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Biodiesel production using fatty acids from food industry waste using corona discharge plasma technology

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ABSTRACT

This article aims to describe an alternative and innovative methodology to transform waste, frying oil in a potential energy source, the biodiesel. The biodiesel was produced from fatty acids, using a waste product of the food industry as the raw material. The methodology to be described is the corona discharge plasma technology, which offers advantages such as acceleration of the esterification reaction, easy separation of the biodiesel and the elimination of waste generation. The best conditions were found to be an oil/methanol molar ratio of 6:1, ambient temperature (25 °C) and reaction time of 110 min and 30 mL of sample. The acid value indicates the content of free fatty acids in the biodiesel and the value obtained in this study was 0.43 mg KOH/g. Peaks corresponding to octadecadienoic acid methyl ester, octadecanoic acid methyl ester and octadecenoic acid methyl ester, from the biodiesel composition, were identified using GC–MS. A major advantage of this process is that the methyl ester can be obtained in the absence of chemical catalysts and without the formation of the co-product (glycerin).

1. Introduction

Waste oils and fats should not be discarded in the public sewage system, because they can cause significant environmental impact (Giraçol et al., 2011). Oils in rainwater and sanitary sewage systems emulsify with organic matter, causing blockages in grease traps and pipes. Due to their immiscibility with water and lower density, there is a tendency toward the formation of oily films on the water surface, inhibiting the exchange of gases with the atmosphere. This leads to the depletion of oxygen and anaerobic conditions in water bodies, resulting in the death of fish and other aerobic organisms (Reis et al., 2007).

In the public sewage system, blockages can cause pressure to build up, leading to the infiltration of sewage into the soil, groundwater pollution and/or surface reflux% (Reis et al., 2007). Furthermore, in areas where sewage treatment is installed, when waste oil enters the system it interferes with the treatment processes and increases the cost by up to 45% (Reis et al., 2007).

As a result of impacts and environmental damage caused by the improper disposal of frying oils, it is necessary to treat these wastes final disposal or, in the reuse of this waste. The utilization of frying oils for biodiesel production is a form of reuse, which is through the transesterification reactions which can be performed through homogeneous catalysis with use of a basic catalyst or acid, enzyme catalysis (biocatalyst) heterogeneous catalyst (zeolites, clays) or in the absence of catalyst, with the use of an alcohol in supercritical conditions (Demirbas, 2006; Ranganathan et al., 2008), or by using corona discharge plasma as a catalyst for reactions.

Biodiesel is the fuel obtained from vegetables oils or animal fat, which can substitute petroleum diesel, total or partially in car engines, trucks, tractors, and also in stationary engines, such as electricity generators, motor pumps, among others (Silva and Freitas, 2008).

Rodrigues and Lunkes (2011) point out that the production of biodiesel does not compete economically with mineral diesel due to its high cost of production, however, offers advantages in environmental and social aspects. In the environmental scope, it shows a reduction in the amount of pollutants emitted upon firing, such as carbon monoxide, sulfur oxides and carbon dioxide. In the social

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scope, it is observed that the production of biodiesel was conceived as a means of social inclusion of family farming in the production chain and the economy as a whole, benefiting from the creation of jobs and income.

The use of waste frying oil as a feedstock for biodiesel production can therefore reduce the cost of the final product, besides being environmentally friendly. Due to the rapid decline in crude oil reserves, the use of vegetable oils for the production of diesel fuels is being promoted in many countries. Depending on the climatic and soil conditions, different nations are looking into different vegetable oils for diesel fuel production. For example, soybean oil in the USA, rapeseed and sunflower oils in Europe, palm oil in Southeast Asia (mainly Malaysia and Indonesia), and coconut oil in Philippines are being considered as substitutes for mineral diesel (ElSolh, 2011).

The world production of waste oils and fats in 2008 was around 154 million tons. A variety of raw materials can be used to produce biodiesel (MPCO, 2008). These include virgin oil feedstock (U.S Energy Information, 2013), waste vegetable oil (WVO), animal fats (Leonard, 2007), algae (Kiong, 2006), oil from halophytes such as *Salicornia bigelovii* (Glenn et al., 1998) and sewage sludge (Casey, 2010). Many researchers have suggested that WVO is the best raw material to produce biodiesel, but since the available supply is considerably less than the amount of petroleum based-fuel that is burned for transportation and home heating globally, this local solution does not scale well.

However, oils and fats undergo several physical and chemical changes when used repeatedly in the frying process. The physical changes observed in vegetable oil after frying include: (i) increased viscosity, (ii) increased specific heat, (iii) a change in the surface tension, and (iv) a change in the color (Cvengros and Cvengrosova, 2004).

During the frying process, different types of reactions occur in the oils, for instance, thermolytic, hydrolytic and oxidative (Kulkarni and Dalai, 2006; Bensmira et al., 2007; Cvengro and Cvengroová, 2004). These reactions can lead to the formation of undesirable compounds which are harmful to human health, such as free fatty acids (FFA). These polar compounds – FFA significantly affects the conversion to alkyl esters (biodiesel) in the conventional transesterification process with basic catalysts. In the transesterification of vegetable oils, a triglyceride reacts with an alcohol in the presence of a strong acid or base, producing a mixture of fatty acids, alkyl esters and glycerol (Schuchardt et al., 1998).

Among the most commonly used alkaline catalysts in the biodiesel industry are potassium hydroxide and sodium hydroxide flakes which are inexpensive, easy to handle in transportation and storage, and are preferred by small producers (Singh et al., 2006). However, these catalysts are now considered to be outdated, since even when using refined vegetable oils with a low content of free fatty acids and low water content, small amounts of soap are formed, promoting the entrainment of esters with varying amounts with glycerin phase, thereby reducing the ester yield in the light phase containing glycerin and generating more contaminants. In biodiesel production carried out through traditional processes the amount of glycerol generated is equivalent to 10% of the biodiesel produced, and this negatively influences the national and international market for glycerin (Dasari et al., 2005).

In this article, different biodiesel production processes which involve the use of a corona plasma reactor are described. For this purpose, a pilot corona discharge plasma system was built for the production of biodiesel, appropriate pilot conditions being set to obtain the best rates for the conversion of waste into biodiesel. The batch production of biodiesel occurred without the use of acid or alkaline catalysts, while the biofuel samples were subjected to chromatography analysis (GC–MS) to confirm the presence of esters (biodiesel). This technology is considered to be more promising than the conventional catalytic processes due to a shorter reaction time, no formation of glycerin and ease of biodiesel separation.

The corona plasma process is also known as corona plasma, as well as dielectric barrier (Ragazzi et al., 2014), plasma jet, electron beam, etc. (Fridman, 2008; Fridman et al., 2007; Kim, 2004; Preis et al., 2013; Pankaj et al., 2014). The corona discharge plasma comprised of a partially ionized gas, in which the average energy of the electrons is considerably higher than the energy of the ions and the gas molecules. Plasma discharges are widely used for processing and are indispensable in many technological applications (Milosavljević et al., 2007).

The plasma discharge is formed by applying an intense electric field, which causes the formation of an electronic self-propagating arc within the gas volume. Once the ionized gas is generated, the electrons collide with molecules, creating chemically-active species known as radicals. Radicals, once produced, can replace the conventional chemical form of the catalyst during transesterification reactions, facilitating the separation of the biodiesel formed (Istadi, 2006; Istadi et al., 2009; Kogelschatz, 2003).

The corona discharge plasma reactor technology offers advantages related to the production of biodiesel compared to conventional methods due to faster reaction times and the easy separation of the final product (Istadi et al., 2009).

2. Methodology

2.1. Raw material acquisition and preparation

The raw material, waste frying oil originating from the food frying process, was purchased from local restaurants. The oils and fats initially underwent a pretreatment step with heating to 50 °C and filtering for the removal of impurities.

Before starting the experiments to obtain biodiesel, the raw material was characterized by determining the acidity number by titration (AOAC n. 940.28, 2005) and the water content by using the Karl-Fischer method (ISO 12937, 2000). Saponification and peroxide values were determined by the AOAC official method 920.160 and 965.33, respectively. The AOAC official method 993.20 (Wijs method) was used to determine the Iodine values.

2.2. Corona discharge reactor

The body of the reactor was comprised of a cylindrical quartz tube (300 × 110 mm), wrapped with a spiral of stainless steel 250 mm in length, which served as an electrode. A stainless steel screw (400 × 5 mm) in the center of the quartz tube was used to seal the exits and keep the second electrode (screw) in the center of the tube (Fig. 1).

The used frying oil with methanol and water was introduced into the reactor through an access positioned at the right side of the reactor cap, throughout the process was injected 1 L/min of argon into the reactor. The final product, methyl ester (biodiesel), is pulled across the reactor and a source of alternating current voltage of 17 kV is used to generate the plasma.

A photo of the system transporting the waste frying oil can be seen in Fig. 2 (note the violet fluorescence emitted by the plasma).

2.3. Pilot optimization

To establish the appropriate conditions for the pilot and obtain better oil to biodiesel conversion rates using the corona discharge plasma technology, tests were carried out varying the residence time of the sample in the reactor (15–120 min), and the sample