A Simple Method For Estimation of Cetane Index of Vegetable Oil Methyl Esters

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This article illustrates a simple method for estimation of cetane indexes of vegetable oil methyl esters from their saponification and iodine numbers. The range of the calculated values covers all the cetane numbers of vegetable oil methyl esters determined experimentally. when it was applied to individual fatty acid methyl esters from C_8 to C_{24}, a straight line parallel to that of Klopfenstein was obtained.

There has been much optimism about the use of vegetable oils or fatty acid methyl esters as alternative fuels for diesel engines. Many oils have been tested successfully in diesel engines. However, cetane number, which measures the ignition quality of diesel fuel, is relatively difficult to measure and rarely has been determined for vegetable oils and fatty acid esters. Recently, Klopfenstein (1) stated that the equation in ASTM Standard D976 (2), using boiling point and density for the calculation of cetane number of petroleum products, is inaccurate for vegetable oils and fatty acid esters. He proposed alternative equations for estimation of the cetane index of a single fatty acid ester and a mixture of known composition. Although fatty acid composition can be determined conveniently by gas chromatography, it takes time to prepare the volatile derivatives, and separation of polyunsaturated fatty acids requires a very efficient column. These facilities may not be available in some laboratories. This paper illustrates an alternative method for estimation of cetane indexes of fatty acid esters by using their saponification and iodine numbers.

PROCEDURES AND RESULTS

Equation [1] is Klopfenstein's equation (1) for estimation of the cetane index of pure fatty acid ester. Where n is the carbon number:

$$\text{Cetane index} = 58.1 + 2.8\,\frac{(n-8)}{2} - 15.9 \times \underset{\text{double bond)}}{(\text{number of}} \qquad [1]$$

Cetane index of the mixture is the average of the product of each fatty acid ester and its percentage in the mixture. According to the above equation, there are two independent variables (chainlength and degree of unsaturation) that affect the cetane index of fatty acid esters. I have assumed similar effects of these two variables but expressed them in terms of saponification and iodine numbers. These two numbers have long been used to specify commercial fats and oils. The saponification number, which is the milligrams of potassium hydroxide required to saponify one gram of fat or oil, is inversely related to molecular weight of fat or oil. Iodine number, on the other hand, is directly related to the degree of unsaturation or number of double bonds in the oil. An equation similar to Eq. [1] (Eq. [2]) was then derived. In it, x is the saponification number, y is the iodine number and a, b and c are constants.

$$\text{Cetane index} = a + b/x + cy \qquad [2]$$

Solving for the three constants (a, b and c) requires at least three independent equations. Hence, Eq. 3, 4 and 5 were generated from palm, peanut and soybean fatty acid methyl esters. Cetane indexes of these fatty acid methyl esters were taken from Pischinger et al. (3). Because saponification and iodine numbers of vegetable oil methyl esters are very close to those of triglycerides, they were used in the calculation without any adjustment.

$$\text{Palm:} \quad 62 = a + b/199 + 52\,c \qquad [3]$$
$$\text{Peanut:} \quad 54 = a + b/192 + 92\,c \qquad [4]$$
$$\text{Soybean:} \quad 45 = a + b/192 + 132\,c \qquad [5]$$

Solving these three simultaneous equations yields values of a = 46.27, b = 5458.3 and c = −0.225. Substituting these values in Eq. [2] gives Eq. [6], which is used as a general equation for estimation of cetane index of vegetable oil methyl esters.

$$\text{Cetane index} = 46.3 + 5458/x - 0.225y \qquad [6]$$

TABLE 1

Comparison of Cetane Indexes of Vegetable Oil Methyl Esters Calculated by Eq. [6], Klopfenstein's equation (1) and their Cetane Numbers (3)

Type of Transesterified oil	Cetane Number	Klopfenstein's	Saponification Number	Iodine Number	Cetane Index
Babassu[a]	63	62.9	240	20.5	64.40
Palm[b]	62	60.8	196-202	48-56	60.7-63.3
Peanut[b]	54	55.0	188-195	84-100	51.8-56.4
Soybean[b]	45	47.95	189-195	120-141	42.5-48.1
Sunflower[c]	49	46.8	188-194	110-143	42.3-50.6

[a]Saponification and iodine numbers calculated from Klopfenstein (1).

[b]Saponification and iodine numbers obtained from Swern (4).

[c]Saponification and iodine numbers obtained from Campbell (5).

Table 1 shows that the range of cetane index estimated by Eq. [6] covered most of the experimental values. The cetane indexes calculated by Klopfenstein (1) also are included.

DISCUSSION

Eq. [6] is a linear equation which quantitatively relates cetane index of vegetable oil methyl esters to their chemical structures. It provides a simple method of estimating the cetane indexes of fatty acid methyl esters by their saponification and iodine numbers. However, these two numbers of vegetable oils vary slightly according to seasons and varieties. Thus, cetane indexes of any particular oil methyl ester might have different values. Table 1 shows that the ranges of the calculated cetane indexes are very close to those determined experimentally. When individual fatty acid methyl esters from C_8 to C_{24} were tested, a parallel straight line three units higher than that of Klopfenstein's was obtained (Fig. 1). Because the general validity of Klopfenstein's equation has not been tested, this difference was not of concern.

Triglycerides and fatty acid methyl esters have almost the same saponification and iodine numbers, but cetane indexes of the oil are much lower than those of methyl ester derivatives (3). Thus, Eq. [6] cannot be used for estimation of cetane index of the oil unless some other terms (eg. viscosity, molecular weight) are introduced to correct the differences.

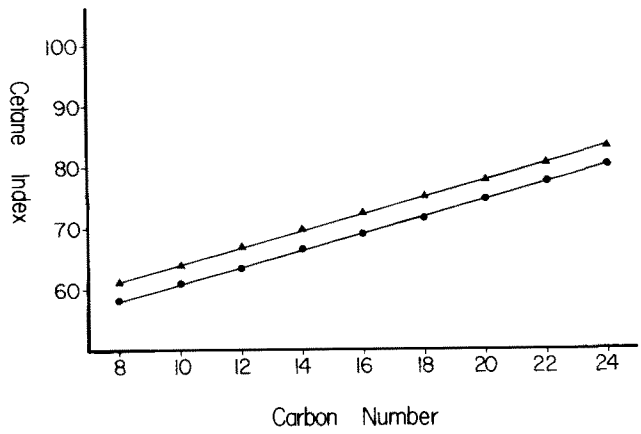

FIG. 1. Cetane indexes of fatty acid methyl esters calculated by Eq. 6 (▲—▲) and by Klopfenstein's equation (●—●).

REFERENCES

1. Klopfenstein W.E., *J. Am. Oil Chem. Soc. 59*:531 (1982).
2. American Society of Testing Materials, *Annual Book of Standards*, Part 23, 1980, p. 471.
3. Pischinger, G.H., R.W. Siekmann, A.M. Falcon and F.R. Fernandes, in *Vegetable Oils as Fuels*, American Society of Agricultural Engineers, Fargo, ND, 1982, pp. 198.
4. Sonntag, N.O.V., in *Bailey's Industrial Oil and Fat Products, Vol. 1*, edited by D. Swern, John Wiley & Sons, 1979, pp. 289-456.
5. Campbell, E.J., *J. Am. Oil Chem. Soc. 60*:387 (1983).

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ERRATUM

An error occurred in "Crystallization and Transformation of α, β- and γ-Polymorphs of Ultra-Pure Oleic Acid," which appeared on pages 1600 through 1604 of the November 1985 issue of the *J. Am. Oil Chem. Soc.*

On pages 1603–1604 of the paper, a comparison of the X-ray diffraction data of Abrahamsson et al. and of the authors was made incorrectly. The correct description is as follows: The data of Abrahamsson et al. (3) for the low-melting form was found to be consistent with those of the metastable γ polymorph.

The paper was written by M. Suzuki, T. Ogaki and K. Sato.