

Application of thermogravimetric analysis method for the characterisation of products from triglycerides during biodiesel production

Carine Tondo Alves^{a,b}, Morenike A. Peters^a, Jude A. Onwudili^{a,*}

^a Energy and Bioproducts Research Institute, School of Infrastructure and Sustainable Engineering, College of Engineering and Physical Sciences, Aston University, Aston Triangle, Birmingham B4 7ET, UK

^b Energy Engineering Department, Universidade Federal do Recôncavo da Bahia, CETENS, Av. Centenario 697, Feira de Santana 44.085-132, Brazil

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ABSTRACT

In this present work, thermogravimetric analysis (TGA) was used to study the thermal degradation of a range of lipids and lipid-derived compounds associated with the production of biodiesel. Thereafter, the procedure was used to successfully quantify the compounds of three process streams from a biodiesel plant. Relevant organic chemicals involved in biodiesel production chemistry, including glycerol, oleic acid (fatty acid), palmitic acid (fatty acid), rapeseed oil (model triglyceride) and fatty acid methyl esters (FAMES) have been studied to determine their volatilisation/thermal degradation patterns. The developed method was then applied for the quantitative characterisation of three samples from a 3-stage biodiesel production plant, including two in-process samples and the final biodiesel product. The method was able to clearly distinguish between two main sets of compounds namely, early - mid volatiles (glycerol, fatty acids and fatty acid methyl esters) and late volatiles (incompletely converted and unreacted triglycerides). In addition, the FAMES in the industrial samples were extracted into petroleum ether and analysed by gas chromatography - mass spectrometry (GC/MS), with good agreement between the two analytical methods. For instance, GC/MS analysis showed that the three industrial samples contained 31.2 ± 0.1 wt%, 60.6 ± 0.2 wt% and 91 ± 0.53 wt% of FAMES, respectively. Similarly, the TGA method gave the FAMES contents of the three samples as 33.9 ± 0.4 wt%, 57.8 ± 0.2 wt% and 85.3 ± 0.52 wt%. This study shows that TGA is a fast and simple method for accurately monitoring the triglyceride conversion stages and the purity of the final product during biodiesel production, without the need for extensive sample preparations and expensive standard solutions.

1. Introduction

Thermogravimetric analysis (TGA) provides information on the thermal, physical and chemical properties of different materials including the decomposition, pyrolysis and combustion, as well as the kinetics and thermodynamics of these processes [1]. It can be used to characterise different materials that can thermally degrade or decompose, and the degradation patterns can be used to reveal important information on individual compounds and mixtures [2]. For instance, TGA has extensively been used to study the controlled thermal degradation of organic materials such as polymers [3–6] and solid fuels e.g., biomass [7–10] and coal [11,12], liquid fuels [13–16] as well as inorganic materials such as catalysts [17–20] and minerals [21]. Therefore, TGA has become one of the oldest and most useful techniques for determining the composition of natural and synthetic chemicals and materials. This

involves measuring mass losses from materials as a function of increasing temperature and time [14]. The degradation patterns known as TGA curves, can be further analysed to determine the degradation stages and the fractions responsible for observed degradation signals.

Individual compounds or polymers can produce distinct thermal degradation patterns, which can be used as specific signatures for their identification. In mixtures however, the identification and quantification of components can be quite complicated. According to Bowley et al. [22] in some cases, the percentages of components cannot be determined directly from the TGA patterns because the thermal degradation of the components occurs simultaneously or overlap. However, careful analysis of the degradation patterns from a TGA can be used to quantify the proportions of components in a mixture or composite material.

For instance, TGA has proven to be a consistent technique to study the impact of polymer structures on thermal stability and understand

* Corresponding author.

E-mail address: j.onwudili@aston.ac.uk (J.A. Onwudili).

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thermal degradation pathways of polymers [2,23–25]. While the degradation of single monomer plastics, e.g., polyethylene [26] and polystyrene [27] are relatively simple to investigate by TGA, those of co-polymeric materials, polymer mixtures/blends and composite/hybrid materials are more complicated. TGA studies of co-polymers and composites such as polyacrylamide [28,29], PVDF copolymer composite films, [3,10] hybrid polysiloxane materials [5] and polymer blends [30] have been extensively studied for various reasons. For instance, Criado et al. [5] investigated the structure of hybrid polysiloxane materials prepared from polymerisation of Si compounds containing different alkoxide groups and observed three distinct weight losses from structural degradation and evolution of matter at different temperatures. The researchers [5] were able to use the TGA curves to identify the mechanisms involved in the formation of volatile products leading to the evaporation of ethanol and water due to scissions within polymer chains or during condensation reactions between Si-OH and Si-OR, the dehydration of silanol groups, and the oxidation or degradation of methyl-triethoxysilane groups, respectively.

Moreover, TGA is a common technique to study the thermal degradation of biomass feedstocks [7–10] and biomass components (cellulose, hemicellulose and lignin) [31–36], prior to thermochemical conversion. For example, Chen et al. [32] investigated the thermal degradation mechanisms of hemicellulose, cellulose, and lignin using pyrolysis–gas chromatography/mass spectrometry to study their decompositions and the compositions of the degradation vapour products. In addition, Yang et al. [33] evaluated the degradation of the three main biomass components (hemicellulose, lignin, cellulose) pyrolysis by TGA method [33] and used the results to model the degradation of whole biomass by identifying the individual components from their decomposition patterns. Singh et al. [34] investigated pyrolysis of waste materials, biomass wood waste, waste tyre, refuse derived fuel and waste plastic. The authors showed that TGA-MS and TGA-FTIR are both complementary techniques to validate qualitative analysis of the gaseous products obtained from pyrolysis.

In addition, Müsellim et al. [35] studied the evolution of gaseous species from degradation of pea waste biomass using TGA and the effects of heating rate and pyrolysis temperature on products. The results showed that the main decomposition step of pea waste was observed between temperatures 220 °C and 450 °C due to the breakdown of hemicelluloses, cellulose and lignin [35]. Burhenne et al. [36] investigated three types of biomass (wheat straw, rape straw and spruce wood with bark) to evaluate lignin, cellulose and hemicellulose by TGA method. The temperature corresponding to the decomposition began at 480 °C, increasing at 510 °C for the herbaceous biomass and at 530 °C for the wood biomass. The thermogravimetric analysis showed that the herbaceous and woody biomass samples was completed at about 830 °C and 900 °C, respectively.

Biodiesel is produced at industrial scale via transesterification of triglyceride feedstocks such as fats and oils. The compositions of biodiesel process streams are usually monitored to determine feedstock quality, triglyceride conversion and final product quality. Different analytical methods are used for these including TGA, gas chromatography and spectroscopy [13,16,37]. Indeed, TGA has become one of the most efficient method to characterise waste cooking oils (WCOs) [35,37] and fatty acid methyl esters (FAMES) [13–16]. In addition, gas chromatography is the analytical method of choice for final product quality measurement [13,16,38–40]. However, GC/MS may not be capable of identifying and quantifying all the components of in the biodiesel process stream due to differences in polarity and molecular sizes. For instance, GC/MS can easily identify FAMES in biodiesel [41–43] but cannot be used to identify the presence of unconverted and incompletely converted components of the feedstock, such as monoglycerides, diglycerides and triglycerides.

In contrast, TGA has been considered as a straightforward and simpler approach for gross analysis of biodiesel process streams [36,37]. TGA can be used in either the pyrolysis or combustion mode to study the

properties of mixtures of compounds or fuels [44,45]. Potentially, all the major components involved in the biodiesel chemistry can be identified and characterised individually and in mixtures for complete quantitative characterisation of process streams in a biodiesel plant. These components include the initial triglyceride feed, free fatty acids (FFAs), glycerol, FAMES and products of incomplete conversion during transesterification process. These components may have different thermal degradation patterns through which they can be identified. According to the literature, commercial biodiesel has been studied with TGA and has been found to undergo two stages of thermal degradation [37,46]. The first stage of the thermal decomposition of biodiesel has been reported to be in the range of 125–230 °C indicating the volatilisation of the fatty acid methyl esters (FAMES) and the thermal conversion of monoacylglycerols [37,46]. The second stage occurs between 230 and 450 °C and has been reported to indicate the degradation of more thermally stable products such as diacylglycerides, triacylglycerides and other heavy biomolecules including gums [13,16,35].

The aim of this present work is to develop and apply a TGA characterisation method for determining the compositions of components in in-process and final biodiesel products. In the present work, TGA volatilisation/degradation patterns of organic compounds related to biodiesel production chemistry have been studied in detail for the first time. These included glycerol, oleic and palmitic acids (as fatty acids) and rapeseed oil (as model triglyceride). These studies have been used to develop a quantitative method of characterising these components. Thereafter, the developed method would be applied to quantify the components of three samples from a biodiesel plant including two in-process samples and the final biodiesel product. It is envisaged that this method will be an inexpensive and accurate technique to quantify lipids and lipid-like compounds in feedstocks and FAMES.

2. Materials and methods

2.1. Materials

Analytical grade chemicals including glycerol, oleic acid and palmitic acid were purchased from Fisher Scientific, Leicester (UK). A sample of fatty acid methyl esters (FAMES) mix was purchased from Thames Restek (UK), while food-grade rapeseed oil was purchased from a local grocery store. These materials were used without further purification. In addition, the three real-world industrial samples from different stages of a biodiesel production process (esterification and two stages of transesterification) were obtained from a UK-based plant and also used without further treatment. The biodiesel plant samples are designated as BPW-A, BPW-B and BPW-C in this present study.

2.2. Experimental methods

2.2.1. Characterisation of samples

Elemental Analysis, Higher Heating Value (HHV), Total Acid Number (TAN), Ash and Density.

The elemental compositions of the pure glycerol, oleic acid, palmitic acid, three biodiesel process stream samples, and rapeseed oil (RSO) are shown in Table 1 [47]. A Flash 2000 Elemental analyser was used to quantify the amount of carbon, hydrogen, nitrogen, sulphur, and oxygen (calculated by difference). Table 1 also shows the HHV of the samples, calculated based on Dulong's Formula [48] according to Eq. (1). Each analysis was carried out in duplicates and the standard deviations reported in Table 1.

$$\text{HHV (MJ/kg)} = 0.3383 \text{ C} + 1.443(\text{H} - (\text{O}/8)) + 0.0942 \text{ S} \quad (1)$$

where C, H, O and S are the wt% composition of carbon, hydrogen, oxygen and sulphur, respectively.

The density is shown in Table 1 and the experiments were conducted

Table 1
Some physicochemical properties of the samples used in this present study.

Sample	Carbon (wt%)	Hydrogen (wt%)	Nitrogen (wt%)	Sulphur (wt%)	Oxygen (wt%)	HHV (MJ/kg)	Density @ 20 °C (kg/m ³)	TAN (mgKOH/g)	Ash (wt%)	Moisture (wt%)
Rapeseed oil	77.0 ± 1.02	11.0 ± 0.15	0.13 ± 0.01	nd	10.9 ± 1.42	41.0 ± 0.65	916.8 ± 0.00	1.40 ± 0.02	nd	0.03 ± 0.00
Glycerol	40.8 ± 0.43	9.86 ± 0.20	0.12 ± 0.01	nd	49.3 ± 0.62	19.1 ± 0.54	1261.3 ± 0.00	5.41 ± 0.01	nd	0.11 ± 0.03
Oleic acid	76.5 ± 0.01	12.2 ± 0.03	0.13 ± 0.00	nd	11.3 ± 0.31	41.4 ± 0.34	892.7 ± 0.00	198.60 ± 1.20	nd	0.08 ± 0.01
Palmitic acid	72.6 ± 0.02	13.1 ± 0.06	0.07 ± 0.00	nd	14.2 ± 0.07	40.8 ± 0.07	853.0 ± 0.00	218.00 ± 0.70	nd	0.08 ± 0.01
BPW-A	74.9 ± 1.13	12.2 ± 0.17	0.16 ± 0.01	nd	12.7 ± 1.29	40.7 ± 0.84	902.6 ± 0.00	5.61 ± 0.12	0.95 ± 0.02	0.11 ± 0.02
BPW-B	74.1 ± 0.72	12.1 ± 0.13	0.16 ± 0.03	nd	13.6 ± 0.63	40.1 ± 0.17	895.3 ± 0.00	2.38 ± 0.08	0.49 ± 0.01	0.15 ± 0.02
BPW-C	75.6 ± 1.05	12.8 ± 0.19	0.13 ± 0.00	nd	11.5 ± 1.23	42.0 ± 0.83	879.0 ± 0.01	2.31 ± 0.03	nd	0.04 ± 0.00

*BPW = Biodiesel Plant Wastes A, B and C; TAN = total acid number, HHV = higher heating value.

using a pycnometer flask with 10 mL of capacity. In addition, the total acid numbers (TAN) of the samples were determined by titration with 0.1 mol/L KOH solution and calculated according to the Eq. (2) [49,50].

$$TAN \left(\frac{mgKOH}{g} \right) = \frac{(B - S) \times C \times 56.1}{W} \quad (2)$$

where B is titre value of blank; S is titre value of sample; C is concentration of KOH (0.1 mol/L); W is the mass of sample used and 56.1 is the molecular mass of KOH.

Clearly, Table 1 shows that BPW-A, BPW-B and BPW-C contained > 70 wt% carbon, which when compared to glycerol (carbon = 40.8 wt%), indicated the presence of long-chain compounds such as fatty acids, FAMES and unreacted oils and fats. In addition, Table 1 shows that their total acid numbers were higher than that of RSO, which indicated the presence of high amounts of free fatty acids. Indeed, direct acid-base titrations of these samples gave acid contents of 3.18 wt%, 1.22 wt% and 1.47 wt% for BPW-A, BPWB and BPW-C, respectively.

2.3. Thermogravimetric analysis (TGA)

TGAs were performed using a Mettler Toledo Thermal Analysis TGA/DSC 2 with a STARE Software System. In each analysis, the sample was placed in an appropriate crucible, which was then heated from 25 °C to 1000 °C, at heating rate of 10 °C/min by using 30 mL/min of nitrogen (N₂) as a flow gas. In this work, the TGA of individual compounds such as pure glycerol, oleic acid, palmitic acid, FAMES and rapeseed oil, were carried out using 2 mg, 3 mg and 4 mg of each sample (Table 2). Also, the TGA of six (6) mixtures containing each individual compound were carried out. Approximately 3 mg of each mixture (Table 3) was used to enable quantification with the derivative TGA curves [49]. The six mixtures were designated as GOPFR-01, GOPFR-02, GOPFR-03, GOPFR-04, GOFR-05 and GOPFR-06, respectively. Each TG analysis

Table 2
Nominal masses of individual compounds used in this study.

Individual Compound	Weight
Pure glycerol (G)	Test 01 – 2.035 ± 0.11 mg Test 02 – 3.110 ± 0.09 mg Test 03 – 4.034 ± 0.03 mg
Oleic acid (O)	Test 01 – 2.067 ± 0.04 mg Test 02 – 3.110 ± 0.09 mg Test 03 – 4.110 ± 0.09 mg
Palmitic acid (P)	Test 01 – 2.053 ± 0.13 mg Test 02 – 3.113 ± 0.09 mg Test 03 – 4.114 ± 0.08 mg
FAMES (F)	Test 01 – 2.069 ± 0.08 mg Test 02 – 3.174 ± 0.09 mg Test 03 – 4.004 ± 0.21 mg
Rapeseed oil (R)	Test 01 – 2.064 ± 0.12 mg Test 02 – 3.122 ± 0.10 mg Test 03 – 4.080 ± 0.07 mg

was carried out in triplicates and averages reported with their standard deviations.

The mixed samples and the amount of each component is shown in Table 3. Since FAMES and glycerol overlap over a wide range of temperatures, lower masses of FAMES (0.30 mg, 0.35 mg and 0.59 mg) were used to ensure that glycerol could be observed in the mixtures. In addition, higher amounts of rapeseed oil (0.71 mg, 0.91 mg, 0.85 mg and 1.21 mg) were used to make it potentially distinguishable from oleic acid due to observed overlap.

2.4. GC/MS analysis of FAMES

The FAMES contents of the three industrial samples (BPW-A, BPW-B and BPW-C) were analyzed using GC/MS. In the procedure, about 0.2 g of each sample was added to 10 mL of deionised water (to remove water-soluble impurities) in a volumetric flask and extracted twice with 5 mL aliquots of petroleum ether. The extracts were combined and dried over anhydrous sodium sulphate for GC/MS analysis. A 1 µL volume injection was made into the injector of a GC/MS maintained at 250 °C using as split ratio 1:10. The equipment used was a Shimadzu GC-2010 GC/MS with electron impact ionisation (70 eV). An RTX-5 ms capillary column (ID 0.25 mm, 30 m in length) was used for the separation with helium (15 mL/min) as carrier gas. The total analysis time was 20 min, and the column oven temperature was initially set at 200 °C and held for 1 min, then increased at a rate of 5 °C/min to a final oven temperature of 250 °C, where it held for additional 9 min. The transfer line temperature was maintained at 280 °C and mass spectra were scanned within in the molecular mass range of $m/z = 35-300$. The combined NIST (National Institute of Standards and Technology) Libraries (NIST17s.lib and NIST17-1.lib) installed on the MS was used to identify the FAMES. Quantitation was achieved by external standard method, using a FAMES standard mix obtained from Thames Restek, Saunderton (UK).

3. Results and discussions

3.1. TGA of individual model compounds and rapeseed oil

The results from the thermogravimetric analyses of glycerol, oleic acid, rapeseed oil (RSO), palmitic acid and FAMES are shown in Fig. 1. Each compound analysed by TGA method was tested using three different masses (2 mg, 3 mg and 4 mg) as mentioned above (Table 2) and the initial and final degradation temperatures as well as the mass losses are shown in Table 4.

The thermal degradation of glycerol, oleic acid, palmitic acid and RSO showed one distinct peak each and the FAME showed two peaks for all experiments. The weight loss temperature ranges for tests involving 2 mg, 3 mg and 4 mg sample sizes were approximately between 118 °C

Table 3
Nominal amounts of components used in the TGA of mixtures in this study.

Component Sample Code	GOPFR-01	GOPFR-02	GOPFR-03	GOPFR-04	GOPFR-05	GOPFR-06
Glycerol (G)	0.60 mg	1.00 mg	0.50 mg	0.50 mg	0.50 mg	0.50 mg
Oleic acid (O)	0.60 mg	0.50 mg	1.00 mg	0.50 mg	0.50 mg	0.50 mg
Palmitic acid (P)	0.60 mg	0.50 mg	0.50 mg	1.00 mg	0.50 mg	0.50 mg
FAMES (F)	0.35 mg	0.30 mg	0.30 mg	0.30 mg	0.59 mg	0.30 mg
Rapeseed oil (R)	0.85 mg	0.71 mg	0.71 mg	0.71 mg	0.91 mg	1.21 mg
Total	3.00 mg	3.00 mg	3.00 mg	3.00 mg	3.00 mg	3.00 mg

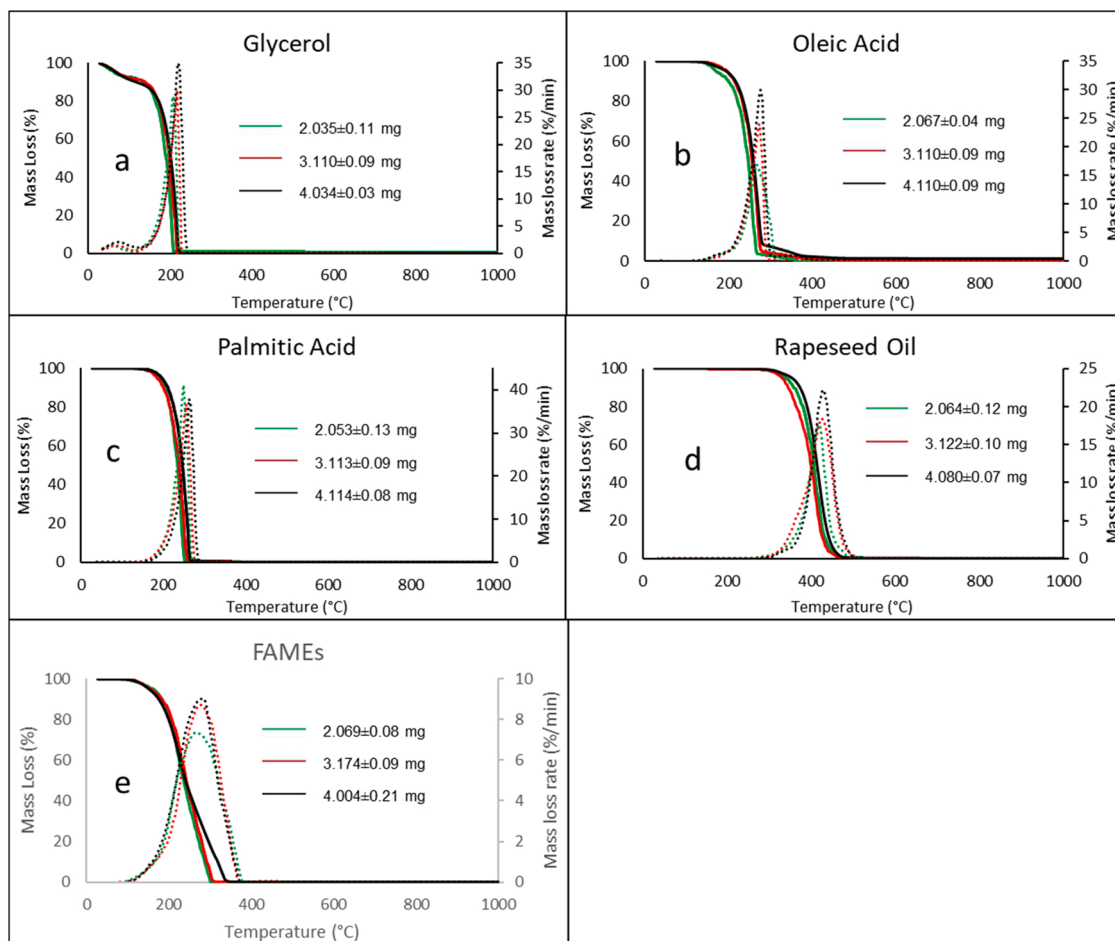


Fig. 1. TGA curves (a) glycerol, (b) oleic acid, (c) palmitic acid, (d) rapeseed oil and (e) FAMES.

Table 4
Thermal degradation characteristics of glycerol, oleic acid, palmitic acid, rapeseed oil and FAMES at different weights.

	2 mg			3 mg			4 mg		
	T _i (°C)	T _f (°C)	Mas Loss (%)	T _i (°C)	T _f (°C)	Mas Loss (%)	T _i (°C)	T _f (°C)	Mas Loss (%)
Glycerol	Stage I			Stage I			Stage I		
	116.01 ± 0.03	211.49 ± 0.03	100.00	116.00 ± 0.07	218.81 ± 0.00	100.00	118.01 ± 0.02	237.75 ± 0.12	100.00
Oleic acid	Stage I			Stage I			Stage I		
	138.22 ± 0.04	284.39 ± 0.02	100.00	138.61 ± 0.07	291.93 ± 0.07	100.00	139.25 ± 0.21	294.16 ± 0.21	98.76
Palmitic acid	Stage I			Stage I			Stage I		
	117.96 ± 0.35	262.38 ± 0.19	100.00	121.57 ± 0.02	265.94 ± 0.12	100.00	121.57 ± 0.13	265.94 ± 0.07	100.00
Rapeseed oil	Stage I			Stage I			Stage I		
	267.03 ± 0.02	476.90 ± 0.35	100.00	276.72 ± 0.09	479.31 ± 0.05	100.00	276.69 ± 0.21	482.87 ± 0.05	100.00
FAMES	Stage I			Stage I			Stage I		
	139.09 ± 0.13	311.81 ± 0.27	100.00	141.42 ± 0.33	313.58 ± 1.76	100.00	142.78 ± 0.10	335.52 ± 1.07	95.59

T_i = initial temperature; T_f = final temperature.

and 238 °C for glycerol, 139 °C and 294 °C for oleic acid, 118 °C and 266 °C for palmitic acid, between 277 °C and 483 °C for rapeseed oil and between 143 °C and 336 °C for FAMES. The TGA curves of pure glycerol for three different amounts (2 mg, 3 mg and 4 mg) are shown in Fig. 1a, with the first little peaks corresponding to the loss of moisture present in the sample as impurity. Thereafter, a major peak corresponding to glycerol can be seen, in which the maximum degradation temperature (Tmax) occurred at 211.49 °C (2 mg), 218.81 °C (3 mg) and 237.75 °C (4 mg), respectively (Table 4). As can be seen from the DTG curves of pure glycerol at the three different amounts of samples, the values of the Tmax shifted to higher temperatures with increasing sample sizes, which agrees with literature [51]. However, all results remained in agreement with the ranges reported in literature [1,52]. Fig. 1b shows the TGA curves of oleic acid and a single well-defined mass loss step can be observed for the degradation or volatilisation of all three samples. Increasing the experimental temperature, small molecule and weak chemical bonds are gradually decomposed, and thermal degradation curves decreases [47], wherever the main weight loss was observed at Tmax of 284.39 °C (2 mg), 291.93 °C (3 mg) and 294.16 °C (4 mg). The small front tailings seen in the TGA curves for oleic acid (Fig. 1b) may be due to hydroperoxides and conjugated impurities, which are often found in unsaturated fatty acids due to their liability to auto-oxidation [53].

Looking at Fig. 1c, TGA curve for palmitic acid shows one distinct peak at Tmax of 262.38 °C (2 mg) and 265.94 °C (3 mg and 4 mg). As shown, no apparent degradation reaction and weight loss of palmitic acid is observed until 117 °C. After that, the palmitic acid volatilised rapidly with the rise in temperature and reached up to 100% mass loss at the Tmax temperatures reported above. Considering the thermal degradation of the rapeseed oil described in Fig. 1d, the TGA curves showed similar patterns for the three samples amount tested and one major peak with total mass loss of 100%. The Tmax were 476.90 °C (2 mg), 479.31 °C (3 mg) and 482.87 °C (4 mg). Fig. 1e show the TGA curves of FAMES and each has one major peak with Tmax of 311.81 °C (2 mg), 313.58 °C (3 mg) and 335.52 °C (4 mg).

This may correspond to the possible overlapping degradation of glycerol and FAMES-rich components such as fatty acids and to the presence of unconverted fats and oils (lipids) from the biodiesel production process (esterification + two stages of transesterification). Thermal degradation properties of FAMES are relative to the alkyl group type in the feedstock and the nature of the alcohol used. FAMES are usually produced through transesterification or esterification reactions using vegetable oils or animal fats and methanol, with the alcohol used for its shorter carbon chain and stronger molecular polarity [37,46]. In fact, it was possible to identify the degradation patterns of individual compounds in FAMES through TGA analysis (Fig. 1 and Table 4) and it was shown that mainly physicochemical processes of volatilisation and carbon chain cleavage are involved.

3.2. TGA of mixtures of model compounds and rapeseed oil

To help with the identification of components or groups of compounds that could be present in a given biodiesel process stream, approximately 3 mg of the mixed samples were analysed according to nominal masses in Table 3. All experiments were done in triplicates and averages reported with their standard deviations in Table 5. The TGA curves of these mixed samples are shown in Fig. 2.

The GOPFR-01 mixture (Fig. 2a) presents the TGA patterns in agreement with Fig. 1a-e, indicating 3 distinct peaks (Table 4) corresponding of pure glycerol (stage I) with Tmax at 211.83 ± 0.04 °C (stage I) and 28.59% of mass loss, degradation of oleic and palmitic acids and FAMES (stage II) with Tmax at 284.62 ± 0.04 °C and 40.68% of mass loss and degradation of rapeseed oil and unconverted oils and fats (stage III) with Tmax at 504.25 ± 0.05 °C and 30.46% of mass loss respectively, as described in Section 3.1.

Accordingly, each mixture sample described in Fig. 2b-f showed

Table 5

TGA parameters of GOPFR-01, GOPFR-02, GOPFR-03, GOPFR-04, GOPFR-05 and GOPFR-06 mixtures.

	Ti (°C)	Tf (°C)	Actual Mass Loss (%)	Expected Mass Loss (%)
GOPFR-01	Stage I			
	116.02	211.83	28.59 ± 0.07	20.00
	± 0.06	± 0.04		
	Stage II			
	211.83	284.62	40.68 ± 0.15	51.70
	± 0.04	± 0.04		
GOPFR-02	Stage I			
	116.27	211.83	40.43 ± 0.03	33.30
	± 0.00	± 0.04		
	Stage II			
	211.83	284.71	31.19 ± 0.01	43.20
	± 0.04	± 0.02		
GOPFR-03	Stage I			
	116.40	211.83	26.06 ± 0.00	16.70
	± 0.18	± 0.04		
	Stage II			
	211.83	284.79	47.28 ± 0.00	59.80
	± 0.04	± 0.03		
GOPFR-04	Stage I			
	116.40	211.80	20.02 ± 0.03	16.70
	± 0.20	± 1.50		
	Stage II			
	211.80	284.80	51.56 ± 0.08	59.80
	± 1.50	± 0.05		
GOPFR-05	Stage I			
	116.72	211.87	20.09 ± 0.09	16.70
	± 0.55	± 1.33		
	Stage II			
	211.87	284.79	48.06 ± 0.15	53.00
	± 1.33	± 0.06		
GOPFR-06	Stage I			
	116.80	211.90	23.37 ± 0.00	16.70
	± 0.10	± 0.15		
	Stage II			
	211.90	284.85	37.94 ± 0.00	43.10
	± 0.15	± 1.20		
GOPFR-06	Stage III			
	284.85	504.60	38.69 ± 0.00	40.20
	± 1.20	± 0.30		
			100.00 ± 0.00	100.00

T_i = initial temperature; T_f = final temperature.

three main peaks and the size of each peak compared with the peaks of the individual compounds in Fig. 1. The GOPFR-02 mixture (Fig. 2b) showed that the highest mass loss of 40.43% (Tmax at 211.83 ± 0.04 °C) corresponded to devolatilization of glycerol, as twice as much glycerol was used in this mixture compared to the other individual compounds. With this result, it was possible to identify the degradation of fatty acids and FAMES with 31.19% of mass loss and the peak corresponding to rapeseed oil and unconverted oils and fats with 26.33% of

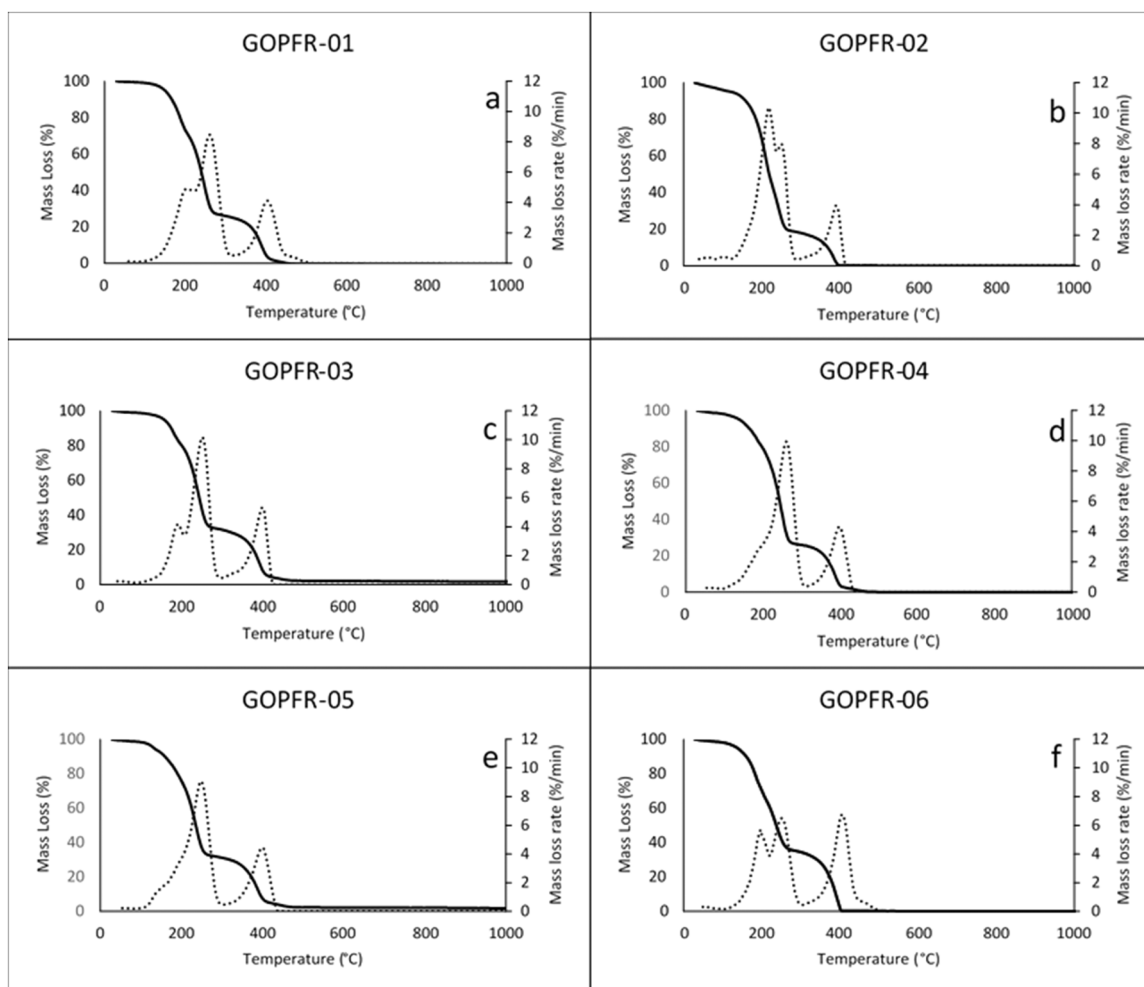


Fig. 2. TGA curves of: (a) GOPFR-01, (b) GOPFR-02, (c) GOPFR-03, (d) GOPFR-04, (e) GOPFR-05 and (f) GOPFR-06 mixtures.

mass loss. Fig. 2c-e present the TGA curves corresponding to the GOPFR-03, GOPFR-04 and GOPFR-05 mixtures with the highest amount of oleic acid, palmitic acid and FAMES and as can be seen, the highest peak of each mixture corresponds to the overlapping degradation of fatty acids and FAMES with 47.28% (T_{max} at 284.79 ± 0.03 °C), 51.56% (T_{max} at 284.80 ± 0.05 °C) and 48.05% (T_{max} at 284.79 ± 0.06 °C) mass losses, respectively. These results can be linked to the TGAs reported in Fig. 1 for individual compounds.

Clearly, Fig. 2f corresponds to the highest amount of rapeseed oil linked to Fig. 1, with the third peak having the highest mass loss observed with 38.69 wt% (T_{max} at 504.60 ± 0.30 °C) corresponding to the degradation of this raw material and the unconverted oils and fats as well as reported Section 3.1 in this present study. In fact, these results showed that the TGA method is an easy and inexpensive technique to identify and quantify compounds even when there is a mixture of individual compounds. Table 5 shows the initial and final temperatures and corresponded mass loss in each peak stage for the mixture samples and linked to Fig. 2. The differences between the mass loss observed and expected in those mixtures showed in Table 6, was attributed to the overlap of the glycerol and fatty acids peaks in the first stage with the FAMES in the second stage. However, the results showed in the Table 5 agrees with the literature [1,37,46,50,54,55] and the highest mass loss in each mixture was in accordance with the compound with the highest amount (Table 3).

3.2.1. Characterisation of biodiesel plant samples by TGA

For the TGA quantification of the three biodiesel plant samples,

Table 6

Compositions of fatty acid methyl esters in the biodiesel plant samples (wt% of extracted FAMES).

Scientific Name	BPW-A	BPW-B	BPW-C
Decanoic acid, methyl ester	0.62	0.27	0.36
Dodecanoic acid, methyl ester	nd	0.39	nd
Tetradecanoic acid, methyl ester	0.97	0.80	0.75
Pentadecanoic acid, methyl ester	0.92	0.27	nd
Hexadec-9-enoic acid, methyl ester	nd	0.81	0.78
Hexadecanoic acid, methyl ester	16.70	16.70	16.20
cis-Heptadec-10-enoic acid, methyl ester	nd	0.32	0.32
Heptadecanoic acid, methyl ester	0.52	0.34	0.31
Octadec-9-enoic acid, methyl ester	72.10	71.30	71.10
9,12-Octadecadienoic acid, methyl ester	5.03	5.53	5.93
Octadecanoic acid, methyl ester	0.53	0.36	0.67
Nonadecanoic acid, methyl ester	nd	0.38	0.86
cis-11-Eicosenoic acid, methyl ester	1.10	1.14	1.21
Eicosanoic acid, methyl ester	0.79	0.74	0.88
Tricosanoic acid, methyl ester	0.72	0.65	0.63

approximately 3.0 mg of each sample was used for the TGA work. The peaks on the DTG curves of the biodiesel plant waste samples were compared to those of rapeseed oil to identify the peak corresponding to unreacted oil and fats. The amounts of FAME and lipid products in each of the three biodiesel plant samples were calculated from weight losses observed at different stages, according to their individual TGA profiles. Fig. 3 compares each TGA of BPW-A (Fig. 3a), BPW-B (Fig. 3b) and BPW-C (Fig. 3c) curves with the food-grade rapeseed oil sample (Fig. 3d).

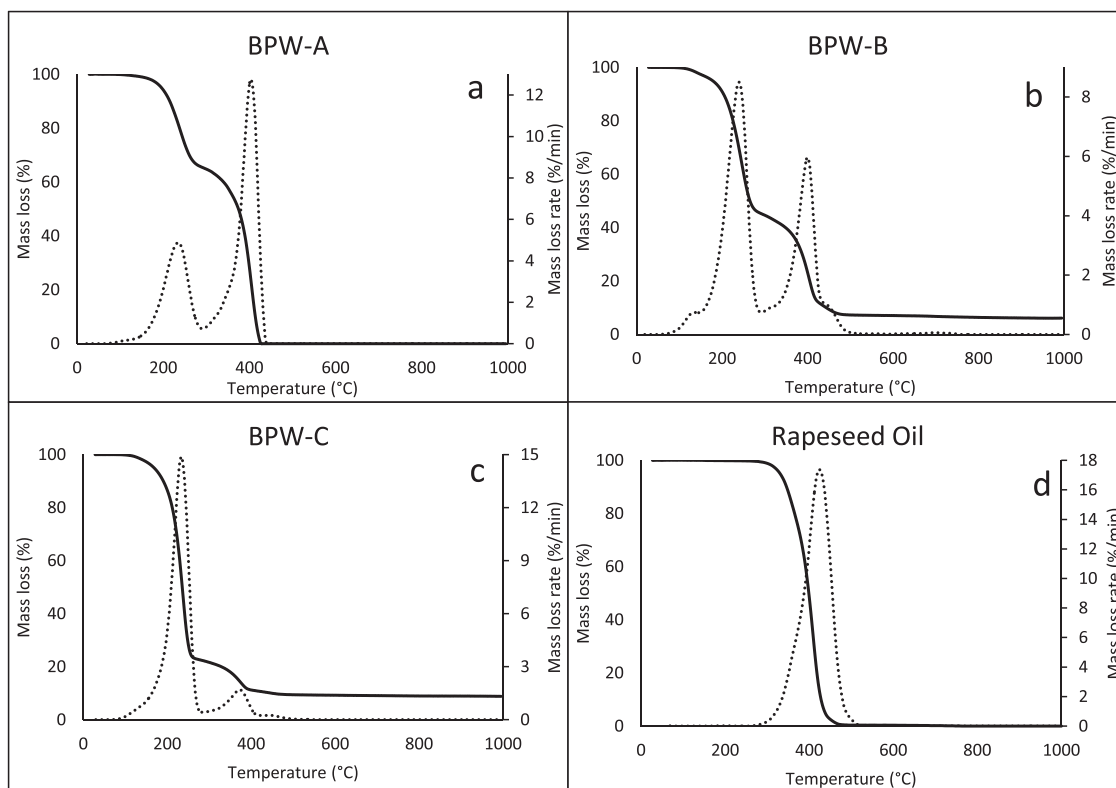


Fig. 3. TGA curves of the three biodiesel plant wastes: (a) BPW-A, (b) BPW-B and (c) BPW-C and (d) Rapeseed Oil.

Clearly, it can be seen that in the first stage of biodiesel production (esterification process) the amount of unreacted rapeseed oil and fats is much higher than in the second and third stages (transesterification processes). In fact, the combination with esterification and transesterification processes significantly increases the production of FAMES, as shown in the TGA curves obtained in this work.

Therefore, by identifying and evaluating the peaks corresponding to lipids from the rapeseed oil degradation pattern, the lipid contents of the samples were calculated to be 65.9 wt%, 41.8 wt% and 14.6 wt% for BPW-A, BPW-B and BPW-C, respectively (Fig. 4). In addition, the GC/MS analysis of the industrial samples showed the presence of FAMES in all three samples (please see Supplementary Information Figs. S11–S14). The compositions of FAMES in the samples are shown in Table 6. Indeed, GC/MS analysis showed that BPW-A contained approximately 32.1 wt%, BPW-B contained 60.6 wt%, while BPW-C contained 91 wt% of FAMES (Fig. 4). The GC/MS results showed very strong consistency with the FAMES contents of the samples from the TGA data. The TGA data (Fig. 4) for the FAME-rich components accounted for 33.9 wt%, 57.8 wt% and 85.3 wt%, in BPW-A, BPW-B and BPW-C samples, respectively.

Therefore, TGA curve of the three industrial samples did not indicate the presence of glycerol, showing that the separation process to remove

aqueous-phase components was effective. Both the TGA and GC/MS data show the progressive conversion of the oil and fats feedstocks in FAMES during of biodiesel production stages. Hence, the GC/MS data (Supplementary Information Figs. S11–S14) and the TGA data in Fig. 4 show that the content of FAMES-rich components in the industrial samples were in the order: BPW-C > BPW-B > BPW-A. Alternatively, Fig. 4 shows that the lipid contents of the samples were in the order: BPW-A > BPW-B > BPW-C, indicating the sequential conversion of triglycerides for FAMES with excellent coefficients of determination (Fig. 4).

4. Conclusions

A thermogravimetric analysis method has been developed and used to quantify the composition of organic compounds involved in biodiesel production chemistry as well as industrial biodiesel process streams. The method showed good reliability with good agreement with GC/MS analysis for fatty acid methyl esters. However, the TGA method went beyond the analysis of FAMES by indicating the chemical composition of biodiesel process streams by differentiating between the volatilisation and degradation patterns of FAMES-rich components and triglyceride-rich components, respectively. The TGA method will be useful for fast and simple characterisation of biodiesel process streams, with the capability of revealing the extent of triglyceride conversion via esterification and transesterification. More importantly, it can become a cheap method of assessing the purity of commercial biodiesel products during production and storage. The acceptability of this innovative TGA method will be enhanced if the analytical data obtained can closely fit with those from the GC/MS standard method, especially for FAMES. As this present study shows, possible overlap of degradation patterns in multicomponent samples presents a technical challenge in accurately determining their mass compositions. Such shortcomings may be overcome by improving the sensitivity of the TGA for this type of analysis and by using a more tailored temperature programme.

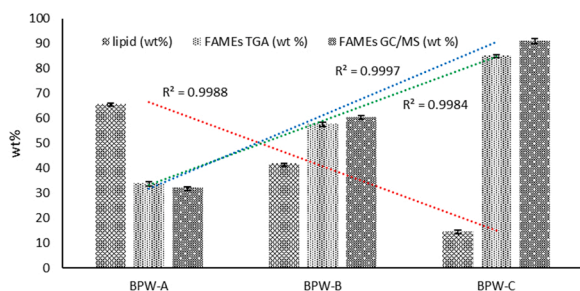


Fig. 4. Compositions of lipids and FAMES in biodiesel plant samples.

CRedit authorship contribution statement

Carine Tondo Alves: Methodology, Investigation, Funding acquisition, Data curation, Formal analysis, Visualization, Writing – original draft. **Morenike E. Peters:** Methodology, Investigation, Formal analysis, Writing – review & editing. **Jude A. Onwudili:** Conceptualization, Funding acquisition, Investigation, Methodology, Project administration, Resources, Supervision, Validation, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:[10.1016/j.jaap.2022.105766](https://doi.org/10.1016/j.jaap.2022.105766).

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