# Evaluation of a glycerol derived biofuel by thermal analysis

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CBRATEC7 Conference Special Issue © Akadémiai Kiadó, Budapest, Hungary 2011

**Abstract** This work describes thermal analysis evaluation of a glycerol derived compound (fatty acid esters of (2,2-dimethyl-1,3-dioxolan-4-yl) methanol) developed to work as a biofuel. Mixtures of these ketal–glyceryl esters with fatty acid methyl esters typical of soybean biodiesel were prepared and evaluated in relation to biodiesel critical thermal properties such as temperature of crystallization, thermal stability and volatilization measured by differential scanning calorimetry and thermogravimetric analysis. The volatility of the products containing fatty acid methyl esters and (2,2-dimethyl-1,3-dioxolan-4-yl) methyl esters could be predicted by thermogravimetric analyses conducted in nitrogen that avoided time consuming distillation and greatly reduced material expenditure.

**Keywords** Glycerol · Thermal analysis · Biofuel · Ketal–glyceryl esters · Dioxolanyl esters · NMR

# Introduction

Due to the success of the implementation of biofuel in Brazil, to its increase in production and to the gradual alteration of the ratio of biofuel in diesel oil, it became urgent to exploit the glycerol by-product. As the amount of glycerol predicted would be more than could be absorbed in a single industrial segment, a molecule derived from glycerol with biofuel features was tailored. One of the main

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Instituto de Química, Universidade Federal do Rio de Janeiro, Rua Athos da Silveira Ramos, 149, bloco A, s/616, Rio de Janeiro 21949-909, Brazil e-mail: veralps@iq.ufrj.br requirements for a compound to act as a fuel is that it must present a high cetane number which reflects the delay in ignition time and also indicates a probable low emission of CO,  $NO_x$  and particulates [1]. Biodiesel from soybean oil presents a high cetane number comparable to that of petrodiesel due to its high O/C ratio and to the predominance of linear alkyl chains (high CH<sub>2</sub>/CH<sub>3</sub>). A second structural feature that can influence the cetane number is the presence of oxygen. Oxygen being an electronegative element leaves a C-H bond at the same carbon atom as oxygen weaker and easier to be broken, which can contribute to the onset of combustion [1]. The better lubricity performance of biodiesel when compared to that of petrodiesel is attributed to the presence of carboxyl groups in alkyl esters [2]. The ketalization of glycerol hydroxyl groups which keeps the oxygen atoms in the molecular structure increases its volatility and reduces viscosity. This is a well known reaction to protect reactive groups or prepare volatile products in organic syntheses. The preparation of glyceryl ketals and glyceryl esters to be used as biofuels has been claimed by some authors; however, neither the fuel performance nor their critical properties have been discussed by them [3, 4].

This paper describes the evaluation of thermal properties of ketal–glyceryl esters developed to work as a biofuel, the study of the influence of these glyceryl derivatives on the thermal properties of a soybean biodiesel and a method to predict products distillation behaviour by thermal gravimetric analysis.

# Experimental

### Materials

The reagents and solvents used were ethanol, methanol, glycerol, chloroform, methyl palmitate (methyl hexadecanoate), methyl oleate (methyl 9Z-octadecenoate), methyl stearate (methyl octadecanoate) and acetone from VETEC S.A., Brazil; methyl linoleate (methyl 9Z, 12Z-octadedienoate) and *p*-toluenesulfonic acid from Aldrich, USA; a commercial soybean oil (SO) and a biodiesel from soybean oil transesterified with methanol (SB). SB was composed of 16% of methyl palmitate, 3% of methyl stearate, 29% of methyl oleate and 52% of methyl linoleate according to gas chromatographic analysis. The purity of all reagents was checked using infrared and nuclear magnetic resonance spectrometry and gas chromatography when appropriate, and they were purified by distillation or recrystallization when necessary.

### Methods

The preparation of the product of interest II (Fig. 1) involved in a first step, the ketalization of glycerol to give product I (Fig. 1) and, in a second step, the esterification of I to furnish the desired product II. For the first step, a mixture of glycerol, propanone, added in excess, and p-toluenesulfonic acid (catalyst) in chloroform were refluxed for 10 h while water was being removed with a Dean-Stark apparatus. The ketal-glycerol (I), that is (2,2-dimethyl-1,3-dioxolan-4-yl) methanol, was isolated by vacuum fractional distillation after adding sodium carbonate to neutralize the catalyst and filtrating the catalyst. The second step was the transesterification of a mixture of methyl esters, consisting of palmitate, oleate, linoleate and stearate in the same proportion as found for biodiesel SB, with the product I. This reaction was conducted in the presence of anhydrous sodium carbonate, for 6 h at 125–140 °C, generating the product **II** that was purified by filtration of the catalyst and distillation of the excess of product I. A transesterification of methyl palmitate with product I was also conducted and produced (2,2-dimethyl-1,3-dioxolan-4-yl) methyl palmitate (PDM).

The products were characterized by solution <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance spectroscopy in an NMR Bruker DPX-200 (4.7 T), by Fourier-transform infrared spectrometry in a Nicolet FT-IR, model Magna 740, and by high resolution gas chromatography with mass spectrometry detector (Agilent Technologies model CG6850 and EM5973), provided with a 30 m capillary column of cross-



Fig. 1 Structure of intermediate I and product II (R = 15-17 carbons;  $R_1$ ,  $R_2 = CH_3$ )

linked (5% phenyl)-methyl-silicone; the column temperature was programmed from 75 to 250 °C at 10 °C min<sup>-1</sup> and the detector voltage was 75 eV.

Two products batches containing ketal–glyceryl esters and methyl esters in the proportions 25:75 (BDM25) and 65:35 (BDM65), respectively, were evaluated in relation to the following thermal properties: temperature of crystallization at a cooling rate of 10 °C min<sup>-1</sup>, in N<sub>2</sub> atmosphere, and oxidation stability from 30 to 300 °C in air atmosphere in a differential scanning calorimeter (Perkin-Elmer model 7); thermogravimetric analysis in N<sub>2</sub> atmosphere, at 20 °C min<sup>-1</sup>, up to 800 °C (Perkin-Elmer model 7e) and distillation behaviour according to ASTM D1160 [5]. A sample of biodiesel was analysed in these same conditions and a sample of (2,2-dimethyl-1,3-dioxolan-4-yl) methyl palmitate (PDM) was submitted to thermal analyses.

#### **Results and discussion**

Products characterization

# *Characterization of (2,2-dimethyl-1,3-dioxolan-4-yl) methanol (I)*

The FTIR spectrum (Fig. 2) of the ketal (I) after distillation presented: the typical C–O band at 1072 cm<sup>-1</sup>, an OH band at 3404 cm<sup>-1</sup> and a C–O band at 1042 cm<sup>-1</sup> relative to the non-reacted hydroxyl, as expected, and the typical CH<sub>3</sub> bend vibrations from the methyl groups at the dioxolanyl radical at 1375–1372 cm<sup>-1</sup>. No carbonyl bands from acetone were detected.

The structure of product **I** was also confirmed by  ${}^{1}$ H NMR (Fig. 3) through the CH<sub>3</sub> signals at 1.36 and 1.43 ppm.



Fig. 2 FTIR spectrum of (2,2-dimethyl-1,3-dioxolan-4-yl) methanol (I)



Fig. 3  $\,^1\mathrm{H}$  NMR spectrum of (2,2-dimethyl-1,3-dioxolan-4-yl) methanol (I)



Fig. 4 FTIR spectrum of ketal-glyceryl esters

# *Characterization of esters of (2,2-dimethyl-1,3-dioxolan-4-yl) methanol (II)*

In Fig. 4 a typical FTIR spectrum of ketal–glyceryl esters (**II**) is depicted, showing ester bands at 1742 and 1213 cm<sup>-1</sup>, and the disappearance of OH bands, while <sup>13</sup>C NMR spectrum (Fig. 5) showed chemical shifts at 173.7 and/or 174.3 ppm for ester carbonyls, depending on the

**Fig. 5** <sup>13</sup>C NMR spectrum of ketal–glyceryl esters



Fig. 6 GC analysis of BDM65 product

acid residue type, and also at 178 ppm due to methyl esters, besides the signal corresponding to the ketal carbon at 109.9 ppm.

It was observed that conversion times longer than 10 h resulted in darkened products, so that it was decided to let some methyl esters in the final mixture. The chromatographic analysis with mass detector (Figs. 6, 7) also confirmed the presence of ketal-glyceryl esters (peaks with retention times between 9.45 and 11.45 min) and methyl esters (peaks between 6.45 and 7.40 min). The interpretations of mass spectra fragments were based on the literature [6–9]. Both spectra have in common the fragments m/z 43 and 101 derived from the 2,2-dimethyl-1,3-dioxolan-4-yl group, as well as the  $[M - 15]^+$  peaks at m/z 355, 379 and 381 corresponding, respectively, to the dioxolanyl-methyl esters of palmitate (PDM), linoleate (LDM) and oleate (ODM). The fragments m/z 312, 336 and 338 correspond to  $[M - 15 - 43]^{+\bullet}$  from PDM, LDM and ODM, respectively, and, although not always abundant, again confirmed that the dioxolanyl-methyl esters were successfully prepared.







Thus, the results of FTIR, <sup>1</sup>H and <sup>13</sup>C NMR and GC–MS analyses confirmed the formation of the ketals (**I**) in the first step and of ketal-esters (**II**) in the second step. The NMR and GC–MS quantitative analyses characterized two product batches as containing ketal–glyceryl esters and methyl esters in the proportions 25:75 (BDM25) and 65:35 (BDM65), respectively. Considering that the methyl esters present in BDM products were constituted of biodiesel main components these products were evaluated in relation to biodiesel critical thermal properties considering them as mixtures of biodiesel and ketal–glyceryl esters.

# Temperature of crystallization

Temperature of crystallization  $(T_c)$  is one of the most critical properties of a biodiesel: as crystallization starts, viscosity increases leading to a higher pour point. In

biodiesel it depends on methyl esters composition [10], specifically, on the percentages of methyl esters of stearic and palmitic acids. These are both solids at ambient temperature, and, on cooling their solution, as in biodiesel, these components precipitate or form a gel [11]. The DSC curve for biodiesel (SB) showed a crystallization onset at -7.9 °C with two peak maxima at about -8.7 and -15 °C, which is typical of soybean methyl biodiesel at the present DSC experimental conditions. The products BDM65 and BDM25 presented a similar qualitative behaviour, but with less intense peaks, that is, a smaller variation of enthalpy per gram, and a small increase in  $T_c$  as shown in Fig. 8. A higher crystallization temperature would be expected for the products containing ketal-glyceryl esters, because of its greater average molecular mass. Corroborating with this expectation, the (2,2-dimethyl-1,3-dioxolan-4-yl) methyl palmitate (PDM), prepared in this work, presented a higher



Fig. 8 Crystallization behaviour of biodiesel, BDM25 and BDM65 by DSC



Fig. 9 DSC of PDM showing  $\mathbf{a}$  melting and  $\mathbf{b}$  crystallization temperatures influenced by the presence of methyl palmitate

melting point (66 °C) than methyl palmitate (30 °C) [11, 12] and crystallized at 51 °C, under the present DSC experimental conditions (Fig. 9). However, the fact that BDM products presented crystallization temperatures near that of biodiesel (SB) can be explained by its high content in unsaturated fatty acid chains that would bring down the  $T_c$  of the mixture relatively to derivatives with saturated fatty acid chains, as it is observed for the methyl esters mixtures that constitute soybean biodiesel and, as well, by the fact that BDM contains methyl esters.

# Oxidation stability

An important characteristic to be considered in soybean oil derived biofuel is its stability with respect to oxidation during storage. The process of oxidation of soybean oil or of its methyl esters, by the action of atmospheric oxygen, starts at the allyl carbon present in the oleate, linoleate and linolenate chains, which constitute about 80% of biodiesel from soybean oil. Hydroperoxides formed at the initiation



Fig. 10 Oxidation behaviour of BDM 25, BDM 65 products and biodiesel

step can either react with other radicals, resulting in high molecular weight insoluble sediments and gums, or break apart to form carboxylic acids [13, 14]. In the present study this process would be a concern as unsaturated chains are present. From DSC analysis (Fig. 10), the BDM65 product presented oxidation onset at 143 °C, BDM25 at 127 °C and SB at 128 °C. This is a significant result indicating that the glycerol part of the structure did not enhance the oxidation process. Its presence in a higher amount, as in BDM65, seemed to work in the opposite direction helping to delay oxidation. It could also be an effect due to the presence of saturated derivatives such as palmitic ester (PDM) that do not oxidize before 200 °C.

# Distillation range determined by TGA and ASTM

The distillation curve gives a pattern of the volatility of the components providing important information. In the case of diesel, the distillation curve following ASTM 1160 is used to determine cetane index (ASTM D4737) [5]. However, this essay requires a great amount of product which is not convenient at an early stage of product development. Instead, a test for volatilization was conducted in a thermogravimetric analyser, in  $N_2$  atmosphere, and compared to the results obtained by ASTM distillation.

According to the Brazilian agency for fuel regulation (ANP), 90% of biodiesel B100 must distillate below 360 °C. Table 1 gives the temperature of distillation determined by ASTM method for the biodiesel SB and product BDM25 at 10, 50 and 90% volume cuts established by ASTM. The product BDM25 and the biodiesel SB were inside the 90% limit.

The TG analysis in  $N_2$  atmosphere (Fig. 11) showed the following mass losses at 360 °C: 98% for biodiesel SB,

 Sample
 Temperature of distillation/°C

 Distilled volume/%
 10
 50
 90

 SB
 188.6
 192.9
 357.9

 BDM25
 199.0
 214.8
 356.8

**Table 1** Distillation behaviour of biodiesel and BDM25, followingASTM



Fig. 11 Thermogravimetric curves in  $N_2$  atmosphere for (*a*) biodiesel; (*b*) BDM25; (*c*) BDM65; (*d*) soybean oil—showing their different volatilization behaviour

93% for BDM25, 87% for BDM65 and 27% for soybean oil that were interpreted as volatilization. The TG curve for (2,2-dimethyl-1,3-dioxolan-4-yl)-methyl palmitate (PDM) was very close to the BDM65 curve.

These results showed that dioxolanyl-methyl esters promoted an increase in the final distillation temperature of the products. However, considering the TG analysis and the ASTM distillation curve for BDM25, it can be inferred that as much as 25% of dioxolanyl esters could be added to biodiesel methyl esters without interfering with its volatilization behaviour. Most interesting, this technique allowed a prediction of the distillation behaviour of the product BDM65 without being necessary to perform a distillation according to ASTM.

### Conclusions

The thermal properties measured for the BDM products, the (2,2-dimethyl-1,3-dioxolan-4-yl)-methyl esters of fatty acids, presented values close to those obtained for a soybean methyl biodiesel. Thus the substitution of methyl alcohol by a glycerol derivative in the structure of fatty esters resulted in a product with good potential to be used as a biofuel according to the measured thermal properties. The conversion of such a glycerol derivative into a product to be added to biodiesel could be a solution to the problem of utilizing the excess of the by-product glycerol.

Acknowledgements The authors gratefully acknowledge CAPES (Coordenação de Aperfeiçoamento de Pessoal de Nivel Superior) for providing a scholarship for Luciano N. Batista.

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