Structure Indices in FA Chemistry. How Relevant Is the Iodine Value?

Gerhard Knothe*

USDA, ARS, National Center for Agricultural Utilization Research, Peoria, Illinois 61604

ABSTRACT: Most common analytical methods in FA chemistry can be categorized as yielding either structure or quality indices. Quality indices often describe components in fats and oils arising from processing, storage, and naturally occurring, nonfatty materials. Common structure indices are the iodine value (IV), the saponification value, and the hydroxyl value. Although modern analytical methods yield more detailed and reliable information, structure indices are still widely used. The IV, which indicates total unsaturation, has even been included in some standards for industrial products such as biodiesel. However, the IV index is too general to allow the correlation of physical and chemical properties with FA composition. The IV is treated in a theoretical fashion regarding biodiesel- and oxidative stability-related issues. That the concept of IV as a structure index is unsatisfactory is shown by the development of a quaternary composition diagram (QCD). The QCD demonstrates the derivation of a specific IV from varying FA compositions. Improved correlations are possible among the structure indices. Alternative indices for the IV are developed. Possible alternatives are the allylic position equivalent (APE) and the bis-allylic position equivalent (BAPE), which better relate structure and amount of common component FA in vegetable oils to observed properties. The APE and BAPE indices are based on the number of reactive positions in oxidation.

Paper no. J10047 in *JAOCS 79,* 847–854 (September 2002).

KEY WORDS: Allylic positions, biodiesel, bis-allylic positions, iodine value, lubricants, quality indices, saponification value, structure indices.

Analytical indices related to fats and oils can be distinguished as structure or quality indices. Structure indices are the iodine value (IV), a measure of total unsaturation of an oil or fat; the saponification value (SV), an indicator of average M.W.; and the hydroxyl value (HV), which is applicable to fatty compounds (or their mixtures) containing hydroxy groups, such as castor and lesquerella oils. Several variations of wet chemical methods have been developed for determining these indices (1–9), although calculative methods based on GC also exist (10,11).

Quality indices are the FFA, peroxide, anisidine, phosphorus, and other similar values. Generally, quality indices relate (i) to the quality of a vegetable oil or fat obtained after processing and possible further derivatization as well as after extended storage or (ii) to the presence of naturally occurring nonfatty materials. Quality indices were formerly termed processing-related parameters (12), but the term "quality indices" appears to be more general. Different ways to categorize these methods have been used, (e.g., Ref. 13). In some cases, oils or fats are subjected to reactions, and the resultant products warrant the inclusion of additional quality indices. For example, in the case of (methyl) ester production from vegetable oils or fats for biodiesel use, these additional criteria are free and total glycerol content (free glycerol arising from the cleavage of the FA chains, total glycerol including glycerol bound in the form of acylglycerols). Note also that structure indices of fatty compounds can be influenced by the presence of accompanying materials (for example, carotenes and squalene mainly affect IV; wax esters and hydrocarbons affect SV; and MAG and DAG affect HV), as these indices often depend on the amounts of all components of a mixture.

The last four decades have seen an exponential increase in the determination of FA structure by spectroscopic methods, often in combination with chromatographic methods. The superior information obtained from these methodologies and their universal use require a more detailed evaluation of the older structure indices, despite the fact that these are relatively easy to grasp. Also, modern analytical methods are often being used for the purpose of determining structure indices such as IV. Thus, the original objective of the introduction of the IV in 1884 (14) and its main use to aid in the analysis of fats and oils have been expanded and even reversed, in that analyses of fats and oils are now carried out to calculate the IV using methods that yield more information than the IV.

Of all the structure indices, the IV especially has been used beyond analytical purposes, having been related to various physical and chemical properties as well as having served as a quality control method in hydrogenations. Although a detailed discussion of these applications is beyond the scope of this work, it may be noted, for example, that IV has been included in the standards of some industrial products derived from vegetable oils and fats, such as biodiesel. It is also occasionally used in assessing oxidative stability of oils and fats and their derivatives, a subject of significant interest for industrial applications such as fuels and lubricants and for physiological applications. Therefore, the technical aspects of the use of such indices, especially the IV, in product standards and property assessments need to be investigated in more detail. Also, alternative indices that more accurately take compound structure and properties into account need to be

---

*Address correspondence at USDA, ARS, NCAUR, 1815 N. University St., Peoria, IL 61604. E-mail: knothegh@mail.ncaur.usda.gov

TABLE 1
Saponification Values, Iodine Values, and FA Compositions of Some Vegetable Oils and Fats[a]

Vegetable oil or fat	Saponification value	Iodine value	FA composition (wt%)							
			12:0	14:0	16:0	18:0	18:1	18:2	18:3	22:1
Canola (LEAR)	110–126	188–193		<0.2	3.3–6.0	1.1–2.5	52–66.9	16.1–24.8	6.4–14.1	0–2
Coconut	248–265	6–11	45.1–50.3	16.8–20.6	7.7–10.2	2.3–3.5	5.4–8.1	1.0–2.1	0–0.2	
Corn	187–195	103–128		0–0.3	8.6–16.5	1.0–3.3	20.0–42.2	39.4–62.5	0.5–1.5	0–0.1
Cottonseed	189–198	99–119		0.6–1.0	21.4–26.4	2.1–3.3	14.7–21.7	46.7–58.2	0–0.4	0–0.3
Linseed	189–195	177 min.			6.1	3.2	16.6	14.2	59.8	
Palm	190–209	50–55	0–0.4	0.5–2.0	40.1–47.5	3.5–6.0	36–44	6.5–12	0–0.5	
Peanut	187–196	80–106	0–0.1	0–0.1	8.3–14.0	1.9–4.4	36.4–67.1	14–43	0–0.1	0–0.3
Rapeseed	168–187	94–120		<0.2	1.5–6.0	0.5–3.1	8–60	11–23	5–13	5–60
Safflower, high–linoleic	186–198	135–150		0–0.2	5.3–8.0	1.9–2.9	8.4–21.3	67.8–83.2	0–0.1	0–1.8
Safflower, high–oleic		90–100		0.1	5.7	2.3	73.6	15.8		
Soybean	189–195	120–143		0–0.2	8–13.3	2.4–5.4	17.7–26.1	49.8–57.1	5.5–9.5	
Sunflower	188–194	110–143	0–0.1	0–0.2	5.6–7.6	2.7–6.5	14–39.4	48.3–74	0–0.2	0–0.2
Tallow[b]		35–48		1.4–7.8	17–37	6.0–40	26–50	0.5–5.0	<2.5	

[a] All values obtained from Reference 15. LEAR, low erucic acid rapeseed.
[b] Tallow contains 0.7–8.8% 16:1 FA.

developed. It is the objective of this work to examine the current uses of the IV and to develop alternative indices that relate structure and properties more closely.

RESULTS AND DISCUSSION

The indices from many common analytical methods in FA chemistry can be classified as structure or quality indices (*vide supra*). The following presentation deals with structure indices, mainly IV and SV.

General observations. The IV is a measure of the average amount of unsaturation of fats and oils and is expressed in terms of the number of centigrams of iodine absorbed per gram of sample (% iodine absorbed) (1–4,10). The SV is expressed as the number of milligrams of potassium hydroxide (KOH) required to saponify 1 g of sample (5–7,11). Many wet chemical methods for determining IV and SV have limited applicability and/or are error-prone as stated in remarks that accompany these methods. Numerous papers have reported on modifications of the aforementioned methods for specific purposes, such as use of less toxic solvents or adjustments for specific kinds of samples. Table 1 contains literature-derived (15) IV and SV for some vegetable oils and other fatty materials.

IV. Table 2 contains the IV of common FA and their triacylglyceryl, methyl, ethyl, propyl, and butyl esters as well as that of a mixture approximating the composition of soybean oil. Free acids have the highest IV. The IV of TAG and methyl esters are nearly identical. The IV of higher esters decrease with increasing size of the alcohol moiety. This is the result of the IV being dependent on the M.W. of the fatty compound. The IV of a pure compound can be computed by Equation 1,

$$\mathrm{IV} = 100 \times \frac{253.81 \times \mathrm{db}}{\mathrm{MW}_f} \qquad [1]$$

in which IV is the iodine value, db is the number of double bonds, MW_f is the M.W. of the fatty compound, and 253.81 is the atomic weight of two iodine atoms that are theoretically added to one double bond.

Accordingly, the IV of a mixture of fatty compounds can be calculated by Equation 2,

$$\mathrm{IV}_{\mathrm{mixture}} = \sum 100 \times \frac{A_f \times 253.81 \times \mathrm{db}}{\mathrm{MW}_f} \qquad [2]$$

in which A_f is the amount (in %) of a fatty compound in a mixture. Equations 1 and 2 assume full iodination, as does the following discussion. Uses of the IV beyond analytical purposes as discussed here also assume full iodination.

With slightly different terminology, Equations 1 and 2 have been discussed in the literature (16). Equations 1 and 2 are generalizations of the equation given in the AOCS GC method for IV determination (10). Research has also been devoted to other methods for determining the IV, including infrared (IR) and nuclear magnetic resonance (NMR)

TABLE 2
Iodine Values of Some Unsaturated Fatty Compounds and a Mixture Close to the Composition of Soybean Oil (computed from Eqs. 1 and 2)

	Iodine value					
		Esters				
Acid	Acid	TAG	Methyl	Ethyl	Propyl	Butyl
Oleic	89.86	86.0	85.6	81.7	78.2	75.0
Linoleic	181.0	173.2	172.4	164.5	157.4	150.8
Linolenic	273.5	261.6	260.4	248.4	237.6	227.6
Erucic	75.0	72.3	72.0	69.2	66.7	64.3
$C_{22:2}$[a]	150.8	145.1	144.8	139.2	134.1	129.3
25% $C_{18:1}$ + 50% $C_{18:2}$ + 10% $C_{18:3}$[b]	140.3	134.3	133.6	127.5	122.0	116.9

[a] 5(*Z*),13(*Z*)-Docosadienoic acid from meadowfoam.
[b] Mixture approximating FA composition of soybean oil.

spectroscopies as well as chromatographic and physical property-based (i.e., refractometric) methods. A detailed discussion of these aspects is beyond the scope of this paper, but Equations 1 and 2 possess the most general applicability and appear to make other methods (of calculation) superfluous.

Equations 1 and 2 give rise to important observations, which sometimes have been considered only sparingly in the literature. These are (i) the IV of a fatty compound depends on its M.W. and therefore that of a mixture of fatty compounds depends on the M.W. of its unsaturated components; (ii) the IV of a mixture of fatty compounds depends on the amounts of the several unsaturated fatty components in the mixture but not on the exact nature of the double bonds in the structure of those fatty compounds (also, wet chemical IV methods do not give satisfactory results for fatty compounds with conjugated unsaturation); (iii) The IV does not depend on the nature of the saturated components but only on their total amount, since the IV treats fats and oils as being composed only of saturates and unsaturates.

Prior literature (e.g., Ref. 13) noted that the IV establishes only the proportion of unsaturated fats but not the kind. In this connection, note that an entity termed the unsaturation number was suggested as being preferable to the IV because it is independent of M.W. (17).

A more general graphical representation, showing that a given IV can be satisfied by different FA profiles, is a quaternary composition diagram (QCD) as shown in Figure 1 for methyl esters. The QCD is constructed as a tetrahedron so that the three edges of the base of the tetrahedron represent the amounts (in %) of the three major unsaturated fatty components $C_{18:1}$ (oleic), $C_{18:2}$ (linoleic), and $C_{18:3}$ (linolenic). Although this procedure does not account for unsaturated FA of non-C_{18} length (such as $C_{16:1}$, $C_{20:1}$, $C_{22:1}$), most major FA occurring in vegetable oils and animal fats are covered by the QCD. The three edges leading from the base to the apex represent the saturated components because all saturates can be combined into one value, as only their amount but not their nature influences the IV. Every FA composition is then given by the coordinates of the four components written in the fashion $C_{\text{saturates}}$, $C_{18:1}$, $C_{18:2}$, $C_{18:3}$. The composition values determining a certain IV (IV_{target}) on the edges of the QCD can then be determined by applying the equation

$$x = 100 \times \frac{IV_{\text{high}} - IV_{\text{target}}}{IV_{\text{high}} - IV_{\text{low}}} \qquad [3]$$

For that purpose, Equation 3 uses two components, IV_{high} and IV_{low}, and x is the amount of the compound with the lower IV. The amount of the compound with the higher IV is then = $100 - x$. The plane that represents compositions with the given or target IV for the full quaternary system is then defined by coordinates determined with Equation 3. Thus, by definition, the composition values of the other two components equal zero in the coordinates determined by Equation 3. Equation 3 is derived from the observation that the given or target IV is the difference between the two IV of the neat components multiplied by the corresponding amounts (in %). Accordingly, for an IV of 115, the shaded area in Figure 1 representing all compositions yielding this IV is given by the coordinates: (33.29, 0, 66.71, 0), (55.84, 0, 0, 44.16), (0, 66.13, 33.87, 0), (0, 83.18, 0, 16.82). There are no coordinates on the edges for the saturates/18:1 and 18:2/18:3 combinations because in the former case all IV are less than 115 and in the latter greater than 115. The volume "below" the plane then represents all compositions with an IV > 115, and the volume "above" the plane represents all profiles with an IV < 115. The value IV = 115 was chosen because of its inclusion in biodiesel standards (see the discussion below).

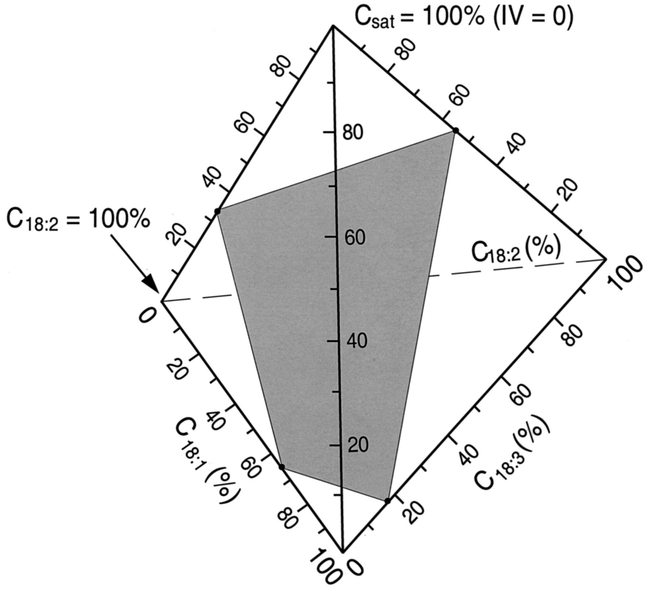

FIG. 1. Quaternary composition diagram for methyl esters of oleic, linoleic, linolenic, and saturated FA with an inscribed plane satisfying the condition of an iodine value (IV) = 115. The construction of the diagram is described in the text. For sake of clarity, no scale is indicated on the "hidden" edge ($C_{18:2}$). • = Intersections of the planes with the edges.

From the coordinates calculated above, the parameters that give the linear equations defining the plane dissecting the QCD can be derived. For this, a 3-D coordinate system with $C_{18:1}$ as the x-axis and the origin at (0, 0, 0, 100) can be envisioned. The y-axis is also in the plane of the base of the tetrahedron (QCD), and the z-axis is perpendicular to the x-y plane. Then the plane for a defined IV dissects the x-axis in the x-y plane (which contains the base of the QCD) at an angle of 29.77° with a slope of 0.572 [= tan (29.77°)] and it dissects the x-axis in the x-z plane at an angle of 30.23° and a slope of –0.583 [= – tan (30.23°)]. With this information and the coordinates of points defined by a given IV, any plane representing the corresponding methyl ester compositions (the procedure holds for any other ester also) of the given IV can be determined. The planes for all IV are parallel to each other.

Applications of the IV. As already indicated, the IV has found applications beyond being a descriptive structure index. Besides being related to various chemical and physical properties of fats and oils, having physiological applications, and serving as a quality control method for hydrogenation, these applications include use in standards for biodiesel and in assessing oxidative stability. It is suggested here that alternative indices can be developed.

Biodiesel. Biodiesel is defined as the mono-alkyl esters of vegetable oils or animal fats. It is suitable as a replacement or complement for conventional diesel fuel (petrodiesel) in a compression-ignition (diesel) engine (18). The most common forms of biodiesel are methyl esters of vegetable oils. The use of methyl esters offers the advantage that the high viscosity of vegetable oils is reduced by an order of magnitude to a value close to that of petrodiesel. This eliminates operational problems such as the formation of engine deposits, which eventually can lead to engine failure. The source of biodiesel usually depends on the crops amenable to the regional climate. Therefore, in the United States, soybean oil is most commonly used as the biodiesel feedstock, whereas in Europe, rapeseed (canola) oil is the most popular feedstock and in tropical countries, palm or coconut oil.

When establishing standards for industrial products from nonpetroleum sources such as vegetable oils, common indices from both sources—the original, usually petroleum-based, product and the alternative source, in this case FA chemistry—are used. Thus biodiesel standards contain indices derived from petrodiesel and also FA chemistry. In the United States an ASTM standard (D 6751) for biodiesel has been developed. In some European standards, the IV has been included, usually being set to a maximum of 115. This would exclude several important vegetable oils, including soybean oil and sunflower oil, at least in the form of their methyl esters, as a source of biodiesel (see Table 1 for a listing of IV of some fats and oils).

Originally, the use of the IV as a fuel index was proposed only for pure vegetable oils and not for derivatives such as mono-alkyl esters (biodiesel). The initial suggestion probably dates from 1938 (19). More recently, a "relatively mild limit" of IV = 135 was suggested for neat vegetable oils (20). The only work that has recommended the use of the IV as an index for methyl esters of vegetable oils, i.e., biodiesel, compared rapeseed methyl ester of IV = 115 and soy methyl ester (SME) of IV = 131 and claimed significant engine deposits when using SME (21). The rationale was that the higher the unsaturation of the biodiesel, the higher the tendency of the unsaturated components to polymerize and form engine deposits. However, the IV difference, 115 vs. 131, of the biodiesel samples used in that study (21) appears low, so that the cause of the problem when using SME must be sought elsewhere, for example, fuel quality problems with the SME used, especially in light of the present discussion. Tables 2 and 3 (discussed below) and the QCD show how the kind of ester can influence IV and how different FA compositions can yield identical IV, which casts doubt on the relatively small IV difference causing such significant differences in engine performance. Besides the countless trips and tests successfully completed by SME-powered vehicles, other studies in this area contradict the use of the IV in biodiesel standards. Work on the use of methyl esters of sunflower oil originally showed that the use of methyl esters alleviated engine operational problems associated with use of neat vegetable oils due to their high viscosity (22). In other early work (23), highly unsaturated linseed

TABLE 3
Mixtures of Methyl Oleate, Methyl Linoleate, and Methyl Linolenate Giving Iodine Values Close to 115 and Corresponding APE and BAPE Values

Entry	Ester	Amount (%)	Iodine value	Double bond equivalents[a]	Allylic position equivalents[b]	Bis-allylic position equivalents[c]
A	18:1	60	51.04	60	120	0
	18:2	20	34.48	40	40	20
	18:3	10	26.04	30	20	20
	Σ	90	111.88	130	180	40
B	18:1	40	34.24	40	80	0
	18:2	30	51.72	60	60	30
	18:3	10	26.04	30	20	20
	Σ	80	112.00	130	160	50
C	18:1	30	25.68	30	60	0
	18:2	20	34.48	40	40	20
	18:3	20	52.80	60	40	40
	Σ	70	111.96	130	140	60
D	18:1	10	8.56	10	20	0
	18:2	15	25.86	30	30	15
	18:3	30	78.12	90	60	60
	Σ	55	112.54	130	110	75

[a] One double bond equivalent is defined as arising from a concentration of 1% methyl oleate (or other monounsaturated compound), which has an allylic position equivalent = 2 (it has two allylic positions in the chain). Thus 1% methyl linoleate has two double bond equivalents and 1% methyl linolenate has three double bond equivalents.

[b] One allylic position equivalent (APE) is defined as 2 for a concentration of 1% methyl oleate, methyl linoleate, or methyl linolenate, as these compounds contain two allylic positions (Eq. 4: see text).

[c] One bis-allylic position equivalent (BAPE) is defined as 1 for a concentration of 1% methyl linoleate. Thus, 1% methyl linolenate yields 2 bis-allylic position equivalents.

oil (with a high IV) was found unsuitable as biodiesel fuel. However, once linseed oil methyl esters were used (23), the problem of engine deposits was almost completely alleviated, again showing that the viscosity of the vegetable oils is the major cause of engine problems. More recently, no maximum IV could be determined (24) in an investigation of mixtures of high-oleic sunflower oil methyl ester (IV = 100) and linseed oil methyl ester (IV = 180). No significant differences in cleanness and formation of deposits in the cylinder, combustion chamber, valves, and injectors were observed. Increasing deposits with increasing IV were found on piston rings of the second ring groove. In another study with vegetable oils with IV of 107, 132, and 150, no significant differences in operability were observed with the exception of a somewhat higher lube oil dilution at higher IV (25). Other authors explicitly state that no relation between IV and polymerization or viscosity increases was observed (26).

Although the application of the QCD illustrates the imprecision of the IV for determining FA composition, the IV of neat fatty compounds and of a mixture simulating methyl soyate given in Table 2 show how, through the application of higher esters, a mixture of fatty compounds that would not meet a biodiesel standard IV maximum of 115 as methyl esters can be tailored to meet such a requirement. Thus, it is theoretically possible for a vegetable oil of higher IV to meet a maximum IV of 115 by using higher esters, although it appears unlikely that higher esters will have any significant effect in terms of reducing alleged engine deposits or significantly improving oxidative stability as discussed below.

The QCD of the IV (Fig. 1) depicts the numerous FA profiles that satisfy a given IV, such as that of 115 used in some biodiesel standards. In relation to the numerous FA compositions yielding a given IV, Table 3 gives examples of how different mixtures of methyl esters of the three most common unsaturated FA—oleic, linoleic, and linolenic—can achieve nearly identical IV just slightly below the value of 115. The number of double bonds in the mixtures listed in Table 3 remains constant, as demonstrated by an entity termed "double bond equivalents" in that table. No saturated FA are explicitly listed because, as noted above, their nature does not play any role in determining the IV of a mixture of fatty compounds. The saturated compounds can be assumed to account for the differences to 100%. Only the relative amounts of total saturated components vs. total *number of double bonds* (not *nature* of the unsaturated FA) determines the IV.

Oxidative stability. In industrial applications, oxidative stability is an issue not only for biodiesel but also for lubricants (27). It is well known that the autoxidation of unsaturated fatty compounds proceeds at rates depending on the number and position of the double bonds (28). The positions of allylic to double bonds are especially susceptible to oxidation. The bis-allylic positions in common PUFA such as linoleic acid (double bonds at Δ9 and Δ12, giving one bis-allylic position at C-11) and linolenic acid (double bonds at Δ9, Δ12, and Δ15, giving two bis-allylic positions at C-11 and C-14) are even more prone to autoxidation than allylic positions. The relative rates of oxidation given in the literature (28) are 1 for oleates (methyl, ethyl esters), 41 for linoleates, and 98 for linolenates. A major drawback of the IV is that it does not distinguish these differences, since it treats all double bonds as being equally reactive toward oxidation. Despite this drawback, oxidative stability has occasionally been discussed in the literature in connection with the IV. Note that reactivity differences are also known for reactions such as polymerization and perhaps heterogeneous catalytic oxidation. Thus, a lower IV implies less reactivity toward these reactions through a reduced number of double bonds, often tacitly implying that a lower IV also means lower amounts of $C_{18:3}$ and possibly $C_{18:2}$. The latter is not necessarily the case, as already discussed in conjunction with data in Tables 2 and 3 and shown by the QCD in Figure 1. The use of IV for assessing oxidative stability also does not consider the fact that, for example, storage conditions may have a greater influence on oxidation than the IV (26), and as numerous other studies not cited here on oxidative stability of FAME investigating the influence of storage conditions show.

Possible alternatives to the IV. The preceding discussion leads to the possibility of developing an alternative to the IV. Generally, this aspect has received only sparse attention in the literature; for an exception see Reference 17. Based on the present discussion, such alternative indices should meet several criteria. They should be independent of M.W. (17), take into account the amounts of unsaturated fatty compounds and specific unsaturation patterns, and reflect the differences in reactivity between different unsaturation patterns. The first criterion, independence from M.W., can be achieved by counting the number of double bonds per molecule and the second criterion, by determining the amount of each FA in a mixture. The third criterion is influenced by the different reactivities of allylic and bis-allylic positions. To distinguish and satisfy these criteria, the adoption of two indices, one for allylic and one for bis-allylic positions, appears reasonable. The indices will be termed allylic position equivalents (APE) and, bis-allylic position equivalents (BAPE). One APE is the equivalent of one allylic position contained in a fatty compound of concentration 1% in a mixture. The same holds for one BAPE. However, since the common $C_{18:1}$, $C_{18:2}$, and $C_{18:3}$ fatty compounds contain two allylic positions, the following equation holds for these fatty compounds:

$$\mathrm{APE} = 2 \times (A_{C_{18:1}} + A_{C_{18:2}} + A_{C_{18:3}}) \qquad [4]$$

in which A again is the amount of each fatty compound, in percentage. Generalized, Equation 4 becomes

$$\mathrm{APE} = \mathrm{ap}_a \times A_{Ca} + \mathrm{ap}_b \times A_{Cb} + \mathrm{ap}_c \times A_{Cc} + \cdots \qquad [5]$$

in which ap_x is the number of allylic positions in a specific FA and A_{Cx} is the amount (%) of each FA in a mixture.

Accordingly, for the BAPE, the relation is

$$\mathrm{BAPE} = A_{C_{18:2}} + 2 \times A_{C_{18:3}} \qquad [6]$$

since $C_{18:2}$ has only one bis-allylic position and $C_{18:3}$ has two bis-allylic positions. Table 3 contains the APE and BAPE values of various mixtures of $C_{18:1}$ and $C_{18:2}$ and $C_{18:3}$ methyl esters giving IV slightly below 115. Figure 2 is a QCD depicting planes with APE = 120 and BAPE = 80. The APE and BAPE indices can be divided by the factor 100 to yield the average number of allylic or bis-allylic positions per molecule in a mixture of fatty compounds.

Considering the greater reactivity usually imparted by polyunsaturation and the often accompanying bis-allylic positions, the BAPE index is the more significant of the two values. The APE and BAPE indices are also useful for unsaturated compounds in which the double bonds are separated by more than one CH_2 group, i.e., fatty compounds that do not contain any bis-allylic positions despite multiple unsaturations. Examples are jojoba oil (29), a mixture of C_{38}, C_{40}, C_{42}, and C_{44} wax esters of 20:1 and 22:1 acids and alcohols with the double bonds occurring in the different chains in the molecules, and 5(*Z*),13(*Z*)-docosadienoic acid (DDA), found in meadowfoam oil. Meadowfoam oil has high oxidative stability (30) despite the presence of the aforementioned acid, which has a relatively high IV (see Table 2). The BAPE contribution of DDA to that of meadowfoam oil = 0 (with the BAPE of meadowfoam oil = 0), showing, in accordance with experimental results, that it does not negatively influence oxidative stability. The high IV of DDA, however, could imply some sensitivity to oxidation. BAPE = 0, though, correctly reflects the oxidative stability of meadowfoam oil. This also shows that high APE values (neat DDA would give APE = 400; DDA has four allylic positions, so that the factor in Eq. 4 would be 4 in this case) do not significantly influence oxidative stability. On the other hand, oxidative stability may depend somewhat on double bond position (e.g., Ref. 30). Also, for fatty compounds with conjugated double bonds such as 9(*Z*),11(*E*),13(*E*)-octadecatrienoic acid (α-eleostearic acid; contained in tung oil), BAPE = 0. Tung oil nevertheless is very reactive and is considered a drying oil. There is only limited understanding of the reactivity of conjugated systems (including IV determination), and this needs to be considered when developing or applying an index to such systems, as discussed here.

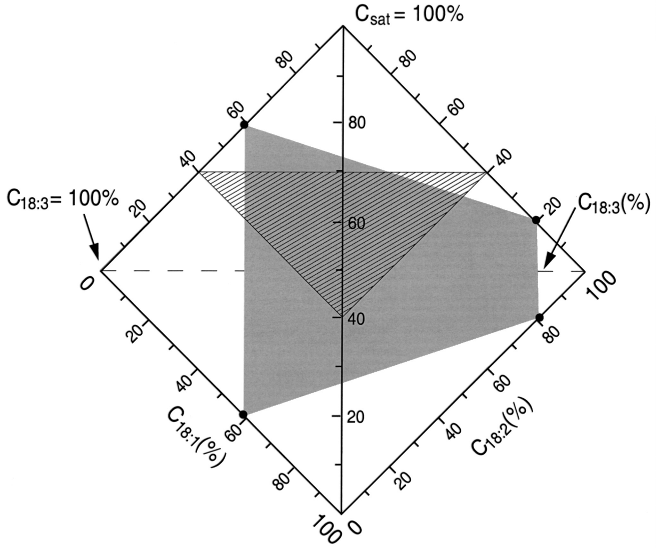

FIG. 2. Quaternary composition diagram for any derivative of oleic, linoleic, linolenic, and saturated FA with inscribed planes satisfying the conditions of the allylic position equivalent = 120 (triangular, striped plane parallel to base of tetrahedron) or bis-allylic position equivalent = 80 (shaded, rhombus-like plane). The intersection of the planes is not indicated for sake of clarity. The construction of the diagram is described in the text.

Maximal and minimal BAPE values are possible for a given IV. Thus, for IV = 115 of methyl esters, the minimum BAPE is 33.87 (calculated for a hypothetical oil consisting of only $C_{18:1}$ and $C_{18:2}$ giving a composition of 66.13% $C_{18:1}$ and 33.87% $C_{18:2}$), and the maximum BAPE is 88.32 (calculated for a hypothetical oil consisting only of saturated and $C_{18:3}$ methyl esters giving a compostion of 55.84% saturates and 44.16% $C_{18:3}$). The multiplication factor between the minimal and maximal BAPE values for IV = 115 is thus 2.61. Conversely, maximal and minimal IV are possible for given BAPE values. Thus, for BAPE = 60, the minimum IV = 78.12 (determined by 30% $C_{18:3}$ giving BAPE = 60) and the maximum IV = 103.44 (determined from 60% $C_{18:2}$ giving BAPE = 60). The corresponding factor is 1.32. Although the maximum and minimum values calculated here are for extreme FA compositions that do not exist in vegetable oils, they are useful for comparing the IV and BAPE. The BAPE can vary more strongly for a given IV than the IV for a given BAPE. This shows the greater sensitivity of the BAPE toward fatty compounds responsible for increased reactivity. Also, the last entry in Table 2, simulating a vegetable oil methyl ester with IV = 134, has APE = 170 and BAPE = 70. Thus, the BAPE is lower here than in other mixtures with higher BAPE affording a lower IV (see last entry in Table 3).

The use of the APE and BAPE indices instead of IV also implies that oxidative stability may be more strongly influenced by the presence of small amounts of more highly unsaturated fatty compounds than by increasing amounts thereof. This concept has been investigated in the past, and the results supported the notion that the more readily autoxidizable compound (methyl linoleate) catalyzes the autoxidation of the less reactive compound (methyl oleate) (31).

The BAPE and APE indices could be determined from data obtained by chromatographic or spectroscopic methods such as GC or NMR.

SV. Generally, the SV has been applied less than the IV to issues beyond analytical purposes. The SV of a monohydric fatty compound is

$$\mathrm{SV} = \frac{56{,}106}{\mathrm{MW}} \qquad [7]$$

Thus, M.W. is analogous to the saponification equivalent (15), which is obtained by dividing 56,106 (1000 × the M.W. of potassium hydroxide) by the experimentally determined SV.

Analogous to the IV, the SV of a mixture is given by

$$\mathrm{SV}_{\mathrm{mixture}} = \sum \frac{A_f \times 56{,}106}{\mathrm{MW}_f} \qquad [8]$$

Equations 7 and 8 are generalizations of the equation given in AOCS Recommended Practice Cd 3a-94 (11) and have been given in the literature (e.g., Ref. 15). For DAG, the numerator in Equations 7 and 8 has to be multiplied by the factor 2, and for TAG by 3. Table 4 contains the SV of some common fatty compounds. The SV increases with decreasing M.W. Because SV and M.W. (and HV and M.W.) are inversely related (Eqs. 7 and 8), the use of average M.W. (saponification equivalent) is more straightforward than the use of the SV.

Analogous to the IV, a QCD for the SV can be applied (Fig. 3). The edges are C_{12}, C_{14}, C_{16}, and C_{18} and the coordinates of a FA composition would be (C_{12}, C_{14}, C_{16}, C_{18}), which accounts for the chain lengths of most FA profiles of vegetable oils and animal fats (some exceptions are coconut oil, which has some shorter FA, and high erucic acid rapeseed oil, which has significant amounts of C_{22}). For C_{18}, the saponification value of methyl oleate is selected since oleic acid (besides linoleic acid) is the most common C_{18} FA, and also provides an intermediary value between the saturated and unsaturated species. The error made by using methyl oleate instead of the saturated compounds as done for the other chain lengths is less than 1%.

TABLE 4
Saponification Values of Fatty Compounds[a]

	Saponification value				
		Esters			
Acid	TAG	Methyl	Ethyl	Propyl	Butyl
Lauric	262.58	261.75	245.68	231.46	218.80
Myristic	232.10	231.46	218.80	207.45	197.22
Palmitic	207.97	207.45	197.22	187.95	179.52
Stearic	188.38	187.95	179.52	171.81	164.73
Oleic	189.66	189.23	180.68	172.88	165.71
Linoleic	190.96	190.53	181.87	173.96	166.71
Linolenic	192.28	191.84	183.06	175.05	167.71
Erucic	159.43	159.12	153.03	147.39	142.16

[a]Computed from SV (saponification value) = 56,106/M.W.

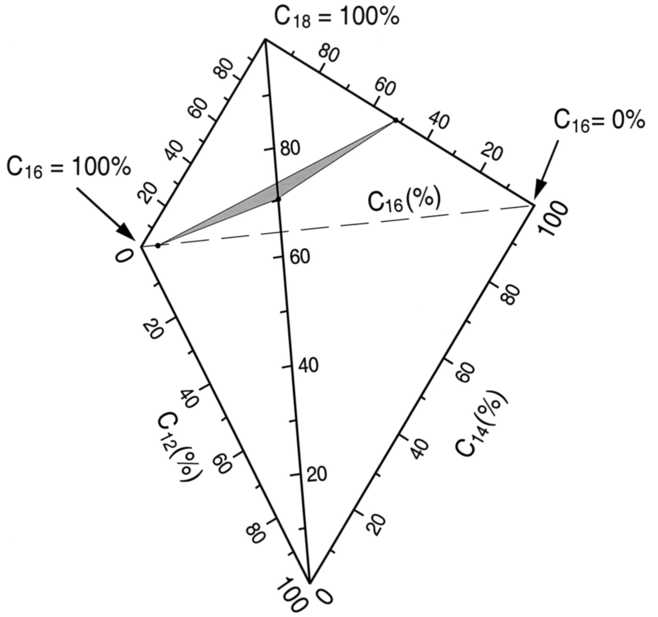

FIG. 3. Quaternary composition diagram for methyl esters of oleic, linoleic, linolenic, and saturated FA with an inscribed plane satisfying the condition saponification value = 200. The construction of the diagram is described in the text.

The QCD (Fig. 3) and the values in Table 4 show that, similar to the discussion of the IV, the SV is not suitable for determining M.W. when considering different kinds of esters, as, for example, methyl esters and TA of the same FA have nearly identical SV and the SV of the propyl ester of the acid with two less methylene groups in the fatty acid chain is also identical to the SV of the methyl ester. However, when it is known that an underivatized vegetable oil is being analyzed, the SV (or, better, the saponification equivalent) may provide an average M.W. The combination of IV and SV also cannot distinguish between the TAG and the methyl ester of a given FA. Therefore, other methods would be needed to determine the nature of a fatty compound mixture.

FA composition can vary more widely in the mid-range of IV or SV than at the “extreme” ends of total saturates or unsaturates for IV or total low M.W. or high M.W. for the SV [IV = 115 discussed here is a mid-range IV; SV = 200 (see Fig. 3) is a lower SV for vegetable oils].

Combination of IV and SV. The number of double bonds in a neat fatty compound can be calculated by combining Equations 1 and 7 and solving for db to give

$$\mathrm{db} = \frac{56{,}106 \times \mathrm{IV}}{25{,}381 \times \mathrm{SV}} = 2.21 \times \frac{\mathrm{IV}}{\mathrm{SV}} \qquad [9]$$

Accordingly, the average number of double bonds in an oil or fat is then

$$\mathrm{db}_{\mathrm{mixture}} = \sum A_f \times 2.21 \times \frac{\mathrm{IV}}{\mathrm{SV}} \qquad [10]$$

This procedure is independent of M.W. but does not consider the other factors accounted for by the APE and BAPE indices. In any case, this combination would have appeared preferable to the use of the IV because values more directly related to structure and even easier to grasp are obtained.

ACKNOWLEDGMENT

The author thanks Professor Frank D. Gunstone for helpful comments.

REFERENCES

1. AOCS Official Method Cd 1d-92, Iodine Value of Fats and Oils, Cyclohexane–Acetic Acid Method, *Official Methods and*

Recommended Practices of the American Oil Chemists' Society, edited by D. Firestone, 5th edn., AOCS, Champaign, 1998.

2. AOCS Recommended Practice Cd 1b-87, Iodine Value of Fats and Oils, Cyclohexane Method, *Ibid*.
3. AOCS Official Method Tg 1-64, Iodine Value, Wijs Method, *Ibid*.
4. AOCS Official Method Tg 1a-64, Iodine Value of Fatty Acids, *Ibid*.
5. AOCS Official Method Cd 3-25, Saponification Value, *Ibid*.
6. AOCS Recommended Practice Cd 3c-91, Saponification Value, Modified Method Using Methanol, *Ibid*.
7. AOCS Official Method Tl 1a-64, Saponification Value, *Ibid*.
8. AOCS Official Method Cd 4-40, Acetyl and Hydroxyl Values, *Ibid*.
9. AOCS Official Method Cd 13-60, Hydroxyl Value, *Ibid*.
10. AOCS Recommended Practice Cd 1c-85, Calculated Iodine Value, *Ibid*.
11. AOCS Recommended Practice Cd 3a-94, Calculated Saponification Value, *Ibid*.
12. Knothe, G., Relation of Some Fat and Oil Indices to Biodiesel, ASAE Paper No. 006011, presented at the July 2000 American Society of Agricultural Engineers International Meeting, Milwaukee.
13. Sonntag, N.O.V., Analytical Methods, in *Bailey's Industrial Oil and Fat Products*, Vol. 2, 4th edn., edited by D. Swern, John Wiley & Sons, 1982, pp. 436-437.
14. Hübl, Eine allgemein anwendbare Methode zur Untersuchung der Fette, *Dinglers Polytechn. J. 253*:281–295 (1884).
15. Gunstone, F.D., J.L. Harwood, and F.B. Padley, *The Lipid Handbook*, 2nd edn., Chapman & Hall, London, 1994.
16. Koman, V., and E. Danielová, Bestimmung der Jodzahl mit Hilfe eines kombinierten Nomogrammes und Ergebnisse der Analysen von Fettsäuren mittels Verteilungs-Gaschromatographie (Iodine Number Determination by Combination Nomogram and Results of Analysis of Fatty Acids by Gas Chromatography), *Chem. Zvesti 28*:218–225 (1974).
17. Glushenkova, A.I., and A.L. Markman, Iodine Number and the Unsaturation Number of Fats, *Khim. Prir. Soedin. 6*:671–675 (1970); *Chem. Abstr. 74*:88935 (1971).
18. Knothe, G., R.O. Dunn, and M.O. Bagby, Biodiesel: The Use of Vegetable Oils and Their Derivatives as Alternative Diesel Fuels, in *Fuels and Chemicals from Biomass*, American Chemical Society, Washington, DC, ACS Symposium Series 666, pp. 172–208.
19. Walton, J., The Fuel Possibilities of Vegetable Oils, *Gas Oil Power 33*:167–168 (1938).
20. Ryan, T.W. III, L.G. Dodge, and T.J. Callahan, The Effects of Vegetable Oil Properties on Injection and Combustion in Two Different Diesel Engines, *J. Am. Oil Chem. Soc. 61*:1610–1619 (1984).
21. Schäfer, A., D. Naber, and M. Gairing, Biodiesel als alternativer Kraftstoff für Mercedes-Benz-Dieselmotoren (Biodiesel as Alternative Fuel for Mercedes-Benz Diesel Engines), *Mineralöltechnik 43*:1–32 (1997).
22. J.J. Bruwer, J.J., B. van d. Boshoff, F.J.C. Hugo, L.M. du Plessis, J. Fuls, C. Hawkins, A.N. van der Walt, and A. Engelbrecht, Sunflower Seed Oil as an Extender for Diesel Fuel in Agricultural Tractors, *Symp. S. Afr. Inst. Agricult. Eng.* (1980).
23. Quick, G.R., B.T. Wilson, and P.J. Woodmore, Injector-Fouling Propensity of Certain Vegetable Oils and Derivatives as Fuels for Diesel Engines, in *Vegetable Oil Fuels* (Proceedings of the International Conference on Plant and Vegetable Oils as Fuels, Fargo, ND, August 1982), ASAE, St. Joseph, MI, pp. 239–246.
24. Prankl, H., and M. Wörgetter, Influence of the Iodine Number of Biodiesel to the Engine Performance, in *Liquid Fuels and Industrial Products from Renewable Resources* (Proceedings of the Third Liquid Fuel Conference, Nashville, TN, September 1996), ASAE, St. Joseph, MI, pp. 191–196.
25. Prankl, H., M. Wörgetter, and J. Rathbauer, Technical Performance of Vegetable Oil Methyl Esters with a High Iodine Number, *Biomass, Proc. 4th Biomass Conf. Am. 1*, edited by R.P. Overend and E. Chornet, Elsevier Science, Oxford, United Kingdom, 1999, pp. 805–810.
26. Bondioli, P., and L. Folegatti, Evaluating the Oxidation Stability of Biodiesel. An Experimental Contribution, *Riv. Ital. Sostanze Grasse 73*:349–353 (1996).
27. Weller, D.E., Jr., and J.M. Perez, A Study of the Effect of Chemical Structure on Friction and Wear: Part 2—Vegetable Oils and Esters, *Lubr. Eng. 57*:20–25 (2001).
28. Frankel, E.N., Lipid Oxidation, The Oily Press, Dundee, Scotland, 1998, p. 19.
29. Spencer, G.F., R.D. Plattner, and T. Miwa, Jojoba Oil Analysis by High-Pressure Liquid Chromatography and Gas Chromatography/Mass Spectrometry, *J. Am. Oil Chem. Soc. 54*:187–189 (1977).
30. Isbell, T.A., T.P. Abbott, and K.D. Carlson, Oxidative Stability Index of Vegetable Oils in Binary Mixtures with Meadowfoam Oil, *Ind. Crops Prod. 9*:115–123 (1999).
31. Gunstone, F.D., and T.P. Hilditch, The Autoxidation of Methyl Oleate in Presence of Small Proportions of Methyl Linoleate, *J. Chem. Soc.*:1022–1025 (1946).

[Received July 30, 2001; accepted May 23, 2002]