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Municipal sewage sludge to biodiesel by simultaneous extraction and conversion of lipids

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ABSTRACT

Two different approaches have been investigated for the production of biodiesel from glycerides and free fatty acids (FFAs) extracted from sewage sludge. The first one is a two-step process consisting of organic solvent extraction followed by acid-catalyzed esterification/transesterification of the isolated oil fraction. The second one is a one-step direct transformation consisting of the simultaneous extraction and conversion of the lipid fraction contained in the sewage sludge. In both alternatives, a heterogeneous acid Zr-SBA-15 catalyst has been used. In the two-step extraction–reaction process, conversion close to 90% of the saponifiable fraction (including FFAs and glycerides) were achieved. Remarkably, the catalyst provided such high conversion in the presence of high amounts of unsaponifiable matter. Furthermore, the catalyst kept its activity in successive catalytic runs in presence of this low-quality lipid fraction. In the one-step direct conversion of the dried sludge, the overall weight FAME yield, based on the initial mass of dried sewage sludge, was around 15.5 wt% for primary and 10.0 wt% for secondary sludge. In contrast, this FAME yield was lower than 6 wt% for two-step process when processing primary sludge (being negligible for the secondary sludge). Finally, the results of this work proof the high potential of Zr-SBA-15 as catalyst for the production of biodiesel from a low quality oleaginous feedstock such as municipal sewage sludge.

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1. Introduction

One of the most important challenging in the conventional biodiesel industry is how to overcome the high costs associated to conventional oleaginous feedstock and eliminate the competition between biofuels and food industries for the same raw material [1–3]. One convenient way to simultaneously overcome both drawbacks is using an inedible, residual and hence inexpensive-oleaginous raw material. Therefore, important efforts are currently being applied in biodiesel production research aiming to find new raw materials fulfilling both requirements. One of the potential candidates is the municipal waste water treatment sewage sludge, which is gaining attraction around the world as a lipid feedstock for biodiesel production. Recent research has indicated that the sewage sludge contains significant quantity of free lipids (mono-, di- and triglycerides, phospholipids and fatty acids), as well as high concentrations of microorganisms. The microorganisms can suppose a significant source of oils, since their cell membranes are lipid-rich and include phospholipids, steroids and fatty acids, mostly in the range of C_{10}–C_{18} [4,5].

Waste water treatment plants continuously produce huge amounts of sewage sludge. More than 20 million ton of dry sludge are produced worldwide every year. This figure is expected to increase in the near future due to the increasing urbanization and industrialization [6]. The management of this waste currently presents difficult environmental challenges. Its incineration results in emissions containing dioxins and metals [7]. In the same way, the use of the sludge for the production of compost and fertilizers is restricted in many countries by the presence of metals [8] and residual pharmaceuticals [9]. Therefore, there is a need to identify sustainable solutions for the utilization of this residue. In this context, the exploitation of sewage sludge for biodiesel production is a promising alternative that would also account as waste valorisation [10], solving at the same time energy and environmental concerns. Municipal sewage sludge thus appears as an alternative non-food feedstock offering a significant potential that could help to overcome the competition between biofuel and food industries. However, this feedstock usually contains, together with relevant amounts of lipids and free fatty acids, unsaponifiable matter such

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as hydrocarbons, carotenes, tocopherols, sterols [7]. This matter could disrupt the activity of catalysts in biodiesel production [1]. Additionally, water can represent more than 50 wt% of the total weight of sewage sludge, compromising the overall yield of biodiesel as a consequence of esterification/hydrolysis equilibrium [11].

Biodiesel production from sewage sludge has received considerable attention during the last years, resulting in the development and application of different methods for extraction and esterification/transesterification of the lipid fraction of such waste feedstock. Nonetheless, there are still few studies focused on the use of heterogeneous acid catalysts, which involve several important technical benefits as compared to their homogeneous counterparts, to drive the production of fatty acid methyl esters (FAME) from sewage sludge (cheaper separation processes; reduced water effluent load, capital and energy costs; the catalyst can be reused; there would be no neutralization products, so a higher grade of glycerol is produced; there would be fewer inputs and less wastes). Nevertheless, the commercial introduction of these catalysts need still important advances to impact in a positive way in the biodiesel synthesis technologies (increasing of the stability of acid sites avoiding their leaching; increasing of thermal stability; enhancement of the mass transfer avoiding diffusional limitations; milder operation conditions and increasing of the resistance to water and other impurities).

Pokoo-Aikins et al. [11] studied the extraction of lipids from sewage sludge using different organic solvents, obtaining lipids yields close to 25 wt%. Pastore et al. [12] proposed a two-step production of FAME from municipal waste water sludge using *n*-hexane in acidic ambient followed by methanolysis with sulfuric acid allowing FAME yields between 12 and 22 wt%. In the same way, Huynh et al. [13] reported the *in-situ* production of FAME, from untreated wet activated sludge under subcritical water and methanol conditions with sulfuric acid. Additionally, Mondala et al. [10] investigated the feasibility of using homogeneous acid catalysts to produce biodiesel from primary and secondary sewage sludge by *in-situ* transesterification process, with sulfuric acid and hexane to improve the solubility in the reaction mixture; obtaining FAME yields close to 15 wt% from primary sludge and 3 wt% from secondary sludge. The *in-situ* approach is gaining great interest since it eliminates the need of extraction with organic solvents and the subsequent separation of lipids and fatty acids from the extraction solvent prior to the esterification/transesterification reaction [14–16].

In this context, the aim of the present study has been to evaluate the catalytic behavior of the acid catalyst Zr-SBA-15 in the production of biodiesel from waste water treatment sewage sludge. In previous works [17–19], Zr-SBA-15 catalyst showed high activity as well as very good stability when treating low-grade oleaginous feedstocks containing significant amounts of free fatty acids (FFAs), water, alkaline metals and unsaponifiable matter. Therefore, the present work seeks to validate the promising properties of this catalyst in the production of biodiesel from sewage sludge. In order to perform this evaluation, primary and secondary sludge from a waste water treatment plant located at Universidad Rey Juan Carlos were explored as renewable sources of saponifiable lipids for biodiesel. Furthermore, the two above commented approaches for the production of biodiesel from sewage sludge, i.e. separated extraction–reaction and *in-situ* processes, have been thoroughly assessed in the present study.

2. Materials and methods

2.1. Chemicals

Methanol (synthesis grade, Scharlab) and *n*-hexane (purity 96%, Scharlab) were used as received for the extraction and reaction assays. Tetraethylorthosilicate (TEOS, Aldrich), Pluronic P123 (Aldrich) and zirconocene dichloride (Aldrich) were used for the preparation of the catalyst Zr-SBA-15 [17].

2.2. Sludge sampling and preparation

Sewage sludge samples used in this study were collected from the pilot-scale waste water treatment plant (WWTP) located at Universidad Rey Juan Carlos at Móstoles, Madrid, Spain. As shown in Fig. 1, the WWTP has two main sludge streams, as usual in waste water treatment facilities employing an activated sludge process. The primary sludge, which is stored in the primary tank (sampling point 1), is a combination of floating grease and solids collected at the top of the flotation tank. After the primary treatment, the effluent is directed to the activated sludge system for the removal of soluble organic contaminants, denitrification and nitrification. The activated sludge collected in the secondary sedimentation tank, and stored in the secondary tank (sampling point 2), is composed mainly of microbial cells and suspended solids produced during the aerobic biological treatment of waste water. Finally, both primary and secondary sludge are collected and further treated and stabilized by anaerobic digestion. The digested sludge is finally dewatered by centrifugation and disposed. The hydraulic retention time (HRT) of the WWTP, calculated from the flow and the volume of the treatment tanks, varies between 3 and 4 h in a season-dependent manner. Some of the operational parameters of the pilot-scale WWTP measured during the monitoring period (2012–2013) are given in Table 1.

Sludge samples tested in the present work were collected at sampling points 1 & 2, for primary and secondary sewage sludge, respectively. Thereafter, they were concentrated by simple settling and, following the work by Mondala et al. [10], the supernatant was discarded and the wet sludge were centrifuged at 3000 rpm for 20 min. The dewatered samples were then dried in an oven at 80 °C. Finally, dried sludge were crushed into a fine powder (with particle size ranging from 0.5 to 1.0 mm) in order to form a sufficiently homogenized suspension during the extraction/transesterification process.

2.3. Extraction assays

n-hexane or methanol are the extraction solvents used in this work. In this stage, the influence of the extraction time (2.5 and 4 h) and sewage sludge to solvent ratio (10 g of dried sewage sludge to 100 mL and 150 mL of solvent) was assessed. The resultant suspension was then filtered with nylon-membrane filters (0.45 μm) and the solvent was removed to yield the crude oleaginous residue. The collected crude oil was quantified and characterized by means of: (i) acid value (UNE EN ISO 660:2000), (ii) fatty acid profile (UNE EN ISO 5508:1996 & 5509:2000), (iii) unsaponifiable matter content following the method described by Plank and Lorbeer [20], and (iv) glycerides and glycerol content (UNE EN ISO 14105:2003).

2.4. Synthesis of Zr-SBA-15

Zr-SBA-15 material was prepared according to a method previously described in literature [17]. In a typical synthesis, triblock copolymer P123, used as structure directing agent, was dissolved in hydrochloric acid (0.67 N) at room temperature. Upon dissolution, zirconocene dichloride, used as zirconium source, was added and the resultant suspension was stirred for 3 h and heated at 40 °C. Afterwards, TEOS was added to the synthesis medium and vigorous stirring was kept for 20 h at 40 °C. The resultant white suspension was hydrothermally aged (130 °C) for 24 h, the solid was recovered by filtration and air-dried overnight. Surfactant

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