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Short Report

Correlation Between the Composition and Flash Point of Diesel-Biodiesel Blends

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Methyl ester biodiesels from vegetable oils, including soy, corn, canola and sunflower, and from swine lard, were prepared. They were mixed with mineral diesel to produce blends from 5% v/v to 50% v/v of biodiesel, i.e., B5, B10, B20 and B50. The flash points of these mixtures, the pure diesel (B0) and the pure biodiesel (B100) were determined. In all cases, it was observed that there was a second order polynomial correlation between the flash point and the percentage of biodiesel in the blend, it was concluded that is possible to estimate the flash point of a diesel-biodiesel mixture if its composition and the flash points of the pure components are known. *Quasi*-linear correlations between the increase of the flash point and the increase in biodiesel content were observed for B0 to B20 mixtures. If a mean linear correlation is applied, independently of the oil or fat used, in this case where the flash point of the petrol diesel is 40.1 °C, the estimated flash points for the blends from B5 to B20 will be approximately 45 ± 3 °C.

Keywords: biodiesel, diesel, diesel-biodiesel blends, flash point

Introduction

Mineral fuels and biofuels are part of the history of modern civilization. Biofuels, including biodiesel, have attained an important status as alternatives to mineral fuels due to oil crises, including rising prices, depletion of oil reserves and atmospheric pollution[1,2] caused by petrol derivatives.[3]

Diesel, the main petrol derivative energy resource, is a hydrocarbon mixture of hundreds of different molecules containing from 7 to 20 carbon molecules, including decane, tetradecane, hexadecane, butyl cyclohexane, naphthalene, etc.[4] Biodiesel is defined as a mono alkyl ester, commonly a methyl or an ethyl derivative,[2] prepared from a vegetable oil or an animal fat with a carbon chain that contains from 10 to 20 carbons.[5,6]

Biodiesel is obtained through transesterification reactions, in which triglycerides react with a short alcohol chain, such as methanol or ethanol and generate glycerol as a byproduct.[7-9] Biodiesel is a renewable fuel that can be used to partially replace mineral diesel when used in mixtures diesel-biodiesel or as a total replacement when it is used in its pure form. However, when biodiesel is used in its pure form, power is lost and the deposition of substances can be observed in engines.[10,11] The direct use of biodiesel results in a 10-15% loss of power in current diesel engines,[12] but blends with biodiesel content up to 20% (B20) show similar performance in comparison to diesel.[13] In light of such observations, some countries use diesel-biodiesel mixtures, which presents the following advantages: it reduces the dependence and use of diesel, decreases emissions of severe pollutants into the atmosphere and uses a renewable fuel.[2]

Austria was the first country to define and adopt standards for biodiesel, which were applied to methyl esters of rapeseed oil.[14] Through the resolution ANP 07/2008,[15] the National Petrol Agency of Brazil (ANP), decided that, from January 2010, all diesel fuel sold in Brazil must present 5% v/v of biodiesel (B5). Recently, through a presidential decision, MP No. 647/2014,[16] the biodiesel content in diesel must be 6% v/v from July 1st, 2014 and 7% v/v from November 1st, 2014. In a couple of years, ANP intends to achieve 20% of biodiesel in the blend (B20). In a couple of years, ANP intends to adopt 20% v/v biodiesel in the blend (B20).

Diesel and biodiesel quality is related to several parameters, including flash point.[17,18] This property has been defined as the lowest temperature at which there is enough gas or vapor to ignite a solution in air.[17] In Brazil, the flashpoint biodiesel is specified by ANP 45/2014,[19] based on ASTM D93 (American standards test methods, ASTM) and on ABNT 14598 (Brazilian standards test methods, ABNT). These regulations fix the minimal flash point temperatures at 100 °C. The European norm, EN 14214

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(European standards, EN) sets the flash point of biodiesel at 120 °C and the ASTM norm D6751 sets it at 130 °C. It is interesting to compare these relatively high biodiesel flash point values defined by regulatory agencies, with those of mineral diesel, which are from 38 °C to 55 °C, depending on the diesel class.[8]

Alcohol residues, remaining from biodiesel synthesis, decrease the flash point of the final biodiesel product, and further purification is necessary to meet the standard.[8,9] In diesel-biodiesel blends, the final flash point values will be between the flash points of the two components. In the present work, a procedure is proposed for estimating the flash point of a diesel-biodiesel mixture, based on the flash points of the components and the composition of the mixture. Conversely, the percentage of biodiesel in diesel-biodiesel blends can be estimated through flash point determination if the flash points of B0 and B100 are known.

Experimental

Materials

Mineral diesel was generously donated by the Brazilian petrol company, Petrobrás. The biodiesels were produced in our laboratory, from refined vegetable oils (soy, canola, corn and sunflower) and from refined swine lard, which were all purchased in the local market. They were used for biodiesel synthesis without further purification.

Biodiesel synthesis

The transesterification reaction was carried out using 1200 g of vegetable oil or swine lard, 240 g of methanol (Synth, Brazil) and 6.7 g of 30% sodium methoxide solution (Synth, Brazil) in methanol. The mixture was stirred for 1 h at 60 °C to 62 °C. It was then transferred to a 2-liter separatory funnel to separate the ester phase (less dense) from glycerol. A new reaction, using 60 g of methanol and 1.6 g of the 30% sodium methoxide solution in methanol, was performed with the ester phase during 1 h. The less dense phase was removed using a separatory funnel. The product was sequentially washed with five 200 mL portions of water. The produced biodiesel was stored in tightly closed amber glass bottles to avoid air and light.[20]

Preparation of diesel-biodiesel blends

Considering that swine lard biodiesel is a solid at the ambient laboratory temperature (ca. 25 °C), a standardized procedure was adopted for all biodiesel used in this work. In all cases, to prepare the blends, the biodiesel was heated to 40 °C and immediately mixed with the mineral diesel under gentle stirring. In addition to the “pure” diesel (B0) and biodiesel (B100), the following blends were prepared for each biodiesel: 5% v/v (B05); 10% v/v (B10); 20% v/v (B20); and 50% v/v (B50).

Flash point

The flash point measurements were performed according to method D93 (ASTM D6751).[21] An automatic closed-cup in an ISL FP93 5G2 (Carpiquet, France) apparatus was used. Measurements were performed in triplicate.

Results and Discussion

Biodiesels were prepared from vegetable oils (soy, corn, canola and sunflower oil) and from swine lard. Diesel/biodiesel blends were prepared in the following proportions (v/v): 0/100, 50/50, 80/20, 90/10, 5/95 and 0/100. The obtained flash points are displayed in Table 1. Second-order polynomial equations describing the dependence between flash point and the biodiesel content of the blend are as follows: canola oil biodiesel, $FP = 40.20 + 0.2957\,C + 0.00536\,C^2$ ($R^2 = 0.9998$); corn oil biodiesel, $FP = 43.13 + 0.0680\,C + 0.00657C^2$ ($R^2 = 0.9954$); swine lard biodiesel, $FP = 40.03 + 0.2169\,C + 0.00618\,C^2$

Table 1. Flash points of diesel, diesel-biodiesel blends and biodiesel

	Biodiesel content / % (v/v)	Flash point / °C					
		Diesel	Canola	Corn	Swine lard	Soy	Sunflower
Diesel-biodiesel blends	0	40.1 ± 1.4	–	–	–	–	–
	5	–	42.5 ± 0.5	44.9 ± 0.2	42.3 ± 0.4	43.7 ± 1.5	45.9 ± 0.8
	10	–	43.5 ± 0.5	46.6 ± 0.5	43.0 ± 1.2	43.1 ± 1.3	46.9 ± 0.8
	20	–	47.5 ± 1.4	48.0 ± 1.0	44.6 ± 2.0	44.6 ± 2.0	48.2 ± 0.7
	50	–	68.8 ± 3.6	61.4 ± 3.1	67.5 ± 4.5	62.8 ± 4.0	71.5 ± 1.4
	100	–	123.3 ± 7.6	116.0 ± 8.1	123.3 ± 3.7	104.2 ± 5.0	140.0 ± 5.7

(R^2 = 0.9986); soy oil biodiesel, FP = 40.67 + 0.2102 C + 0.00427 C^2 (R^2 = 0.9972); sunflower oil biodiesel, FP = 42.55 + 0.1915 C + 0.00782 C^2 (R^2= 0.9979), where FP is the flash point, C is the biodiesel content of the blend in% v/v and R^2 is the square of the correlation coefficient of the curve (determination coefficient).

From B0 to B20, *quasi*-linear correlations between the increase in the flash point and the increase in the biodiesel content are observed. If a mean linear correlation is applied, independently of the oil or fat used, in the case where the flash point of the petrol diesel is 40.1 °C, the estimated flash points for the blends from B5 to B20 are approximately 45 ± 3 °C.

Conclusions

According to the experimental results, there is a clear correlation between the biodiesel quantity in a diesel-biodiesel blend and its flash point. This means that the experimental determination of a flash point temperature also provides information regarding the biodiesel content of diesel-biodiesel blends. Conversely, if the percentage of biodiesel in a diesel-biodiesel blend is known, the flash point can be estimated if the flash points of B0 and B100 are known. From the obtained results, it is also clear that, for diesel-biodiesel blends with lower contents of biodiesel, the flash point is mainly determined by that of the mineral diesel.

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