Determination of Vapor Pressures of FAME Industrial Mixtures by Ebullioscopic and Thermogravimetric Experimental Methods

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Abstract

Vapor pressure is a parameter that characterizes, by principle, only pure compounds. Nevertheless, it can be refereed also to mixtures, in order to characterize their volatility or to be inserted in technical documents. The measurement of vapor pressure for mixtures is strongly dependent on the possible variation of the composition, during experiments, due to the different volatility of the constituent compounds. It is possible to calculate the vapor pressure of the mixture starting from its composition, but the different thermodynamic scenarios must be considered. Moreover, for industrial samples possible effects due to the presence of impurities must be considered. In this work, two different experimental methods have been employed to determine vapor pressure of some acetates esters and two industrial mixtures of Fatty Acid Methyl Esters (FAME). The first method is a direct ebullioscopic method while the second is an indirect thermogravimetric analysis (TGA). An error function was calculated to compare the experimental results of vapor pressures obtained with the two methodologies with the theoretical ones. Ebullioscopic measures resulted suitable only for acetates esters, as FAME mixtures are characterized by too low vapor pressures to be quantified with this technique. On the contrary, TGA methodology is more accurate for FAME than acetates. It allows to collect a great number of vapor pressure values with a very fast analysis. This method is less accurate than others, but it can be useful for a fast screening of the FAME mixtures, also contaminated with light impurities.

Keywords: Vapor Pressure, Biodiesel, Ebullioscopic Methods, FAME, Mixtures, TGA.

1 INTRODUCTION

In the quest for sustainable energy sources, biodiesel (BD) has emerged as a viable and environmentally friendly alternative to traditional fossil fuels. Derived from renewable and green materials like vegetable oils, greases, and animal fats, biodiesel has the potential to play a pivotal role in the circular economy [1][2]. Fatty Acid Methyl Esters (FAME) are the main constituents of these biofuel mixtures and they are produced by the transesterification reaction, promoted by homogeneous or heterogeneous catalysis, of the triglycerides molecules using methanol, or as possible alternative, ethanol [3] [4]. Other important advantages of BD are biodegradability, non-toxicity, possibility of production in small scale plants and low environmental impact. Moreover, a huge advantage for BD is the possibility of using any blend between biodiesel and petrodiesel in any proportion in the modern engines [5]. However, the possibility of using FAME blends directly in the current fuel market requires that these respond to specific requests for standards, such as ASTM D6751 and EN 14214 [6], as regards their main chemical-physical characteristics. The determination of these properties is particularly challenging because they depend on the composition of the biodiesel, which can vary according to the initial raw material and the conditions of synthesis and purification [4]. Therefore, each

produced mixture requires a detailed characterization study [7] by experimental techniques or, when possible, through predictive methods [8]. Moreover, the presence of impurities can influence the measurements [9]. The most important physical characteristics of BD mixture are calorific value, or heat of combustion, cloud point, viscosity, density, flash point, melting point and vapor pressure (VP) [10]. This last parameter is strictly correlated with the volatility and it is fundamental both for safety reasons and for a good functioning of the internal combustion of the engines [6]. BD characterized by a too high vapor pressure has problems of too fast evaporation, but too low values of this parameter means delayed ignition, due to poor BD atomization, and consequently cause not efficient combustion [11]. VP can be defined as the pressure of a vapor in thermodynamic equilibrium with its condensed phase in a closed container [12] and it is, by strictly definition, a characteristic of a pure compound. The experimental measure of VP for BD is a not easy task for different reasons. BD is actually a mixture of several FAME, it is characterized by very low vapor pressure and it can change composition or it can be degraded during the experiments [12]. Moreover, the presence of impurities can strongly affect the experiments [13]. In order to determine correctly the VP of a mixture it is important to maintain the composition constant during the experiment. It is also possible to calculate the vapor pressure of a mixture by knowing the VP of the single compounds and the composition, but it is necessary to know the thermodynamic characteristic of the mixture, ideal or not ideal. FAME mixtures are largely considered as ideal mixture in literature [11], also if not ideal approaches that take into account the activity coefficients calculation have been reported [14].

Different experimental methods have been proposed to determine VP of FAME mixtures. In the manometric procedures the tested material is in equilibrium in the liquid or solid phase and the vapor pressure is directly measured. The main problem of this approach is the possible presence of volatile contaminants in the sample that strongly increases the pressure of the container. This problem occurs also with extremely pure BD, as it can absorb impurities also from the surrounding air [15]. This problem can be solved by applying cycle measurements or pre-treating the sample [13]. Other possible experimental procedures are represented by "gas saturation method" and "concatenated gas saturation methods" proposed from National Institute of Standard and Technology (NIST) [16], based on the stripping of the vapor for a calibrated volume of carrier gas followed by a cold trap (or adsorber) and then on the measuring of the collected weight of the condensed liquid. These methods are able to give very accurate data, but they are quite complex from an experimental point of view and, moreover, they are

not fully suitable for liquid mixtures, due to the possible change of composition during the experiments. Correlation Gas Chromatography methodology was proposed by Lipkind et al. [17] to measure vaporization enthalpies and vapor pressure of single, not mixed, saturated FAME. Ebullioscopic equipment was used to measure the boiling temperatures of single FAME and one binary mixture [6]; also for this method complex experimental equipment is needed and few data about multicomponent mixtures are available in literature.

An interesting procedure, based on the interpretation of thermogravimetric analysis (TGA), was proposed by Goodrum [18] [19]. TGA method is based on the evaporation rate of single and mixed FAME in function of the TGA heating rate [20]. VP obtained in this way resulted accurate, requiring very small amount of samples and fast analysis. The possible presence of impurities in the samples was detected by the shape of TGA curves and no thermal degradation effect were observed. The experiments were conducted with a commercial TGA instrument, working under vacuum (100 kPa) and using laser-drilled capsules. The great advantage of this method is represented by its simplicity and speed of measurement. The main limitation is given by the experimental measurement conditions, in particular for pressure. As described by Goodrum [19] "*the pressure and temperature condition of these TGA test are much lower than those encountered as fuel volatilizes in a diesel engine*" and the possibility to perform TGA experiment at higher pressure was suggested. On the other hand, this method seems to be the fastest, simplest and most suitable for vapor pressure measurements of BD mixtures of different composition or production compared to the other different techniques reported in literature.

The accuracy of the measurements may be lower than in other methodologies [16] [13], but it is still suitable for obtaining characteristic values of the many possible mixtures on the market. For this reason, in the present work, a study was conducted to determine the vapor pressure of industrial blends of FAME using a modified TGA methodology respect the one proposed by Goodrum [18]. The operating conditions of the analysis were studied, first of all the best temperature ramp, to carry out TGA analyses at ambient pressure.

The presence of experimental vapor pressure values, in particular for FAME mixtures is still considered too limited from several Authors [16][13][12][11]. The reason is that the experimental measure of BD VP is cumbersome and time consuming [16]. To overcome this limiting situation, several estimation methods were proposed [12] [21] and an interesting overview was suggested by Saxena et al. [22]. Despite the good results obtained from these predictive methodologies, experimental data are often needed both due to the possible presence of impurities in

commercial FAME mixtures and due to the huge variety of BD produced or which will potentially be produced in the future. In fact, more than 350 oil bearing crops have been identified as potential raw material for the production of BD based fuels [23]. Therefore, accurate, fast and not complex methodology for the measure of VP of real industrial FAME mixture are still required to be optimized.

In the present work, two different methodologies for the VP measurement of two real industrial FAME mixtures (FAME_01 and FAME_02), produced by Sabio Fuels s.r.l. company (Brescia, Italy) were tested, based on ebullioscopic methodology [24] and TGA analysis. The effect of impurities and the accuracy of both methodologies were investigated and optimized, using standard compounds (ethyl acetate, butyl acetate as pure compounds and their mixtures, generally labelled in this paper as "acetates") and then FAME. TGA methodology resulted to be the most suitable for the measure of the vapor pressure of FAME mixtures and it was seen how it is possible to operate at ambient pressure if an appropriate heating ramp is used.
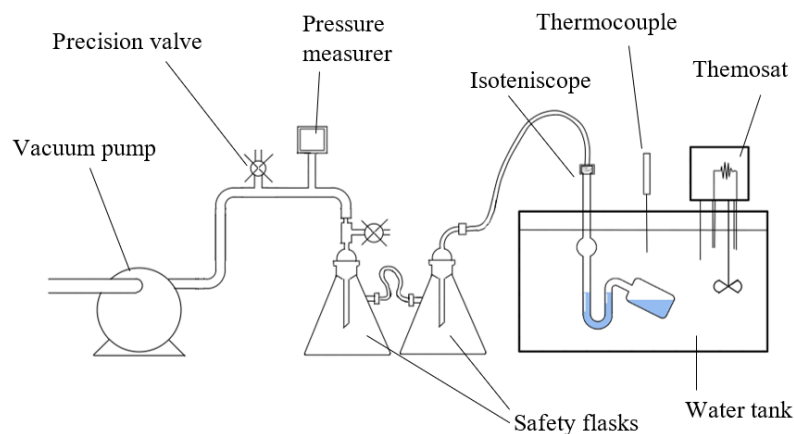

2   METHODS

Butyl and ethyl acetate were bought from Merck company and used as received. FAME mixtures FAME_01 and FAME_02 were received from Sabio Fuels s.r.l. company.

In this section the two experimental methods employed for the determination of the vapor pressure of industrial mixtures of FAME are described. The first method is a direct ebullioscopic method while the second is an indirect thermogravimetric analysis.

The vapor pressures of pure compounds tested in this paper were calculated by the Process Simulation software AVEVA PRO II, using the internal database. Vapor pressures of the mixtures (acetates and FAME) were calculated applying the Raoult's law on the basis of their composition, i.e. assuming ideal thermodynamic behavior [14]. In the paper, all the vapor pressures calculated in this way will be labelled as "calculated".

2.1 Direct ebullioscopic method

The scheme of the plant used for the determination of vapor pressures of acetates and FAME pure compounds and mixtures at different temperatures is reported in Figure 1. This experimental setup was proposed by Belletti et al. [25] and the working procedure was explained in detail in our previous work [24].

FIGURE 1: *Scheme of the experimental plant for ebullioscopic method.*

In each experiment, the tiny tank of the isoteniscope is filled with 25 ml of the sample (pure compound or mixture) and placed in a thermostatic water bath for temperature regulation of the liquid and gas phases. After establishing isothermal conditions at the specified temperature T, air trapped inside the plant is removed using the vacuum pump. It is crucial to attain a pressure lower than the estimated vapor pressure of the sample. The pressure within the line is measured using a Pirani vacuum gauge, which can detect pressure in the range from vacuum (about 65 Pa) to 101325 Pa.

The U-tube of the isoteniscope filled with the same liquid shifts to the left when the pressure on the left side of the instrument is lower than the liquid's vapor pressure (due to vacuum). This apparatus measures the pressure difference between the two branches of the tube, that is the difference between the unknown vapor pressure and the apparatus pressure. The precision valve is then opened to enable a small amount of air to enter, gradually increasing the pressure within the apparatus. When the U-tube inside the isoteniscope is balanced, the opening of the valve remains constant, enabling the instruments to monitor the pressure. When the liquid inside the syphon of the isoteniscope is at the same level in both branches by visual observation, a reading is taken. The error due to this visual inspection is extremely low considering the low specific weight of the measured compounds. Under these conditions, the pressure of the line and the unknown vapor pressure in the glass lungs are equal and opposing. This line pressure, registered by the Pirani vacuum gauge, is equivalent to the vapor pressure of the sample at bath temperature.

2.2 Indirect thermogravimetric analysis

Thermogravimetry analyses (TGA) are, in principle, suitable for high-boiling substances that are otherwise challenging to examine. The data collected by TGA refers to the sample's mass as a function of temperature and time. These two parameters are linked by the configuration of a furnace's heating ramp. In addition to the predetermined temperature, the analysis also records the actual temperature of the sample. This study employs the Langmuir equation (equation 1), which describes the spontaneous evaporation of a substance, to establish a relationship between mass loss rate and temperature [20]:

$$-\frac{dm}{dt} = p\alpha\sqrt{\left(M/2\pi RT\right)} \tag{1}$$

In this equation, *-dm/dt* represents the measured mass (*m*) change in function of the time of analysis (*t*), *p* represents the vapor pressure of the compound, *M* represents the molar mass, *T* represents the furnace temperature in Kelvin, α represents the vaporisation coefficient and *R* is the gas constant. This equation can be rearranged as *p=kv*, where $k = \sqrt{(2\pi R)}/\alpha$ and $v = dm/dT\sqrt{T/M}$. In this manner, *k* can be obtained through linear regression and utilised for all subsequent analyses with the same instrument and under the same conditions. This calibration can be done from an initial calibration analysis on the basis of a TGA experiment with a compound whose vapor pressure and molar mass are perfectly known, in the same pressure range of the compound for which vapor pressure must be determined. The detailed calculations of this procedure are reported in the paragraph 3.2.

Before measuring the vapor pressure of FAME mixtures, TGA methodology was tested using acetates compounds with well known vapor pressure. In particular, the parameter *k* was derived from butyl acetate as calibration standard and validated checking the vapor pressure values of a second standard, i.e. ethyl acetate. Measurements were performed using a heating ramp of 5 K/min between 303 K and 973 K in a constant nitrogen flow of 20.0 NmL/min and values were collected every second. The resulting curves were not satisfactory. Therefore, measurements were conducted with a gradient of 25 K/min, in order to modify the evaporation rate of the samples.

The parameter *k* for FAMEs mixtures was determined using a sample of methyl palmitate, and the accuracy of the method was validated by comparing VP results for pure methyl-decanoate with the theoretical ones. All measurements were conducted using both 5 K/min and 25 K/min as gradient, increasing the temperature between 303 K and 973 K in a constant nitrogen flow

of 20.0 NmL/min, and values were collected every second. Each sample contained approximately 35 mg of the substance.

All results obtained for FAME mixtures were calculated using the molecular mass of the samples as the average weighted on the composition of the molecular masses of the major components. The obtained values were compared with vapor pressure curves assumed always as the weighted average of the vapor pressures of the main components based on the percentages listed in Table 1, i.e. assuming ideal thermodynamic behaviour of the mixture and then using the Raoult's law, as already reported for this kind of BD mixtures [13].

Sample	FAME Total	Methyl Caparilate C08:0	Methyl Caproate C10:0	Methyl Myristate C14:0	Methyl Palmitate C16:0	Methyl Stearate C18:0	Methyl Oleate C18:1	Methyl Linoleate C18:2	Methyl Arachidate C20:0	Methyl Eicosenoate C20:1
		% weight								
FAME_01	99.5	0.3	0.3	2.2	31.6	6.6	35.0	18.0	0.2	0.9
FAME_02	89.0	<0.1	<0.1	0.1	10.8	11.2	49.0	22.6	0.7	1.6

TABLE 1: *Compositions of FAME industrial samples (% weight) by Sabio fuels s.r.l. The remaining part of composition to close at 100% the "FAMEs total column" is formed by impurities.*

2.3 Error evaluation

An error function has been calculated for all the experiments in order to compare the results with the theoretical values, using the following Equation (2).

$$error\ function = \frac{\sum_{i=1}^{n}|p°_{exp,i}-p°_{calc,i}|}{n}x100 \tag{2}$$

It takes into consideration the total sum of the difference between all the experimental vapor pressures $(p^0_{exp,i})$ and the reference values calculated by Clausius Clapeyron equation for pure standard compounds or by assuming ideal behaviour for mixtures $(p^0_{calc,i})$ divided for the total number of experimental points (n).

3 RESULTS

Both the methodologies (Ebullioscopic and TGA) were tested with acetate esters and FAME, as single compounds and mixtures. Ethyl acetate and butyl acetate have a normal boiling point

of 350 and 399 K respectively, while FAME constituting FAME_01 and FAME_02 (Table 2) have a normal boiling point in the range 569-647 K. Then, ebullioscopic and TGA methods were compared for these classes of compounds with strongly different vapor pressures, in order to shed light on what is the best experimental approach with compounds having very different characteristics.
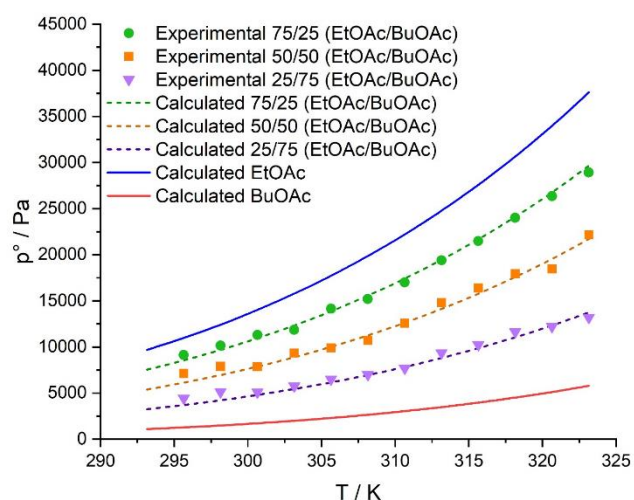
3.1 Ebullioscopic method

To validate the methodology the vapor pressures of pure ethyl acetate and butyl acetate and of the mixtures thereof were determined. The isteniscope's accuracy were confirmed by the results of the vapor pressure of the pure compounds. These values are extremely close (average error function for butyl acetate (BuOAc) and ethyl acetate (EtOAc) equal to 8.6% and 2.0% respectively) to the calculated vapor pressure curves (Figure 2).
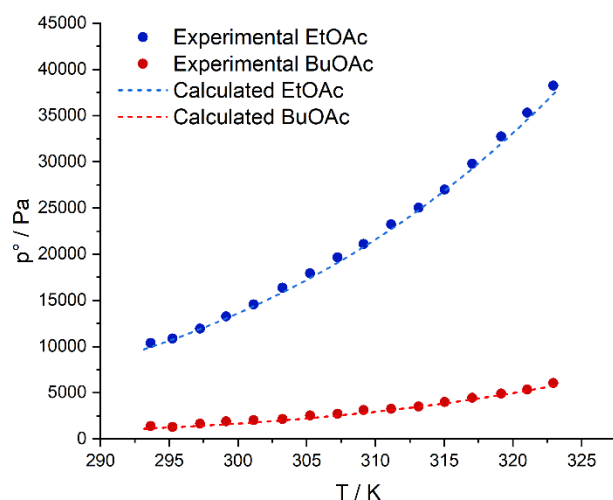
FIGURE 2: Experimental and calculated vapor pressure curves of pure butyl and ethyl acetate obtained using the ebullioscopic method.

To compare the data of the mixtures instead, the weighted averages were used, approximating the mixtures as ideal and considering Dalton's law for total pressure as valid. This approximation appears satisfactory (Figure 3) given that we were working with small polar molecules, very similar to one another; as a result, interactions in the gas phase were uniform across the mixture and therefore negligible.

FIGURE 3: *Experimental and calculated vapor pressure curves of butyl and ethyl acetate mixtures obtained using the ebullioscopic method.*

As shown in the graph above (Figure 3), experimental points are very close to the calculated curves (Table 2), demonstrating the accuracy of the isoteniscope and validating the hypothesis of ideality of the mixtures.

Sample	Error Function (%)
BuOAc	8
EtOAc	2
75/25 (EtOAc/BuOAc)	2
50/50 (EtOAc/BuOAc)	5
25/75 (EtOAc/BuOAc)	6

TABLE 2: *Error function values of isoteniscope measurements for acetates. The mixture composition is expressed as molar ratio for ethyl acetate (EtOAc) and butyl acetate (BuOAc).*

For all the compounds and mixtures, the error function results < 10%. Furthermore, the error decreases significantly for samples with higher vapor pressure.

The isoteniscope measurements on FAME mixtures (FAME_01 and FAME_02) were conducted at 298 K, 308 K, 318 K and 328 K. Preliminary results showed an irregular trend of the experimental values, that were also very difficult to stabilize. This bad result could be explained by considering that during an analysis, especially for long times, there is a removal

of the most volatile components, such as water and other impurities, and this provokes not stable conditions in the experimental device. Moreover, the resulting pressures are not the real vapor pressure of the mixture but actually represent a gas mixture in which the volatile molecules give the most important contribution. This result is coherent with the observations reported by Castellanos Diaz et al. [13].

To limit the effect of water and other volatile compounds, it was verified that, given the high-boiling nature of methyl esters, the maintenance of the mixtures under vacuum for a fixed time before the measure didn't change the FAME mixture composition, then succeeding in selectively removing volatile impurities. The presence of low-boiling impurities strongly influences the vapor pressure measurement of FAME mixtures by isoteniscope method. The difference in volatility between water (the most important impurity) and FAME compounds is sufficient to significantly increase the vapor pressure detected by isoteniscope, as clearly shown in Figure 4, where the measured vapor pressure is reported in function of the duration of the experiments. Clearly, a stable value is expected if the mixture composition remains constant and only if this stability is verified the vapor pressure measure can be considered as meaningful and correct. Methyl caproate (M-caproate) is the lightest FAME present in the FAME mixture and then its vapor pressure can be considered as the maximum theoretical limit of the mixture. If vapor pressures higher than the corresponding one for pure methyl caproate (dashed line in Figure 4) are obtained, this means that impurities with vapor pressure higher than FAME are present in the mixture. For this, the dashed line reported in Figure 4 can be considered as a reference to understand when light impurities are still present in mixture. This behaviour is exactly the same reported in Figure 4, where it results that only after 80 minutes of vacuum application all the impurities can be considered as removed from FAME mixture. Only in these conditions the detected vapor pressures can be actually representative of the FAME mixture.

On this basis, the variation of the vapor pressure generated by the mixtures during the vacuum evaporation process was therefore monitored until a constant measurement was obtained (Figure 4).
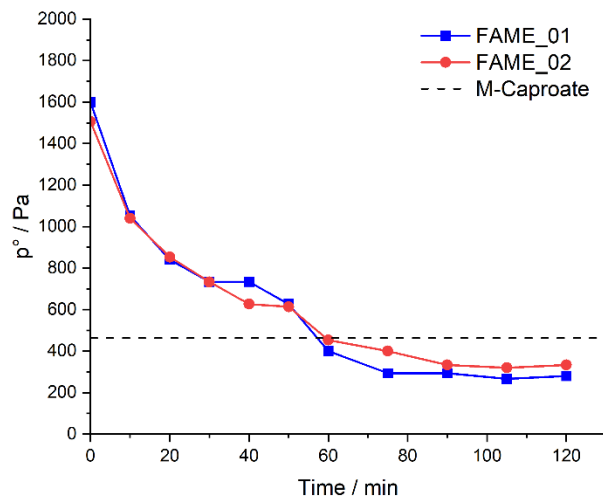
FIGURE 4: Variation of the vapor pressure generated by the FAME mixtures during the the isoteniscope measure under vacuum and at a constant temperature of 298 K.

On the basis of the results reported in Figure 4, in order to remove light impurities, vacuum conditions (P<200 Pa) were applied for 2 hours before the vapor pressure measurements. After this step, the dependence of vapor pressure on temperature was studied, again carrying out measurements between 298 K and 328 K, with temperature step equal to 5 K (Figure 5).
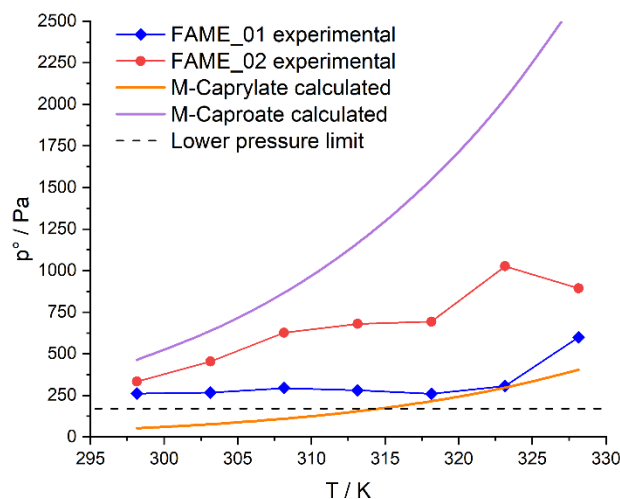
FIGURE 5: Dependence of vapor pressure on temperature of FAME samples, after the vacuum distillation process inside the isoteniscope. The dashed line represents the lowest pressure limit, i.e the minimum pressure obtainable in the experimental plant.

As it can be seen in Figure 5, the measurements at the lowest temperatures of both the mixtures are very near to the pressure limit (dashed line), so the vapor pressures are too low to be measured by isoteniscope method. The degree of vacuum obtainable by the equipment is not low enough to carry out these measurements, therefore the vapor pressures obtained correspond to the minimum vacuum obtainable in the system. Nevertheless, in measurements at higher temperatures, an increase in vapor pressures is observed, as expected for the normal correlation between this parameter and temperature. Moreover, it is observed that almost all values of vapor pressure appear confined between the vapor pressure curves of the two most volatile methyl esters present in the mixtures, tending to overlap more with the methyl-caprylate curve, especially for higher temperatures. From these tests it is evident that through the isoteniscope measurements of the vapor pressure of a mixture, in the case of high-boiling compounds, there is a tendency to observe only the vapor pressure of the most volatile compounds, even if it is present in very small quantities.

Summarizing, on the basis of our investigations, the minimum vapor pressure detectable by isoteniscope method is about 250 Pa and it is important to be sure that not volatile impurities are present in the mixture. This method can be considered as not suitable for high temperature boiling mixtures as BD (average error function > 100%).

3.2 TGA method

In order to validate the TGA method, measurements on butyl acetate and ethyl acetate, as pure compounds, were initially performed. Moreover, butyl acetate was used as standard for the calculation of the calibration constant k. This calibration must be done for each different heating ramp applied in the TGA experiment.

For this goal, an equation describing its temperature-dependent vapor pressure is needed. The parametric Clausius-Clapeyron equation, available in the Aveva PRO II simulation software, was applied:

$$\ln p° = A + \frac{B}{T} + C \ln T + DT^E \tag{2}$$

where, for butyl acetate $A = 122.82$, $B = -9253.2$, $C = -14.99$, $D = 0.00001047$, $E = 2$.

TGA experiment was performed with butyl acetate and, for each couple of measures (n and $n+1$), recorded during the TGA, the parameter v was calculated as $v = \frac{(m_{n+1} - m_n)}{(t_{n+1} - t_n)}$.

$\sqrt{\frac{(T_{n+1}+T_n)}{2} \cdot \frac{10^{-3}}{M}}$, where m is the mass measured, t the time from the start of the analysis, T the sample temperature in K, M the molecular weight of the butyl acetate and the factor 10^{-3} is for the correction from g to mg for the molecular weight. For each average temperature between the two points the vapor pressure in logarithmic form $ln\ p°$ was obtained applying the Equation (2). An example of these calculations, for two different consecutive times of TGA analysis, is reported in Table 2, where:

$$v = \frac{80.77651 - 80.6829}{(1.00002 - 0) \cdot \sqrt{[(291.449 + 291.476)/2 \cdot (0.001/270.45)]}} = 0.000412$$

$$p° = e^{[122.82 - 9253.2/\ 291.463\ -\ 14.99 \cdot ln(291.463)\ +\ 0.00001047 \cdot 291.463^{\wedge}(2)]} = 986.507\ Pa$$

time (min)	t(s)	mass (mg)	T (K)	ν	ln p	p (Pa)
0	0	80.77651	291.44	0.000412	6.89E+00	986.507
0.016	1.00	80.76829	291.47			

TABLE 3: *Numerical example for the first two measures of TGA experiments (heating ramp of 25 K/min).*

This calculation is repeated for every point measured and p° is plotted against v, as reported in Figure 6.
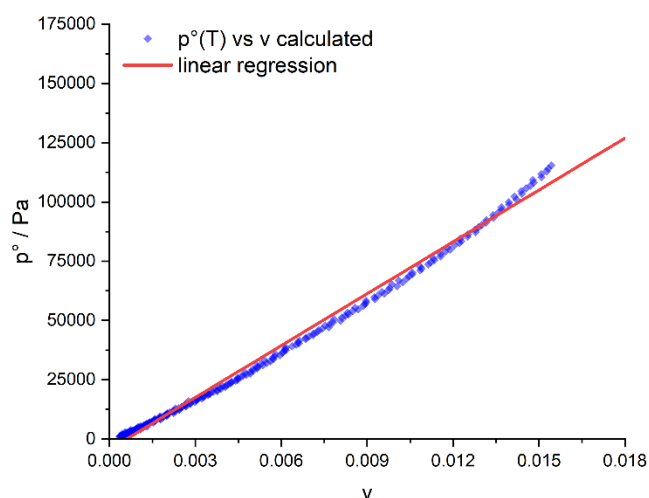
FIGURE 6: Calibration curve for the determination of k value, using butyl acetate (heating ramp of 25 K/min).

From the linear regression of the points of $p°$ and v, it is possible to obtain the slope of the line, that corresponds to the parameter k for all the measurements conducted in the same conditions and with compounds with similar vapor pressures. For BuOAc, the k calculated and used for all the acetates elaborations (temperature ramp of 25 K/min) was equal to 7.3×10^6.

As a verification, k parameter was used to determine the vapor pressure values of both pure butyl and ethyl acetates, by elaborating the TGA results.

The same procedure was previously used for the analysis with a slower temperature ramp (5 K/min). In this case the k value obtained with BuOAc resulted 5.3×10^6. The analyses were performed using different temperature ramps because this parameter is important for the quality of the results, due to the specific liquid vapor equilibria of the sample. A too slow heating rate in fact can provoke a different evaporation rate for which the TGA sensibility is not sufficient to give mass variation vs. time suitable for our interpretation. The increase of the temperature ramp in TGA has the effect of leaving the sample in the furnace of the instrument for less time, covering a greater temperature range before the complete evaporation of the analyzed liquid. In the case of mixtures, a shorter analysis time might result in a lower variation of the composition of the liquid fraction due to evaporation effect, remaining for a greater range equal to the initial composition and to the vapor pressure of interest.

As a verification, *k* parameter was used to determine the vapor pressure values of both pure butyl and ethyl acetates, by elaborating the TGA results. The obtained vapor pressures values are compared with the calculated ones (Figure 7).
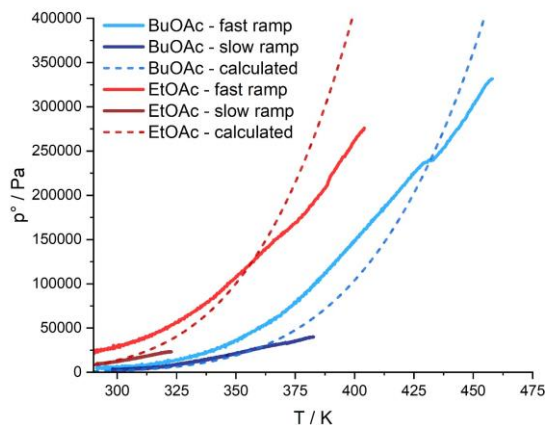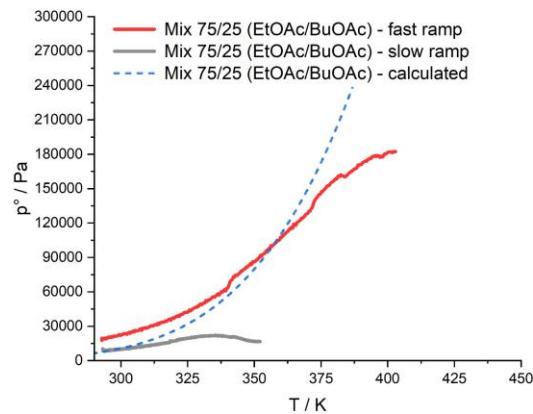

FIGURE 7: Comparison between experimental (TGA) and calculated vapor pressure curves of pure ethyl acetate (EtOAc) and butyl acetate (BuOAc) samples, using fast and slow temperature ramp.

The elaborations fail to correctly describe the behaviour of the two pure chemicals with a satisfactory accuracy, for both the applied temperature ramps. In particular, for EtOAc with slow ramp, data are only provided for a limited temperature range of around 30 K, because the measurement deviates almost early from the predicted curve and moreover the sample is consumed quickly as consequence of its high vapor pressure.

TGA method was tested also for acetates mixtures. In particular, a mixture 75/25 of ethyl and butyl acetate was analyzed using the two different heating ramps (Figure 8).

FIGURE 8: *Comparison between experimental (TGA) and calculated vapor pressure curves of ethyl and butyl acetate mixtures, using fast and slow temperature ramp.*

It is clear, by observing Figure 8, that the vapor pressures determined by TGA method are not satisfactory also for the acetates mixture.

The accuracy of TGA methods for the measure of vapor pressures of acetates was evaluated by referring to the error functions calculated with Equation (1), for pure compounds and their mixture. In order to correctly evaluate these results, it is important to consider that the values of vapor pressure quantified by TGA were collected in a very large range of temperatures. For example, for ethyl acetate TGA was performed from 290 to 400 K with a theoretical value of vapor pressures corresponding to 8850 Pa and 418000 Pa, respectively. It makes little sense to calculate an average error for such a large range of measurements. It must also be considered that the TGA measurements become representative of the evaporation process starting from a minimum temperature, at which the weight loss of the sample starts to be detectable with sufficient accuracy by the instrument. For acetates this minimum temperature corresponds to room temperature, while for FAME blends it is higher. On the other side, the maximum temperature at which the vapor pressure can be detected depends on the analysis time (and then temperature) in which all the sample under analysis is evaporated, and therefore depends on the quantity of sample used and the thermal ramp applied. As happens in every measuring instrument, the accuracy is low in the measurement intervals close to the lower sensitivity limit, while it increases in the central detection areas. For this reason, Table 4 shows the error calculated for vapor pressures between 150 and 2500 Pa ($\text{Error}_{150\text{-}2500\ Pa}$) with low accuracy and that calculated for higher vapor pressures ($\text{Error}_{>2500\ Pa}$) with higher accuracy. The absolute values of the numerical values may seem high, but it should be kept in mind that the proposed

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technique should be used as a method to quickly obtain a large number of data on the vapor pressure of pure or mixed compounds.

A very important parameter is the minimum vapor pressure that can be detected during TGA analysis, and the corresponding temperature. For this reason, a very low vapor pressure value (150 Pa) was selected as reference and the temperature in which this vapor pressure can be detected was determined from the derivative term of the TGA elaboration. Thanks to this reference value, it is possible to state that under this minimum temperature the vapor pressure of the sample is below 150 Pa. The same approach was used to assess the corresponding temperature at 2500 Pa as reference for the error function with higher accuracy. These reference temperatures are labelled as T_{150Pa} and T_{2500Pa}, respectively, and are reported in Table 4 for acetates and Table 5 for FAME.

|	BuOAc		EtOAc		75/25	
	Slow Ramp	**Fast Ramp**	**Slow Ramp**	**Fast Ramp**	**Slow Ramp**	**Fast Ramp**
Error$_{150-2500\ Pa}$ (%)	82	>100	--	--	--	--
Error$_{>2500\ Pa}$ (%)	24	29	15	39	34	40
T$_{150Pa}$ (K)	RT	RT	RT	RT	RT	RT
T$_{2500Pa}$(K)	307	306	RT	RT	RT	RT

TABLE 4: *Error functions and T_{150Pa} and T_{2500Pa} of TGA measurement for acetates. RT= Room Temperature (about 295 K). Error$_{150-2500\ Pa}$ for EtOAc and 75/25 mixture can't be calculated as it is higher to 2500 Pa also at the lower temperature tested in TGA.*

For all the measures conducted on the acetates the error function results significantly higher than the ones obtained with the ebullioscopic method, making this analysis less accurate for these compounds and then, not suitable for these measures.

FAME mixtures were then evaluated by TGA methodology. Two different *k* constants (for slow and fast heating ramps) for the elaboration of the FAME measurements were calculated from TGA data of pure methyl palmitate, a compound present in all the samples and with a vapor pressure similar to the mixtures. Vapor pressure curve of pure methyl palmitate was calculated

using Equation (2) and the following parameters (available in the Aveva PRO II simulation software) *A = 110.985, B = -14440.4, C = -11.7854, D = 1.01 E-18, E = 6.* The calculated calibration constants *k* were equal to 5.1×10^5 for the fast temperature ramp of 25 K/min and 6.0 for the slow temperature ramp of 5 K/min.

TGA methodology was then applied to measure VP of pure methyl decanoate and methyl palmitate, by comparing the results with the calculated curves. In this case, both the ramps used describe well the behaviour of the two compounds (Figure 9 and Table 5).
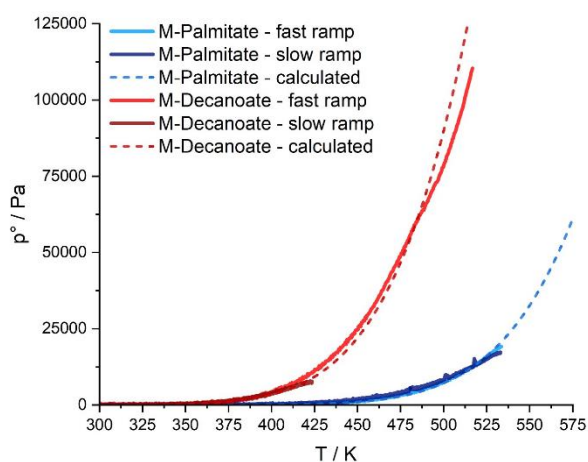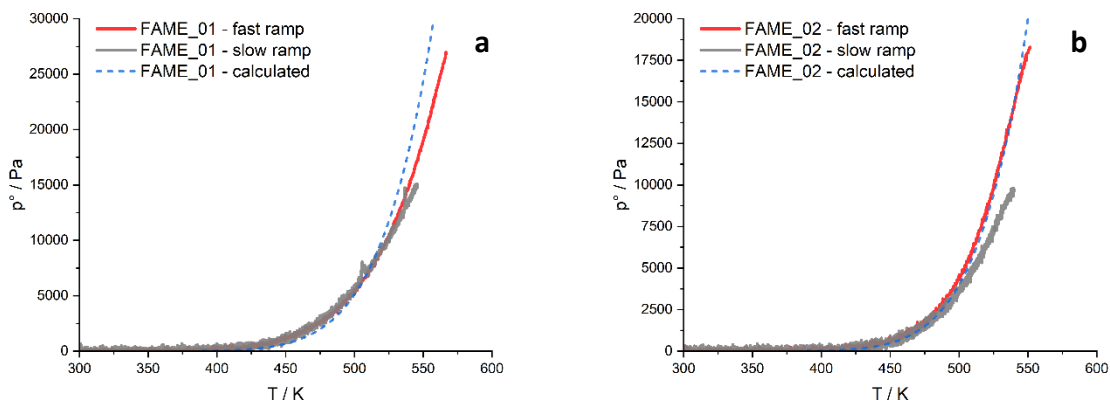

FIGURE 9: Comparison between experimental (TGA) and calculated vapor pressure curves of pure M-Palmitate and M-Decanoate samples, using fast and slow temperature ramp.

TGA method was finally tested for the measure of the vapor pressures of two real industrial FAME mixtures from Sabio Fuel Company (Brescia, Italy), whose composition is reported in Table 1. The experimental VP values were compared with the theoretical ones, calculated by assuming ideal behaviour for the mixtures, as before justified.

These analyses were conducted with the two temperature ramps of 5 K/min and 25 K/min and, as can be seen in Figure 10, the fast ramp gave better results, but the difference between those two is less significative than for the acetate mixtures previously discussed.

For these mixtures, as for the standards, the accuracy of the results was satisfactory (Table 5). Moreover, even though volatile impurities are present they do not seem to interfere with the measure.

FIGURE 10: *Comparison between experimental (TGA) and calculated vapor pressure curves of a) FAME_01 and b) FAME_02 mixtures, using fast and slow temperature ramp.*

As discussed for the acetates (Table 4) the accuracy of the measurements on FAME mixture was evaluated by referring to the error function in different pressure range and by determining the temperature for which vapor pressure is equal to 150 and 2500 Pa. The values reported in Table 5 demonstrate that for these high-boiling point compounds TGA analysis offers a valuable tool to determine in a very fast way the most important volatility and evaporation characteristics of a sample. The temperatures corresponding to vapor pressures of 150 and 2500 Pa were detected correctly and they do not result dependent of slow or fast temperature ramp. The identification of T_{150Pa}, in particular, is noteworthy as it is possible to state that under this reference temperature the vapor pressure of FAME mixtures is extremely low. As expected, the errors in the range 150-2500 Pa are quite high and then they must be considered as a rough indication of the vapor pressures just above the 150 Pa limit. On the contrary all the errors for vapor pressure higher than 2500 Pa are lower than 20 % and with the fast ramp the errors for both FAME mixtures are below the 15%. This is a very satisfactory results for the aim of the work as it is possible, using an analysis of about 15 minutes, to determine the vapor pressures of an industrial FAME mixture, also with light impurities inside, with an acceptable level of accuracy. Clearly, this method is not suitable for different aims, such as the rigorous collection of experimental data for modelling or for the fully characterization of the mixtures. For this purposes, other methods already reported in literature, must be considered.

	M-Palmitate		M-decanoate		FAME_01		FAME_02	
	Slow Ramp	Fast Ramp	Slow Ramp	Fast Ramp	Slow Ramp	Fast Ramp	Slow Ramp	Fast Ramp
$Error_{150-2500\ Pa}$ (%)	84	29	36	44	76	80	31	37
$Error_{>2500\ Pa}$ (%)	18	5	8	14	17	14	18	11
T_{150Pa} (K)	412	412	341	341	421	421	428	428
T_{2500Pa} (K)	471	471	393	393	481	481	488	488

TABLE 5: *Error functions and T_{150Pa} and T_{2500Pa} of TGA measurement for FAME.*

In addition to the speed of execution, other advantages of this methodology are the possibility of obtaining numerous experimental values of VP as a function of the temperature in a single analysis, the possibility of measuring VP also for mixtures containing impurities and the non-thermal degradation of FAME. On the contrary, TGA analysis are significantly less accurate to measure VP at fixed temperature respect other methodologies elsewhere described [16].

When TGA method involves FAME mixtures, it results accurate in the temperature range where the minimum temperature is above the instrument's limit of detection for mass variation over time and below the temperature where the mixture's composition is not sufficiently constant (or the sample is quite totally evaporated). In the case of the FAME mixtures here analysed the maximum temperature limit was considered equal to 550 K and for this limit the error functions were calculated as reported in Table 5. Different results can be achieved changing the experimental conditions (mass of the sample, temperature ramp, initial temperature), depending on the aim of the measure.

4   CONCLUSIONS

Two different experimental methods, namely isoteniscope and TGA, were tested to determine vapor pressure of some acetates esters, as pure and mixtures, and of two industrial mixtures of Fatty Acid Methyl Esters (FAME). The experimental results were compared with the calculated ones through the AVEVA ProII software simulation, defining an error function. Ebullioscopic measures result suitable only for acetates esters, as FAME mixtures are characterized by too low vapor pressures to be quantified with this technique. On the contrary, TGA methodology

is suitable and more accurate for FAME than acetates mixtures and it allows to collect a great number of vapor pressure values with a very fast analysis. This method is less accurate than others reported in literature, but it can be suitable for a useful screening of the FAME mixtures, also contaminated with light impurities, and to determine the temperature at which the vapor pressure of the mixture is equal or greater to a fixed value.

Acknowledgment

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