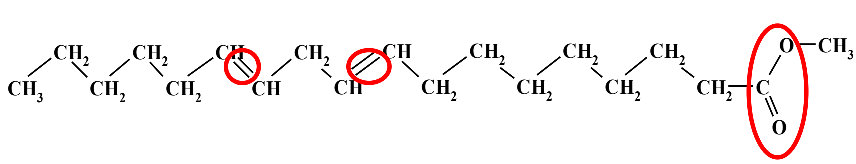

Fig. 2. Structure of fatty acid methyl ester molecule (methyl linoleate).