♣ Estimation of Cetane Index for Esters of Fatty Acids

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ABSTRACT

Cetane indexes have been calculated for the esters of the individual saturated fatty acids in the C_8-C_{24} range plus palmitoleic, oleic, linoleic, and linolenic acids. Two methods were used for these calculations: ASTM 976 and a method involving simultaneous equations relating the experimentally determined cetane numbers for several transesterified oils and the fatty acid compositions of the oils. Cetane indexes calculated according to ASTM 976 produced values which were too low for ester mixtures high in saturated acids and low in polyunsaturated acids, and were somewhat high for ester mixtures high in polyunsaturated acids. When cetane indexes calculated according to the simultaneous equation method were applied to the fatty acid mixtures, the agreement with those experimentally determined was approximately the error of determination of the cetane number.

INTRODUCTION

With the recent interest in the use of vegetable oils and fatty acid esters prepared from vegetable oils as alternative fuels for diesel engines, it is of interest to be able to predict the behavior of these compounds compared to the traditional diesel fuel. Since diesel fuel quality is indicated by cetane number, and cetane numbers are not available for many ester mixtures, I have mathematically estimated the cetane number for the esters of several fatty acids and com-

pared those results to experimentally determined cetane numbers for esters prepared from several vegetable oils.

PROCEDURES AND RESULTS

The equation in ASTM standard D976 (1) was used to calculate estimated cetane indexes for esters of saturated fatty acids from 8 to 18 carbons, and 18-carbon unsaturated acids as well as for several linear hydrocarbons from 7 to 18 carbons in length. The equation relates cetane index to density at 15 C (D) in g/mL and mid-boiling temperature (B) in degrees C as follows:

$$\text{cetane index} = 454.74 \text{-} 1641.416D + 774.74D^2 \text{-} 0.554B + 97.803 (\log B)^2$$

Densities for the hydrocarbons are from Egloff (2). Densities for the ethyl esters were extrapolated to 15 C from the data of Shigley et al. (3). Densities for the methyl esters were determined at several temperatures and extrapolated to 15 C. Boiling points at atmospheric pressure were used for the mid-boiling temperature. Boiling points for the hydrocarbons are from Egloff (2), while those for the fatty acid esters are from the Handbook of Chemistry and Physics (4). These calculated cetane indexes are shown in Figure 1. The cetane indexes for the fatty acid esters are listed in Table I.

Cetane indexes for methyl ester mixtures produced by transesterification of several vegetable oils were calculated using the estimated cetane indexes for the individual fatty acid esters calculated above and the fatty acid compositions of the oils found in the Handbook of Chemistry and Physics (5). These cetane indexes are included in Table II.

Cetane indexes for the individual fatty acid esters were also calculated based on the cetane numbers found experimentally for the transesterified oils (6) and their fatty acid compositions (5) using simultaneous equations. Although at first it appears that there are more variables than equations, the situation may be simplified since the "unknowns"
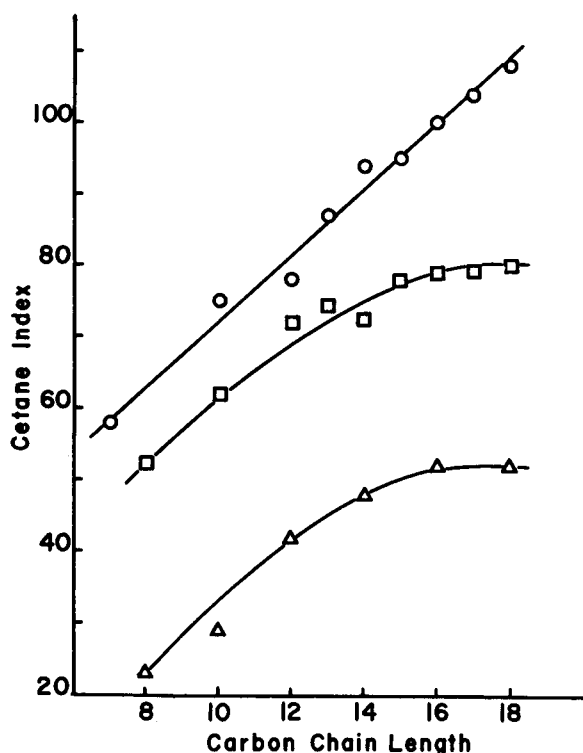

FIG. 1. Effects of chain length on cetane index. —o—, Experimentally determined cetane ratings for a series of linear, saturated hydrocarbons (7). —□—, Cetane indexes for the series of linear saturated hydrocarbons calculated according to ASTM standard D 976 (1). The boiling points for the compounds were used as the mid-boiling temperatures. —△—, Cetane indexes for fatty acid methyl or ethyl esters calculated according to ASTM standard D 976 (1).

TABLE I

Cetane Indexes of Fatty Acid Esters

Fatty acid ester	ASTM 976	Equation 6
8:0	23[a]	58.1
10:0	29[a]	60.9
12:0	42[a]	63.7
14:0	48,48[a]	66.5
16:0	52	69.3
16:1	—	53.4
18:0	52	72.1
18:1	51	56.2
18:2	48	40.3
18:3	46	24.4
20:0	—	74.9
22:0	—	77.7
24:0	—	80.5

[a]Cetane index calculated for ethyl esters. All other data are for methyl esters.

Cetane indexes were calculated from density and boiling point data using the equation in ASTM 976, or alternatively by sets of simultaneous equations relating fatty acid compositions with experimentally determined cetane numbers (6) for a number of transesterified vegetable oils (equation 6).

TABLE II

Comparison of Calculated Cetane Indexes for Transesterified Oils with Cetane Numbers

Oil transesterified	Experimentally determined cetane numbers (6)	Cetane index ASTM 976	Equation 7
Babassu	63	43.8	62.9
Palm	62	53.1	60.8
Peanut	54	50.5	55.0
Soybean	45	49.2	45.7
Sunflower	49	49.1	46.8

Cetane indexes shown in Table I for the individual fatty acid esters were used to calculate cetane indexes for the transesterified oils according to equation 7. Fatty acid compositions used were those listed in reference 5.

are members of a series of compounds and therefore differ from one another in predictable ways.

Since the homologous series of hydrocarbons show a linear relationship between chain length and cetane number, I have assumed a similar relationship for the fatty acid esters. This reduces the number of variables for chain length of the saturated esters to two, the base cetane index for the reference compound, and the increment for changing chain length. If the effect of a double bond is independent of the number of double bonds present already, the number of variables due to unsaturation is reduced to one. This reduces the total number of variables for chain length and unsaturation to three while we have five independent equations. These assumptions were used in deducing the cetane indexes of the constituent fatty acid esters. With these assumptions we can write an equation for each ester mixture relating its fatty acid composition to its cetane index. For sunflower oil we obtain equation 1, where x is equal to the cetane index of the shortest chain ester included in the study (methyl octanoate), y is the increment in the cetane index for increasing the fatty acid chain of the ester by two carbons, and z is the increment in the cetane index attributable to the presence of a double bond in the molecule.

$$49 = 0.056 (x+4y) + 0.022 (x+5y) + 0.009 (x+6y) + 0.251 (x+5y+z) + 0.662 (x+5y+2z) \quad [1]$$

Thus, (x+4y) is the cetane index for methyl palmitate, (x+5y) that for methyl stearate, and (x+5y+z) that of methyl oleate, etc.

This equation can be reduced to

$$49 = x + 4.95y + 1.57z \quad [2]$$

Similar equations can be generated for each of the methyl ester mixtures for which a cetane number is available. These equations in their reduced forms are shown in Table III. An average was obtained which was then solved in terms of x.

$$x = 54.6 - 4.44y - .99z \quad [3]$$

The equations for the individual ester mixtures were then rearranged and each solved for y. From these equations an average equation for y was calculated.

$$y = 13.2 - 0.237x - 0.208z \quad [4]$$

After the above value of x (equation 3) was substituted into this equation, the equation simplified to:

$$y = -5.66 - .53z \quad [5]$$

Next, the values of x and y (equations 3 and 5, respectively) were substituted into each of the equations for the individual ester mixtures, and each solved for z. The average

TABLE III

Simplified Equations Relating the Experimentally Determined Cetane Numbers (6) with Cetane Index for Methyl Octanoate and Cetane Index Increments for Chain Length and Unsaturation for Methyl Esters Prepared by Transesterification of Various Oils

Babassu	63	= x + 2.77y + 0.189z
Palm	62	= x + 4.57y + 0.633z
Peanut	54	= x + 5.05y + 1.08z
Soybean	45	= x + 4.89y + 1.49z
Sunflower	49	= x + 4.95y + 1.58z
Average	54.6	= x + 4.44y + 0.994z

value for z obtained was -15.9. This was substituted into equation 5 to produce a value for y of 2.77. Substituting the values of y and z into equation 3 produced a value of 58.1 for x. Using these values of x, y, and z, the cetane index for the methyl ester of a fatty acid may be computed by equation 6.

$$\text{Cetane index} = 58.1 + 2.8 \left(\frac{n-8}{2}\right) - 15.9 \text{ (number of double bonds)} \quad [6]$$

The cetane indexes for the methyl esters of the common fatty acids calculated as above are included in Table I.

The cetane index for a mixture of methyl esters may be calculated according to equation 7, which takes into account the fatty acid composition of the mixture and the cetane indexes (CI) of the individual constituents.

$$\text{Cetane index} = \frac{(\%A \times CI \text{ of } A) + (\%B \times CI \text{ of } B) + \dots (\%W \times CI \text{ of } W)}{100} \quad [7]$$

Cetane indexes calculated by this method for the transesterified oils included in this study are included in Table II.

DISCUSSION

The calculated cetane indexes for the series of hydrocarbons and methyl esters are shown in Figure 1. These two series of compounds show similar relationships between carbon number and cetane index, as exemplified by the similar slopes and shapes of the curves. However, comparison of the calculated cetane index with the experimentally determined cetane numbers (7) for the hydrocarbons indicates that the calculated index is considerably lower than the experimentally determined number, with the effect increasing above 14-15 carbons. ASTM standard 976 (1) states that the equation is not intended for calculation of cetane indexes for pure compounds. Furthermore, these calculations are based on densities and boiling points which were determined at different times in different laboratories which probably contributed to the deviations from the lines observed for some of the compounds. The deviations from the line for the experimentally determined cetane numbers for the hydrocarbons arise from the precision of the process. ASTM standard 613 states that two single determinations in different laboratories on a sample having a cetane number of 56 should deviate by more than 3.2 cetane numbers in only one case in 20 (8). Thus, some deviation from a least-square line is to be expected and is not inconsistent with a linear relationship between cetane number and MW in this MW range.

Table I compares the cetane indexes of the fatty acid esters calculated according to ASTM 976 and by equation 6. The cetane indexes calculated by the ASTM method for the shorter chain acids were for ethyl esters as more data were available on the densities of these esters than for methyl esters. Although the greater MW of the ethyl esters might be expected to result in a higher cetane index, for

myristic acid both the methyl and ethyl esters yielded cetane indexes of 48.

It is evident that the ASTM method produced cetane indexes which were lower for the shorter chain esters and higher for the polyunsaturated esters than those produced by equation 6. This difference can also be seen in the cetane indexes for the transesterified oils, Table II. The ester mixtures which are higher in shorter chain acids or low in polyunsaturated acids show cetane indexes which are low compared to the experimentally determined indexes (6) when the ASTM-calculated indexes for constituent esters are used. On the other hand, cetane indexes for these mixed esters agree within the stated limits for determination of cetane number (8) when the cetane indexes for the constituents of the mixtures calculated according to equation 6 are used. Close agreement might be expected here since the cetane indexes for the individual esters were derived from these experimentally determined cetane numbers. However, the fact that the agreement was close for all of the vegetable oil-derived ester mixtures which have quite wide variations in their fatty acid compositions lends credence to the cetane indexes estimated for the fatty acid esters. The minor differences observed may be attributable to one or more of the following sources: (a) precision of the cetane number determinations; (b) use of fatty acid composition data which might not match the fatty acid compositions of the ester mixtures on which the cetane number data were obtained; and (c) possible nonlinearities of cetane index with chain length and unsaturation.

The method described above provides a convenient means of estimating the cetane indexes for methyl ester mixtures containing the ordinary range of fatty acids.

Recently, the cetane number for the ethyl esters prepared from soybean oil has been reported to be 50.0 (9) and 48.2 (10), both on samples obtained from the same source. Since the cetane number for the methyl ester prepared from soybean oil was reported to be 45 (6) and the cetane index calculated in this study was 45.7, it appears that ethyl esters have cetane indexes between two and five units higher than the corresponding methyl esters.

REFERENCES

1. Annual Book of ASTM Standards, Part 23, 1980, p. 471.
2. Egloff, G., Physical Constants of Hydrocarbons V, Reinhold, New York, NY, 1953.
3. Shigley, J.W., C.W. Bonhorst, C.C. Liang, P.M. Althouse and H.O. Triebold, JAOCS 32:213 (1955).
4. Weast, R.C., CRC Handbook of Chemistry and Physics, 60, CRC Press, Boca Raton, FL, 1981, pp. C-271, 281, 332, 403, 406 and 512.
5. Weast, R.C., Ibid., pp. D-225, 226.
6. Pischinger, G.H., R.W. Siekmann, A.M. Falcon and F.R. Fernandes, in Vegetable Oil Fuels, Proc. International Conference on Plant and Vegetable Oil as Fuels, Fargo, ND, 1982, pp. 198-208.
7. Goodger, E.M., and A.P. Valvade, Inst. Pet., Paper IP 80-002, 1980.
8. Annual Book of ASTM Standards, Part 47, 1980, p. 236.
9. Kusy, P.F., in Vegetable Oil Fuels, Proc. International Conference on Plant and Vegetable Oils as Fuels, Fargo, ND, 1982, pp. 127-137.
10. Pienaar, P.G., S.F. Clark and M.D. Schrock, Ethyl Alcohol Soybean Esters, A Renewable Fuel for Diesel Engines. Paper presented at International Conference on Plant and Vegetable Oils as Fuels, Fargo, ND, 1982.

✗ A Gas Chromatographic Reactor to Measure the Effectiveness of Antioxidants for Polyunsaturated Lipids[1]

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ABSTRACT

A method and apparatus consisting of a gas chromatographic reactor was developed to study the effect of antioxidants on lipid-containing systems. The oxygen uptake during the oxidation tests was continuously measured. The relative efficiencies, expressed as protective index, for butylated hydroxytoluene (BHT), propyl gallate (PG), α-tocopherol, citric acid, and ascorbic acid on the oxidation of linoleic acid at 85 C and 55 mmHg were determined. The effect of increasing the concentration of BHT (0.025, 0.05, and 0.1%) on the oxidation of safflower oil at 70 C and 45 mmHgO$_2$ was observed. The method was found to be a rapid and reproducible approach to investigate the effect of antioxidants on polyunsaturated lipids.

INTRODUCTION

Modern methods of food processing and handling require the addition of antioxidants in lipid-containing foods to ensure high storage stability. The most common antioxidants in food processing are the free radical scavengers

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(Type 1) which can donate a hydrogen to a radical and the free radical production preventors (Type 2) which inhibit oxidation by chelating trace metals normally present in foods (1). Examples of the Type 1 include butylated hydroxytoluene (BHT), tertiary butylhydroquinone (TBHQ), propyl gallate (PG), and tocopherols. Citric acid, ascorbic acid, phosphoric acid, and ethylene diaminetetraacetic acid (EDTA) are examples of the Type 2 which are also classified as synergists (1-2). Because of possible toxicity of the synthetic antioxidants, other natural compounds have been reported. For instance, the active antioxidant component in the extracts of rosemary and sage has been shown to improve the flavor stability of soybean oil and of fried food such as potato chips (3). In addition, antioxidant activity of amino acids (4,5) and of caffeic acid and its esters (6) are other examples of natural inhibitors of lipid oxidation.

The mechanism of protection given by an antioxidant is postulated to occur at the initial stage of autoxidation (1, 2,7,8). The free radicals formed by an initiator (light, metals) or by chain reaction are inhibited or interrupted by the free radical acceptor (phenolic structure), thus stopping the chain reaction. Such protection mechanism leads to an increase in the induction period of antioxidation and therefore a longer