



Biodiesel production from wastewater sludge using exchange resins as heterogeneous acid catalyst: Catalyst selection and sludge pre-treatments

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ABSTRACT

Three different ion-exchange resins (Amberlyst 15, 36 and IR120) were used as heterogeneous catalysts for the transesterification of the secondary sludge lipids. Catalyst performance was evaluated based on the biodiesel yield and quality; the best biodiesel yield, with the best properties was obtained with Amberlyst IR120. Microwaves (MW) and ultrasounds (US) were studied as a pre-treatment step to increase lipid extraction. US treatment shows the highest biodiesel yield, providing a biodiesel that fulfils the current regulations. The sludge particle size effect was also studied obtaining the best results using the smallest one. However, in these conditions, ultrasound damage the lipids, decreasing the biodiesel yield. Temperature and catalyst/sludge ratio have been optimized. The maximum biodiesel yield (32.9% FAMES/lipids) was obtained with Amberlyst IR120, catalyst/sludge ratio 1:2, MeOH/sludge ratio 33:1, 120 °C, 21 h reaction time and US as pre-treatment. The catalyst was also reused for six times under the optimal reaction conditions with negligible catalytic activity loss.

1. Introduction

Despite its environmental and technological advantages, biodiesel (mainly fatty acids methyl esters, FAMES) is usually more expensive than petroleum-based diesel, especially when it is produced from vegetable oils or animal fats [1]. In addition, its current manufacture competes with the food industry, since it is synthesized from edible oils and fats [2]. Therefore, new raw materials are needed for reducing costs and avoid competition with food supply. In this way, several authors propose the use of waste cooking oil [3–4] or microalgae [5–9] as raw materials. Another potential feedstock is sewage sludge, a by-product of biological wastewater treatment plants. The fatty acid content of the sludge is mainly in the range of C10 to C18, which can yield appropriate biodiesel qualities [10]. Wastewater treatment plants produce large quantities of sludge as a by-product, which make them a good feedstock for biodiesel production.

Previous studies have demonstrated the potential of sewage sludge as feedstock by *in situ* transesterification with acid or basic homogeneous catalyst, but both methods have several drawbacks. In the case of basic catalysts, when free fatty acids (FFA) are present, soap formation can take place, consuming the catalyst and reducing biodiesel yields [11]. On the other hand, homogeneous acid catalysts provide a lower reaction

rate, as well as important corrosion problems [12].

To overcome the drawbacks of homogeneous catalysts, heterogeneous catalysts have been proposed. These catalysts improve the transesterification efficiency and enable catalyst separation and reutilization [13]. Although there are several studies about the use of heterogeneous catalysts, very few propose sludge as raw material. When the FFA content is higher than 1%, an alkali catalyst is not recommended, since the reaction is inhibited by the FFAs, leading to soap formation [14–15]. For this reason, recent advances are focused on heterogeneous acid catalysts, since they provide several advantages, such as high catalytic efficiency, removal of biodiesel washing step, ease of recovery and reuse, and reducing corrosion of reactors [16]. Siddiquee et al. and Zhang et al. checked different acid heterogeneous catalysts under a two-step process (extraction-reaction). Siddiquee et al. obtained a biodiesel yield of 30.14% (based on lipids) using SBA-15 impregnated with a heteropolyacid (PW12) as catalyst, without studying the catalyst reuse [17]. Zhang and co-workers prepared different $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3/\text{SnO}_2$ catalysts, reporting biodiesel yields close to 73% (weight of biodiesel product/weight of dried crude fat), also without catalyst reuse [18].

On the other hand, Melero et al., studied the catalytic behaviour of the acid catalyst Zr-SBA-15, obtaining a maximum FAMES yield of 15.5% (FAMES/dry sludge), demonstrating the high potential of the

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catalyst [19]. In this case, they also studied the catalyst reusability in a second consecutive run, with negligible decreases of the FAMES yields.

Although the use of heterogeneous catalysts for sludge-based processes is scarce, solid acid catalysts were proposed for biodiesel production from common oils: zeolites, organic polymers, acidic ion-exchange resins, heteropolyacids, etc.). Many of these studies are focussed on the esterification of fatty acids using ion-exchange resins as catalysts, since they present good properties in terms of esterification efficiency [11,20–22]. Acidity seems to be a determining factor in transesterification reactions, therefore strong acidic ion-exchange resins are an attractive alternative [1], with appropriate thermal and mechanical stability [11]. On the other hand, resins are more hydrophobic than other inorganic materials, which is also considered as a key factor for these reactions [23]. However, to the best of our knowledge, ion exchange resins have not been used before for sludge transesterification.

Although catalyst selection is a key parameter to obtain a good esterification efficiency, biodiesel yield also depends on the extraction process of the lipids present in the sludge. The extraction is carried out with an organic solvent; but it can be improved by different physical processes for promoting mass transfer from sludge particles to the liquid medium. Microwaves and ultrasounds, among other pre-treatments, have been used to increase lipids extraction [24–25]. Although it has been shown that these pre-treatments increase the lipid extraction yield, there is no agreement about the best technique, as it is highly dependent on the considered raw material.

On the other hand, since the extraction depends on the contact between the sludge and the organic solvent, milling and sieving of the raw material could increase the mass transfer, thus increasing the extraction capacity. For this reason, a study about the particle size effect is also interesting.

In the present study, three different ion exchange resins – Amberlyst 15, 36 and IR120 – with different physico-chemical properties, were selected as heterogeneous acid catalysts for biodiesel production from sewage sludge by *in situ* transesterification. The screening was performed to select the catalyst, providing the best results both in terms of yield and quality of the resulting biodiesel. The effect of reaction conditions, such as temperature, catalyst loading, as well as catalyst reusability for several reaction cycles, were also studied; analysing the results based on biodiesel yield and quality.

An additional investigation was done to determine the effect of pre-treatments (microwaves and ultrasound) and the effect of sludge particle size on the performance and quality of the biodiesel.

2. Materials and methods

Samples of floating sludge correspond to the sewage treatment plant of “La Reguerona” in Gijón, Spain. Three different commercial resins were used as heterogeneous acid catalyst: Amberlyst 15 (A-15, Sigma Aldrich), Amberlyst 36 (A-36, Sigma Aldrich) and Amberlyst IR120 (A-IR120, Merck). Chloroform (99.8%, Baker) was used for determining the total lipid content in the sludge samples. For the *in situ* transesterification process, methanol (MeOH) ($\geq 99.8\%$, VWR) was employed as solvent. Sodium hydroxide ($\geq 98\%$, Sigma Aldrich) and sodium chloride ($\geq 99\%$, Sigma Aldrich) were used to titrate the catalyst acid sites. A commercial mixture of 37 FAMES from C₄ to C₂₄, supplied by Supelco was used for identification and quantification of the fatty acid methyl esters (FAMES).

2.1. Sample preparation and characterization

The total lipid content was determined according to the method proposed by Siddiquee and Rohani [26]. This method uses chloroform ($\geq 99.8\%$, J.T. Baker) as solvent, with a dry sludge/solvent ratio of 1 g/25 mL at 75 °C for 4 h under stirring. After extraction, the samples were filtered, and residual particles were removed by centrifugation, using a Kubota 6500 centrifuge at 3000 rpm for 5 min. The solvent of the

supernatant was removed in a Heidolph VV 2000 rotavapor at 70 °C, and the lipids were weighted in order to obtain the lipid content, expressed as lipid (g)/dry sludge (g).

The swelling capacities were obtained according to the method proposed by Özbay et al. [1]. The resins were dried in an oven at 105 °C, then a volume of each resin was placed into a measured tube and methanol was added. The contact was kept at 50–60 °C for 2 h and the initial and final volume of the resins were measured. Percentage of swelling can be calculated according to the following equation:

$$\text{Swelling (\%)} = \frac{\text{swollen volume}}{\text{initial volume}} \times 100 \quad (1)$$

2.2. Catalyst characterization

The textural characterization of the resins was based on nitrogen adsorption tests and performed in a Micromeritics ASAP 2020 surface analyser. The catalysts acidity was measured by acid-base titration, following the method proposed by Melero et al. with NaOH as ion exchange agent [27].

2.3. Experimental procedure

The reactions were carried out by *in situ* transesterification in a 0.5 L stirred batch autoclave reactor with a PID temperature controller and a back pressure regulator (Autoclave Engineers, MAWP 5500 PSI). Three different ion exchange resins were checked as catalyst: Amberlyst 15, 36 and IR120. For the study of the different catalysts, the reactor was loaded with 0.3 L of methanol, and MeOH/sludge ratio of 33:1 and sludge/catalyst ratio of 2:1, following the optimum ratio proposed by Carrero et al. [2]. The reactor was heated up to the desired temperature (120 °C), while stirring at 1000 rpm, using a reaction time of 21 h, long enough to ensure maximum lipid extraction has been achieved.

Once the optimal catalyst has been selected, different pre-treatments were checked for maximizing extraction efficiency: Microwaves at 2450 MHz for 10 min and sonication at 10 kHz during 50 min. The sludges underwent these pre-treatments before being introduced in the transesterification reactor [28].

On the other hand, since the sludge particle size can affect the extraction step, three different fractions (50–100 µm; 100–255 µm; and 255–350 µm) were tested. In all cases, experiments were performed at the same experimental conditions that the catalyst selection experiments.

To optimize the experimental conditions, different temperatures were studied from 40 °C to 120 °C, whereas different catalyst/sludge ratios was also tested (1:1, 1:2 and 1:4).

2.4. FAMES analysis

Product distribution was evaluated by gas chromatography. The qualitative analysis of FAMES was analysed using a SHIMADZU GC-MS QP2010 Plus with a TRB-5MS (30 m × 0.25 mm × 0.25 µm) column. 1 µL of the sample was injected with a split ratio of 30. Injection port temperature was kept at 260 °C, MS source at 200 °C and interface temperature 250 °C. Column temperature was operated to start at 100 °C, kept for 5 min, then raised from 100 °C to 240 °C with a rate of 4 °C/min, and held at this temperature for 30 min.

The quantitative analysis was carried out using a SHIMADZU GC2010 with a FID detector and a CP-Sil 8CB (30 m × 0.25 mm × 0.25 µm) column. The detector temperature was 260 °C and the temperature program was the same than for the qualitative analysis.

FAMES yield (ϕ_{FAME}) was calculated according to the Eq. (2), expressed as g FAME/g lipid.

$$\phi_{\text{FAME}} = \frac{\sum C_{i,\text{FAME}} \cdot V_{\text{T}}}{\text{TL}} \cdot 100 \quad (2)$$

where $C_{i,FAME}$ is the concentration of all detected FAMES, V_T , the total volume and TL the total lipid content.

2.5. Biodiesel properties

The main physicochemical properties of biodiesel produced were obtained, since these properties are closely related to the composition profile of the obtained FAMES. All the physicochemical properties – long chain saturated factor (LCSF), saponification value (SV), degree of unsaturation (DU), cold filter plugging point (CFPP), iodine number (IN), kinematic viscosity, density, higher heating value (HHV) and cetane number (CN) – were estimated according to the equations shown in different articles [4,29–32].

3. Results and discussion

3.1. Catalyst selection

The reaction profile for the different catalysts is shown in Fig. 1a. The activity of the studied catalysts, expressed as FAMES/lipids yield, decreases in the order: A-IR120 (21.23%) > A-36 (20.20%) > A-15 (14.98%). Results obtained for A-IR120 and A-36 are very similar, reaching the maximum biodiesel yield after 16 h reaction time. In the case of A-15, the slope obtained during the first 16 h is much lower, but the yield also stabilizes after this reaction time.

Taking into account the catalysts properties (Table 1), surface acidity and pore diameter are the key parameters governing catalyst performance. Among these two properties, acidity has the most evident effect, since in the case of A-36 and A-IR120, although A-36 presents the highest particle diameter, the final yield obtained is lower than for A-IR120, the catalyst with the highest acidity. When the FAMES yield is normalized per acid sites, an opposite trend than the described in Fig. 1a is obtained — A-IR120 (8.23) < A-36 (9.27) < A-15 (14.41). This fact indicates that, even though A-IR120 has a higher acidity value, not all active sites are used in the selective FAMES production. Obtained results suggest that diffusional effects on the resins play a key role in the catalyst performance, which is consistent with the large molecular size of the triglycerides involved in the reaction. Thus, the low porosity material (that also has the acid sites in the external surface) present the best performance, whereas in the case of mesoporous materials, a large fraction of the acid sites is not fully accessible to the reactants.

On the other hand, previous studies have demonstrated that resins with lower crosslinking have higher swelling capacity, which affects positively in the esterification rate [1]. The swelling capacity follows the order: A-IR120 (37%) > A-36 (22%) > A-15 (10%), which matches with the trends observed for the biodiesel yields. Thus, high acidity and swelling capacity play a more determinant role than the other

morphological parameters. This fact is congruent with the low esterification rate obtained with A-15, with higher surface area and mesoporous volume, but lower acidity and swelling capacity.

Besides, Park et al., found that the water produced during the esterification reaction acts as inhibitor from the acid sites of the resin A-15 [22]. They also compared A-15 with A-BD20, a resin with similar S_{BET} and V_{meso} than A-36, for which they obtained better results, since the interaction of the acid sites with the released water is weaker, keeping constant its activity [22].

3.2. Biodiesel quality

The feasibility of a process based on wastewater sludge for obtaining biodiesel will depend not only on the FAME yield, but also on the quality of the resulting biodiesel. Obviously, this quality will mainly depend on the raw sludge, but catalyst can also play a role in these properties. The FAMES profile obtained for each catalyst, is shown in Fig. 1b. In all cases, the percentage of saturated FAMES is similar and close to 90%. Although the ratio between saturated and unsaturated FAMES can influence the biodiesel quality, the optimal ratio has not been established yet [33]. Saturated FAMES offer better burning properties; meanwhile unsaturated ones are associated with better fluidity under cold temperature [34]. The FAMES profile is similar for A-15 and A-IR120, for which the biodiesel obtained is predominantly composed of methyl esters of palmitic acid (C16:0) and stearic acid (C18:0). In the case of A-36, the proportion of palmitic acid decreases, increasing the amount of the methyl ester of C15:0. This unexpected effect suggests a specific interaction of the triglycerides with the catalyst, probably because of the abovementioned diffusional effects. These effects are negligible in the A-IR120 catalyst, but not for the others. This differentiation could be attributed to the difficulty of the compounds to access the active centers, as the catalysts have different pore diameter (Table 1).

From the FAMES profile, the biofuel properties can be determined to study the viability of the biofuel obtained according to the standard specification for biodiesel fuel by ASTM D975 and EN 590 (Table S1). The biodiesel obtained with the three different catalysts are quite similar. The main differences are related to the iodine number (IN), kinematic viscosity (η_i) and higher heating value (HHV). Although ASTM D975 and EN 590 provide no specifications for IN, EN14111 specified a maximum value of 120. The values obtained in this study follow the order: A-36 (8.12) < A-15 (9.71) < A-IR120 (10.41) and all of them are far from the maximum recommended. In the case of the kinematic viscosity, one important parameter that define the capability of fuel, only the biofuel obtained with A-IR120 as catalyst meets the requirements of the standard specifications, with a value of 2.03 mm²/s. Although there is no standard requirement in the case of HHV, the typical value for a diesel is close to 49 MJ/kg, and it was found to be

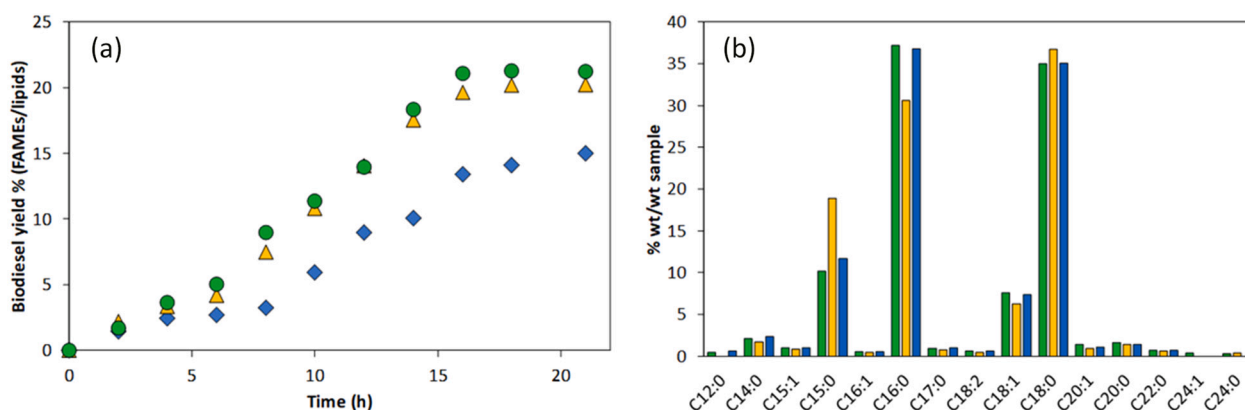


Fig. 1. Temporal evolution of the biodiesel yield (a) and FAMES composition after 21 h reaction time (b), with different catalysts: ● A-IR120 ▲ A-36 and ◆ A-15. Catalyst/sludge ratio 1:2, MeOH/sludge ratio 33:1 and 120 °C reaction temperature.

Table 1
Morphological properties of the catalysts used in this work.

	Acidity (meq H/g cat)	S _{BET} (m ² /g)	V _{meso} (cm ³ /g)	D _p (nm)	Swelling capacity (%)
A-15	1.04	80	0.4	26	10
A-36	2.18	35	0.3	33	22
A-IR120	2.58	2	0.01	29	37

between 39 and 43 for biodiesel from different raw materials [35]. In this case for A-IR120 the value is close to that obtained for mineral diesel, whereas A-15 provides a fuel more similar to conventional biodiesel. In the case of A-36, the value obtained is higher than that obtained for mineral diesel.

In relation with the other parameters with standard specifications — saponification value (SV), density, and cetane number (CN), in all cases the values obtained comply with the standards without significant differences among the three catalysts.

As for the other properties, there is not regulation-fixed values for degree of saturation (DU), since it is not a final property of biofuels. Long chain saturated factor (LCSF) is in the same situation. Regarding the Cold Filter Plugging Point (CFPP), in these cases, the value is close to 58 °C. The CFPP for diesel fuel is between 0 and 12 °C, but in the case of biodiesel it is usually higher and depends on the raw material, so it will be necessary additives to decrease CFPP [36].

To sum up, A-IR120 achieved not only the maximum biodiesel yield but also the best biodiesel quality, being the only catalyst that complies with all the values set by the regulations. For these reasons, it is the catalyst selected to carry out the optimization of the transesterification process.

3.3. Effect of different pre-treatments on the biodiesel yield

The biodiesel yield not only depends on the transesterification process, but also on the extraction process. In the samples obtained by the *in situ* transesterification with A-IR120 as catalyst, no lipids were detected in the final samples, which suggests that all the extracted lipids have been trans-esterified. Therefore, the option of a pre-treatment to favour the lipids extraction is a good alternative to increase the biodiesel yield. Thus, pre-treatments of the sludge with microwaves (MW) and ultrasounds (US) were tested for improving the extractability of the sludge, as they have been shown to maximize the lipid extraction from biological samples [24].

As observed in Fig. 2a, both methods have resulted in improved lipid extraction, since the maximum biodiesel yield increases with MW and US. These results show that the use of these techniques favour the cellular breakdown, and, as a consequence, larger amounts of lipids were extracted. This increase leads to a significant increase in biodiesel yield. The increase in the maximum yield obtained was 12% and 3% for

MW (yield, 23.8%) and US (yield, 27.6%) respectively. In both cases no lipids were detected in the final samples, which suggests that all the lipids extracted have been trans-esterified, which confirms that extraction is a limiting step.

On the other hand, the yield profile (Fig. 2a) is quite similar for both pre-treatments (MW and US) during the first hours, and the *in situ* transesterification is faster when these pre-treatments are applied, since more lipids are available for the transesterification process. The maximum biodiesel yield is obtained after 14 h in both cases, faster than without pre-treatments. At this point is also important to mention that no FFAs were detected in the final samples, which confirms that all the extracted FFAs have reacted.

Regarding to the best technique, there is no unanimity in the bibliography about which pre-treatment achieves a greater improvement, being dependent on the raw material and the experimental conditions. Martínez Guerra et al., studied the effect of these pre-treatments for the extractive-transesterification of algal lipids (*Chlorella*, sp.), obtaining the highest yield and conversion for MW, although both methods produce better results than the conventional one [25]. But nevertheless, Prabarakan and co-workers obtained higher lipid content by using the sonication method, when compared with MW using *Chlorella*, sp. and *Nostoc* sp. as raw material [37]. In this work, MW and US are applied on sludge sample after a storage period in waste treatment facility. Thus, these sludges will be more compacted than fresh sludges. US pre-treatment leads to sludge floccules fragmentation that enhances lipid extraction hence the best performance with US. This effect is not so marked with the MW pre-treatment.

3.4. Effect of pre-treatments on the biodiesel quality

Although the best biodiesel yield was obtained with US, it is important to check the biodiesel quality in all cases, since the different pre-treatments could modify the lipidic fraction and, consequently, the biodiesel quality.

As observed in Fig. 2b, the FAMES profile changes when MW and US are used. The fraction of palmitic acid methyl esters (C16:0) increases with both pre-treatments, being more marked for the case of MW. On the contrary, the amount of C15:0 decrease drastically. On the other hand, with US, the percentage of C18:0 increase in a small percentage, meanwhile it decreases a bit for MW. The fraction of saturated FAMES

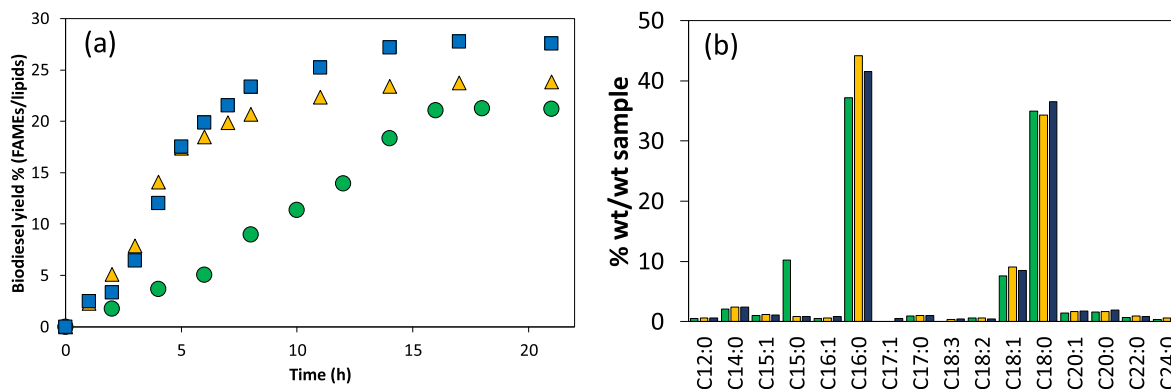


Fig. 2. Temporal evolution of the biodiesel yield (a) and FAMES composition after 21 h reaction time (b), with different pre-treatments: ● no pre-treatment, ▲ MW, ■ US. A-IR120 as catalyst, catalyst/sludge ratio 1:2, MeOH/sludge ratio 33:1 and 120 °C reaction temperature.

decreases from 88% (no pre-treatment) to 85.8 and 85.7% for MW and US respectively. The monounsaturated one's increase from 10.9% (no pre-treatment) to 12.4% (MW) and 12.6% (US). The greatest difference is obtained in the case of polyunsaturated FAMES, for which the percentage increases from 0.6 (no pre-treatment) to close to 1.2% for MW and US. However, although polyunsaturated FAMES can lead to undesired gums formation reactions, which decrease the product stability, a 1.2% is considered a small percentage that would not cause problems (in the interval of plant biodiesel).

Regarding to the fuel properties regulated by the ASTM D975 and EN590 standards (Table S1), there is a change when using MW as a pre-treatment, decreasing the kinematic viscosity below the set limits, with a value of 1.94 mm²/s (Table S2). It is not a value very far from the standards, but in the case of US, it fulfils all the regulation standards. This difference in terms of the fuel properties is due to the different effects of both treatments in the lipid extraction. In general terms, all the properties improve when the studied pre-treatments are applied, with the exception of the saponification value (SV), but they are very close to the initial ones.

3.5. Effect of sludge particle size on the biodiesel yield

Since it has been demonstrated that extraction is a limit stage, it is interesting to carry out the *in situ* transesterification at different sludge particle sizes, as a smaller particle size could favour the extraction process by increasing the contact surface. As can be seen in Fig. 3a, the biodiesel yield follows the order: 50–100 μm (24.3%) > no sieving (21.23%) > 100–250 μm (18.6%) > 250–355 μm (15.2%). Only the particle size of 50–100 μm, the smallest one, get an improvement in the final yield, with an increase in 14.1%, even higher than the obtained with MW (23.8%). The lipid content of each fraction was analysed,

without relevant variations in the results. Therefore, the difference in yield cannot be due to a difference in the lipid content, but an improvement in the lipid extraction.

This difference in performance is attributed to the fact that a smaller particle size results in a better sludge/solvent contact, which lead to greater lipid extraction and higher biodiesel yield. Since the non-pre-treated sludge is a mixture of all particle sizes, there is not a net improvement of the extraction efficiency comparing the yield of each individual fraction and the whole sludge.

Regarding the yield profile, it is quite similar during the first 8 h, and the maximum lipid extraction capacity and therefore maximum biodiesel yield, was reached after 14 h for 250–355 μm, and after 17 h in the case of 50–100 and 100–250. Since the biodiesel yield remains constant after 17 h in all cases and no free lipids were detected in the final samples, the different lipid availability in each fraction is the main responsible of the observed yield differences.

Since US has resulted in a higher performance, they were applied to the different particle sizes to check if this could further increase the maximum yield obtained, giving a synergistic effect of both pre-treatments (sieving and US). As observed in Fig. 3b, a decrease in yield between 5 and 10% is observed compared to sieving without ultrasound, being larger to smaller particle sizes. These results suggest that the US can damage lipid content, the smaller the particle size, the greater the damage, which has already been reported in previous works [38–39]. When ultrasound without sieving was used, the biodiesel yield was higher since the raw material contains mostly particles greater than 355 μm. In fact, the raw sludge is composed mainly of larger particles, being the small range (50–100 μm) the least representative.

Regarding the yield profile, as when sieving was checking without US, it is quite similar during the first 8 h. The difference after this time is due to the different amount of lipids available due to the extraction

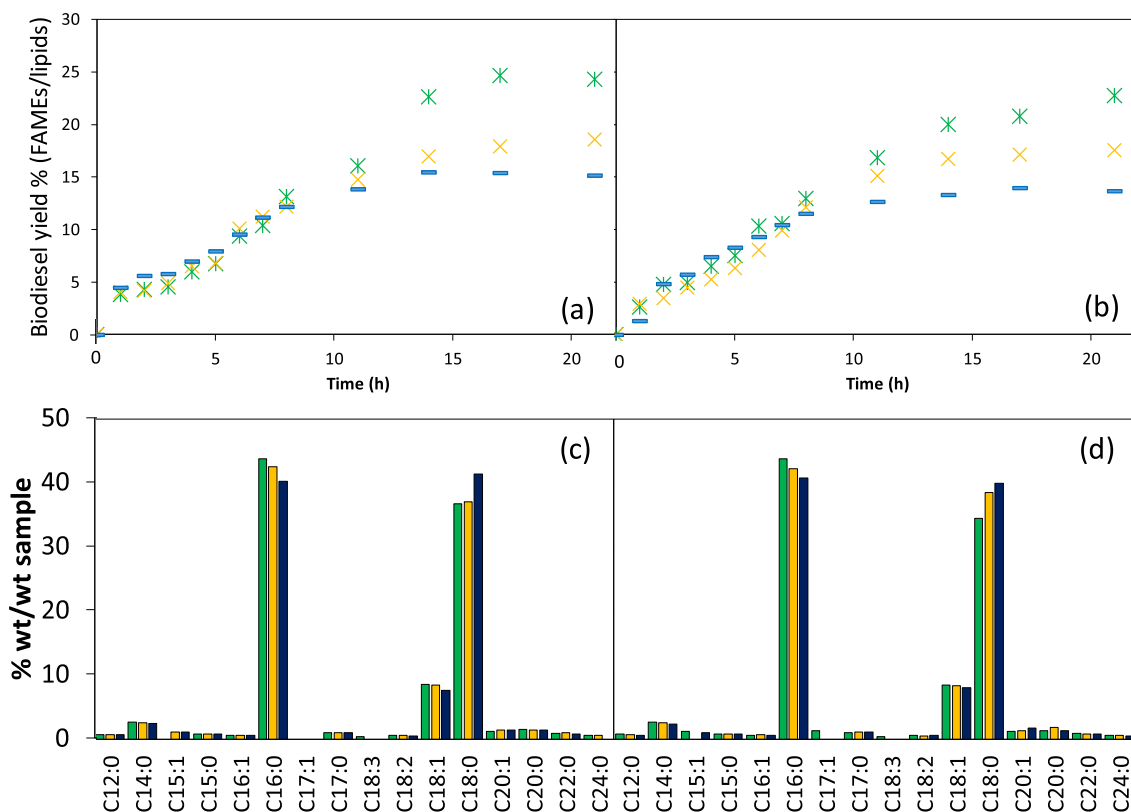


Fig. 3. Temporal evolution of the biodiesel yield at (a) different sludge particle size and (b) different sludge particle size and US, and FAMES composition (after 21 h), at (c) different sludge particle size and (d) different sludge particle size and US. 50–100 μm (green), 100–250 μm (yellow) and 250–355 μm (blue). Catalyst/sludge ratio 1:2, MeOH/sludge ratio 33:1 and 120 °C reaction temperature. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

process, which leads to a different final yield. In the case of 100–250 and 250–355 μm a constant profile was obtaining after 14 h, meanwhile for 50–100 μm , it seems that more time is necessary to reach the maximum biodiesel yield.

3.6. Effect of sludge particle size on the biodiesel quality

Comparing the FAMES profile obtained at different particles sizes, the C16:0 fraction decreases by increasing the particle size, whereas C18:0 increase at increasing particle sizes (Fig. 3c). This is due to the different composition depending on the particle size of the sludge, since only a differentiation by size has been carried out, without modifying the starting raw material or subjecting it to any other treatment. The fraction of saturated compounds remains almost constant (around 88%), but there are small differences in the unsaturated moieties. As particle size decreases, the resulting biodiesel shows a slightly higher fraction of polyunsaturated and *vice-versa*, which implies the opposite effect in the monounsaturated FAME yields.

About the biodiesel properties (Table S2), these properties hardly differ from the result obtained without sieving, except the kinematic viscosity. This last parameter is, in all cases, lower than regulated standards. For this reason, although smaller sieving results in an increase in the biodiesel yield, it is not a good alternative, since the kinematic viscosity is found below the standards.

When sieving and US were combined (Fig. 3d), there are no major differences in the FAMES profile, except in the amount of C18:0, which increase when US is applied to the particle size 100–250 μm . Besides, taking into account the properties of the final biodiesel, shown in Table S2, it does not imply an improvement in the fuel quality. Regarding to the regulated properties, the kinematic viscosity remains below the minimum value set by the standards, as in the case of the abovementioned treatments.

3.7. Effects of reaction temperature

In situ esterification reactions were carried out at three different temperatures (40, 80 and 120 $^{\circ}\text{C}$) below to the upper temperature limit of the catalyst operation. The catalyst selected was A-IR120 with catalyst/sludge ratio 1:2, MeOH/sludge ratio 33:1 for 21 h and US as pre-treatment, since it was proven to be the best alternative for an increase in the process performance.

As observed in Fig. 4, as the temperature increases, the biodiesel yield also increases following the order: 120 $^{\circ}\text{C}$ (27.6%) > 80 $^{\circ}\text{C}$ (22.5%) > 40 $^{\circ}\text{C}$ (14.5%) [40]. This fact is a good agreement with an endothermic equilibrium-limited overall process. Besides, the slope before to reach the maximum biodiesel yield, also increase with the

temperature, so the reaction rate increases with temperature. Similar trend has been reported by other authors [11,20–21]. In the final samples, no lipids were detected in any case, suggesting that the amount of extracted lipids increases as temperature increases. Therefore, the slope in the biodiesel profile (formation rate) increases because there are more lipids available for the transesterification reaction. Therefore, temperature plays a key role in the lipids extraction, which determines the maximum biodiesel yield.

In the case of 40 $^{\circ}\text{C}$ the maximum biodiesel yield was reached after 8 h reaction time, meanwhile for 80 $^{\circ}\text{C}$ and 120 $^{\circ}\text{C}$ it was achieved after 11 h. Maximum lipid extraction was reached in all the cases, since the biodiesel yield remains constant with the time. In the same way, negligible lipid presence was detected in the final samples, suggesting that lipid extraction efficiency, and therefore biodiesel yield, increase as temperature increases.

3.8. Effect of temperature on biodiesel quality

As in the previous sections, it is also important to study the effect of the reaction temperature on the biodiesel quality. Fig. 4b shows the FAMES profile at different temperatures. In the case of 80 $^{\circ}\text{C}$ and 120 $^{\circ}\text{C}$, the FAMES profile is quiet similar, with small variations in the amount of C16:0 and C18:0, but it changes drastically for 40 $^{\circ}\text{C}$. Not only the FAMES profile changes, but also the FAMES variety. At 120 $^{\circ}\text{C}$, 17 different FAMES were obtained, 15 at 80 $^{\circ}\text{C}$ and only 4 at 40 $^{\circ}\text{C}$ (C15:0, C16:0, C18:1 and C18:0), which will affect the biodiesel properties. When the temperature is lowered to 80 $^{\circ}\text{C}$, the profile of saturated, monounsaturated and polyunsaturated FAMES is rather similar. On the contrary, at 40 $^{\circ}\text{C}$, polyunsaturated FAMES are not obtained, and the percentage of monounsaturated decreases from close to 12% at 120 $^{\circ}\text{C}$ and 80 $^{\circ}\text{C}$ respectively, to 1.07%.

The different biodiesel properties as a function of temperature are shown in Table S3. Due to the drastic variation in the FAMES profile, and the large decrease in unsaturated ones at 40 $^{\circ}\text{C}$, some biodiesel properties are extremely modified, such as, DU, IN, kinematic viscosity and HHV. Of these properties, the only one with a value set by the regulations is the kinematic viscosity, which decrease by half, far from the minimum set by the standards. At 80 $^{\circ}\text{C}$, although there is no great variation in the biodiesel properties, the highest differences are in the HHV and kinematic viscosity, where the latter no longer meets with the regulation. Thus, considering both the biodiesel yield and quality, the higher temperature offers the best results.

3.9. Kinetic modelling

A kinetic model is proposed for gaining further understanding about

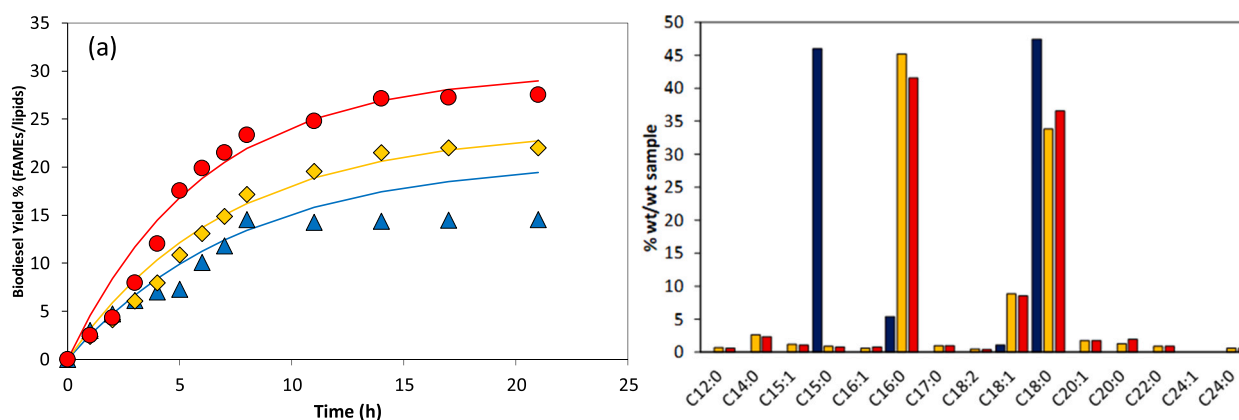
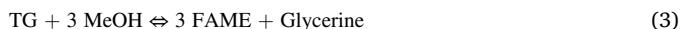


Fig. 4. Temporal evolution of the biodiesel yield (a) and FAMES composition (after 21 h) (b), at different temperatures: 40 $^{\circ}\text{C}$ (blue), 80 $^{\circ}\text{C}$ (yellow) and 120 $^{\circ}\text{C}$ (red). Lines corresponds to kinetic model predictions. Catalyst/sludge ratio 1:2, MeOH/sludge ratio 33:1 and US as pre-treatment. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the reaction mechanism, and as a starting point for designing purposes. The overall transesterification reaction is given by:



Due to the large methanol excess, its concentration was considered constant, and the reaction was considered as irreversible. A first-order reaction is proposed, and the concentration of FAMES can be obtained according to the Eq. (4):

$$C_{\text{FAMES}} = 3 C_{\text{TGO}} (1 - e^{-kt}) \quad (4)$$

where C_{FAMES} is the concentration of FAMES with the time ($\text{mmol}\cdot\text{L}^{-1}$), C_{TGO} is the initial concentration of triglycerides ($\text{mmol}\cdot\text{L}^{-1}$, limited by extraction equilibrium), t the time and k is the apparent kinetic constant which can be obtained by applying the Microsoft Excel Solver tool.

Fig. 4a shows the good fit of the proposed model at 80 °C and 120 °C (r^2 of 0.97 and 0.98 respectively), whereas Table S4 summarizes the values of the kinetic constant.

On the other hand, as observed in Fig. 4a, the model does not provide good data fitting at 40 °C, especially after the first hours of reaction time. This fact suggests that the process is limited by lipid extraction at the lowest temperatures, leading to lower biodiesel yields than the expected ones.

3.10. Effects of catalyst/sludge ratio

The sludge/catalyst ratio is one of the most important reaction parameters, which affect the reaction efficiency. Different sludge/catalyst ratios were studied keeping constant the sludge loading. As expected, and shown in Fig. 5, higher catalyst loadings provide higher biodiesel yields and faster reaction rates: 1:1 (32.9%) > 1:2 (27.6%) > 1:4 (16.5%). For 1:2 and 1:4 there is no big difference during the first 3 h, although it can be seen that after this time, the reaction rate is higher for 1:2 than for 1:4, which agrees with literature [11,18].

As observed in the Fig. 5, the FAMES profile does not change at different catalyst/sludge ratios, since the amount and variety of extracted lipids, does not depend on the catalyst loading. This can also be corroborated from the biodiesel properties, which remain unaltered in the experiments changing catalyst loadings (Table S3).

Since there are no significant variations, the biodiesel quality obtained at the three different catalyst/sludge ratios meets the standards, so the 1:1 ratio is chosen as optimal since it results in a higher reaction rate and biodiesel yield (32.9%). The summary of the properties obtained under optimal conditions can be seen in Table 2.

The maximum biodiesel yield obtained under optimal conditions can be compared with the obtained in other works with heterogeneous catalyst and sludge as raw material. Siddiquee et al., studied biodiesel

Table 2

Biodiesel properties obtained under optimal conditions: catalysts/sludge ratio 1:1, MeOH/sludge ratio 33:1, 120 °C and US as pre-treatment.

Degree of unsaturation (DU)	14.85
Long chain saturated factor (LCSF)	25.67
Cold Filter Plugging Point (CFPP, °C)	64.16
Saponification value (SV, mgKOH/g)	190.4
Iodine number (IN, $\text{gI}_2/100 \text{ g}_{\text{biodiesel}}$)	13.43
Density at 15 °C (ρ , kg/m^3)	907
Kinematic viscosity at 40 °C (η_i , mm^2/s)	2.01
Higher heating value (HHV, MJ/kg)	80.3
Cetane number (CN ₁)	71.8
Cetane number (CN ₂)	68.8
Cetane number (CN ₃)	68.0

production using SBA-15 impregnated with a heteropolyacid as heterogeneous catalysts, and wastewater sludge as raw material. The maximum biodiesel yield was 30.14% (on the basis of lipid), a little lower than that obtained in this work [17]. The results can also be compared with those obtained by Wu et al., by using alkali catalyst for biodiesel production from sewage sludge. In this case, they obtained a yield of FAME of 6.8% (on the basis of dry sludge) [41]. In this work, the biodiesel yield was 32.8% FAMES/lipids; taking into account that the percentage of lipids in the dry sludge is 20.54%, the maximum biodiesel yield was 6.7% FAMES/dry sludge. The results obtained in this work are comparable with those obtained by Wu et al., adding the advantages of using heterogeneous acid catalyst, already mentioned.

The proposed kinetic model was applied at different sludge/catalyst ratio. As shown in Fig. 5a, the model fits with the experimental data in all cases, with a correlation coefficient higher than 0.95 (Table S4). The amount of acid catalyst has a significant effect on the reaction rate (Table S4). Mondala et al., attributed this observation to the increase in the rate of formation of the reaction intermediates, caused by the presence of a higher catalyst loading [42].

3.11. Catalyst reuse

It is fully accepted that resins need to be regenerated after a period of use in order to recover their initial performance, which entails an increase in operating costs. That is why it is important to study the reuse of the resin. In this study the catalyst was used directly after filtration, for several reaction cycles. The reusability reactions were carried out under optimal conditions: A-IR120 as catalyst, catalyst/sludge ratio 1:1, MeOH/sludge ratio 33:1 for 21 h at 120 °C and US as pre-treatment. The amount of catalyst hardly varied in successive batch reactions, since the catalyst losses during filtration were negligible.

As it can be observed in Fig. 6, the same resin has been employed for 8 reaction cycles. The biodiesel yield remains constant for sixth cycles

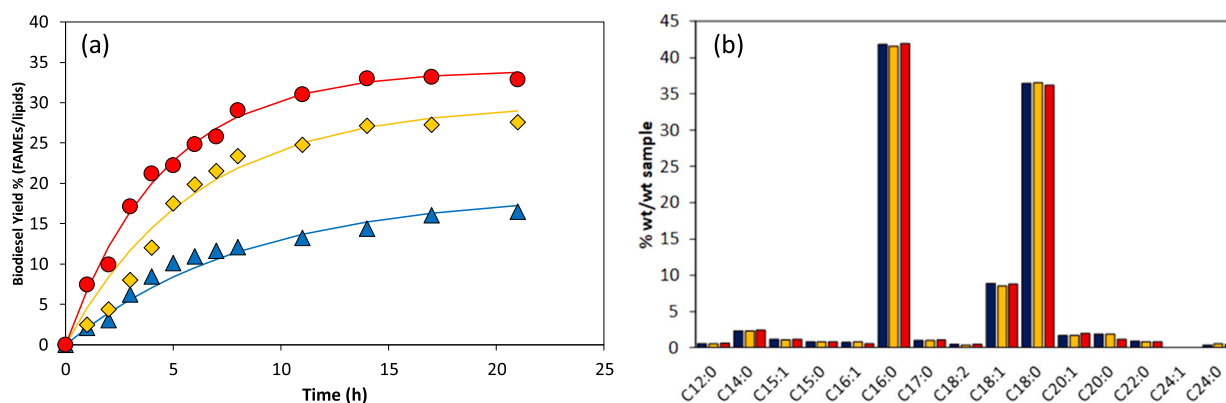


Fig. 5. Temporal evolution of the biodiesel yield (a) and FAMES composition (after 21 h) (b), at different catalysts/sludge ratios: 1:1 (red), 1:2 (yellow) and 1:4 (blue). MeOH/sludge ratio 33:1, 120 °C and US as pre-treatment. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

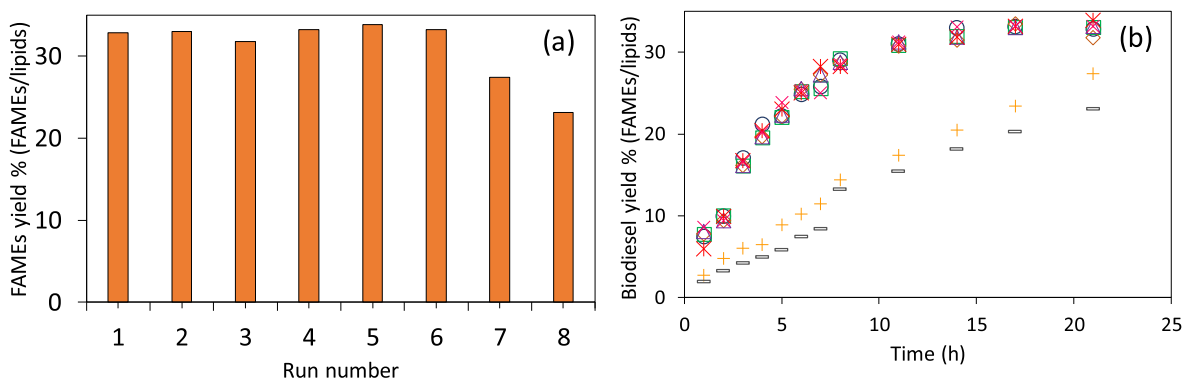


Fig. 6. Reusability of A-IR120 catalyst. Reaction conditions: catalyst/sludge ratio 1:1, MeOH/sludge ratio 33:1 for 21 h at 120 °C and US as pre-treatment. (a) Biodiesel yield at different runs and (b) reaction profile at different runs: ○ 1st run, □ 2nd run, ◇ 3rd run, △ 4th run, * 5th run, × 6th run, + 7th run and – 8th run.

with a variation of 2.1% in the biodiesel yield (values from 31.8% to 33.2%). For the seventh and eighth run the performance loss is noticeable with a decrease of 16.6% and 29.7% respectively from the initial value (Fig. 6a). This behaviour on the decrease in the catalyst activity have been reported in previous studied and it has been associated to water blocking the active sites of the catalysts [11,43].

Regarding to the reaction profile, it practically the same during the first 6 runs. For the sixth and seventh runs, a decrease in the reaction rate can be seen due to the decrease in the active centres available (Fig. 6b). Even in the last two runs, it seems that not all lipids reacted after the reaction time.

The catalyst reusability cannot be compared with other authors with sludge as raw material and heterogeneous catalyst, since to the best of our knowledge, there are no studies with several reaction cycles. However, the reuse of ion-exchange resins to obtain biodiesel can be compared with studied that checked other raw materials. Zanette et al., studied the catalyst reutilization in five successive batch experiments with Amberlyst 15 as catalyst and *Jatropha curcas* as raw material [13]. They found a decrease in FAME yield as the number of reuse increases, from the first run. On the other hand, Ilgen, investigated the esterification of oleic acid with Amberlyst 46 as catalyst, and the conversion was almost kept constant for 10 runs [20].

Taking all this into account, the experimental results obtained are promising and confirm the viability of Amberlyst IR120 as heterogeneous catalyst for *in situ* transesterification with sewage sludge as raw material. The catalyst not only offers good results, but it can also be reuse for at least six runs without a decrease in the biodiesel yield.

4. Conclusions

Amberlyst IR120 is the catalyst with the highest biodiesel yield and the best biodiesel quality, due to the catalyst acidity and swelling capacity. MW and US as pre-treatments improve the biodiesel yield, however, only the product obtained by US meet with the standards.

Although sludge sieving (50–100 µm) leads to an improvement in the lipid extraction, there is a deterioration in the biodiesel quality. Besides, US can damage lipid structure, which results in lower quality fuels.

The maximum biodiesel yield obtained was 32.9% at the optimal conditions. After reuse, the activity of A-IR120 did not decrease for 6 runs.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jwpe.2021.102335>.

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