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Full Length Article

Experimental data and prediction of normal boiling points of partial acylglycerols

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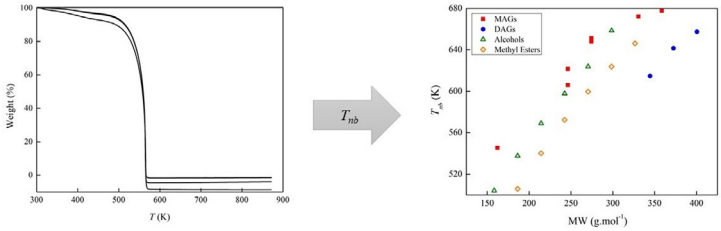
GRAPHICAL ABSTRACT



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ABSTRACT

Normal boiling point is an important thermophysical property for quality control of biofuels, as biodiesel, and is related to purification processes as distillation. Monoacylglycerols and diacylglycerols are formed during transesterification reaction of oils, and directly affect quality parameters of biodiesel, as its viscosity. Nevertheless, to the best of our knowledge, normal boiling point data of partial acylglycerols are completely absent in the open literature. This paper goals at providing experimental data of normal boiling points for five monoacylglycerols, monobutyrin, monocaprin, monolaurin, monopalmitin and monoestearin, and three diacylglycerols, dicaprylin, dinonanoin and dicaprin using the thermogravimetric analysis (TGA) technique. Predictive capacities of available methods in the literature were also evaluated.

1. Introduction

Currently, nonrenewable sources of energy are considered as a major threat to the environment, for this reason seek for alternatives forms of energy is an issue of modern society. In this sense, biodiesel figures as an interesting alternative for diesel fuel, particularly in transport sector, considering that it produces a lower global pollution in comparison with a conventional source of fuel [1].

During transesterification reaction, monoacylglycerols (MAG) and diacyglycerols (DAG) are produced together with fatty esters (biodiesel). These compounds directly affect biodiesel quality parameters, as viscosity, and its content is controlled by the standard for total glycerine (0.25% m/m, max.) [2,3]. In this way, during purification of biodiesel, mono- and diacylglycerols need to be removed. Besides, partial acylglycerols are widely used in food industry, as surface-active agents and emulsifiers [4], and are purified by molecular distillation [5].

Normal boiling point is the basis for estimating critical properties, and temperature-dependent properties such as vapor pressure, density, latent heat of vaporization, viscosity, and surface tension of chemicals [6]. In general, there is a lack of experimental data for thermophysical properties of compounds related to the lipid technology. For normal boiling points of partial acylglycerols, to the best of our knowledge, experimental data are completely absent. In fact, there are only two data for triacylglycerols provided by Santander et al. [7] using the thermogravimetric analysis technique: 692.25 K for triolein

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(MW = 885.4 g·mol^{-1}) and 690.02 K for tripalmitin (MW = 807.3 g·mol^{-1}). Very few data are still available for boiling points of partial acylglycerols [8–10], and they are concentrated at low pressure values (up to 13.2 kPa).

Normal boiling points can be measured by thermogravimetric analysis (TGA) [11]. This method provides a rapid mean for quantifying boiling points of pure compounds or mixtures, for example: n-paraffins, alcohols, fatty acids, fatty esters, triacylglycerols, biodiesel, and others [7,11–13]. Boiling point is taken from a plot of weight loss versus temperature (thermogram), provided by the TGA equipment. The extrapolated onset point of the thermogram is the boiling point of the sample [11]. As any other analytical technique, the TGA technique can be affected by many factors, as: impurities, heat rate, crucible configuration, amount of mass, among others [7–9,14]. In fact, some of these issues have been addressed when using the DSC technique to determine boiling points of organic compounds. For instance, Troni et al. [14] developed a systematic study to test the influence of two factors that affect the results of the DSC technique when measuring boiling points of pure compounds at low pressures: sample sizes (mg) and heating rates (K.min^{-1}). Also, the TGA analysis provides important information about thermal stability, oxidation and degradation of pure compounds or mixtures. Further investigations could address similar studies for the TGA technique. Furthermore, one important advantage of the TGA technique is that it requires very low sample mass (7 mg approx.), which is cost-effective for fatty compounds [7,12]. In a recent work, the TGA technique was applied for measuring normal boiling points of pseudobinary mixtures of biodiesel/diesel, biodiesel/oil and diesel/oils [13].

For contributing to the lipid technology field, this work measured novel normal boiling point data for five monoacylglycerols (MAGs) and three diacylglycerols (DAGs), i.e.: monobutyrin, monocaprin, monolaurin, monopalmitin, monoestearin, dicaprylin, dinonanoin and dicaprin using the TGA technique. In the case of monocaprin and monolaurin, two different lots were tested. Also, the ^{13}C-Nuclear Magnetic Resonance (NMR) analysis was used for both lots of monocaprin to qualitatively verify the presence of isomers 1,3-MAG and 1,2-MAG [15]. The predictive capacities of the methods of Ceriani et al. [16], Marrero and Gani [17], Joback and Reid [18], and Zong et al. [19] were also evaluated.

2. Methodology

2.1. Materials

Table 1 lists all the reagents used in this study (CAS Registry numbers, purities in mass fraction, IUPAC names and suppliers). All chemicals were used without any further purification step.

2.2. Experimental procedures

2.2.1. The thermogravimetric analysis (TGA) technique

The TGA technique was performed according with Goodrum and Geller [12] and Santander et al. [7]. The equipment used was a TGA/DSC1 – Mettler Toledo. All measurements were conducted at ambient pressure at campus of the State University of Campinas (UNICAMP), in the city of Campinas, São Paulo State, Brazil. Ambient pressure (p) registered by the CEPAGRI (Centro de Pesquisas Meteorológicas e Climáticas Aplicadas à Agricultura) during the days of our analysis was 95.54 kPa with $u(p)$ = 0.52 kPa. Nitrogen purge flow through the cell was 50 mL/min and a heating rate of 10 K/min was used. This heating rate value enables to detect whether some irregular situations arise in the experiment [7]. Each assay was obtained using a pair of sealed crucibles (40 μL), one empty (reference) and the other with a sample of approximately 7 mg (± 1 mg) of reagent. To assist for achieving isothermal boiling, 1.0 mg (± 0.2 mg) of α-alumina (standard grade) was added to the sample [12]. Crucibles were sealed with drilled lids using a Mettler Toledo pressing device. Pinhole diameter was within 0.25–0.31 mm range. All measurements were conducted in triplicates. Based on Troni et al. [14], we developed a method to select the onset temperatures from the TGA curves, considering the limitations and differences from both thermal analyses, this information is explained in detail in Supplementary material – “Selection of the onset temperatures of TGA”.

2.2.2. Nuclear magnetic resonance (NMR) spectroscopy

According to Gunstone [15] and Compton et al. [20], ^{13}C-NRM analysis allows to qualitatively verify the presence of isomers of monoacylglycerols. In fact, the glycerol carbon atoms in each type of isomers of monoacylglycerol give a specific ^{13}C NMR signal, which it can be used to identify the presence of 1-MAG or 2-MAG [15]. ^{13}C – NMR spectra were obtained on a Bruker Avance 500 MHz spectrometer (125.69 MHz 13C) using a 5 mm BBI probe. All samples were dissolved in $CDCl_3$, and all spectra were acquired at 298.2 K.

2.3. Estimation of normal boiling point (T_{nb})

Group contribution methods were used for estimating the normal boiling point (T_{nb}) of mono- and diacylglycerols. The methods applied were Ceriani et al. [16], Marrero and Gani [17], and Joback and Reid [18]. Besides that, the chemical constituent fragment approach for partial acylglycerols developed by Zong et al. [19] was also checked. Table 2 lists equations of each method and their description.

Table 3 shows the functional groups present in mono- and diacylglycerols according to each group contribution method selected in this work.

Table 1
List of compounds with their respective IUPAC name, CAS Registry No., supplier and purity.

Compound	IUPAC name	CAS Registry No.	Supplier	Purity (mass fraction)
n-tetradecane	Tetradecane	629-59-4	Sigma-Aldrich	0.99
n-hexadecane	Hexadecane	544-76-3	Sigma-Aldrich	0.99
Glycerol	Glycerol	56-81-5	Sigma-Aldrich	0.99
Monobutyrin	2,3-dihydroxypropyl butanoate	557-25-5	Sigma-Aldrich	0.99
Monocaprin[a]	2,3-dihydroxypropyl decanoate	2277-23-8	Nu-Chek Prep, Inc.	0.99
Monolaurin[a]	2,3-dihydroxypropyl dodecanoate	142-18-7	Nu-Chek Prep, Inc.	0.99
Monopalmitin[a]	2,3 dihydroxypropyl hexanodecanoate	542-44-9	Nu-Chek Prep, Inc.	0.99
Monoestearin[a]	2,3 dihydroxypropyl stearate	123-94-4	Nu-Chek Prep, Inc.	0.99
Dicaprylin[b]	2 hydroxy-3octanoyloxypropyloctanoate	36354-80-0	Nu-Chek Prep, Inc.	0.99
Dinonanoin[c]	2-hydroxy-1,3-propanediyl dinonanoate	618443-08-6	Nu-Chek Prep, Inc.	0.99
Dicaprin[b]	3 decanoyloxy 2 hydroxypropyldecanoate	53988-07-01	Nu-Chek Prep, Inc.	0.99

[a] Thin layer chromatography showed only the monoacylglycerol moiety present according to the certificate of analysis provided by Nu-Chek Prep, Inc.
[b] Thin layer chromatography showed only the diacylglycerol moiety present (may contain trace amounts of 1,2-DAG) according to the certificate of analysis provided by Nu-Chek Prep, Inc.
[c] Thin layer chromatography showed only the diacylglycerol moiety present according to the certificate of analysis provided by Nu-Chek Prep, Inc.