# Effect of Molecular Weights of Fatty Acid Esters on Cetane Numbers as Diesel Fuels

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## ABSTRACT

Cetane numbers for various esters of the saturated fatty acids from C8 to C18 have been determined according to ASTM D-613. For the methyl esters the cetane numbers were found to increase in a nonlinear relationship with the chain length of the fatty acid. Cetane numbers of esters in which the fatty acid is kept constant while the alcohol esterified is altered also increased with the molecular weight of the ester. However, increases in the molecular weight of the fatty acid portion of the ester produce greater increases in cetane number than the same change in molecular weight in the alcohol portion of the ester. Except for the esters of octanoic acid, all of the esters tested had cetane numbers above the value of 40, which is specified as the minimum cetane number for commercial diesel fuel.

## INTRODUCTION

The use of fatty acid esters as alternative fuels for diesel engines has attracted considerable attention over the past several years. Much of this work has been involved with experiments to determine the effects of using vegetable oils, usually mixed with diesel fuel (1-5), or with esters prepared by transesterification of the vegetable oil (6-8), on the long-term performance of the engines. While such work is necessary before esters are used as fuel on a large scale, it does not yield much information on the question of the contributions of the various structural features of the esters to their performance as diesel fuels.

One of the characterizations of diesel fuel is combustibility as indicated by cetane numbers. Although cetane numbers have been reported for several ester mixtures prepared by transesterification of several vegetable oils (6,9,10, 11), no cetane numbers performed by the prescribed ASTM D-613 method have been reported for individual fatty acid esters. Johnston and Harrington (12) have reported cetane number rankings of ester mixtures prepared from several seed oils and several esters of oleic acid by a non-ASTM method.

I now report the cetane numbers of the series of methyl esters of the saturated fatty acids from 8 to 18 carbons and esters other than methyl for several of the fatty acids, as determined by ASTM D-613.

## MATERIALS AND METHODS

Esters were prepared from commercial grades of fatty acids. The octanoic, decanoic and lauric acids were provided by Armak Chemical Co., McCook, Illinois. Myristic, palmitic and stearic acids were purchased from Eastman Kodak Company, Rochester, New York. Esterifications were carried out using reagent grade alcohols without further purification. One percent $H_2SO_4$ was used as catalyst. After esterification, the reaction mixtures were washed with $H_2O$, dried over anhydrous $Na_2SO_4$ and distilled under vacuum. Fatty acid compositions were determined by gas-liquid chromatography.

Cetane numbers of the esters were determined by Waukesha Engine Division, Dresser Industries, Waukesha, Wisconsin, according to ASTM D-613 (13). All of the esters were used neat except that methyl palmitate was subjected to the determination both neat and in an ester-petroleum ether mixture (70:30, v/v). Decanoic acid and methyl stearate were tested only as the 70:30 mixtures with petroleum ether. The cetane numbers for the decanoic acid and methyl stearate were calculated from those of their mixtures with petroleum ether, by using a calculated cetane number for petroleum ether. This cetane number for petroleum ether was calculated by equation 1, where x equals the cetane number for the petroleum ether, y equals the cetane number of the methyl palmitate and 57.7 is the cetane number for the 70:30 mixture of methyl palmitate and petroleum ether.

$$57.7 = 0.3x + 0.7y = 0.3x + 0.7\ (74.5)$$

$$x = 18.3 \qquad [1]$$

Using that value as the cetane number for petroleum ether, the cetane numbers of the pure decanoic acid and methyl stearate were calculated using analogous equations.

Boiling points for the fatty acid esters were estimated by gas-liquid chromatography. Retention times for a series of normal, saturated hydrocarbons on OV-101 were determined. A plot was prepared of log of retention time versus boiling point. From this curve, boiling points of the fatty acid esters were estimated from their retention times.

## RESULTS AND DISCUSSION

The purities of the compounds used in this study and the cetane numbers determined are listed in Table I. Also included in Table I are cetane indexes calculated previously

TABLE I

Cetane Numbers of Fatty Acid Esters

| Ester | Common name | Purity (%) | Cetane # | Cetane index (14) |
|---|---|---|---|---|
| Me 8:0 | Methyl octanoate | 98.6 | 33.6 | 58.1 |
| Bu 8:0 | Butyl octanoate | 98.7 | 39.6 | |
| $H^+$ 10:0 | Decanoic acid | 98.0 | 47.6 | |
| Me 10:0 | Methyl decanoate | 98.1 | 47.2 | 60.4 |
| Et 10:0 | Ethyl decanoate | 99.4 | 51.2 | |
| i-Pr 10:0 | Isopropyl decanoate | 97.7 | 46.6 | |
| n-Pr 10:0 | Propyl decanoate | 98.0 | 52.9 | |
| Bu 10:0 | Butyl decanoate | 98.6 | 54.6 | |
| Me 12:0 | Methyl laurate | 99.1 | 61.4 | 63.7 |
| Me 14:0 | Methyl myristate | 96.5 | 66.2 | 66.5 |
| Et 14:0 | Ethyl myristate | 99.3 | 66.9 | |
| Bu 14:0 | Butyl myristate | 99.0 | 69.4 | |
| Me 16:0 | Methyl palmitate | 93.6 | 74.5 | 69.3 |
| Me 18:0 | Methyl stearate | 92.1 | 86.9 | 72.1 |

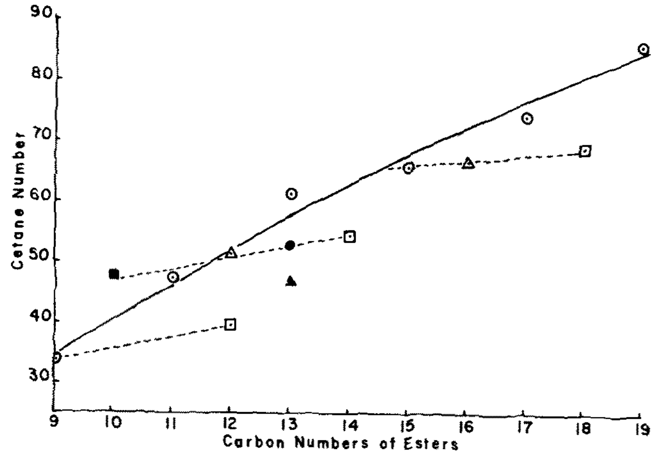

FIG. 1. Fatty acid esters were subjected to cetane number determinations according to ASTM standard D-613 (13). Cetane numbers were plotted against the total number of carbon atoms in the ester. The solid line connects the homologous series of methyl esters. The broken lines connect esters of different alcohols and the same acid. ○, methyl esters; △, ethyl esters; ●, 1-propyl ester; ▲, 2-propyl ester; □, butyl ester, and ■, free acid.

from the cetane numbers reported for fatty acid ester mixtures and the fatty acid compositions of the mixtures (14). Comparison of the cetane indexes with the cetane numbers reveals close agreement between the two for methyl myristate. For shorter chain esters the cetane indexes are high, while for the longer esters they are low. This indicates that the effect of the fatty acid chain length on the cetane number was underestimated in the earlier study.

Figure 1 depicts the relationship between cetane numbers and total numbers of carbon atoms of the fatty acid derivatives. It appears that for the methyl esters there is a nonlinear increase in cetane number with increasing chain length of the fatty acid. The line shown was calculated according to equation 2, where y = fitted cetane number and x = chain length of the fatty acid.

$$y = 24.48 + 8.431\,x - 0.1299X^2 \qquad [2]$$

The nonlinearity of the relationship between carbon chain length and cetane number for the methyl ester is in contrast to the linear relationship for the normal hydrocarbon (18), although the data presented by those authors suggests a nonlinearity at longer chain lengths of the hydrocarbons.

Cetane numbers of several derivatives other than methyl ester also are shown on Figure 1. The carbon numbers represent the sum of the carbon atoms in the fatty acid and alcohol portions of the ester. Thus, decanoic acid has a carbon number of 10, while butyl decanoate has a carbon number of 14. It is apparent from Figure 1 that increases in carbon number which result from increasing the molecular weight of the alcohol portion of the ester do not have the same effect on increasing the cetane numbers as does a similar increase in molecular weight of the fatty acid. At present only suggestions can be presented to account for this observation. ASTM standard D-976 (15) provides a method for calculating a cetane index for petroleum-derived mixtures using the density and mid-boiling temperature of the mixture. Although this method of calculating cetane index is limited in application to mixtures of petroleum-derived hydrocarbons whose cetane numbers fall between 30 and 60 and is expressly stated to be not applicable to pure hydrocarbons and synthetic fuels, I felt that comparisons of the trends observed for the cetane numbers of the esters with the predicted directions of cetane indexes would be instructive. The form of the equation is such that a higher cetane index results from either elevated mid-boiling temperature or reduced density. Although boiling points are not available for many of the fatty acid esters at atmospheric pressure, retention times of the ester on gas chromatographic analysis using a non-polar liquid phase should provide an indication of relative vapor pressures of the various esters. Table II contains boiling points estimated in this manner along with literature values for some of the esters. The boiling points determined by gas-liquid chromatography are, in all cases, higher than the literature values, presumably determined by conventional methods. Two possibilities exist to explain these discrepancies. The first is that small quantities of impurities would have the effect of lowering the observed actual boiling temperature while having no effect on retention time by gas-liquid chromatography. The second is that, although the OV-101 liquid phase is among the least polar phases available, the carbonyl of the fatty acid esters might cause the ester to be retained slightly longer than expected from boiling point alone.

**TABLE II**

**Boiling Points and Densities of Fatty Acid Esters**

| | Boiling points (°C) | | |
|---|---|---|---|
| | Estimated | Literature (16) | Densities (20°') |
| Me 8:0 | 197 | 193 | 0.8778 |
| Bu 8:0 | 246 | 240 | 0.8620 |
| Me 10:0 | 233 | 224 | 0.8724 |
| Et 10:0 | 249 | 242 | 0.8655 |
| 1-Pr 10:0 | 268 | | 0.8614 |
| 2-Pr 10:0 | 257 | | 0.8552 |
| Bu 10:0 | 289 | | 0.8583 |
| Me 12:0 | 277 | 262 | 0.8683 |

When esters having the same carbon numbers but differing in structure are compared, we find that for carbon numbers of 12, butyl octanoate has a lower cetane number and boiling point than ethyl decanoate. This is in agreement with the prediction of ASTM D-976. A similar correlation is seen among the three esters having 13 carbons. Methyl laurate has the highest boiling point (and the highest cetane number) followed for both boiling point and cetane number by 1-propyl decanoate and then 2-propyl decanoate. Thus, there appears to be a positive correlation between boiling points of the esters and cetane number. This correlation also can be seen for the homologous series of methyl esters. Thus the effect of boiling point on cetane number for fatty acid esters resembles that for mixtures of petroleum-derived hydrocarbons.

The effects of density on cetane numbers of the esters are more difficult to determine. For mixtures of petroleum origin, the equation in ASTM D-976 (15) predicts a negative correlation between density and cetane number. For esters of one alcohol the density decreases with increasing molecular weight of the ester (17). Thus we would expect the observed increases in cetane numbers obtained with increasing chain length for the homologous series of methyl esters. However, density also decreases with molecular weight of the alcohol portion of the ester when the fatty acid is kept constant. Furthermore, experiments in my laboratory show that for esters of the same carbon number, the one containing the lowest molecular weight alcohol and the longest fatty acid will have the highest density. Esters of 1-propanol have higher densities than those of 2-propanol. Thus densities decrease in the series ethyl decanoate > butyl octanoate and methyl laurate > 1-propyl decanoate > 2-propyl decanoate. Cetane number also decreases in that order for those series, in contrast to the observation above for the homologous series of methyl esters, and the negative correlation between density and cetane number in ASTM D-976. When this equation is used to calculate the cetane indexes of sets of esters having the same carbon numbers using the boiling points and densities from Table II, we find cetane indexes which are essentially the same for all members of the set. For example, for the esters with 13 carbon atoms, the calculated cetane indexes were 43.24, 43.61 and 43.84 for methyl laurate, 2-propyl decanoate and 1-propyl decanoate respectively. This occurs because the increase in cetane number which is predicted to accompany an increase in boiling point is almost exactly offset by the decrease in cetane number predicted to accompany an increase in density.

These results demonstrate that, although ASTM D-976 may be useful in predicting trends in cetane numbers for a homologous series of fatty acid esters, it is not able to predict variations in cetane numbers when more complex structural variations are being considered. Perhaps physical properties other than just boiling point and density, for example surface tension and heat capacity, need to be considered before accurate cetane numbers may be calculated for fatty acid esters.

Cetane numbers for the methyl esters of the saturated fatty acids varied in a non-linear manner with chain length of the fatty acid. Cetane numbers also increased with increasing molecular weight for esters of the normal alcohols when fatty acid was kept constant. The cetane number increase resulting from an increase in the molecular weight of the alcohol of the ester was less than that for the same increase in molecular weight of the fatty acid portion of the ester.

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# ♣Purification and Properties of the Lipase from *Candida deformans* (Zach) Langeron and Guerra

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## ABSTRACT

Palm oil being solid at room temperature could be converted into a fluid oil by substitution of about 40-50% of its palmitic acid. This could be achieved by a fermentation process or using yeast lipase.

*Candida deformans* CBS 2071 seemed suitable for this purpose; therefore, its lipase was isolated and studied. This enzyme was purified by acetone precipitation followed by chromatographies on Sephadex C 50 and Sephadex G 150. The purification factor achieved was ×70, and the protein and activity yields were 0.25% and 18%, respectively. The homogeneity of the purified enzyme was verified by polyacrylamide gel electrophoresis. The enzyme molecular weight was estimated at 207,000. Its activity is optimal between 40 C and 50 C and its optimum pH is 7.0. This enzyme is thermoresistant and loses only 14% and 18% of its activity, respectively, when heated to 45 C and 55 C for 30 min. Its activation energy was 2.75 kcal.mole$^{-1}$ and its inactivation energy was around 21 kcal.-mole$^{-1}$. This enzyme is activated by $Ca^{++}$, $Mg^{++}$ and $Co^{++}$ and inhibited by $Cu^{++}$, $Zn^{++}$, and p-chloromercuribenzoate (pCMB) and EDTA.

The synthesis of this lipase is induced by lipid substrates in the culture medium and inhibited by glucose. This enzyme attacks primarily the 1- (or 3-) position of all triglycerides tested. Hydrolysis was preferential for triglycerides containing short chain fatty acids. The triglycerides with monounsaturated monoacids were more quickly hydrolyzed than those with saturated monoacids. The presence of two and especially three double bonds in the fatty acid chain seemed to slow down the rate of hydrolysis.

## INTRODUCTION

Numerous papers relative to lipase-producing microorganisms have been published, and most of them are concerned with selection and identification of strains, growth characteristics, lipase production mechanisms and, in some cases, with the purification and enzymatic properties of lipases. These microbial lipases have received much attention because of their potential use in industry. Seitz (1) and Macrae (2) reported some interesting new applications for microbial lipases, developed particularly in the oils, fats and dairy industries, to make foods palatable and acceptable. For the purpose of biofashioning palm oil, it may be possible to exploit the potential of some microorganisms.

Crude palm oil is solid at room temperature because of