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Investigation of the effects of the fatty acid profile on fuel properties using a multi-criteria decision analysis

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ABSTRACT

The structural features of fatty acids in biodiesel, including degree of unsaturation, percentage of saturated fatty acids and average chain length, influence important fuel properties such as cetane number, iodine value, density, kinematic viscosity, higher heating value and oxidation stability. The composition of fatty acid esters within the fuel should therefore be in the correct ratio to ensure fuel properties are within international biodiesel standards such as ASTM 6751 or EN 14214. This study scrutinises the influence of fatty acid composition and individual fatty acids on fuel properties. Fuel properties were estimated based on published equations, and measured according to standard procedure ASTM D6751 and EN 14214 to confirm the influences of the fatty acid profile. Based on fatty acid profile-derived calculations, the cetane number of the microalgal biodiesel was estimated to be 11.6, but measured 46.5, which emphasises the uncertainty of the method used for cetane number calculation. Multi-criteria decision analysis (MCDA), PROMETHEE–GAIA, was used to determine the influence of individual fatty acids on fuel properties in the GAIA plane. Polyunsaturated fatty acids increased the iodine value and had a negative influence on cetane number. Kinematic viscosity was negatively influenced by some long chain polyunsaturated fatty acids such as C20:5 and C22:6 and some of the more common saturated fatty acids C14:0 and C18:0. The positive impact of average chain length on higher heating value was also confirmed in the GAIA plane.

1. Introduction

Biodiesel is a mixture of fatty acid alkyl esters produced by transesterification of animal fat or vegetable oil [1]. Biodiesel standards ASTM D6751 (American Society for Testing and Materials) and EN 14214 (European Standard) were introduced to ensure high product quality and to improve consumer confidence [2]. The use of neat fatty acid methyl esters (FAME), or as a blend with petroleum diesel, is a promising alternative to the use of pure petroleum diesel because it is renewable, reduces emissions of particulate matter, hydrocarbons, carbon monoxide, and life cycle net carbon dioxide emission [3–7].

The suitability of a vegetable oil for biodiesel ultimately depends on its fatty acid composition and many of the fuel properties are determined by the structure of the fatty esters comprising biodiesel [2,8,9]. These fatty acid ester-influenced biodiesel fuel properties include cetane number (CN), iodine value (IV), higher heating value (HHV), density (ρ), kinematic viscosity (KV), cold filter plugging point (CFPP) and oxidation stability (OS). The influence of fatty acid composition on fuel properties CN, IV, CFPP, ρ, KV and HHV were explained in previous work [10] using PROMETHEE–GAIA. A variety of multi-criteria decision analysis (MCDA) software, e.g. ELECTRE, PROMETHEE and REGIME, are being used in different research fields. However, PROMETHEE–GAIA has significant advantages (compared to other MCDA programs), facilitating rational decision making processes [11]. Recently, PROMETHEE was used for selecting microalgae species, and evaluating the biodiesel production process [12,13]. All these fuel properties were estimated using algorithms from literature [14,15] and included microalgae feedstocks with similar fatty acid

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Nomenclature

ASTM	American Society for testing and materials	KV	kinematic viscosity ($mm^2\ s^{-1}$)
ACL	average chain length	MAME	microalgae methyl ester
CFPP	cold filter plugging point (°C)	MUFA	monounsaturated fatty acid
CN	cetane number	OS	oxidation stability (h)
CNL	canola	POME	palm oil methyl ester
CSO	cotton seed oil	PUFA	polyunsaturated fatty acid
DU	degree of unsaturation	SFAs	saturated fatty acids
FAME	fatty acid methyl ester	WCO	waste cooking oil
HHV	higher heating value ($MJ\ kg^{-1}$)	P	density ($g\ cm^{-3}$)
IV	iodine value ($g\ I_2 100\ g^{-1}$)		

composition. However, this study investigates the influence of individual fatty acids on measured fuel properties from nine different feedstoks (8 from non-algae, 1 from algae) to identify the accuracy of the algorithms over a wide range of carbon chain length.

The CN is one of the important indicative parameters for combustion characterisation of fuel [6,16]. The ASTM D613 is a widely recognised standard for CN testing, but there are some drawbacks including the large amount (~1 L) of fuel sample required, the time consumed, high reproducibility error and relatively high cost [17]. To reduce the time and cost for CN testing, several equations have been published to predict the CN, based on the fatty acid composition in the biodiesel all correlating a CN increase with increased carbon chain length, molecular weight and decrease with number of double bonds in the FAME profile [14,15,18,19]. This study investigates the goodness of fit between the estimated CN and the measured CN according to DIN 51773 in order to answer the question as to whether the CN can be accurately predicted based on fatty acid ester-based calculations.

Another important parameter for biodiesel is density (ρ), because the injection system pumps and the injector should deliver the appropriate amounts of fuel for complete combustion [20,21]. It has been shown that ρ is the most influential parameter for the amount of mass injection [22,23]. Several models for calculating ρ for biodiesel fuel [15,24,25] have been proposed and reported that ρ increases with increasing amounts of double bonds in the FAME profile. In this study, the ρ of FAME was estimated from mass fraction of each fatty acid and compared with the measured value according to ASTM D4052 [15]. PROMETHEE–GAIA was then used to assess the influence of each fatty acid on fuel properties.

The higher viscosity of neat vegetable oils or fats compared to petroleum diesel is the main reason for transesterification to reduce the KV before use in engines [26]. Despite transesterification, the viscosities of biodiesel are still slightly higher than petroleum diesel. The influence of fatty acid composition on viscosity has been discussed in the literature [15,27–30]. The structural features of fatty acids, such as chain length and degree of unsaturation (DU), have a positive influence on KV of the biodiesel. The present work investigates the influence of fatty acid structure between estimated [15] and measured kinematic viscosities according to ASTM D445.

The higher heating value (HHV) of biodiesel is an important parameter, which can be predicted from the chemical composition of biodiesel. The HHV of biodiesel is around 10% lower than petroleum diesel (44 $MJ\ kg^{-1}$). The HHV, also called the gross calorific value of fuel, considers the complete combustion of fuel with all carbon converted to CO_2 and all hydrogen to H_2O [31]. Numerous works have been published to relate the HHV of fuel to the chemical compositions (amount of carbon, hydrogen, nitrogen, oxygen) and reported an increase in HHV with increasing amounts of increased average chain length of the fatty acid profiles [15,32–35]. This work presents the influence of individual fatty acids and their composition in a fuel to the estimated [15] and measured HHVs according to ASTM D 240-09. The oxidation stability (OS) and iodine value (IV) of biodiesel are two important properties which are directly related to the amount of unsaturated fatty acid methyl esters. It has been reported that the IV increases linearly with DU, whereas OS decreases linearly with an increase in polyunsaturated fatty acids [36,37].

2. Materials and method

2.1. Materials

Nine types of FAME from different sources – 1 animal fat, 7 plant oils (4 fractionated palm oils, canola, cotton seed oil, waste cooking oil) and 1 microalgal oil (*Crypthecodinium cohnii)* – were investigated in this study. Microalgae fatty acid methyl esters (MAME) were derived from extracted lipids in a pilot scale extraction process, whereas canola oil methyl esters (CNL), tallow and four different fractionated palm oil methyl esters (POME) named by their dominant carbon chain lengths, i.e. POME810, POME1214, POME1618, and POME1822 [38] were collected commercially from Procter and Gamble Chemicals. The detailed fatty acid methyl ester composition is shown in Table 1. Waste cooking oil biodiesel (WCO) and cotton seed oil biodiesel (CSO) were supplied by EcoTech biodiesel, and the Centre for Tropical Crops and Biocommodities (CTCB), Australia, respectively. The detailed procedure for the transesterification of microalgal lipids is described in [39].

2.2. Methyl ester property analysis

Physical and chemical properties such as CN, ρ, KV, and HHV were measured following standard DIN 51773, ASTM D4052, and ASTM D445 respectively. Along with these properties, OS and IV were also estimated from the fatty acid profile of all FAMEs (Table 1). FAME analysis was carried out as per literature [40] in scan-mode, on an Agilent 7890 GC equipped with a flame ionisation detector (FID) and connected to an Agilent 5975C electron ionisation (EI) turbo mass spectrometer (Agilent Technology Australia Pty Ltd.). The detailed process of fatty acid peak identification is outlined in literature [41].

Fuel properties, CN, ρ, KV, HHV, IV and OS, were estimated using empirical equations proposed by [6,15,36,14] and compared with measured values of CN, ρ, KV, HHV to assess the accuracy of proposed calculation methods. PROMETHEE–GAIA (a multi-criteria analysis) was used to determine the influence of individual FAMEs on particular fuel properties and to identify estimation methods that did not accurately predict fuel properties. Biodiesel names were set to "action" whereas fuel properties and individual FAMES were set to "criteria" in PROMETHEE. The preference functions of all criteria were selected as "V-shape" and modelled as