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# A comprehensive evaluation of the cetane numbers of fatty acid methyl esters

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## HIGHLIGHTS

- Cetane number determination of geometric and positional isomers of fatty acid methyl esters.
- Cetane numbers predicted for compounds with difficult experimental determination.
- Methyl oleate discussed as standard for cetane testing.
- Cetane numbers predicted for mixtures of fatty acid methyl esters (biodiesel).

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## ABSTRACT

The cetane number (CN), being related to ignition and combustion behavior, is a prime indicator of the quality of diesel fuels, including those derived from renewable resources such as biodiesel. While many effects of compound structure are known or have been postulated, experimental data have not always been available for the various ester components of biodiesel and a comprehensive evaluation including some structural features not yet experimentally investigated such as double bond configuration and position is lacking. In this work, existing CN data of fatty esters are complemented by studying C18 esters with differing double bond positions and double bond configurations. For the first time, CNs, determined as derived cetane number (DCNs), of neat *trans* fatty acid methyl esters, methyl elaidate (methyl 9(*E*)-octadecenoate) and methyl linolelaidate (methyl 9(*E*),12(*E*)-octadecenoate), were determined as were the CNs of the C18:1 positional isomers methyl petroselinate (methyl 6(*Z*)-octadecenoate) and methyl asclepate (methyl 11(*Z*)-octadecenoate). The CNs of the positional and geometric isomers of methyl oleate are close to the CN of methyl oleate. These data are compared to other previously determined CN data. Furthermore, the applicability of CN data is evaluated using an extensive collection of CN determinations for methyl oleate as "standard" fatty acid (methyl) ester. The average CN value for methyl oleate is in the range of 56–58 with a CN of 57 suggested for calculating purposes. Similarly, uncertainty ranges could be established for CNs of other fatty materials. The data are also useful for predicting CNs of compounds for which CNs are not readily available or easily determinable.

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## 1. Introduction

One of the prime quality aspects of any fuel is its ignition and combustion behavior. To serve as an indicator for the ignition and combustion quality of diesel fuels, the cetane number (CN) has been established with its determination described in standards [1,2]. The CN is now also regularly applied to biodiesel [3,4], a biogenic alternative to petrodiesel derived from vegetable oils, animal fats, or other materials based on triacylglycerols, composed of the fatty acid mono-alkyl esters (usually methyl esters) thereof. Generally, the CN is a dimensionless descriptor for the ignition delay time a fuel experiences upon injection into the combustion chamber of a diesel engine. The shorter the ignition delay time, the greater the CN and vice versa. The CN is based on the cetane scale for which hexadecane ($C_{16}H_{34}$; trivial name: cetane; giving the CN its name) is the high-quality reference compound with an assigned CN of 100 and 2,2,4,4,6,8,8-heptamethylnonane (HMN; also $C_{16}H_{34}$) is the low-quality reference compound with a CN of 15. Generally, higher CNs are regarded as desirable due to reduced engine knock, and a positive influence on nitrogen oxides ($NO_x$) exhaust emissions has also been reported [5,6]. An early compilation of CNs of various compounds, mainly hydrocarbons as they are the major components of petrodiesel, was published by Puckett and Caudle [7] while a more recent one is by Murphy et al. [8]. The CN is included in the American Society for Testing and Materials (ASTM) and European petrodiesel [9,10] and biodiesel standards

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[11,12] with the prescribed minimum CN in these standards listed in Table 1.

Compound structure strongly influences the CN. This influence of structure on combustion in a diesel engine was recognized when originally the cetene number was developed [13], in which cetene (1-hexadecene) and mesitylene (1,3,5-trimethylbenzene) were the high- and low-quality reference materials for ignition delay in a diesel engine. Because of stability problems with cetene, cetane was suggested as the high-quality standard material by the ASTM in 1934 [14] with the relationship between the CN and the cetene number being [14]

$$\mathrm{CN} = 7/8 \times \text{cetene number} \quad (1)$$

According to Eq. (1), the CN of cetene is 87.5. Similarly, mesitylene as the low-quality reference compound was soon replaced by 1-methylnaphthalene for cost reasons [14]. In the ASTM cetane test standard, HMN replaced 1-methylnaphthalene in 1962 because of better storage stability and availability [1]. The CN of HMN was determined as 15 on the scale using cetane and 1-methylnaphthalene. The CN of mixtures of hexadecane and HMN is then given by the equation

$$\mathrm{CN} = \mathrm{vol} - \%\ \text{cetane} + 0.15(\mathrm{vol} - \%\mathrm{HMN}) \quad (2)$$

as described in Ref. [1].

Probably the first CN determination of what is now known as biodiesel, namely the mono-alkyl esters of vegetable oils, animal fats or related materials [11] was reported in 1942 [15]. Here, palm oil ethyl esters were synthesized and used as a fuel. The CN of the palm oil ethyl esters was reported to be higher (83; giving a cetene number of 95) than that of the other materials tested for comparison purposes.

These historical perspectives illustrate several important effects of compound structure on CN, which have been confirmed many times in more recent literature. The effects that can be deduced from this earlier work are that long straight-chain (or only lightly branched) hydrocarbons, i.e. alkanes, are "ideal" diesel fuels in terms of ignition and combustion as they have high CN; double bonds reduce CN as the comparison of cetane and cetene shows; branching in the chain reduced CN as shown by the comparison of hexadecane and HMN; aromatic compounds have low CN although CN will increase with increasing size of an alkyl side chain; and that saturated long-chain esters, such as those found abundantly in palm oil alkyl esters, impart high CN. A related discussion of the effect of compound structure of hydrocarbons on CN can be found in [16]. CNs were also found to increase with chain length for saturated fatty acid alkyl esters [17]. Finding its experimental expression in the CN, the structural similarity of fatty compounds with hexadecane, namely the long hydrocarbon chain, can thus explain the suitability of fatty esters as diesel fuel. The CN of alkyl esters did not increase as strongly with increasing size of the alcohol moiety [17,18]. Esters of octanoic acid had CN below 40 [16], the minimum CN specified for petrodiesel in the standad ASTM D975 (Table 1). An alternative to the CN, termed the "lipid combustion quality number," was suggested to accommodate long-chain fatty esters with CN > 100 [19]. In a theoretical paper, various effects of compound structure such as chain length and increasing number of double bonds on the CN of fatty compounds were discussed [20]. When double bonds are present, it was surmised that the CN increases if the double bond "migrates" towards one end of the chain with the same effect holding for branching of the chain [20].

**Table 1**
Minimum cetane numbers prescribed in petrodiesel and biodiesel standards.

| Standard | Type | Cetane number (minimum) |
|---|---|---|
| ASTM D975 | Petrodiesel | 40 |
| EN 590 | Petrodiesel | 51 |
| ASTM D6751 | Biodiesel | 47 |
| EN 14214 | Biodiesel | 51 |

The calculation and prediction of the CNs of individual fatty acid methyl esters (FAME) and their mixtures, i.e. biodiesel, has also received attention in the literature, a major reason being the considerable amount ($\geqslant$1 L) of fuel sample consumed by the ASTM D613 method. In early work on this subject matter, several authors predicted the cetane index of FAME [21,22] which is, however, designed to estimate the CN of petrodiesel fuels from API gravity and mid-boiling point and for which a separate standard exists [23]. Correlation with physical properties was used to predict the CN of FAMEs also with the boiling point giving the best correlation in that study [24]. Recently, more complex methods, such as regression analysis, artificial neural networks with application of other methods such as principal component analysis, have been proposed for the determination of CNs of vegetable oil methyl esters [25–31]. Any predictions, however, are affected by the issue of variability of results addressed below.

Issues such as the significant amount of fuel sample consumed by cetane testing, as mentioned above, besides ease of operation and the aforementioned variability, prompted the development of test procedures using a constant volume combustion apparatus requiring less sample [32]. Eventually, an Ignition Quality Tester (IQT) resulting from this research was developed and a corresponding standard, ASTM D6890 [33], established with CNs of some fatty acid alkyl esters determined with the IQT at that time [34]. The IQT procedure provides what is termed a derived cetane number (DCN) which can be correlated with the CN as determined by D613 through means of an equation. Thus, many CN test results in the literature utilize this method including the results reported and discussed here.

In light of the discussion above, this work presents an evaluation of the CN of biodiesel components taking structural features such as double bond position and configuration besides chain length into account with the first cetane tests of positional and geometric isomers, the prediction of CNs of compounds which are not readily determinable under ambient conditions as well as the prediction of the CN of mixtures. Furthermore, an issue affecting both experimental determination and prediction is that of experimental variability of CN. This issue also is addressed.

## 2. Experimental

Straight-chain fatty acids and esters were obtained from Nu-Chek Prep (Elysian, MN). To ensure purity and nature of the samples, some samples were randomly checked by GC–MS and NMR (solvent $CDCl_3$; 500 MHz for $^1$H NMR, 125 MHz for $^{13}$C NMR). All samples were found to be of advertised purities or higher (>99%). NMR also served structure verification purposes, including the double bond position for unsaturated fatty acids and esters. The position and separation of the olefinic carbon signals in $^{13}$C NMR of monounsaturated fatty acid chains depends on the proximity of the double bond to the terminal ester or methyl group [35]. Thus, for a double bond "migrating" from the 5- to the 15-position in the monounsaturated samples investigated here, a decrease in the difference of the signals of the olefinic carbons from 2.9 ppm (C20:1 $\Delta$5) to 0.03 ppm (C22:1 $\Delta$13) to 0 ppm (C23:1 $\Delta$14 and C24:1 $\Delta$15) was observed.

Cetane numbers were determined as described in the literature [34] as DCNs following the standard ASTM D6890 using an IQT located at Southwest Research Institute in San Antonio, TX.