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Biodiesel production from olive–pomace oil of steam-treated alperujo

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ABSTRACT

Recently interest has been revived in the use of plant-derived waste oils as renewable replacements for fossil diesel fuel. Olive–pomace oil (OPO) extracted from alperujo (by-product of processed olives for olive oil extraction), and produced it in considerable quantities throughout the Mediterranean countries, can be used for biodiesel production. A steam treatment of alperujo is being implemented in OPO extraction industry. This steam treatment improves the solid–liquid separation by centrifugation and facilitates the drying for further extraction of OPO. It has been verified that the steam treatment of this by-product also increases the concentration of OPO in the resulting treated solid, a key factor from an economic point of view. In the present work, crude OPO from steam-treated alperujo was found to be good source for producing biodiesel. Oil enrichment, acidity, biodiesel yield and fatty acid methyl ester composition were evaluated and compared with the results of the untreated samples. Yields and some general physicochemical properties of the quality of biodiesel were also compared to those obtained with other oils commonly used in biodiesel production. As for biodiesel yield no differences were observed. A transesterification process which included two steps was used (acid esterification followed by alkali transesterification). The maximum biodiesel yield was obtained using molar ratio methanol/triglycerides 6:1 in presence of sodium hydroxide at a concentration of 1% (w/w), reaction temperature 60 °C and reaction time 80 min. Under these conditions the process gave yields of about 95%, of the same order as other feedstock using similar production conditions.

1. Introduction

Biofuels are sustainable and renewable energy sources derived from biological materials wastes. The production and consumption of biofuels continues to increase as more attention is paid to the environment protection, the rapid rate of growth in world energy requirements mainly in developing countries and the depletion of conventional fossil-fuel resources. Biodiesel, a fuel produced from natural/virgin edible

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and non-edible vegetable oils including used cooking oils or animal fats like tallow and fish oil [1], is a good substitute for petroleum-diesel fuel representing an alternative source of energy, which can supplement or totally replace fossil fuels in diesel engines without any major modification. According to the United States Environmental Protection Agency (EPA), biodiesel may be blended with conventional diesel to obtain different blends such as B20 (20% biodiesel) or it can be used as 100% biodiesel (B100). Biodiesel is technically defined as a mixture of long-chain fatty acid methyl esters (typically C_{14}–C_{22}). Biodiesel is non-toxic, biodegradable and significantly reduces pollutant emissions such as carbon monoxide (44%), particulate matter (40%), and sulfur dioxide (100%) [2].

The benefits to using biodiesel have promoted research on a variety of raw materials that can be used to produce it. Exploring other sources of renewable oils is of interest, not only to further increase the economic viability of biodiesel, but also to increase the potential supply of this fuel. It is observed that there is a close relationship between the availability of oils and the publication of papers since, depending upon the climate, soil conditions and geographical location, each country studies mostly those vegetable oils which has available: for example, soybean oil in the US; rapeseed and sunflower oils in Europe and palm oil in Asia [3–5]. In the Mediterranean region countries, the corresponding renewable feedstock and one of the possible sources for biodiesel production would be olive–pomace oil (OPO) extracted from solid waste called two-phase pomace or "alperujo". OPO is a by-product very abundant, in the 2005–06 season, the annual OPO production is estimated at 56,000 tonnes in Spain (Agency for Olive Oil) [6]. In the last years, only a very few authors have explored the possibility of using OPO for biodiesel production and have concluded that it can be considered as a good potential feedstock [7–9] for this purpose. On the other hand the problems concerning the detection of benzopyrene in OPO discovered in 2001 have drastically reduced the human consumption. Therefore, biodiesel production is converted into an important alternative commercial for the OPO. OPO extraction plants would not have to perform the refining process of crude OPO, increasing biodiesel profit margins. However, although alperujo is easily available (only Spain generates approximately 4–6 million tonnes every year) and a low-cost raw material, it should be taken into consideration other important aspects such as its high moisture (50–70%) and low oil content. The technological changes performed in olive oil mills have introduced more efficient methods of olive oil extraction such as the two-phase centrifugation system. Moreover, alperujo is usually treated in a second centrifugation to extract the residual oil, with which final oil content is left around 1–2.5%. With these data, production costs from a solid so exhausted increase as a result of drying the alperujo and subjected it to solvent extraction with hexane in order to obtain OPO. The oil content is of fundamental significance and the price of oil may mean between 60 and 75% of the total cost [10] of biodiesel production and, in the future, is likely to become the main competitive factor determining on international markets [11].

It is possible to reduce the moisture content and to increase oil yield of alperujo to make of OPO an alternative economically competitive for biodiesel production. From an environmental point of view, alperujo represents a serious trouble in the Mediterranean area countries due to its highly polluting organic load which limit its biodegradation because of their high toxicity. In recent years, many management options have been proposed for the treatment and valorization of alperujo. One of the most interesting is a steam treatment developed and patented by Fernández-Bolaños and co-workers [12] already implemented at industrial scale by one of the most important OPO extraction industries in Spain, so that all processed alperujo will be treated by means of this system in a future. This treatment is conducted in a continuous reactor using steam at high pressures and temperatures (150–170 °C, 5–8 kg/cm^2) and allows the separation of alperujo into two phases (liquid and solid), operation that is practically impossible without treatment. Therefore, the solid fraction resulting has a lower moisture content (30–35%). The treatment combines a physicochemical effect that helps break cell wall structure, cellulose depolymerization and autohydrolysis of hemicellulosic material due to the generation of acids such as acetic and formic. As a consequence of this a release of phenolic compounds (hydroxytyrosol, 3,4-dihydroxyphenylglycol), fermentable simple sugars, oligo and polysaccharides and other high-added value compounds is produced. The result is a significant solubilization of the solid fraction in the liquid phase. The solubilization causes a substantial reduction of dry weight of alperujo (20–50%) and together with the efficient solid–liquid separation lead to a final solid material enriched in components such as cellulose and proteins. The oil is also concentrated in it producing an extra yield of OPO [13], making more interesting to recover this non-edible waste oil for biodiesel. The effects of the steam treatment on both fractions separated from the treated alperujo are reported in Table 1 (the data shown on this table correspond to one of the alperujo samples used in this study).

In this work, crude olive–pomace oil (non-refined) from steam-treated alperujo was used for the production of biodiesel by alkali-catalyzed transesterification. The aim of the paper was to study the use of OPO extracted of steam-treated alperujo for biodiesel production and to check whether the steam treatment has some effect on yield of biodiesel production and there are differences between OPO from steam-treated and untreated alperujo samples. The possibility of obtaining valuable products such as biodiesel from OPO not only is a solution environmentally friendly, but also is important because increase the value of alperujo.

2. Methods

2.1. *Materials*

Two fresh alperujo samples from different olive cultivars and consecutive seasons (2007–2008 and 2008–2009) were supplied by an experimental olive oil mill plant located at the Instituto de la Grasa (CSIC) in Seville (Spain) and directly collected from two-phase centrifugal system decanter. In particular the alperujo of the 2007–2008 season was obtained from olive fruit of marteña variety while the alperujo of the 2008–2009 season corresponds to picual variety. The reason is that this olive oil mill plant often processes olive fruits from