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Physical and chemical properties of fish oil biodiesel produced in Brazil

Gislaine Iastiaque Martins [a], Deonir Secco [a], Helton Aparecido Rosa [a,b,*], Reinaldo Aparecido Bariccatti [a], Bruna Dresch Dolci [a], Samuel Nelson Melegari de Souza [a], Reginaldo Ferreira Santos [a], Tiago Roque Benetoli da Silva [c], Flavio Gurgacz [a]

[a] UNIOESTE–State University of West Paraná–Post-graduation Program, Master Course of Energy in Agriculture, Rua Universitária, 2069, CEP: 85.819–130 Bairro Faculdade, Cascavel, Paraná, Brazil
[b] FAG-Assis Gurgacz Faculty, Cascavel, Paraná, Brazil
[c] Department of Agricultural Sciences, UEM-State University of Maringá, Maringá, Brazil

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ABSTRACT

Due to the energy crisis caused by the progressive depletion of fossil fuel sources, the search for alternative fuels from renewable sources is in growing demand. Therefore, the manufacturing of biodiesel from fish waste might help the environment as an alternative for the reduction of residues that are harmful if incorrectly disposed. Biodiesel from residual oil of tilapia waste was manufactured by means of transesterification, basic catalysis and methyl route. This study assessed mandatory parameters regulated by the Brazilian National Agency of Petroleum, Natural Gas and Biofuels (ANP) for biodiesel commercialization. It also determined values for specific mass, kinematic viscosity, water content, acidity level, flash point, oxidative stability and calorific value of fish oil biodiesel. Biodiesel calorific value analysis reported levels that are similar to those of diesel. Other parameters that characterize fish oil biodiesel physically and chemically according to specifications of ANP resolution No. 7/2008 were evaluated, and indicated that fish oil is a promising alternative for biodiesel manufacturing.

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1. Introduction

The main materials utilized in biodiesel production are vegetable oils such as soybean, sunflower, canola, castor bean and palm, as well as animal fats, such as beef tallow and poultry fat,

* Corresponding author at: UNIOESTE–State University of West Paraná– Post-graduation Program, Master Course of Power Engineering in Agriculture, Rua Universitária, 2069, CEP: 85.819–130 Bairro Faculdade, Cascavel, Paraná, Brazil. Tel.: 55 45 3220 3151.
E-mail address: helton.rosa@hotmail.com (H.A. Rosa).

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and also waste frying oil [1]. Most of biodiesel production comes from soybean oil, which provides more than 70% of feedstock.

The use of biofuels from vegetable and animal oils has been receiving more and more incentives from government institutions such as measures that put biodiesel in the market by means of its compulsory mix with diesel in gas stations [2].

In that sense, the development of alternative fuels from several renewable sources has drawn remarkable attention. One alternative is the use of residues originated from tilapia processing plants for biodiesel production [3].

Tilapia is the most processed freshwater fish in Brazil. It is processed as fresh or frozen fillets and presents an average fillet yield of approximately 30%, whereas the other 70% are residues that include head, skeleton, guts, skin and scales [4].

From the total fish caught, roughly 60% are used in the fresh fish market, processed as frozen, canned or smoked, generating a considerable volume of disposed material. It is estimated that the volume of residues generated by processing units reaches around half of the total production [5]. The production of tilapia in Brazil in 2013 is estimated to have exceeded 250,000 t, and it is an alternative to reduce the country's high dependence on the use of oleaginous species as raw material [6].

In Brazil, most oils used in biodiesel production come from traditional oilseeds; however, using only one raw material in such a diverse country as Brazil would certainly be a mistake. In Europe, the most used oil is extracted from colza due to lack of alternatives. Biodiesel is also manufactured from waste frying oil and fats. In Brazil, there are several possible alternatives, as shown in experiments carried out on oilseeds such as castor beans [7], soybeans [8], sunflower [9], cotton [10], canola [11], babassu [12], corn [13], beef tallow [14], fish and others [15].

Because of the variety of oils and fats and the convenience in manufacturing biodiesel, it is difficult to assure its quality, once that producing it in a way that meets all the compulsory parameters for its commercialization is complex. In Brazil, biodiesel is regulated by the National Petroleum Agency (ANP) [16]. The resolution of physicochemical features is done according to national standards of The Brazilian National Standards Organization (ABNT), as well as international standards of ASTM, ISO, and CEN [17].

Parameters associated to chemical features of the fuel can be evaluated by methods of analysis. Thus, it is important to gain the confidence of the market and automotive industry, ensuring the success of the new fuel. Some of the methods for physical-chemical biodiesel analysis are classic methods known for mineral diesel analysis. The remaining methods are analytical methods that have been employed for a long time in determining the quality of oils and fats [18].

Along with vegetable oils [19–21], fish oil presents great potential to be used as a substrate for biodiesel production, not only because of its lipid composition, which presents long chain fatty acids [22], but also for being abundant in Brazil. It is important to mention that fish oil is often in an advanced oxidation state, affected by the procedures employed in its handling, what may limit its usage as a substrate for biodiesel synthesis [23].

This study aimed to describe the physicochemical features of the fish-based biodiesel obtained from tilapia oil and check if it meets the standard requirements of ANP. Parameters such as specific mass, kinematic viscosity, water content, acidity level, flash point, oxidative stability and calorific value were assessed in order to provide enlightening results concerning to biodiesel quality.

2. Materials and methods

The experiment was carried out using tilapia oil provided by Consolata Agroindustrial Cooperative–COPACOL (Copacol Industrial Fish Unit), in Nova Aurora–PR. The oil was previously neutralized with NaOH 16% solution. To every 100 mL of oil, 4.0 mL of NaOH solution was added. It was then placed on a hot plate agitator for 15 minutes. When agitation was turned off, the solution was heated up to 60 °C. The neutralized oil was transferred to a glass funnel with a paper filter for complete draining. The filter was disposed alongside with the organic phase retained. During transesterification, the oil presented acidity level of 0.28 mg KOH g^{-1}.

The transesterification reaction was performed with an alkaline catalyst (potassium hydroxide-KOH) and methanol. A 5:1 M oil/methanol ratio was used, with 0.6% catalyst. The potassium methoxide solution previously prepared under mechanical agitation was slowly added to the fish oil (approximately 1 min). The reaction time was 20 minutes, with temperature up to 60 °C and constant mechanical agitation of 600 rpm.

Once reaction time ended, the mixture was taken to a separatory funnel to rest for about eight hours. During that period, a glycerol layer was formed at the bottom of the funnel due to its thickness and biodiesel sat on top of it. Both parts were collected separately.

Biodiesel was washed three times with portions of hot water at 60 °C containing 30% of its volume, that is, water was added to biodiesel in a separatory funnel that had been agitated manually. Afterwards, the aqueous part was disposed. The biodiesel was dried out in a stove at 85 °C for 48 hours.

2.1. Biodiesel description

2.1.1. Moisture

Moisture level was determined based on the evaporation principle of water and other volatile materials when the sample is submitted to high temperature. Determination was performed in accordance with the Official Methods and Recommended Practices of the AOCS [24].

2.1.2. Acidity level

Acidity level analysis was carried out in triplicate and in accordance with the analytical standards of Adolfo Lutz Institute [25].

ANP resolution No. 07 from 19.3.2008–DOU 20.3.2008 determines the national quality standards for biodiesel and stipulates that its acidity level must be below 0.50 mg KOH g^{-1}.

2.1.3. Specific mass at 20 °C, Kg m^{-3}

This method consists in introducing a glass hydrometer in a 1.000 mL glass test tube containing the sample to be analyzed. It covers the specific mass determination of petroleum distillates and viscous oils that may be handled normally as liquids on test temperatures between 15 °C and 35 °C.

Readings were performed on the superior meniscus part, with the sample at 20 °C. A hydrometer with a metric density range from 850 to 900 Kg m^{-3} was used.

2.1.4. Kinematic viscosity at 40 °C, mm^2 s^{-1}

This test is a procedure that is used to determine the kinematic viscosity of both transparent and opaque liquid products, by measuring the time in which a liquid volume flows under gravity through a capillary glass calibrated viscometer. The test was performed using a Cannon-Fenske viscometer in thermostatic bath at 40 °C.

2.1.5. Flash point, °C

This test was carried out in a place with low light and no air flow. The test container was filled with the sample to a specific level. Sample temperature was increased in a fast initiation hot