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Oil from the acid silage of Nile tilapia waste: Physicochemical characteristics for its application as biofuel

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ABSTRACT

In this work, a chemical silage technology was employed to obtain a high yield – 42.8% (m/m) – of the oily fraction of filleted Nile tilapia (*Oreochromis niloticus*) waste. The waste-fish-oil (WFO) was analysed to determine its potential as a biofuel. The objective of this paper was to characterise the WFO and its blends with diesel oil regarding its physicochemical and rheological properties. Binary mixtures of WFO-diesel were prepared at 25%, 50% and 75% (m/m). Ash content, density, flashpoint, viscosity, acidity, iodine, peroxide and saponification values were determined for each blend. The WFO presented high levels of acidity for biofuel use, which indicates that the adopted process requires adjustment. However, the WFO presented low peroxide values, indicating that the addition of alpha-tocopherol in the silage process was effective in preventing oxidation. Other physicochemical parameters suggest a potential use of the WFO as a biofuel with low ash content, flashpoint and density in accordance to the Brazilian National Petroleum, Natural Gas and Biofuels Agency specifications, which are similar to the European specifications. Rheological analyses of the blends indicated time independent Newtonian behaviour. Moreover, low concentration mixtures are better suited for use as biofuel due to the high viscosity of WFO.

1. Introduction

Nile tilapia (*Oreochromis niloticus* L.) is one of the most important farmed fish worldwide [1]. In Brazil, tilapia represents approximately 37% of freshwater aquiculture and is considered the most promising species for aquiculture because of its robustness, strength and fast growth [2].

The growth of the fishery industry results in the production of large quantities of waste, especially fish viscera, which are usually discarded to the environment. This waste constitutes a serious hygiene threat to facilities that benefit from or commercialise the fish. Moreover, this waste also affects production and cost efficiency since it represents approximately 50% of the initial weight and essentially consists of heads, carcass, viscera, waste from filleting operations, dark meat and fish that do not meet the size criteria for industrialisation [3–7].

Nowadays, the silage process is emerging as a potential technology to produce oil from industrialized fish waste. Fish silage is defined as a liquid product obtained from the whole fish or parts of it, to which acids, enzymes or lactic-acid-producing bacteria are added. Liquefaction is then provoked by the action of enzymes from the fish [5]. The final product or silage, is a potential source of lipids and proteins. Chemical silage is the most prevalent method among the silage preparation methods. In this approach, the feedstock is mixed with organic or mineral acids and liquefied due to enzymes that are naturally present in the fish. Microbial growth is inhibited by maintaining low pH values. According to many authors, in addition to promoting autolysis and pH reduction, the addition of acid generates a stable product free from pathogenic microorganisms [4,5,8,9]. The majority of the published literature employs silage as a protein source for animal feed and discards the oily fraction in order to increase the stability of the protein product [8,9]. In the present work, the silage process is employed with focus on recovering the oily fraction of the waste, which would allow the

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application of the waste-fish-oil (WFO) as an alternative renewable fuel.

The need for sustainable and renewable energy, as well as the desire to decrease our dependency on fossil fuels, has driven interest and research toward the development of fuels derived from biomass resources. According to Lin et al. [10], fossil fuels accounted for 88% of global energy demand in 2009, with a share of 35% for oils. Furthermore, the IEO2013 – International Energy Outlook [11] projects a use of more than 18 million m^3 of liquid fuels per day in 2040, and biofuels, such as ethanol or biodiesel, are expected to supply almost 715 thousands m^3 per day in 2040. The major obstacle to the widespread use of fats and oils as fuels and chemicals is the high cost of the finished products relative to petroleum [12].

Usually diesel substitutes are transesterified bio-oils – called biodiesels. The use of transesterified bio-oils is advantageous because these oils are quite similar to regular diesel and almost no changes in the feeding and combustion systems are necessary, although the cost and technology requirements of the transesterification process are high [13]. In Brazil, the financial reality of the fishing industry does not allow significant investments in new technologies. However, WFO from silage has the advantage of being produced by an easily transferrable and simple technology and it can even be considered for use as a diesel substitute in a fishing company's own fleet.

To replace diesel as fuel, the substitute must have similar properties since it will be used in the same equipment. Flow properties, such as pour and cloud point, viscosity and surface tension play an important role in the viability of employing a particular fuel. These properties are also important to the combustion quality due to their influence on spray formation. Considering flow properties, there are previous studies which evaluate straight vegetable oils (SVO), animal fat, residues and its esters as diesel substitutes.

For example, Thangalazhy-Gopakumar et al. [14] studied the properties of a bio-oil produced from the fast pyrolysis of pinewood. It was reported that the viscosity showed a Newtonian behaviour for shear rates greater than 20 s^{-1}, a value higher than that of diesel fuel but lower than regular SVO. As expected, the viscosity decreased with temperature: more precisely, viscosity was 6–7 times greater at 30 °C than at 80 °C. According to Berrios et al. [15], biodiesel from used frying oil did not meet EN 14214 standards for specification [16] due to the fatty acid methyl ester content and kinematic viscosity requirements. The kinematic viscosity upper limit is 5 $mm^2\ s^{-1}$ at 40 °C, and the values obtained for used frying oil varied from 5.13 to 5.64 $mm^2\ s^{-1}$ [15,17]. Franco and Nguyen [18] examined various straight vegetable SVOs oils, such as canola, corn, olive, peanut, soybean and sunflower. It was shown that the least viscous oil (corn) was approximately 5–12 times more viscous than diesel when the temperature was decreased from 80 to 20 °C. At 40 °C, the viscosity of soybean oil is approximately 0.031 Pa s, while the viscosity of diesel is approximately 0.0025 Pa s. Measurements showed that SVOs and its diesel blends exhibited time-independent Newtonian behaviour in the temperature range investigated (20–80 °C). A simple and general model based on the Andrade viscosity mixing rule [19] was developed, which can be applied to predict the blend viscosity at any temperature and composition. The use of SVO was not recommended by Franco and Nguyen [18] because its viscosity values are much higher than that of diesel, even if it is lowered by increasing its temperature and/or blending it with diesel.

As for density, SVOs are usually 10% denser than regular diesel, so this property must be considered in the adjustment of fuel flow rates since fuel pumps are volumetric devices [17,13,20,21].

In addition to flow properties, physicochemical properties which depend on the source of the biofuel are quite important to combustion, degradability, wear and fuel transport. Iodine and peroxide values are mainly related to oil degradation. However, a lower degree of unsaturation also improves the combustion properties, thus decreasing deposits and wear. Conversely, highly saturated oils may show a poor low temperature performance [13,21–23]. The acidity value and saponification are related to wear, while the flash point is important for transport and storage issues [13,20–22].

In the present work, a chemical silage technology was employed to obtain a high yield of the oily fraction from filleted Nile tilapia waste. The major objective of this work was to characterise the waste-fish-oil (WFO) resulting from the silage process and its blends with diesel oil regarding its physicochemical and rheological properties, and consequently assess the applicability of the WFO as biofuel. Binary mixtures of WFO-diesel were prepared and the ash content, density, flashpoint, viscosity, acidity, iodine, peroxide and saponification values were determined for each blend.

2. Material and methods

The waste material used to obtain the chemical silage consisted of four lots of approximately 6 kg of Nile tilapia (*O. niloticus*) originating from commercial cultivation in the city of Ivoti (Brazil). The waste was collected during spring and summer, when tilapias increase their body weight and was composed of approximately 59% heads and fishbone tissue, 33% viscera and 8% flippers by mass.

2.1. Chemical silage

A meat grinder was used to grind the waste into particles approximately 4 mm in size and placed in polyethylene containers. A mixture of 1:1 formic acid and propionic acid was added at 3% (m/v) and the antioxidant alpha-tocopherol was added at 0.02% (m/m). The addition of the synthetic antioxidants TBHQ (terc-butyl hydroquinone) [24], vitamin E and alpha-tocopherol is recommended due to the presence of unsaturated fatty acids in the fish oil [4,25]. The silage was stirred daily with a spreader for a period of seven days to ensure homogeneous acidification.

The silage was maintained at ambient temperature (24°C ± 2 °C) and stable pH (4.0 ± 0.2) during the seven days. After this period, it was centrifugated (3500 × G) in a Combi – 514R – Hanil Science Industrial Co., Ltd. multi-purpose centrifuge for 30 min at 35 °C to separate the phases.

Two different fractions were obtained: a solid fraction, which was stored, and an oily fraction (WFO). The WFO was bottled in an amber flask at 4 °C for 12 h, then blended with diesel for physicochemical and rheological analysis. The storage time of 12 h was kept constant among the four batches. Refrigeration was employed in order to reduce the effects of oxidative degradation. Fig. 1 shows the process flowchart.

2.2. Fish and diesel oil blends preparation

In the present study, WFO-diesel blends were prepared using an analytical balance with a precision of 0.1 mg. Measured amounts of WFO and mineral diesel were blended in a 600 mL beaker under continuous stirring. Based on mass percentages, the following blends were prepared: WFO100 (100% WFO), WFO75 (75% WFO), WFO50 (50% WFO) and WFO25 (25% WFO). The notation D100 is employed herein for pure diesel.

2.3. Physico-chemical characterisation of the products

The physical properties of the WFO and WFO-diesel blends were determined using ASTM standard methods, including density