Volatility and boiling points of biodiesel from vegetable oils and tallow

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Abstract

Quality control of fuel-related properties of Biodiesel, such as volatility, is needed to obtain consistent engine performance by fuel users. The vapor pressures and boiling points of selected methyl esters and vegetable oils are proposed as quality control metrics for Biodiesel. This type of data was obtained by a rapid new method using thermogravimetric analysis (TGA). One atmosphere boiling points (bps) and temperature-dependent vapor pressures from 1 atm down to 5.332 kPa (40 mmHg) were measured for methyl and ethyl esters of rapeseed oil, canola oil, soybean oil, and tallow. Boiling points (1 atm) ranged from $340°C$ to $375°C$. Methyl and ethyl esters of a given oil differ by ca. $5°C$ in bps. These results are discussed in terms of the fatty acid composition of the esters and oils. Calibrations showed that the TGA/laser orifice capsule method gave accuracy of ±5%. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Biodiesel; Vapor pressure; Boiling point; TGA; TGA/laser orifice; Methyl ester; Ethyl ester; Tallow; Vegetable oil

1. Introduction

Standards and quality control in the manufacture and distribution of Biodiesel are being developed to assure that reliable and consistent fuels are supplied to users. Vapor pressure, P_v, and boiling point (bp) data hold promise as key fuel properties for Biodiesel since they have played a vital role in quality control in the petroleum based diesel fuel (D2) industry. D2 is defined by a specific bp range; its manufacture is based on control of the fuel's bp range. Further, D2 is winterized or regionally adjusted by changing its boiling range slightly.

If a practical method for fast, routine measurement of bp and temperature dependence of vapor pressure

were available, a specified bp would be a key test for quality of a Biodiesel fuel. For example, multiple bps for a single solution indicate the presence of chemically distinct components. Therefore, two bps would indicate the presence of approximately 20% or more of impurities, such as un-reacted vegetable oil, glycerol, etc. In addition, one may use vapor pressure data to calculate heat of vaporization by use of the Clausius/Clapeyron model [1]. The heat of vaporization values may be used, for example, to compare the rates of vaporization for two Biodiesel fuels.

It is assumed that Biodiesels, being mixtures of methyl esters, will have physical property trends analogous to those of pure methyl esters. That is, the mixtures of methyl esters found in Biodiesels are expected to show volatility and bp values which are dependent on fatty acid composition, mainly chain lengths and number of double bonds. Since other fuel properties,

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Table 1
Fatty acid content of vegetable oils (% weight)

	Palmitic (C16:0)	Stearic (C18:0)	Oleic (C18:1)	Linoleic (C18:2)
Safflower	5	1	20	70
Soybean	9	2	32	53
Sunflower	5	2	35	57
Cotton-seed	21	2	25	50
Rapeseed[a]	3	1	13	11
Peanut	8	4	55	25
Palm	42	4	42	10
Tallow	23	19	42	3

[a]Lenolenic (18:3) 8%, eicosic (20:1) 8%, erucic (22:1) 50%.

Table 2
Boiling points of pure methyl esters at 1 atm (100 kPa) (literature values)

Composition	CAS registry number	Boiling point (°C)	Reference
Methyl undecanoate (C11:0)	1731-86-8	248	[4]
Methyl laurate (C12:0)	111-82-0	262	[5]
Methyl myristate (C14:0)	124-10-7	296	[6]
Methyl palmitate (C16:0)	112-39-0	415	[4, p. C-412]
Methyl stearate (C18:0)	112-61-8	442	[4, p. C-518]
Methyl oleate (C18:1)	112-62-9	218[a]	[4, p. C-408]

[a]Measured at 2.66 kPa.

such as iodine number, have been associated with fatty acid chain lengths and double bonding character, vapor pressure of Biodiesels is expected to be related to other fuel properties. The major constituents of some commercial vegetable oils are given in Table 1 [2]. Biodiesels from these oils will have the same fatty acid composition. For a given Biodiesel, the actual bp will be the effective average of the types and amounts of fatty acids present. Other properties such as Iodine number also appear to be controlled by the types and quantities of fatty acids present [3].

In Table 2, the bps of pure methyl esters commonly present in Biodiesels are listed. These literature values [4, p. C-412, C-518, C-408; 5,6] illustrate the increase in bp with molecular chain length. Note that methyl oleate bp was only available for the low pressure of 2.66 kPa, a common occurrence in the literature. Other current bp techniques are not useful as thermal decomposition often occurs in larger organic

molecules such as those studied here. This breakdown of the sample occurs under the high pressure and temperature conditions used to determine bps. Because of these obstacles, there is generally a lack of detailed vapor pressure data for methyl esters of fatty acids and almost no data for biodiesels near 1 atm pressure.

A thermogravimetric analysis (TGA) laser aperture method has been developed by Goodrum [7–9]. This method shows promise as a rapid means of measuring the effective bp and vapor pressures of many organic compounds, including vegetable oils or methyl esters of vegetable oils. Boiling points and vapor pressure measurements of many organic compounds, including lipids, have often required considerable laboratory effort and thermal decomposition is normally a major concern, especially at absolute pressures greater than 6.7 kPa (50 mmHg). The TGA method for bps requires very small samples (typically 5 mg), is rapid, uses standard commercial equipment, and has given accurate ($\pm 5\%$) vapor pressure values up to at least 1 atm for a variety of oils, alcohols, and methyl esters in the 500 g molecular weight range. No evidence of thermal decomposition has been observed for pressures up to 101.3 kPa (1 atm) [7–9].

The objectives of this study were (1) to illustrate the usefulness of the new TGA method for relatively quickly obtaining otherwise unavailable data for Biodiesel fuels. This was to be accomplished by (2) measuring the effective bps for several Biodiesel fuels. Also, (3) the temperature dependence of vapor pressure ("volatility") was to be measured for pressures from 101.3 kPa (1 atm) down as low as 5.3 kPa (40 mmHg) absolute pressure. (4) In addition to verifying the TGA method, this study was intended to yield a body of basic physical property data.

2. Equipment and procedure

Thermogravimetric analysis (TGA) data were obtained with a TA Instruments Model 951 thermobalance with quartz furnace tube. At ambient pressure, a 50 ml/min nitrogen purge flow was used. Sub-atmospheric pressures were obtained with a mechanical vacuum pump (Edwards, model 5, 2 stage) and manually controlled airflow restriction valves. The platinum sample support was shaped to accommodate
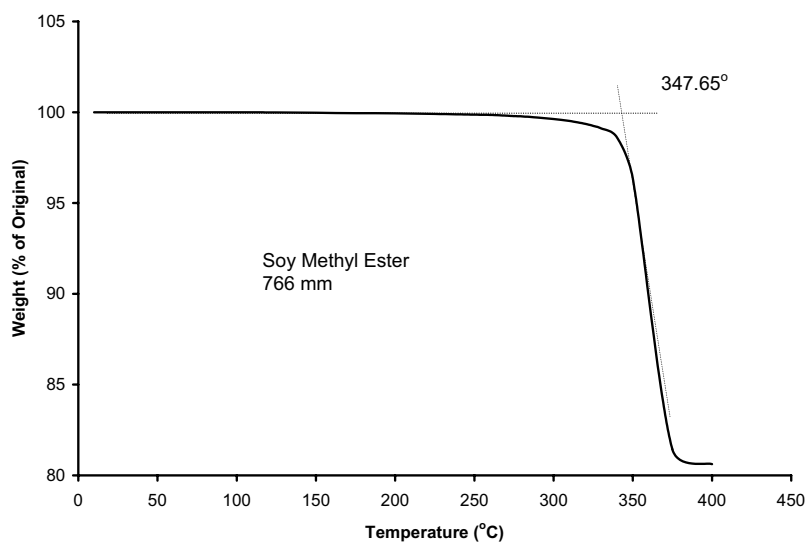
Fig. 1. Typical TGA plot of weight loss vs. temperature.

laser-drilled capsules obtained from the Perkin-Elmer Corp. (part no.N5190788). The drilled openings are 0.050–0.100 mm in diameter.

Typically, 5–8 mg samples were sealed in 20 μl pans with vented covers. To assist in achieving isothermal boiling, 0.2–0.5 mg of alumina powder was added to the sample as an inert diluent. The heating rate was set at 10°C/min. Each experiment was conducted at constant pressures so that temperature dependence of transitions could be measured. Pressure was maintained at ±0.13 kPa (1 mmHg) by manually adjusting a micrometer type valve. To check the accuracy of the TGA unit for vapor pressure, two well-characterized compounds, nonanol (CAS 143-08-8) and decanol (CAS 36729-58-5), were selected as reference standards [8].

Vapor pressure properties were found for samples of fuel grade rapeseed, canola, soybean, and tallow *methyl* esters, supplied by C.L. Peterson at the University of Idaho, Moscow, ID. Fuel grade *ethyl* esters of the above oils were also obtained from C.L. Peterson. Fuel grade is based on the National Biodiesel Board specification for Biodiesel [10]. This defined analysis is based on monoalkyl esters which may contain maximum traces of water, glycerine, and sulfur by weight. Alumina powder was from Baker Chemical, chromatography grade.

3. Discussion

One objective of this work was to evaluate the relative speed and convenience of finding vapor pressures and bps of methyl ester derivatives of oils at pressures near 1 atm by use of a TGA method. In Fig. 1, typical TGA bp transitions are shown for a nominal pressure of 1 atm. The plot is easily analyzed for 1 atm bps of ester by using the temperature onset method [7]. The dotted lines in Fig. 1 illustrate the use of this method. The TGA software is used to draw the tangent lines and compute the boiling temperature.

There was no visible evidence that any of the ester samples were decomposing prior to or during boiling. More importantly, our TGA measured bp value at 1 atm for methyl undecanoate was 241.5°C (not shown). This was within 3% of the literature value of 248°C [4], this suggests the TGA method is accurate for this series of molecules. Other comparisons between TGA-derived bps and older methods have shown good agreement (typical 5% error or less) for organics in the 200 to 600 molecular weight range [7–9].

In Fig. 2 we have a TGA plot for a mixture of 70% Biodiesel and 30% food grade vegetable oil. From the relative weight losses, one may calculate the Biodiesel/oil ratio and identify the Biodiesel fuel and
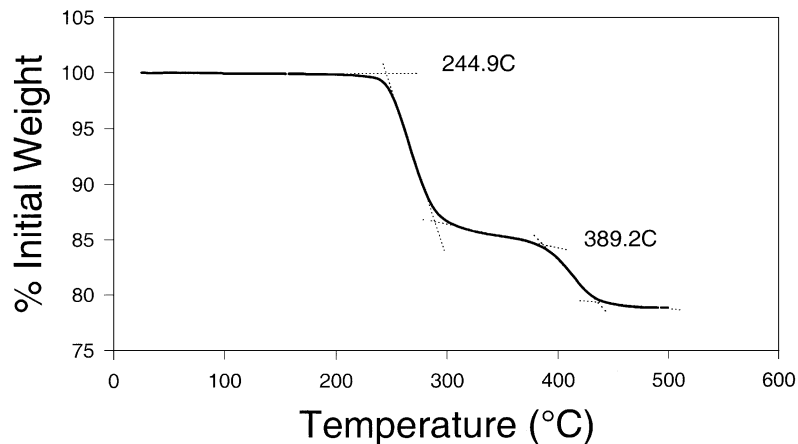
Fig. 2. Typical TGA plot for mixtures boiling separately: 30% peanut oil in rapeseed methyl ester at atmospheric pressure (100 kPa).

Table 3
TGA derived boiling points of oil methyl esters at 1 atm (100 kPa)

Composition	Boiling point (°C)
Rapeseed methyl ester	368.99
Tallow methyl ester	338.10
Canola methyl ester	338.13
Soy methyl ester	347.65
Rapeseed ethyl ester	362.24
Tallow ethyl ester	338.58
Canola ethyl ester	358.37
Soy ethyl ester	355.24

oil by their bps (in this case, rape methyl ester, RME, mixed with peanut oil).

Table 3 shows the TGA-derived 1 atm bps of several methyl and ethyl esters. It should be remembered that these are actually ester mixtures which are derived from the mixture of fatty acids in each type of vegetable oil. The tallow methyl and ethyl esters were prepared from a refined tallow. Tallow is a mixture of triglycerides, most of which are saturated; tristearin (CAS 555-43-1) is usually the major component [11]. Note that the bps of esters from this tallow material are close to bps of esters from vegetable oils. Note also that all esters shown had bps near 350°C. It should be observed that the ethyl and methyl esters differed very little in bp.

The typical temperature dependence of vapor pressure of these Biodiesel fuels is given in Figs. 3

and 4. In Fig. 3, the volatility of rapeseed and soybean methyl esters is compared, along with the vapor pressure for diesel, D2. Fig. 4 gives comparisons for the methyl esters of tallow and rapeseed oils, and for D2. The tallow ester, as was seen in Table 3, has characteristics generally similar to those of vegetable oil esters.

In both Figs. 3 and 4, the bp and the temperature coefficient of vapor pressure (curve slope) of the ester fuels are reasonably similar to D2. This behavior agrees with engine screening results which showed very similar performance for esters and D2 in engines. The vapor pressure data provided in Figs. 3 and 4 may be of value to guide the winterization of Biodiesel, following the approaches now used to winterize D2. Note that the Clausius/Clapeyron plot ($\log P$ vs. $1/T$ (K)) would yield values for the vaporization energy of Biodiesel fuels, since the linear slope of these regressions is equal to the heat of vaporization. Also, the linear regression of this type plot is readily extrapolated to give estimates of bp at higher pressures.

Fig. 5 gives a comparison of TGA-derived temperature dependence of ethyl and methyl ester vapor pressures for tallow. Fig. 6 gives an analogous comparison of TGA-derived temperature dependence of ethyl and methyl esters vapor pressures for soy. Note in Figs. 5 and 6 that the volatility properties of the methyl and ethyl esters differ only slightly for Biodiesels derived from the same oil. Methyl esters appear to have a slightly higher P_v than ethyl esters for a given
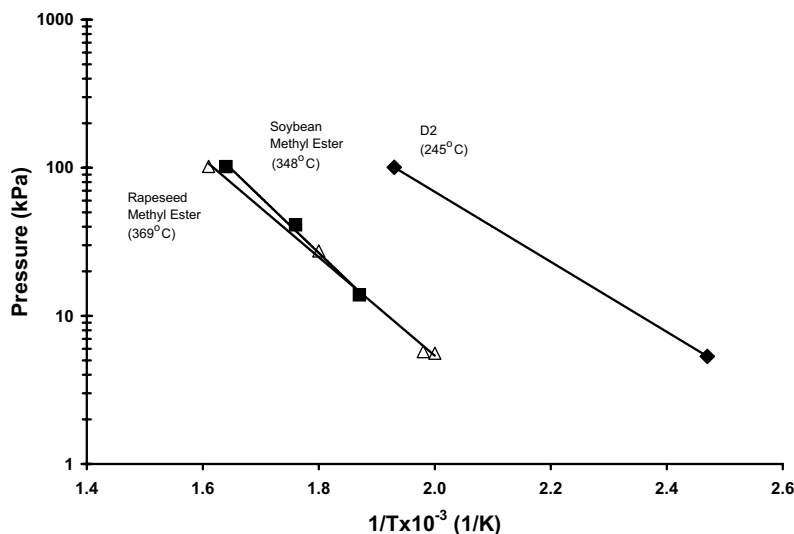
Fig. 3. Comparison of TGA-derived temperature dependence of vapor pressures for △, rapeseed methyl esters; ■, soybean methyl esters; and ◆, D2. Number in parentheses indicates bp at 1 atm (100 kPa).

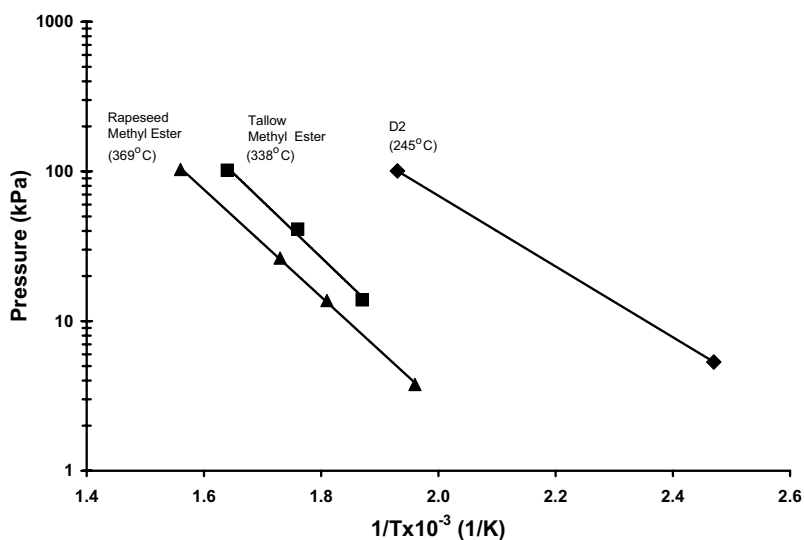Fig. 4. TGA-derived vapor pressures of ▲, rapeseed methyl esters; ■, tallow methyl esters; and ◆, D2. Number in parentheses indicates bp at 1 atm (100 kPa).

temperature, as one would expect for the shorter molecule length.

The TGA method appears to avoid thermal decomposition of relatively large organic molecules commonly observed as boiling temperature occurs at temperatures greater than 50 mmHg. The method does not resolve bp peaks for the several fatty acids present in, for example, the Biodiesel of soybean oil. It is assumed that the small isothermal samples boil as ideal solutions at a constant temperature. This greatly simplifies the interpretation of TGA plots for purposes of routine quality control. This relatively
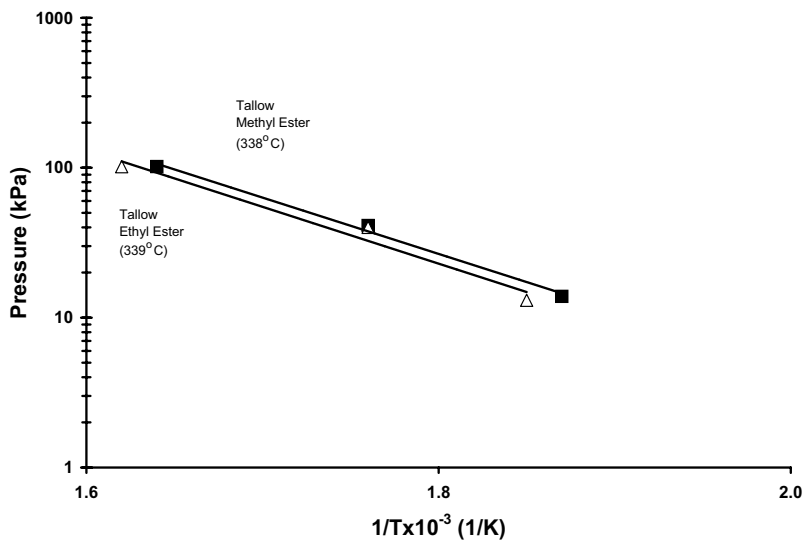
Fig. 5. Vapor pressures of △, ethyl; and ■, methyl esters of tallow. Number in parentheses indicates bp at 1 atm (100 kPa).
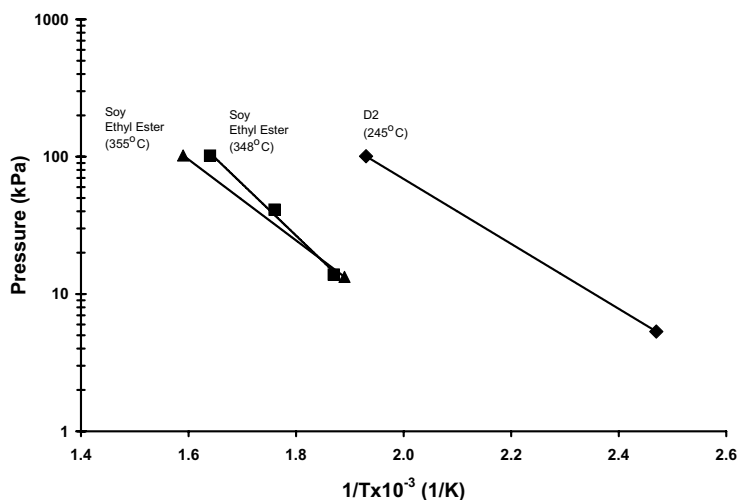

Fig. 6. Vapor pressures of ▲, ethyl; and ■, methyl esters of soybean oil; and ◆, D2. Number in parentheses indicates bp at 1 atm (100 kPa).

simple data format is a convenient means of comparing the volatility of Biodiesels formed from different oils and may be useful for tentative identification a given Biodiesel.

The pressure and temperature conditions of these TGA tests are much lower than those encountered as fuel volatilizes in a diesel engine. However, one may extrapolate these linear Clausius/Clapeyron plots to obtain an estimate of relative volatility at much higher pressures and temperatures. It is planned to conduct tests in a high pressure TGA unit to determine the limits of the linear Clausius/Clapeyron model.

4. Conclusions

a. Volatility and bp of ester products of oils, and diesel fuel (D2) were rapidly determined to ±5% with TGA method.

b. The TGA method yields data at relatively high pressures, up to 1 atm.
c. Data for six methyl and ethyl ester products were obtained.
d. Influences on the vapor pressure properties of esters were related to fatty acid composition of the esters.
e. Evaluation of data suggests this TGA method will be useful as the Biodiesel industry develops.

Acknowledgements

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