Determination Model for Cetane Number of Biodiesel at Different Fatty Acid Composition: a Review

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Abstract
The most accepted definition of biodiesel is stated at the EU technical regulation EN 14214 or in the USA in ASTM 6751-02. Because of this highly strict description only methyl esters of fatty acids conform to these definitions, nevertheless the term “biodiesel” is spread out to other alkyl fatty esters. Some countries have adopted bioethanol for replacement of methanol in biodiesel transesterification and thus assuring a full biological fuel. Of course, such position brings some problems in fulfilling technical requirements of EN 14214 or ASTM 6751-02. Biodiesel is actually a less complex mixture than petrodiesel, but different feedstock origins and the effect of seasonality may impose difficulties in fuel quality control. Since biodiesel is an alternative diesel fuel derived from the transesterification of triacylglycerol comprised materials, such as vegetable oils or animal fats, with simple alcohols to furnish the corresponding mono-alkyl esters, its composition depends on the raw material used, the cultivated area location, and harvest time. The choice of the raw material is usually the most important factor for fluctuations of biodiesel composition, because different vegetable oils and animal fats may contain different types of fatty acids. Important properties of this fuel vary significantly with the composition of the mixture. Cetane number, melting point, degree of saturation, density, cloud point, pour point, viscosity, and nitrogen oxides exhaust emission (NOx), for instance, deserve to be mentioned. One of the most important fuel quality indicators is the cetane number; however, its experimental determination may be an expensive and lengthy task. To weaken situation concerning biodiesel, the availability of data in the literature is also scarce. In such scenario, the use of reliable models to predict the cetane number or any other essential characteristic may be of great utility. We reviewed available literature to describe model, which will correlate cetane number of single mono-alkyl esters of fatty acids and their mixtures (biodiesels) with structural characteristics achieved by hydrogen nuclear magnetic resonance spectra. We suggest that this could be done through the application of a three stages process, combining statistical tools, fuzzy logic and artificial neural networks. Both treatments pointed to two major characteristics as determinants for the cetane number values: the number of carbon-carbon double bonds and the structure of alcohol moiety in each fatty ester. Neural Networks predicted cetane number quantitatively. The results are beneficial for the further development of analytical models addressing the quality of biofuels.

Keywords: biodiesel, cetane number, fat acid, model, raw material.

1. Introduction
Current oil and gas reserves would be enough to last only a few more decades. To deal with the rising energy demand and declining petroleum reserves, fuels from renewable stocks such as ethanol, biodiesel, and hydrogen are at the forefront of alternative technologies [1-4]. Process technology and engineering companies were striving for continuously improving the required biodiesel quality and for reducing production cost with an increasing number of such companies providing reliable quality at low investment cost [5]. Biodiesel is an alternative diesel fuel obtained through the transesterification of vegetable oils or other materials largely comprised of triacylglycerols (also known as triglycerides), such as animal fats or used frying oils, with

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monohydric alcohols to give the corresponding monoalkyl esters [6, 7]. Since biodiesel is an alternative diesel fuel derived from the transesterification of triacylglycerol comprised materials, such as vegetable oils or animal fats, with simple alcohols to furnish the corresponding mono-alkyl esters, its composition depends on the raw material used, the cultivated area location, and harvest time [8, 9].

2. Specifications limiting fatty contaminants in the biodiesel standards

Because of the transesterification reaction, biodiesel contains small amounts of glycerol, free fatty acids, partially reacted acylglycerols (monoacylglycerols and diacylglycerols), as well as residual starting material (triacylglycerols). These contaminating trace materials are limited in biodiesel standards such as the American Society for Testing and Materials (ASTM) standard D-6751 and the European standard EN 14214, as well as other standards under development around the world. Biodiesel can be defined as fatty acid of ethyl and methyl esters from vegetable oils or animal fats, with high cetane number and, generally, its boiling point and viscosity are suitable for use as fuels in diesel engines. Because this fuel is produced from renewable resources and involves lower emissions than petroleum fuel, it can be used as an attractive alternative fuel. Although the use of biodiesel increases nitrogen oxides slightly, it can cause a reasonable reduction in the main pollutant emissions like particulate material, total hydrocarbons, and carbon monoxide [10]. Biodiesel is an alkyl monoester originated from vegetable oils, waste cooking oils or animal fats. It has been derived through a transesterification process with a presence of methanol as a catalyst. Technical regulations regulate the biodiesel to conform the standard in the fuel production process when removing glycerin, catalyst and alcohol in minimal levels. The transesterification process is functioned to remove the unnecessary constituents include dirt and water from the oil. Studies conducted by different researchers around the world revealed that biodiesel is proven as a substitute for mineral diesel and at the same time reducing the emission significantly [11-14].

In general, biodiesel that originated from palm oil has different properties as compared to other biodiesel made from other organic sources as well as mineral diesel. Palm oil has greater density and viscosity compared to mineral diesel [15]. Therefore, a comprehensive data of biodiesel and their blend fuel physical properties is required to analyze the characteristics of biodiesel when operated with conventional diesel engines. The fuel physical properties are very critical parameters in the atomization process in compression ignition engines. Viscosity plays important roles in the atomization quality of fuel injection within the combustion chamber, distribution of fuel droplet size and the uniformity of the mixture. In addition, larger surface tension affects the dissolution of a liquid jet into smaller fuel droplets [16]. Biodiesel is produced on the industrial scale by methanolysis of vegetable oils (usually rape or soybean) or waste fat, particularly using frying oils. Methanolysis proceeds with modest amounts of base catalyst, provided the levels of free fatty acid and water in the oil are low [17]. The fatty acid content may be reduced by physical or chemical treatment before methanolysis but for waste fats, alternative processes that do not use base catalysis may be preferred. Lipase catalyzed methanolysis is less sensitive to fatty acid and water in the oil and has been tested in batch [18] and fixed-bed reactor [19] conversion of waste oil and grease to biodiesel. Viscosity can be defined as resistance of oil to flow smoothly or the measurement of internal friction. The viscosity of biodiesel is higher compared to mineral diesel, but approximately less than straight vegetable oils. Fuel viscosity can be significantly reduced by using a transesterification process. Viscosity has a greater impact under low temperatures that resist the fuel to flow smoothly from the storage tank into the engine. Higher viscosity causes poorer atomization of the fuel spray and inaccurate fuel injectors operation. In addition, fuel density is a weight of unit volume of fuel. The minimum value of density is desirable to obtain the maximum engine power through the fuel flow control in the injection pump. It also required minimizing the smoke formation when operates with maximum power [20]. Acid value number is defined as the amount of potassium hydroxide (KOH) in milligrams that is necessary to neutralize free fatty acids contained in 1 gram of oil. It possesses as
the vegetable oil quality indicator to monitor the oil degradation during storage period. According to ASTM D 6751, the maximum value of acid number is 0.5 mgKOH.g⁻¹ [21].

Cetane number is the ignition quality indicator of the fuel. It defines whether the fuel has longer or shorter ignition delay during the combustion period. An increase in cetane number is because the carbon chain length increases. Typical diesel engines accept the cetane number between 40 and 55 while below 38, a more rapid increase in ignition delay is occurred. In general, alcohol has lower cetane number compared to mineral diesel and biodiesel. Among effects that could describe when operated with the fuel that has lower cetane number are engine noise and longer ignition delay. The cetane number of neat alcohols is very low (8 for ethanol and 3 for methanol) which defines them as poor compression ignition engine fuels. Furthermore, the cetane number of diesel-alcohol blend fuel depends on the diesel ignition quality, the percentage of the alcohol in the blend, and the addition of cetane improver additives [22]. The objective of the study by [16] was determined the fuel properties of the biodiesel B100, B20, B20-alcohol blend fuels of 5%/v and 10%/v with mineral diesel as a baseline fuel. For these reasons, in recent years many different techniques to analyze biodiesel properties have been developed to infer the quality of these fuels [23-25]. One of the most important fuel quality indicators is the cetane number; however its experimental determination may be an expensive and lengthy task. To weaken situation concerning biodiesel the availability of data in the literature is also scarce. In such a scenario, the use of reliable models to predict the cetane number or any other essential characteristic may be of great utility [26-30]. Cetane number is characterized according to EN ISO 5165 by a minimum limit 51 for European biodiesel. Cetane number is a dimensionless indicator that characterizes ignition quality of fuels for compression ignition engines. Since in the compression ignition engines burning of the fuel-air mixture is initiated by compression ignition of the fuel, the cetane number is a primary indicator of fuel quality as it describes the ease of its self-ignition. Theoretically, the cetane number is defined in the range of 15-100; the limits are given by the two reference fuels used in the experimental determination of the cetane number: a linear-chain hydrocarbon, hexadecane \( \text{C}_{16}\text{H}_{34}, \) also called n-cetane, very sensitive to ignition, having a cetane number of 100, and a strongly branched-chain hydrocarbon, \( 2,2,4,4,6,8,8\)-heptamethylnonane (HMN, also called isocetane), having the same chemical formula \( \text{C}_{16}\text{H}_{34}, \) with high resistance to ignition, having a cetane number of 15. The cetane number is the percentage by volume of normal cetane in a mixture of normal cetane and heptamethylnonane, which has the same ignition characteristics as the test fuel. Thus, the cetane number is given by the formula:

\[ \text{CN} = \text{n-cetane} \% \text{, v/v} + 0.15 \times \text{HMN} \% \text{, v/v}. \]

Determination of the cetane number on the monocylinder engine specially designed for this purpose (EN ISO 5165, ASTM D613) is an expensive and lengthy operation. A cheaper and faster alternative is to determine the derived cetane number through ignition delay in a constant-volume combustion chamber (ignition quality tester – IQT), a widely accepted method described in ASTM D6890 and ASTM D7170, accepted by the biodiesel quality standard ASTM D6751. The cetane number indicates ignition delay, i.e. the time elapsed since the injection of fuel into the combustion chamber and self-ignition of the fuel-air mixture. Thus, ignition time lag means a low cetane number and vice versa. The upper and lower limits of the cetane number ensure the proper functioning of the engine. If the cetane number is too low, start of the engine will be difficult, especially at low temperatures, the engine will function unevenly and noisily, with cycles without combustion, it will warm more slowly, combustion will be incomplete and engine pollution will increase, especially hydrocarbon emissions. In case of a fuel with a very high cetane number, ignition will be carried out before a proper mix with air, resulting in incomplete combustion and the increase of the amount of exhaust smoke. In addition, if the cetane number is too high the fuel will ignite close to the injector causing it to overheat, and unburned fuel particles can plug the injector nozzles. The optimal range of the cetane number is between 41 and 56, but must not be higher than 65 [31].

The minimum cetane number of biodiesel is 51 in the European Union, 47 in the United States and 45 in Brazil. The minimum cetane number for diesel oil is 40 in the USA (ASTM D 975) and 51 in Europe (EN 590) [32, 33]. The cetane number of a substance depends on its molecular structure.
The cetane number decreases with the number of double bonds, nd, in fatty acid ester molecules (degree of unsaturation, characterized by the iodine number) and increases with the number of carbon atoms, nc. Generally, the cetane number of ethyl esters is higher than that of methyl esters. Methyl- and ethyl palmate as well as methyl- and ethyl stearate have a high cetane number, but methyl- and ethyl linoleate has a low cetane number. The cetane number of biodiesel depends on the concentration of the esters it is made up of. The cetane number of biodiesels is higher than that of the vegetable oils from which they are produced (34.6 < CN < 42), and is between 39 and 67 [33-37].

3. The cetane number prediction model

Cetane number is a dimensionless parameter used to correlate the ignition delay time of a fuel upon injection into the combustion chamber. A high cetane number implies a shortening of the ignition delay time, and is correlated with reduced nitrogen oxides (NOx) exhaust emission [38]. Biodiesel has several advantages in comparison to mineral diesel, but a prominent exception is its NOx exhaust emission rate [22, 38, 39] who chose model procedure, obtained interesting results. They have correlated the cetane number of single mono-alkyl esters of fatty acids and their mixtures (biodiesels) with structural characteristics achieved by Hydrogen Nuclear Magnetic Resonance spectra. This was done through the application of a three stages process, combining statistical tools, fuzzy logic and artificial neural networks. Fatty acid esters were prepared by alkylation of the fatty acid potassium salt by the corresponding alkyl bromide in N,N-dimethylformamide. Hydrogen Nuclear Magnetic Resonance spectral data from Spectral Database for Organic Compounds (SDBS), as well as Hydrogen Nuclear Magnetic Resonance spectra simulated with gNMR 5.0.6 [40] were used as well. Data processing was carried out with the software R, an environment for statistical computing and graphics [41], and related packages (stats, cluster and ANN) developed by R users community. R is freely distributed under GNU General Public License, with thorough documentation, and supported by a highly active user’s network. Data processing was developed in three steps: exploratory analysis through PCA, data set categorization through Fuzzy Clustering, predictive modeling through a back propagation Neural Network. The data set was composed by chemical shift and signal integration of 35 fatty esters. The study of Hafizil et al. [16] presents the results of seven types of fuel. The study includes mineral diesel, biodiesel (B100), B20 (biodiesel 20% blend with 80% mineral diesel), B20 E5 (biodiesel 20% blend with 80% mineral diesel and 5% ethanol), B20 E10 (biodiesel 20% blend with 80% mineral diesel and 10% ethanol), B20 M5 (biodiesel 20% blend with 80% mineral diesel and 5% methanol) and B20 M10 (biodiesel 20% blend with 80% mineral diesel and 10% methanol). All the test methods are conformed to the strict ASTM procedures as recommended by manufacturers. Those tests were conducted under controlled room temperature, pressure and relative humidity to ensure that the result is not influenced from environmental errors. The cetane number of the biodiesel is significanly higher when compared to mineral diesel. The mineral diesel has the lowest cetane number value of 71.6 while the biodiesel B100 has the highest of 98. The cetane number is increasing with an increasing percentage of biodiesel in blend. This is because the cetane number of biodiesel depends on the distribution of fatty acids in the original oil or fat. Despite all problems concerning to fatty acid composition described above, structural variation at the fatty acid moiety is somewhat limited. Typical variation is observed at carbon chain length (C16–C22), presence of one or more C=C cis double bond, and the presence of hydroxyl group (usually at position 9) [2, 9, 42, 43]. Oxidation rates of organic compounds have a good correlation with the strengths of the weakest C-H bonds in the molecule [44, 45]. Considering these two points, Nadai et al. [22] aimed to correlate the effect of these structural variations with the C-H bond weakening and then infer fatty ester and biodiesel cetane number. In order to increase the usefulness of this approach, we also have drawn a parallel between C-H bond strength and its chemical shift in Hydrogen Nuclear Magnetic Resonance spectra. Hydrogen Nuclear Magnetic Resonance spectra spectroscopy furnishes good quantitation of fatty acid composition.
4. Conclusion

a) Biodiesel is stated at European Union technical regulation EN 14214 (2005) for European conditions.

b) Biodiesel is actually a less complex mixture than petrodiesel, but different feedstock origins and the effect of seasonality may impose difficulties in fuel quality control. Since biodiesel is an alternative diesel fuel derived from the transesterification of triacylglycerol comprised materials, such as vegetable oils or animal fats, with simple alcohols to furnish the corresponding mono-alkyl esters, its composition depends on the raw material used, the cultivated area location, and harvest time.

c) Cetane number is the ignition quality indicator of the fuel. It defines whether the fuel has longer or shorter ignition delay during the combustion period. An increase in cetane number is because the carbon chain length increases. Typical diesel engines accept the cetane number between 40 and 55 while below 38, a more rapid increase in ignition delay is occurred.

d) One of the most important fuel quality indicators is the cetane number; however its experimental determination may be an expensive and lengthy task.

e) Interesting results were obtained by model procedure. The cetane number of single mono-alkyl esters of fatty acids and their mixtures (biodiesels) was correlated with structural characteristics achieved by hydrogen nuclear magnetic resonance spectra. This was done through the application of a three stages process, combining statistical tools, fuzzy logic and artificial neural networks.

f) Processing of literature knowledge provide relevant information for the further development of analytical models addressing the quality of biofuels.

Acknowledgements

Study was elaborated within the Grant project of Ministry of Education of the Slovak republic VEGA 1/0857/12 „Reduction of unfavourable impacts of agriculture and transport machinery on environment”. The research leading to these results has received funding from the European Community under project no 26220220180: Building Research Centre “AgroBioTech”.

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