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Variability in sunflower oil quality for biodiesel production: A simulation study

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ABSTRACT

Biodiesel is an alternative fuel made from vegetable oils or animal fats. The fatty acid composition of the feedstock, which varies among and within species, is the main determinant of biodiesel quality. In this work we analyze the variability in biodiesel quality (density, kinematic viscosity, heating value, cetane number and iodine value) obtained from sunflower oil, by means of a validated crop model that predicts the fatty acid composition of one high-oleic, and three traditional (high-linoleic) sunflower hybrids. The model was run with a 10-year average weather data from 56 weather stations in Argentina, and simulation results were compared to the biodiesel standards of Argentina, USA and Europe. We show that biodiesel produced from sunflower oil does not have one fixed quality, but different qualities depending on weather conditions and agricultural practices, and that intraspecific variation in biodiesel quality can be larger than interspecific differences. Our results suggest that (a) sunflower oil from high-oleic hybrids is suitable for biodiesel production (within limits of all analyzed standards), regardless of growing conditions and (b) sunflower oil from traditional hybrids is suitable for biodiesel production under the standards of Argentina and USA, while only certain hybrids grown in warm regions (e.g., Northern Argentina, Southern USA, China, India, Pakistan) are suitable for biodiesel production according to the European standard.

1. Introduction

Biodiesel is an alternative fuel that can be commercially produced from a variety of oils and fats. The literature abounds in descriptions of the quality of biodiesel obtained from different raw materials, without taking into account, in most cases that a great variation in quality can occur within a certain raw material, sometimes higher than among different raw materials. For instance, it is well-known that the fatty acid composition of sunflower oil, one of the main characteristics that determines its quality for biodiesel production, can vary according to the location and sowing date, and in different years. This is because the oleic/linoleic ratio depends on the temperature during the early stages of oil

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synthesis in the seeds [1]. Moreover, the effect of temperature can be different according to the genotype [2].

Despite the relative simplicity in its production, the importance of maintaining a high quality is similar than with any fuel used in modern diesel engines. An efficient agro-industrial production needs to well know the quality of raw materials that can be obtained in different regions during different moments of the year, as well as the ranges of variation of the quality in different years. This knowledge is helpful to determine if biodiesel produced from a given raw material could be within a given quality standard. Biodiesel standards have been established or are being developed in various countries and regions around the world [3]. These standards are based on the physical and chemical properties needed for satisfactory diesel engine operation.

Several quality parameters of biodiesel (e.g., density, kinematic viscosity, heating value, cetane number and iodine value) are highly dependent on fatty acid composition. Moreover, there are several well validated equations in the literature that allow to predict the above-mentioned parameters from the oil fatty acid composition. Recently, a simulation model of yield and grain and oil quality of sunflower has been established [4]. The model allows to simulate the effects of temperature and crop management on the oil fatty acid composition of a traditional sunflower cultivar. More recently, important differences in this response of oil fatty acid composition to temperature among sunflower hybrids were reported [2].

Integrating relationships between temperature and fatty acid composition, and relationships between fatty acid composition and fuel-quality parameters into a sunflower crop simulation model would allow to simulate the effect of cultivar selection in addition to the effect of other crop management practices (sowing date, sowing location) on the final quality of biodiesel. The objective of this work was to analyze the variability in the quality of biodiesel produced from sunflower oil, in different regions of Argentina (one of the main sunflower producing countries), different sowing dates, and for different cultivars. This was achieved by means of a crop simulation model adapted to simulate the genetic differences in the response of fatty acid composition to temperature, and validated by comparison to independent experimental data. Simulations were performed and biodiesel quality was assessed by comparing quality parameters to the two main standards (ASTM D6751 from the US, and EN 14214 from Europe) and to Argentina's standard (IRAM 6515-1).

2. Materials and methods

2.1. *The model*

We used a simulation model which can predict growth, development, yield and quality (including fatty acid composition) of a sunflower crop [4]. In this model, fatty acid composition of the oil is predicted through its relationship with the minimum temperature during a critical period of grain filling (between 100 and 300 degree-days after flowering) [2]. The timing of this period is dependent on phenological development, which is predicted through its relationship with temperature. In this model, fatty acid composition is not directly linked to other quality traits (e.g., grain size, oil content) or grain yield.

This model, established for only one hybrid (Dekalb G100), was recalibrated for the prediction of development and fatty acid composition of four sunflower hybrids: high-oleic hybrid 'Trisol 600', and traditional (high-linoleic) hybrids 'Paraíso 20', 'ACA885', and 'MG2'. These four hybrids have marked differences in fatty acid composition or in its response to minimum temperature [2].

Recalibration for the prediction of development was achieved by modifying the parameter which determines the amount of thermal time required for flowering. This parameter was estimated, for each of the 4 hybrids, from experimental data obtained in 16 experiments performed in 7 locations in Argentina (latitude ranging from 26 to 38°S) [2]. This parameter was found to be dependent on photoperiod at emergence, in a way similar to that found by authors of Ref. [5]. Therefore, a sigmoid curve was fitted to the relationship between the thermal time to flowering and the photoperiod at emergence, for each hybrid.

In order to predict the fatty acid composition (oleic, linoleic, stearic, and palmitic acids) for each hybrid, the model was recalibrated. The parameters of the equations which relate the fraction of oleic, linoleic, and stearic acids to the minimum temperature during the critical period (between 100 and 300 degree-days after flowering) were modified for each hybrid, according to Ref. [2]. The fraction of palmitic acid was fixed for each hybrid, with a value taken also from Ref. [2].

The predicted values of fatty acid composition obtained with the model were used for predicting quality properties of biodiesel: iodine number, kinematic viscosity, density, cetane number and higher heating value (or gross calorific value).

The density, heating value and cetane number of mixture were predicted using a simple linear mixing rule [6], based on the values of pure fatty acid methyl esters:

$$\delta_{mix} = \sum (A_i \times \delta_i), \quad (1)$$

$$H_{mix} = \sum (A_i \times H_i), \quad (2)$$

$$CN_{mix} = \sum (A_i \times CN_i), \quad (3)$$

in which δ_{mix}, H_{mix} and CN_{mix} are density, heating value and cetane number of biodiesel, respectively; A_i is the fraction of fatty acid, δ_i and H_i are the density and heating value [7] and CN_i the cetane number [8] of each pure fatty acid methyl ester.

A logarithmic rule was used for predicting the kinematic viscosity [6,9,10]. The following equation was used to predict the kinematic viscosity of biodiesel based on fatty acid methyl ester composition:

$$\ln(\upsilon_{mix}) = \sum [A_i \times \ln(\upsilon_i)], \quad (4)$$

where υ_{mix} is the kinematic viscosity of biodiesel, A_i is the fraction of each fatty acid, and υ_i is the kinematic viscosity of each pure fatty acid methyl ester [11].

The iodine value is a measure of the average amount of unsaturation of fats and oils and is expressed in terms of the number of centigrams of iodine absorbed per gram of sample (% iodine absorbed). Iodine value (IV) was calculated from the fatty acid methyl ester composition as follows: