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Iodine value of tung biodiesel fuel using Wijs method is significantly lower than calculated value

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Abstract

The tung tree (*Vernicia fordii*) is a non-edible oil plant native to southern China and was introduced in Japan in the nineteenth century. The tree produces tung oil, which is composed of approximately 80% α-eleostearic acid (9*c*, 11*t*, 13*t*-octadecatrienoic acid), 7% linoleic acid, and 6% oleic acid. Tung oil may be a non-edible source of biodiesel fuel (BDF) production. The iodine value (IV) is one of parameters to guarantee BDF quality, and the most common method for the determination of IV is the Wijs method. The IV can be calculated from the average molecular weight and the number of double bonds from the GC–MS data. In this study, the IVs of olive, castor, soybean, linseed, and perilla BDF using the Wijs method were found to be almost the same as the calculated IV. On the other hand, the IV of tung BDF by the Wijs method indicated a significantly lower value than that of the calculated value. To determine the cause of this discrepancy, the samples before and after halogenation using the Wijs method, were analyzed by ^{1}H NMR. The conjugated double bond signals did not disappear, and a broad double bond signal remained in the tung BDF spectrum after halogenation. These results demonstrated that iodine, with a large atomic radius, could not react completely with the three conjugated double bonds in α-eleostearic acid. Therefore, the IV of tung BDF was significantly lower than the calculated value.

Keywords: α-Eleostearic acid, BDF, Conjugated fatty acid, FAME, Halogenation, Iodine value, *Vernicia fordii*, Wijs method

Introduction

Biodiesel fuel (BDF) has recently received attention as a renewable, non-toxic, and biodegradable fuel. BDF is composed of fatty acid methyl esters (FAMEs), which are usually synthesized by the transesterification of vegetable oils with methanol [1, 2]. The transesterification process reduces the high viscosity of vegetable oils, increases the volatility of the oil, and closes to properties such as petroleum diesel. The primary raw materials for the production of BDF are edible oils. Rapeseed is the most commonly used BDF feedstock in Europe, soybean is the most popular feedstock in America, and palm and coconut oil are used in Southeast Asia. However, the mass production of edible oils for BDF may encourage global food crisis. Therefore, non-edible vegetable oils are promising alternatives for the production of BDF [3]. The use of non-edible oils is very significant because the plants are seed-bearing shrubs and trees, which can be grown on non-cropped marginal lands and wastelands that are not suitable for the cultivation of other oil and fat plants.

The tung tree (*Vernicia fordii*) is a non-edible oil plant native to southern China and was introduced to Japan in the nineteenth century [4, 5]. The seeds of tung fruits contain approximately 40–50% of oil, and the tree produces tung oil from 300 to 450 kg/ha. Tung oil is composed of approximately 80% α-eleostearic acid (9*c*, 11*t*, 13*t*-octadecatrienoic acid), 7% linoleic acid, and 6% oleic acid. The oil is readily oxidized because of the three conjugated double bonds in α-eleostearic acid [6]. Drying oil

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is used as a drying agent for paint and varnish, and the oil is also used as a raw material for producing waterproofing paper, ink, linoleum, resin, and artificial leather [7–9]. Recently, tung oil has attracted attention as a non-edible source of BDF production [10–12].

The BDF quality was checked by determining several parameters to guarantee quality. The iodine value (IV) is one of the parameters [13–15]. The IV has classically been used to measure the total degree of unsaturation in oils and fats. It is defined as the mass of iodine (I_2) in grams consumed by 100 g of sample [1]. Determination of the IV in BDF is useful for preventing problems in engines such as polymerization and deposit formation on engine nozzles, piston rings, and piston ring grooves. The most common method for the determination of IV is the Wijs method, which is adopted in EN 14214 and JIS K2390 [16, 17]. The quality standard IVs are less than 120–130 g I_2/100 g.

The IV can be calculated from the average molecular weight and the number of double bonds acquired from the gas chromatography–mass spectrometry (GC–MS) data. In this study, we reported that the IVs of olive, castor, soybean, linseed, and perilla BDF obtained using the Wijs method were almost the same as the calculated IVs. However, the IV of the tung BDF by the Wijs method was significantly lower than that of the calculated value. To determine the cause of the discrepancy, the samples before and after halogenation using the Wijs method were analyzed by ^{1}H nuclear magnetic resonance (NMR).

Materials and methods

Plant materials

Tung tree fruits were harvested from a farm in Sanuki City, Kagawa prefecture. Tung seeds were separated from the fruit, crushed with a blender, and squeezed with a press machine (KT23-160, Sun Seiki, Japan) to obtain tung oil. Castor oil and soybean oil were purchased from Fujifilm Wako Pure Chemical Corporation. Olive oil, linseed oil, and perilla oil were purchased from a local grocery store. All other chemicals used were of analytical grade and were purchased from Fujifilm Wako Pure Chemical Corporation or Nacalai Tesque, Inc.

Preparation of BDF

Potassium hydroxide (0.3 g) and methanol (30 mL) were added to 100 mL of each plant oil, dissolved with a magnetic stirrer, and heated at 60 °C for 2 h [10–12]. The reaction solution was left to achieve room temperature and it separated into two phases. The upper phase was washed three times with water and further washed with a saturated NaCl solution. The upper methyl ester phase was dried over calcium chloride and filtered using a silica gel column to obtain BDF.

Determination of IV by the Wijs method

The IV of BDF was determined using the Wijs method [18, 19]. Approximately 0.15 g of BDF was added to 10 mL of cyclohexane and 25 mL of Wijs solution. After 2 h in the dark, the solution was added to 10 mL of 10% KI solution, 70 mL of water, and 1 mL of 1% starch solution, and it was titrated against a 0.1 M $Na_2S_2O_3$ solution.

Calculation of IV from the FAME compositions

The FAME compositions were analyzed by GC–MS (QP-2010SE, Shimadzu, Japan) [20, 21]. The capillary column was InertCap 225 (GL science) with a length of 30 m, a film thickness of 0.25 μm, and helium was used as the carrier gas. The oven temperature was set to 180 °C and was increased to 230 °C at a rate of 1 °C/min. The mass spectrometer was operated at an ionization energy of 70 eV and scanned from *m/z* 50–600. The FAMEs were identified by the comparison with standards and Wiley library data. The calculated IV was acquired by considering the number of olefinic protons (n) and the average molecular weight (M):

$$\text{Calculated IV} = \frac{\text{Iodine (g)}}{\text{BDF (g)}} \times 100 = \frac{n \times 253.8(\text{g/mol})}{M(\text{g/mol})} \times 100.$$

Analysis of BDF and halogenated BDF by ^{1}H NMR

(1) Preparation of halogenated BDF

Each BDF (0.15 g) was added to 10 mL of cyclohexane and 25 mL of Wijs solution. After 2 h in the dark, to the solution were added 10 mL of 10% KI solution, 70 mL of water, and *n*-hexane. The upper phase was washed three times with water and further washed with a saturated NaCl solution. The halogenated BDF was dried over calcium chloride, filtered with a silica gel column, and concentrated under reduced pressure.

(2) ^{1}H NMR analysis of BDF and halogenated BDF

Approximately 120 mg of each BDF sample was dissolved in 0.6 mL of $CDCl_3$ (99.8% D) with 0.03% tetramethylsilane (TMS) as an internal standard, and placed into a 5 mm i.d. NMR tube [22, 23]. In the case of halogenated BDF, approximately 20 mg of the sample was dissolved in 0.7 mL $CDCl_3$ with 0.03% TMS. ^{1}H NMR

spectra were obtained using a JEOL JNM under the following conditions: spectral width, 500 Hz; relation delay, 4 s; data points, 32768; and number of scans, 60.

Results and discussion

The FAME compositions of the BDFs obtained from GC–MS are shown in Table 1. These results were almost the same as those reported in previous studies [1]. The calculated IVs were determined from the average molecular weights and the number of olefinic protons. The tung BDF mainly consisted of methyl eleostearic acid (78.4%), methyl linoleic acid (9.04%), methyl oleic acid (6.82%), methyl palmitic acid (3.32%), and methyl stearic acid (2.47%) [20, 21]. The average molecular weights and the average number of olefinic protons of tung BDF can be estimated as 292.3 g/mol and 2.60/molecule, respectively, and the calculated IV of the tung BDF was 226, which was the highest calculated value in this study.

Table 2 lists the experimental IVs acquired using the Wijs method. The data for olive, castor, soybean, linseed, and perilla BDF were almost the same as the calculated IVs in Table 1. The IV of the perilla BDF was 194, which was the highest value calculated by the Wijs method. However, the IV of the tung BDF obtained using the Wijs method was approximately 70 lower than the calculated value in Table 1. The IV of the tung BDF was 156, which was almost the same as that reported in the literature (IV: 159–161) [11, 12, 20].

Over 60 years ago, oil and fat chemists reported that the IV value of tung oil could not be determined using conventional halogen absorption methods, such as the Wijs, Hubl, and Hanus methods [24, 25]. They expected the erroneous results that arisen from the incomplete absorption of the halogen reagents, and they tried to accurately measure the IV value of tung oil by incorporating longer reaction times, excess reagents, and more reactive reagents [26]. However, there has been no study that explains why tung oil shows a lower IV value in conventional halogen absorption methods, using NMR.

The BDF samples before and after halogenation using the Wijs method were analyzed using ^{1}H NMR spectroscopy (Fig. 1). In the spectrum of the perilla BDF (a), there was a broad singlet signal at δ 5.2–5.3, which belongs to non-conjugated double bonds [22, 23]. The signal disappeared after halogenation, indicating that all double bonds in the perilla BDF were halogenated (b).

In the spectrum of the tung BDF (c), there are some conjugated double bond signals at δ5.2–6.4 ppm. The signals were shifted to a lower magnetic field compared to the non-conjugated double bond signal in the perilla BDF. After halogenation, the conjugated double bond signals did not disappear completely in the spectrum (d). A broad double bond signal at δ5.7–6.0 ppm remained, which indicated that one double bond of α-eleostearic acid methyl ester in the tung BDF was not halogenated.

Linolenic acid methyl ester with three unconjugated double bonds, which are the main components of the

Table 1 The FAME compositions obtained from GC–MS and the calculated IV

	Olive	Castor	Soybean	Linseed	Perilla	Tung
Methyl palmitic acid (16:0)	14.7		11.8	6.05	6.69	3.32
Methyl palmitoleic acid (16:1)	1.34					
Methyl stearic acid (18:0)	2.58		4.51	3.94	2.07	2.47
Methyl oleic acid (18:1)	71.7	4.29	28.01	21.8	16.4	6.82
Methyl ricinoleic acid (18:1)		88.2				
Methyl linoleic acid (18:2)	9.71	7.47	49.8	17.9	16.2	9.04
Methyl linolenic acid (18:3)			5.9	50.3	58.6	
Methyl eleostearic acid (18:3)						78.4
Average molecular weight	292.1	310.5	292.3	292.6	292.1	292.3
Number of olefinic protons	0.924	1.07	1.45	2.09	2.25	2.60
Calculated IV (g I_2/100 g)	80.4	87.9	126	181	195	226

Table 2 The IV obtained from Wijs method (g I_2/100 g)

	Olive	Castor	Soybean	Linseed	Perilla	Tung
Wijs method	80.7 ± 0.11	85.4 ± 0.38	131 ± 0.14	180 ± 0.25	194 ± 0.76	156 ± 2.22

The data are the mean ± SE (n = 3)

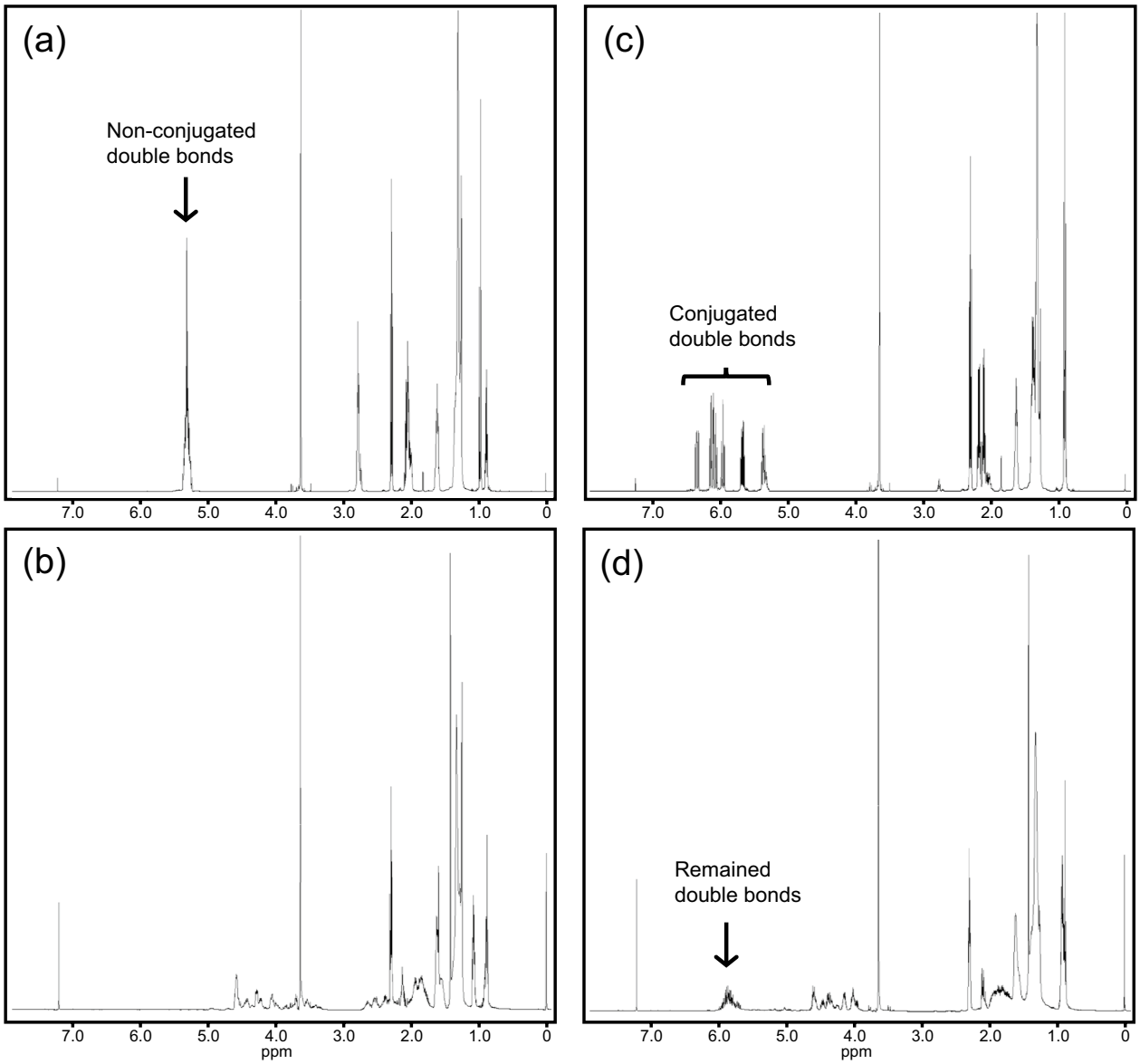

Fig. 1 Spectra of BDF and halogenated BDF obtained with the Wijs method: **a** perilla BDF, **b** halogenated perilla BDF, **c** tung BDF, and **d** halogenated tung BDF

perilla and linseed BDF, can react with the iodine monochloride in the Wijs reagent (Fig. 2). Therefore, the IVs of these BDFs from the Wijs method show almost the same value as the calculated IVs. However, in the case of α-eleostearic acid methyl ester with three conjugated double bonds, which is the main compound of the tung BDF, there would not be enough distance between the conjugated double bonds for halogenation. The halogen reaction would not proceed completely due to steric hindrance and electrostatic repulsion. As a result, the IV of the tung BDF from the Wijs method would be lower than the calculated IV. Assuming that one double bond of α-eleostearic acid methyl ester would remain in the tung BDF after halogenation, the assumed IV would be 158. The assumed value is almost the same as the measured IV (156) of the tung BDF from the Wijs method in this study (Table 2). These results demonstrate that the Wijs method is inadequate for measuring the IV of a sample containing conjugated double bonds, such as tung BDF.

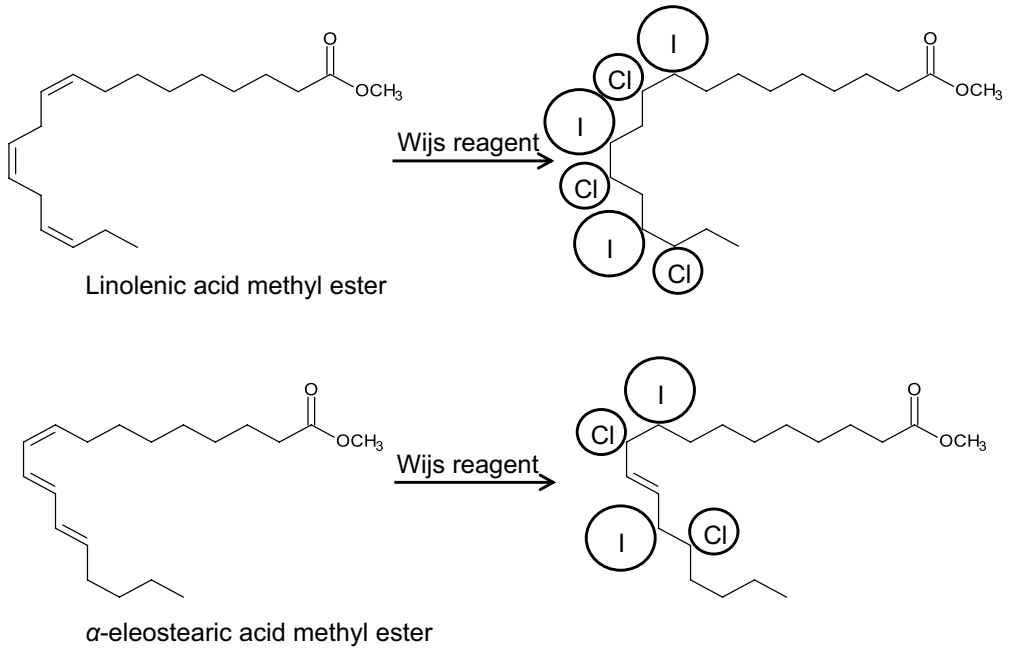

Fig. 2 Predicted halogenation reaction of linolenic acid methyl ester and α-eleostearic acid methyl ester by the Wijs method

Conclusions

The old oil and fat chemists reported that the IV value of tung oil could not be determined using conventional halogen absorption methods. There has not been much attention towards this for some time. Modern researchers have reported that tung BDF, blended with other plant oils such as canola, palm, and coconut BDF can be used to overcome the shortcomings of tung BDF. The IVs measured using the Wijs method in these studies might be lower than the actual values. The IV index is too general as a factor to allow for the correlation of the physical and chemical properties of BDF [27]. The BDF quality should be checked using several parameters to prevent engine problems.

Abbreviations

BDF: Biodiesel fuel; FAME: Fatty acid methyl esters; GC–MS: Gas chromatography–mass spectrometry; IV: Iodine value; NMR: Nuclear magnetic resonance.

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Authors' contributions

TS designed this study and wrote the manuscript. KS measured IVs of BDFs. KF and TK discussed the results and revised the manuscript. All authors read and approved the final manuscript.

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Availability of data and materials

The datasets used and analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Competing interests

The authors declare that they have no competing interests.

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