

## Short communication

## Determining the residual alcohol in biodiesel through its flash point

Jorge Henrique Faber Boog, Eva Lúcia Cardoso Silveira, Lilia Basílio de Caland, Matthieu Tubino\*

University of Campinas, Institute of Chemistry, Campinas, P.O. Box 6154, 13083-970 SP, Brazil

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## ABSTRACT

A simple low cost method is proposed for the quantitative analysis of residual alcohol in biodiesel through determination of the flash point, with which it is correlated. Methyl ester biodiesels from vegetable oils such as corn, soy and sunflower were prepared. The ethyl ester was obtained from soy oil and methyl biodiesel was also synthesized from bovine fat. In all cases it became very evident that there is a direct correlation between the flash point and the residual alcohol content in the prepared biodiesel. Therefore this parameter can be used to directly determine the residual alcohol content of the product.

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## 1. Introduction

Nowadays there is an intense search for new renewable, pollutant free sources for energy. Several facts motivate this situation; among them the atmospheric pollution caused by petrol derivatives. The increase of petrol prices also pushes research on this subject.

Biodiesel is a renewable fuel that is increasingly gaining strength in Brazilian and even in an international context. Brazil presents available climate, sun light, soil and water supply, characteristics that turns it into an important biofuel producer, including both biodiesel and ethanol. Biodiesel is defined as a mixture of mono-alkyl esters produced from vegetable oil (e.g. soy oil) or animal fats (e.g. swine lard) through transesterification reactions with a short chain alcohol, usually, methanol or ethanol, induced by a catalyst. Other alcohols that can be used in the transesterification reaction for biodiesel production are propanol and amyl alcohol although methanol and ethanol are more frequently used, mainly methanol, due to its lower cost and some chemical advantages [1–4]. However, in Brazil bio-ethanol can be used directly as fuel or in biodiesel synthesis is readily available, produced from sugar cane.

Biodiesel quality depends on several factors, being a reflection of its chemical and physical characteristics. The flash point is one of them. This parameter is the minimal temperature where enough vapors of the liquid form an inflammable mixture with the air. Biodiesels present elevated flash points (usually from ca. 160 to 170 °C), if compared with mineral biodiesel whose minimum flash

point can be as low as 38 °C [5]. With respect to the minimal flash point regulated for biodiesel, ASTM norm D6751, is the most restrictive, as it fixes the minimal temperature at 130 °C, whereas the European norm, EN 14214, regulates the minimal flash point at 120 °C and the Brazilian ANP 07/2008 at 100 °C [6]. Very small quantities of residual alcohol present in biodiesel provoke a significant decrease in the flash point and, therefore, according to the regulations, both the alcohol content and the flash point must be determined for each batch of biodiesel produced. Several analytical methods have been developed for the determination of the residual alcohol in biodiesel. Most of them use gas chromatography and, more recently, some of them involve NIR spectrophotometry, which needs the use of quimiometric tools [7,8]. A flow injection method has been proposed by Araujo et al. [9].

The development of other methods for the determination of the alcohol content of the biodiesel are necessary in order to offer a better range of analytical possibilities. Thus, the objective of this work was to verify the correlation between the residual alcohol content and the flash point of biodiesels prepared from several different oils and fats. The intention is to propose an analytical method based on the flash point determination that could also inform the alcohol content. Therefore, the two parameters could be determined using only one procedure.

## 2. Experimental

## 2.1. Materials

Refined oils (soy, corn and sunflower) were purchased in the local markets and employed for biodiesel synthesis without further

\* Corresponding author. Tel.: +55 19 35213133; fax: +55 19 35213023.

E-mail address: [tubino@iqm.unicamp.br](mailto:tubino@iqm.unicamp.br) (M. Tubino).

purification. Bovine fat was heated and treated with calcium oxide to eliminate humidity.

Calcium oxide, methanol and ethanol were analytical grade reagents. Sodium methoxide, 30% in methanol, an industrial product, was used as catalyst.

## 2.2. Biodiesel synthesis

The transesterification reaction was done using 1000 g of vegetable oil or animal fat, 150 g of methanol and 5 g of catalyst (sodium methoxide). The mixture was stirred for an hour between 60 and 62 °C and then transferred to a 2 L separation funnel in order to separate the ester phase (less dense) from the glycerol. The esters were again submitted to reaction using 50 g of methanol and 2 g of the catalyst. After another separation the upper part was washed with five 100 mL portions of water. Afterwards the biodiesel produced was filtered through Amberlite BD10 Dry resin and then heated at 110 °C during 1 h to complete the drying process and the elimination of the residual alcohol. It is known, there are no other low molecular weight components in the raw biodiesel to be removed.

To produce ethyl biodiesel the same procedure was used except that the mass of ethanol that was twice that of methanol.

## 2.3. Sample treatment

In order to verify the dependence of the flash point on the alcohol content, different biodiesels were prepared to contain from 0.0% to 1.0% w/w alcohol/biodiesel, weighing on an analytical balance. To the methyl esters, methanol was added and to the ethyl ester, ethanol was added.

## 2.4. Flash point

The flash point measurements were done according to method D93 (ASTM D6751). A closed cup Pensky–Martens device was used, with aliquots of 65 mL. Measurements were done in triplicate (three different solutions).

## 2.5. Gas chromatography

The methanol content introduced by weight into the biodiesel from corn oil was checked according to method EN 14110 by gas chromatography to verify the accuracy of the concentration of the alcohol added. The procedure was carried out using an Agilent 6890 N Headspace CombiPal-CTC Analytics chromatograph. A 2.0 mL aliquot of the sample was introduced into the headspace flask which was ultrasonicated for 5 min, followed by incubation at 80 °C for 45 min with stirring at 500 rpm. Five hundred microliters of the vapor were taken and immediately injected into the chromatograph. Chromatograph conditions: column: RTx-1-Res-tek-10184; oven temperature: 50 °C; injector temperature: 150 °C; detector temperature: 150 °C.

## 3. Results and discussion

Biodiesels prepared from vegetable oils (corn, soy, sunflower) and bovine fat were analyzed. In the case of soy oil the ethyl ester was also synthesized. The biodiesels obtained were carefully washed with water and dried at 110 °C. The flash point was determined and the process was repeated until a constant value was obtained, supposing that, in this case, the residual alcohol was completely removed. In one case the residual methanol was analyzed by gas chromatography in order to confirm the zero concentration of the residual alcohol in the washed biodiesel. This result

can be seen in the first line on the left in Table 1S, in the Supplementary material, in the case of the biodiesel from corn, confirming the zero or, at least, very low methanol content (<0.004% w/w).

To verify the flash point dependence on the biodiesel alcohol content, methanol or ethanol were added to biodiesel. The added quantity was determined by weight. In order to confirm that the procedure, i.e., that the addition and homogenization, was correct, the corn oil biodiesel, to which a range of methanol quantities were added, was analyzed by gas chromatography. The results are reported in the two first columns of Table 1S, where excellent agreement is observed. Therefore it can be assumed that for the other biodiesels, using the same synthesis and washing procedure, the methanol or ethanol values of the concentrations added by weight are reliable, i.e., none was lost by evaporation. For each biodiesel solution the flash point was determined three times and a mean was calculated. It is very clear that the flash point temperature strongly depends on the residual alcohol content. Considering the ASTM D6751, EN 14110 and ANP 07/2008 values for the flash point limit (ASTM D93, 130 °C; EN ISO 3679, 120 °C; NBR 14598, 100 °C) and for residual alcohol content (EN ISO 14110, 0.2% w/w; NBR 15343 0.2% w/w), an apparent contradiction is found, as, at these methanol or ethanol concentrations, the flash point falls to values as low as 71–87 °C. In contrast, the flash point for mineral diesel is fixed in the range from 38 to 55 °C, depending on the diesel class, i.e., much lower than the limits established for biodiesel. Therefore, with respect to the biodiesel residual alcohol content, concentrations up to about 0.7% w/w should be accepted as, in these cases, the lowest flash point temperature observed is 39 °C, which is similar to that of petrol diesel. Such a simple change in the allowed residual methanol or ethanol content will certainly lead to lower production costs and to lower environmental consequences as the industrial process will be simplified and shortened, consuming less energy and less water for washing, presenting lower levels of liquid effluents.

The results are shown in Fig. 1. The high sensitivity of the flash point with respect the residual alcohol content of the biodiesel is very clear. Based on this observation, the use of the flash point temperature for determination of the residual alcohol content of biodiesel can be proposed. Presently, the regulations (EN ISO 14110 and ABNT NBR 15343) require such residual alcohol analysis be through gas chromatography. However, from the data presented herein, it is obvious that the determination of the flash point according to the ASTM D6751 (130 °C), EN 14214 (120 °C) and ANP 07/2008 (100 °C) regulations already informs the residual alcohol content, making the GC procedure unnecessary. Also, it is

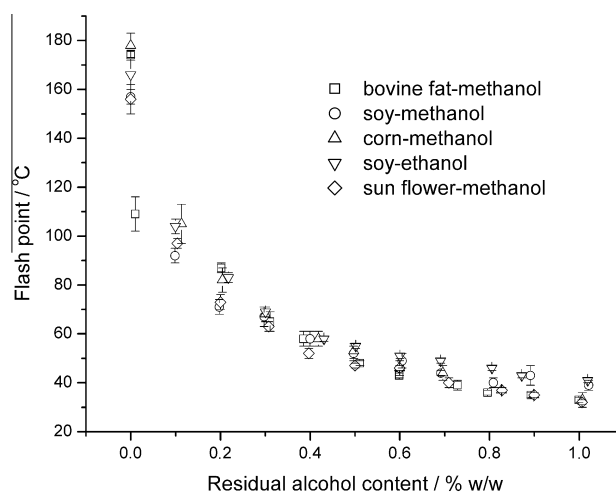


Fig. 1. Dependence of the biodiesel flash point on the residual alcohol content.

very clear that the regulated maximum limit of the residual alcohol content (0.2% w/w) does not agree with the flash points presented in the regulations. To achieve agreement between flash point and residual alcohol, the alcohol concentration cannot be higher than 0.1% w/w or, inversely, the flash point temperature cannot be fixed above ca. 70 °C.

In terms of toxicity, it is very interesting to compare the methanol and ethanol regulated limits in alcoholic distillates with those of biodiesel. Of course, about ethanol there is nothing to say as its concentration in alcoholic beverages is much higher than that fixed for biodiesel. In the case of methanol, however, a very toxic substance that causes damage if consumed even in small quantities, it is curious that the limit established by the regulations is similar, or even lower for biodiesel than is for beverages. For example, in Brazilian law [10] methanol can be present up to 2000 mg/L of the corresponding anhydrous ethanol (ca. 0.1% w/w for 1 L of a beverage containing 40% ethanol). This applies to cachaça (Brazilian sugar cane distillate), whiskies and other distillates from cereals. The limit is even higher, at 4000 mg/L of ethanol (ca. 0.2% w/w for 1 L of a beverage containing 40% ethanol) for cognacs and distillates from fruits. In American legislation the methanol limit is ca. 0.4% w/w for 1 L of a beverage containing 40% ethanol [11].

The limits presented above clearly show that regulations related to the residual alcohol content in biodiesel tend to be more rigorous than those for beverages. In terms of toxicological caution this can certainly be considered an exaggeration, mainly in the ethanol case. In terms of security for stocking and use, mineral diesel presents a lower flash point than the limits established for biodiesel. Also, gasoline, whose flash point is below 0 °C, and ethanol (flash point 13 °C) are currently used as fuels for combustion engines.

#### 4. Conclusion

The results presented here show that there is a correlation between the flash point and the residual alcohol content of a biodiesel. This means that the experimentally determined flash point temperature also informs the methanol or ethanol concentration in the biodiesel. This last analysis is now currently done by gas chromatography, a more expensive procedure.

The present regulations of the biodiesel flash point and the residual alcohol content present ambiguous values as the observed correlation between these two parameters does not agree with the values fixed in the regulations.

In terms of toxicity the limit of residual alcohol content is more rigorous than those established for alcoholic beverages.

With respect to the security aspects, the biodiesel norms are also more rigorous than those for other fuels, such as mineral diesel, gasoline, ethanol, methanol and even gases such as methane, propane, butane, etc.

In consideration of the above, a revision of the regulations related to the residual alcohol content of biodiesel and its flash point can be proposed. A suggestion is that 39 °C could be an interesting admitted flash point with a corresponding 0.7% w/w residual alcohol content. The establishment of such limits will certainly simplify biodiesel production, being a factor to lower the prices of the product and also would be beneficent with respect to environmental aspects as it will economize energy and water and decrease liquid effluents.

Finally, it must be emphasized that the above discussion supposes the use of “pure” biodiesel in engines, whereas the current use is in blends with mineral diesel. This reality makes stronger the above arguments about the possible changes in the regulated values for the flash point and for the residual alcohol content of biodiesel.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.fuel.2010.10.020](https://doi.org/10.1016/j.fuel.2010.10.020).

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