Fuel 233 (2018) 497–503

Contents lists available at ScienceDirect

Fuel

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

Full Length Article

Thermophysical behavior of three algal biodiesels over wide ranges of pressure and temperature

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ARTICLE INFO

Keywords:
Biodiesel
Microalgae
Cyanobacteria
Density
Viscosity

ABSTRACT

The knowledge of density and viscosity is important both for the optimization of diesel engines operation and the fuel quality specification. To this end, the present work focuses on the study of these thermophysical properties for three algal biodiesels. The samples were produced by transesterification of dry biomass supplied from different microorganisms, the marine strain *Nannochloropsis gaditana*, the freshwater strain *Scenedesmus almeriensis* and the freshwater cyanobacteria *Spirulina platensis*. The protocol of production is detailed. The purity of biodiesels is low, ranging from 63,7% to 68,1% because the produced biodiesel was not purified in order to evaluate the characteristics of the crude biodiesel produced from microalgae. The relative new technique based on a simple process is attractive for an industrial point of view. The (FAMEs) profile of the biodiesels were characterized using a GC–MS technique. The density measurements were performed over expanded ranges of pressure [0,1–140 (MPa)] and temperatures [293,15 (K)–353,15 (K)] compatibles with their engines applications. The isothermal compressibility and the isobaric thermal expansion were estimated within the same experimental range by density differentiation. The cinematic viscosity was also measured for the three biodiesels at atmospheric pressure for temperatures ranging from 293.15 (K) to 353.15 (K). The storage stability of the biodiesels was assessed in terms of reproducibility of the measured properties. Spirulina biodiesel was not affected by oxidation process. Additionally, its density and viscosity values meet the standards specifications that support the use of this production process.

1. Introduction

The energy demand is continuously increasing due to the rapid development of new emergent economics. The global needs in energy are mainly supplied from fossil fuels although in the last years up to 19% of global energy demand is supplied from renewable sources, the enhancement of this percentage being a compromise of most of nations in worldwide. Both the high depletion rate of fossil fuels and the increasing emission of greenhouse gases, particularly CO_2, have incited much demand for alternative and renewable fuels especially for transport [1,2]. Among the alternative, biodiesel is of great prominence over petro-diesel considering safety, renewability, non-toxicity, and lubricating property. In this scenario, production of algal biodiesel received much attention due to their high biomass productivity (up to 100 t/ha·year), and lipid content (30–60%d.wt.) [3–5], thus it being proposed to achieve lipids productivities up to 40.000–50.000 L/ha·year [6]. Moreover, the production of lipid from microalgae have environmental advantages due to their ability to grow in contaminated waters, to sequester atmospheric CO_2, and to recover nutrients from wastewaters, in addition to their capacity to be produced in non-arable land and in continuous mode with low generation time for the development of sustainable fuel. However constrains also exist due the still high production cost and uncertainty about the quality of final biodiesel produced [6].

The physical and chemical properties of algal biodiesel depend on the type of strain and culture conditions, in addition to the downstream processing, both determining the fatty methyl ester composition and finally the fuel properties [7]. Production of freshwater strains is most recommendable because the fatty acids are mainly saturated and monounsaturated whereas using marine strains the content of polyunsaturated fatty acid increases; concerning culture conditions low dilution rates allows to increase the fatty acids content of the biomass the accumulation of saponifiable fatty acids increasing [8]. Different strategies has been proposed to produce biodiesel from microalgae, the most promising being the direct transesterification of biomass [9]. Although the thermophysical properties of biodiesel produced from a

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https://doi.org/10.1016/j.fuel.2018.06.091
Received 12 September 2017; Received in revised form 16 March 2018; Accepted 21 June 2018

wide variety of natural feedstock have been largely investigated, still the studies focusing on algal biodiesel remains scarce. Most of these studies are restricted to limited pressure and temperature ranges [10,11]. In order to size engines and injection systems, it is relevant to assess the accurate knowledge of the thermophysical properties within pressure and temperature conditions compatibles with the operating ranges.

Among them, density and compressibility are of importance to optimize the injection process. Density is the fundamental property that influences the conversion of volume flow rate into mass biodiesel flow rate [12] whereas the compressibility linked to a bulk modulus controls the fuel injection timing [13]. Density depends upon the raw materials used for biodiesel fuel production and the biodiesel methyl ester profile [14]. The knowledge of viscosity is also an important concern to automotive manufacturers as higher viscosity values tend to alter injection spray characteristics, resulting in fuel impregnement on the chamber [15]. So, fuel which is too highly viscous can damage the fuel pump.

In this context, this study details the main features of biodiesel produced from three selected microalgae. Biomass from three largely different microorganisms were used: (i) the marine strain Nannochloropsis gaditana, (ii) the freshwater strain Scenedesmus almeriensis and (iii) the freshwater cyanobacteria Spirulina platensis. Biodiesel was obtained from the three different biomasses by direct transesterification, using the same methodology and conditions, thus the quality of final biodiesel being only a function of composition of raw material used. The produced biodiesel was not purified in order to evaluate the characteristics of the crude biodiesel produced from microalgae. Very scarce information is available about the biodiesel produced from microalgae in spite that it has been widely reported that it could be easily produced. It is a relative new and simple process with good efficiency and interest from an industrial point of view. This work aims at characterizing theses biodiesel obtained from this particular production method using the thermophysical properties as main indicators. In this sense, density measurements were carried out within extended ranges of pressure (0.1–140 (MPa)) and temperature (293.15 K–353,15 K). The isothermal compressibility and the isobaric thermal expansion were derivated from the density measurements. The viscosity was also measured at atmospheric pressure on a wide temperature range (293,15 K–353,15 K). The reproducibility of these properties was checked for each sample thus assessing the storage stability of the microalgal biodiesel. Section 2 reports information on the materials production whereas section 3 details the experimental techniques and reports the whole results obtained for the thermophysical properties.

2. Materials and methods

2.1. Microalgae biomass

Biomass from three different microorganisms were used, the marine strain *Nannochloropsis gaditana*, the freshwater strain *Scenedesmus almeriensis* and the freshwater cyanobacteria *Spirulina platensis*. Biomass of *Spirulina platensis* was supplied by the company Biorizon (Almería, Spain) and it is produced in China using raceway reactors. Biomass of the other two microalgae was produced in industrial scale outdoor tubular photobioreactors (3 m^3), in continuous mode at 0.30 l/day dilution rate, on Almería (Spain) at research center Las Palmerillas from Fundación Cajamar [16]. Culture medium used was prepared on freshwater or seawater using fertilizers ($NaNO_3$, KH_2PO_4, micronutrients). The cultures were performed at pH = 8.0 by on-demand injection of CO_2, and temperature was controlled below 30 °C by passing thermostated water through a heat exchanger located inside the reactor. The biomass was daily harvested by centrifugation, then being lyophilized and stored at − 18 °C. Dry biomass was used as raw material whatever the microalgae/cyanobacteria used.

2.2. Production of biodiesel from microalgae

The production of biodiesel from microalgae biomass is performed by direct transesterification of dry biomass, by using methanol and sulfuric acid as alcohol and catalyst respectively, under inert nitrogen atmosphere conditions. The reaction is carried out in a 5 L stainless steel reactor, equipped with manometer and temperature sensors, and valves for the inlet and outlet of gases. Mixing is provided by a vertical stirrer (RZR2020 Heidolph) whereas temperature is controlled by Heat-On 5-Liter block (Heidolph).

To perform the reaction the first step is to prepare the methylation mixture. For this 85 mL of sulfuric acid (sulfuric acid 95–98% PRS, Panreac) is slowly added into 1700 mL of methanol (methanol 99.5% PRS, Panreac) under continuous stirring in the reactor, then 200 g of dry biomass being finally added. The second step is to perform the reaction. For this the reactor is closed, and nitrogen is inlet to create an inert atmosphere inside the air chamber, then temperature is increased up to 95 °C and maintained at this value for one hour, pressure increasing up to 3 bar. The third step is to cool the reaction mixture up to room temperature the pressure reducing till atmospheric value.

After reaction the biodiesel is extracted from the methanolic phase using hexane. For this 1700 mL of hexane (hexane 95% alkanes mixture PRS, Panreac) is added to the reactor and stirred gently for 20 min, then stirring being stopped and two phases appearing. Hexane phase is removed, then it being washed with 1700 mL of water. Finally hexane is removed by vacuum evaporation in a rotary evaporator at 80 °C and 20 mbar to obtain biodiesel product, which is weighted and analyzed.

2.3. Fatty acids analysis and evaluation of yield

The fatty acids content of whatever sample (biomass, biodiesel) is determined by gas-chromatography using flame ionization detection (GC-FID) (7683 Series Injector, 6890N Network GC system, Agilent Technologies, column Omegawax™250-Supelco) [17]. All the measurements are performed over fatty acids methyl esters (FAMEs), then the preparation of the sample is different according to nature of the sample. Biomass is methylated before GC-FID determination, while the biodiesel samples are only diluted in solvent and enriched with internal standard before GC-FID.

To evaluate the yield of the process different parameters are determined [18–20]. The conversion yield is determined as the ratio between the mass of FAMEs into biodiesel with respect to FAMEs from the biomass. The purity of biodiesel is determined as the ratio between the mass of FAMEs into biodiesel with respect to mass of biodiesel weighted. The FA extraction yield is determined as the ration between the total fatty acids into the biodiesel with respect to total fatty acids into the biomass. To determine the FA extraction yield it is necessary to perform an additional reaction of transesterification to biodiesel samples to ensure that no fatty acids remains as free fatty acids into the biodiesel sample. This parameter is the most relevant to evaluate the recovery of total fatty acids contained into the biomass, including if transesterification is not performed at 100% yield.

2.4. Analysis of FAME: analytical conditions

Fatty acid methyl esters (FAME) profile of the three biodiesel prepared from the three different microalgae *Nannochloropsis, Scenedesmus* and *Spirulina* were estimated using Thermo Scientific™ ISQ™ LT Single Quadrupole GC–MS System. The column used was Thermo Scientific™ Trace GOLD TG-5MS with dimension 0.25 μm thickness – 0.25 mm ID – 30 m length). The oven temperature was initially held at 160 °C for 2 min, increased to 180 °C at 2 °C/min and held for 2 min, increased continuously to 250 °C at 10 °C/min and then help for 2 min. The injector, transfer and source temperatures were 250 °C, 260 °C and 240 °C respectively. Carrier gas was helium and total scan time 24 min. EI mode of ionization was applied and mass scan rang was from 50 to