Fuel 103 (2013) 232–238

Contents lists available at SciVerse ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Density of alkyl esters and its mixtures: A comparison and improvement of predictive models

Manuel García *, Juan-José Alba, Alberto Gonzalo, José Luis Sánchez, Jesús Arauzo

Thermochemical Processes Research Group (GPT), University of Zaragoza, Mariano Esquillor s/n, I+D Bld., 50018 Zaragoza, Spain
Aragón Institute of Engineering Research (I3A), Universidad de Zaragoza, Mariano Esquillor s/n, I+D Bld., 50018 Zaragoza, Spain

HIGHLIGHTS

- The aim of this work is to improve existing models to predict biodiesel density.
- New density data with methanol and ethanol and detailed composition are presented.
- A correlation for biodiesel acentric factor has been developed for theoretical prediction.
- A ethanol biodiesel density empirical model is proposed.

ARTICLE INFO

Article history:
Received 27 February 2012
Received in revised form 8 June 2012
Accepted 19 July 2012
Available online 10 August 2012

Keywords:
Biodiesel
Density
Modeling
FAME
FAEE

ABSTRACT

Biodiesel density is a key parameter in biodiesel simulations and process development. In this work we selected, evaluated and improved two density models; one theoretical (Rackett–Soave) and one empirical (Lapuerta's method) for methanol based biodiesels (FAME) and ethanol based biodiesel (FAEE). For this purpose, biodiesel was produced from vegetable oils (sunflower, rapeseed, soybean, olive, safflower and two other commercial mixtures of vegetable oils) and animal fats (edible and crude pork fat and beef tallow) using both methanol and ethanol for the transesterification reactions, and blended to get 21 FAME and 21 FAEE, reporting their density and detailed composition. Bibliographic data have also been used. The Rackett–Soave method has been improved by the use of a new acentric factor correlation, whereas the parameters of the empirical one are improved by considering a bigger density data bank. Results show that the evaluated models could be used to estimate the biodiesel density with a good grade of accuracy but the performed modifications improve the accuracy of the models: ARD (%) for FAME; 0.33, and FAEE; 0.26, both calculated with the modification of Rackett–Soave method and ARD (%) for FAME; 0.40 calculated with the modification of Lapuerta's method.

1. Introduction

The physicochemical properties of biodiesel have attracted much attention in the last years. As a mixture of different alkyl esters, fatty acid methyl esters (FAMEs) or fatty acid ethyl esters (FAEEs), biodiesel composition depends on the raw materials that are used. Vegetal oils and some kinds of animal tallows are typically used [1] to produce biodiesel but depending on the composition of the used raw materials, biodiesel properties can show a low quality performance in some aspects.

For its commercialization, biodiesel must fulfill the conditions established by relevant standards, such as EN 14214:2008 + A1:2009 (EU) or ASTM 6751-07 (USA). In addition, the raw materials cost represents more than 80% of the total, [2] which is why the search of new triglycerides sources [1,3] is currently a major issue.

Modeling the final properties of biodiesel could be an interesting tool to find a combination of low-cost raw materials which can be used to produce biodiesel within the ranges established by quality standards. Along these lines, many papers dealing with modeling and estimation of physical properties of biodiesel can be found in available literature. Some properties such as cetane number [4] and iodine value [5] can be estimated by using empirical correlations, as well as Cold Filter Plug Point or Cloud Point [6,7]. A comprehensive study of prediction models for biodiesel properties, including density, was conducted by Su et al. [8].

Biodiesel density is an important variable which has strong influence in the combustion process, engine injection system [9] and spray atomization. The presence of biodiesel in diesel blends affects the fuel thermophysical properties in a high degree and that

* Corresponding author at: Thermochemical Processes Research Group (GPT), University of Zaragoza, Mariano Esquillor s/n, I+D Bld., 50018 Zaragoza, Spain. Tel.: +34 976 762961; fax: +34 976 761879.
E-mail address: manuelgr@unizar.es (M. García).

0016-2361/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.fuel.2012.07.049

Nomenclature

Abbreviations

FAME	fatty acid methyl esters
FAEE	fatty acid ethyl esters
FFA	free fatty acid
UD	unsaturation degree
LC	length chain
RD (%)	relative deviation
ARD (%)	average relative deviation
LP	Lapuerta's Method

Greeks symbols

ω	acentric factor
ρ	density (g cm^{-3})

Symbols

T	temperature (K)
P	pressure (kPa)
V	volume (m^3 mol^{-1})
R	universal gas constant (J K^{-1} mol^{-1})
Z_{Ra}	compressibility factor
MW	mass weight (g mol^{-1})

Subscripts

nb	normal boiling point
atm	atmospheric
c	critical
r	reduced
m	relative to mixture
i	component i

influence must be taken into account in all estimations and technical calculations such as combustion models, atomization and combustion processes [10]. Moreover, density values are needed to design the biodiesel production process including separation units, such as decanters, centrifugal units, distillation columns and piping. For that reason a prediction tool, capable of estimating the biodiesel density, could be a very useful way to improve the commercial and production strategies by selecting the raw materials prior to the biodiesel production.

In order to estimate biodiesel density two different methodologies are typically used; theoretically based approaches and empirical or semi-empirically based correlations.

One of the most commonly employed methods for estimating the saturated liquid density is the Rackett equation and its modifications [11]. A summary of works dealing with biodiesel density estimation using this method was reported in our previous work [12].

Reid et al. [13] summarize a number of theoretical methods for estimating the saturated liquid density. The Hankinson and Thomson method was modified by Thomson et al. [14] to allow the prediction of compressed liquid volumes and comprises a set of equations in terms of critical properties, tabulated constants and a specially computed acentric factor. Another significant method is the Bhirud [15] method for nonpolar fluids. Using a group contribution method, Elbro et al. [16] reported a method for the prediction of liquid densities as a function of temperature from the triple point to the normal boiling point.

The theoretical models discussed in the previous paragraphs have been developed for the estimation of the density of any liquid, regardless of its composition and origin. A different approach is the use of empirical models or correlations specifically fitted for biodiesel. Just as the theoretical models, the empirical ones use composition as input, and additionally, can use other empirical measurements or composition/structural derived coefficients and improve the accuracy of the predicted density.

The existing models in the literature for estimating biodiesel density are generally based on the composition of biodiesel, usually taking into account the influence of temperature. A summary of equations which represent the dependency of density with temperature was reported by Lapuerta et al. [9]. Moreover, they proposed an equation in terms of the number of atoms in the original alcohol, the number of atoms in the original fatty acid and the number of double bonds in the fatty acid molecule (they use the average values for different biodiesels). The coefficients of the equation were correlated using data available in literature reported by Sanford et al. [17].

Other empirical models have also been used to predict the density of biodiesel–diesel blends. Alptekin and Canacki [18] and Yoon et al. [19] reported models for predicting sunflower, soybean, canola, corn, cottonseed, and waste palm biodiesels–diesel blends. The methodology of these models usually deals with the correlation of experimental data using a linear or polynomial equation. In the same way, Ramírez-Verduzco et al. [20] reported a simple empirical correlation to predict the density of biodiesel blends at various temperatures, which is characterized by only three adjustable parameters.

Recently, artificial neural networks (ANNs) have been used for predicting the final properties of biodiesel with good results [21]. In the same way, Baroutian et al. [22] used an ANN in order to model the temperature dependency of palm oil based biodiesel density.

In this work, a comparison and validation of different selected models (explained in following sections) to estimate biodiesel (FAME and FAEE) density were performed at the temperature established by standards EN 14214 and ASTM 6751 (15 °C).

In order to achieve representative results, biodiesels departing from different raw materials have been produced, mixed and the ester profile and density were analyzed. A bibliographical search was carried out in order to expand the data bank with the aim of selecting the most accurate estimation model for biodiesel density, for both, methanol and ethanol based biodiesel. Using the new experimental data and the bibliographical ones, the reported models were tested and some modifications were introduced in order to improve its accuracy.

2. Materials and methods

2.1. Materials and biodiesel preparation

Sunflower, rapeseed, soybean, olive, safflower and other two kinds of vegetable oils (mixtures of vegetable oils) were purchased, mixed and used directly. Three different animal raw materials were used in this work: commercial edible pork fat, which was purchased and used directly, crude pork fat, which was provided by the Spanish company LIPSA (Santa Perpetua de Mogoda, Barcelona, Spain), and natural beef tallow, acquired in some slaughterhouses in Tudela (Navarra, Spain). Fat was extracted from this beef tallow by heating it and removing the solid residue. The obtained product was finally filtered and stored. The acid value of the animal fats was determined by volumetric titration according to the standard ISO 660 (2002) and all values were below 1 wt.% FFA.