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Fatty acid based prediction models for biodiesel properties incorporating compositional uncertainty

Carla Caldeira [a,b,*], Fausto Freire [a], Elsa A. Olivetti [c], Randolph Kirchain [d]

[a] ADAI-LAETA Department of Mechanical Engineering, University of Coimbra, Pólo II, Rua Luís Reis Santos, 3030-788 Coimbra, Portugal
[b] INESC Coimbra, University of Coimbra, Pólo II, Rua Sílvio Lima, 3030-290, Portugal
[c] Department of Materials Science & Engineering, Massachusetts Institute of Technology, MA, USA
[d] Materials Systems Laboratory, Massachusetts Institute of Technology, MA, USA

HIGHLIGHTS

- Uncertainty was integrated in prediction models for biodiesel properties.
- 3 virgin oils and a waste oil were used to assess the models.
- The models results present lower variation than the reference values.
- Prediction models should report information on model uncertainty.

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ABSTRACT

Biodiesel is globally produced by transesterification of vegetable oils. Each vegetable oil possesses a typical fatty acid (FA) profile that will influence the final properties of the biodiesel. Models have been developed to express the relationship between the FA composition and the fuel properties. However, as the FA sources are variable and because the chemical composition of a FA source are not always fully characterized, this variability translates into uncertainty for the production planner. This paper explores the underlying variability associated with the FA composition and assesses the results of these models incorporating FA compositional uncertainty. Models for viscosity, density, cetane number, iodine value, cold filter plugging point and oxidative stability were considered. The potential range of properties given by the models was compared with values reported in the literature. The main goal is to assess the influence of compositional uncertainty and the potential existence of systematic deviations in the results provided by these models. This assessment can be used to improve production plans with tools that account for compositional uncertainty and variability, allowing the biodiesel producer planner to determine blends that minimize the risk of noncompliance with the technical requirements.

1. Introduction

According to the OECD-FAO outlook 2011–2020, biodiesel use in the European Union (EU) will increase by almost 85% over the projection period, and more than 75% of global biodiesel production is expected to come from vegetable oil in 2020 [1]. Each vegetable oil possesses a typical fatty acid (FA) profile that will influence the final properties of the biodiesel. It is generally assumed that FA compositional profiles remain unchanged during conversion of the feedstocks to fuels via transesterification [2]. For this reason, the biodiesel properties are directly related to the FA profile [3].

The modification of the final FA composition can lead to a specific value for a property of the biodiesel to guarantee its compliance with quality standards (that ensure that the biodiesel has quality to be used as automotive diesel fuel) like ASTM D6751 [4] and EN 14214 [5]. This can be done by blending different vegetable oils that used individually would not comply with the standard for a specific property. However, as the FA sources are variable and because the chemical composition of a FA source are not always fully characterized, this variability translates into uncertainty for the production planner in determining quantity and types of oils to blend. Different growing conditions, geographical location,

* Corresponding author at: ADAI-LAETA Department of Mechanical Engineering, University of Coimbra, Pólo II, Rua Luís Reis Santos, 3030-788 Coimbra, Portugal.
E-mail addresses: carla.caldeira@dem.uc.pt (C. Caldeira), fausto.freire@dem.uc.pt (F. Freire), elsao@mit.edu (E.A. Olivetti), kirchain@mit.edu (R. Kirchain).

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harvest times, etc. can influence maturity of the crop and seed and thus the fatty acid composition [2]. Models have been developed that express the relation between the FA composition and biodiesel properties showing agreement with experimental data [6–14]. Nevertheless, these models provide deterministic results and do not explore the underlying variability associated to the FA composition. This paper analyzes the results of prediction models for biodiesel properties that are directly based on the FA composition, integrating the FA compositional uncertainty. The main goal is to provide a quantified range of the variation of the model results when considering the uncertainty in the FA composition and show how the different composition-based models available in the literature reflect the FA composition. We selected three feedstocks widely used in biodiesel production: palm, rapeseed and soya, and a secondary material that possesses higher compositional variability due to diverse origin of sources [2] and has been gaining prominence as a feedstock for biodiesel production: waste cooking oil (WCO). We firstly performed a review on prediction models for biodiesel properties that are directly related to the FA composition (presented in Section 2); secondly, we determined the range of values of the models incorporating the FA composition uncertainty and finally, we compared the results of the models with reported values in the literature (designated in this paper as reference values). With this analysis we assess the influence of the compositional uncertainty and the potential existence of systematic deviations in the results provided by these models. This assessment can be used to improve production plans with tools that account for compositional uncertainty. This information can be integrated in stochastic optimization models allowing the producer planner to determine the optimal blend that minimizes the risk of noncompliance with the technical requirements. This becomes even more relevant if the producer wants to use feedstocks such as waste cooking oils (WCO) that possess high compositional uncertainty.

2. Material and methods

The following two sections present a review of existing prediction models that are directly related to the FA composition (Section 2.1) and the procedure followed to integrate the FA compositional uncertainty in the models (Section 2.2).

2.1. Prediction models for biodiesel properties

The most common process to produce biodiesel is by transesterification of vegetable oils. Vegetable oils are mainly composed of triglycerides, an ester derived from glycerol and three fatty acids (FA). Transesterification is the reaction of a triglyceride and an alcohol in the presence of a catalyst to produce esters of fatty acids and glycerol [15]. The most used alcohol in the transesterification reaction is methanol and in this case, the biodiesel is a fatty acid methyl ester (FAME). Since the FA compositional profiles remain unchanged during conversion of the feedstocks to fuels via transesterification, the biodiesel properties are directly related to the FA profile [2]. Biodiesel properties that are directly related with the FA profile are: viscosity, density, cetane number (CN), iodine value (IV), cloud point (CP), pour point (PP), cold filter plugging point (CFPP), and heating value (HHV) [16]. Oxidative stability (OS) is related to the FA composition but it is also influenced significantly by the conditions that biodiesel is exposed during storage, transport and handling (e.g. light, temperature). Moreover, this property can also be modified by anti-oxidant additives [2,15,17]. In the following subsections we present a short description of the features that influence these properties and the prediction models found in the literature.

2.1.1. Viscosity

Viscosity measures the resistance to flow of a liquid due to internal friction of one part of a fluid moving over another at a given temperature [15]. Biodiesel viscosity is higher than diesel and it affects the behavior of fuel injection. Kinematic viscosity (at 40 °C) is limited to 3.5–5.0 mm^2s^{-1} in EN 14214 and 1.9–6.0 $mm^2\ s^{-1}$ in ASTM D6751.

Chemical features that influence viscosity are: (i) Carbon chain length and molecular weight: the increase in the length chain (of the FA and of the alcohol segment) and molecular weight increases the degree of intermolecular interactions and consequently, the viscosity. This effect becomes more evident at lower temperatures, where the molecular movements are even more restricted [18,19]; (ii) Presence of double-bonds and their configuration (viscosity increases with increasing degree of saturation and trans-configuration) [18]. Prediction models for viscosity based on the FA composition applying a logarithmic equation were investigated by Allen et al. [20] and Rabelo et al. [21] and verified by Noor et al. [22] and Boyak et al. [23]. Ceriani et al. [24] proposed a group contribution method based model to predict the viscosity of fatty acid esters. A set of parameters for the description of the viscosity of pure FAMEs was presented by Krisnangkura et al. [25]. Yuan at al. [26] presented a model to describe the relationship between viscosity-temperature of pure FAME based on the Vogel Tammann-Fulcher (VTF) equation where the equation parameters were determined by fitting experimental viscosity data. The viscosity of biodiesel based on FAME composition was then determined through the mixture model (1), where η_m is the dynamic viscosity of the mixture, η_{FA} is the dynamic viscosity of an single compound, and x_{FA} is the mole fraction.

$$\ln \eta_m = \sum_{FA} x_{FA} \ln \eta_{FA} \quad (1)$$

Freitas et al. [13], proposed a revision of the Yuan et al. model and calculated results for several biodiesel systems with a higher correlation with the experimental data: an average deviation of 4.65%, compared to 5.34% for Yuan's model, 8.07% for Ceriani's model, and 7.25% for Krisnangkura's model. In the revised Yuan's model the parameters of the VTF model were refitted. Since the model provides dynamic viscosities, their conversion into kinematic viscosities was performed by considering the density data for pure FAMEs reported by Pratas et al. [8].

A similar approach was taken by Knothe & Steidley [12] that predicted the kinematic viscosity of several biodiesels from the kinematic viscosity values of the single components. No composition-based model for viscosity prediction that presents an explicit relation with the FA compositions was found in the literature. All models are based on the weighed sum of the viscosity of each FAME.

The revised version of Yuan's model [13] was applied in this work.

2.1.2. Density

The density of a fuel is critical to determine the quantity of mass injected and consequently, the air–fuel ratio and energy content within the combustion chamber. Density is limited to 860–900 kg m^{-3} at 15 °C in EN 14214 but there is no specification for density in the ASTM D6751. Biodiesel density is affected by: (i) chain length, with higher chain length leading to lower fuel density and (ii) degree of unsaturation, with higher unsaturation leading to increased density [15].

In the research developed by Pratas et al. [27], three versions of Kay's mixing rules and two versions of the group contribution GCVOL model to predict biodiesel density were investigated. It is shown that Kay's mixing rules and the revised form of the GCVOL