Biodiesel production from sewage sludge lipids catalysed by Brønsted acidic ionic liquids

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Abstract

Production of biodiesel from sewage sludge lipids was catalysed by six different Brønsted acidic imidazolium and long chain ammonium ionic liquids; both with an alkane sulfonic acid group and with different anions. Among the ionic liquid tested, 4-(3-methylimidazolium)butanesulfonic acid trifluoromethanesulfonate, [mimC$_4$SO$_3$H][SO$_3$CF$_3$], was selected as the best catalyst due to its high catalytic performance and purer biodiesel obtained than the equivalent ammonium ionic liquid, 4-(trihexylammonium)butanesulfonic acid trifluoromethanesulfonate, [N$_{6\,6\,6}$(C$_4$SO$_3$H)][SO$_3$CF$_3$]. The influence of different reaction variables on the biodiesel yield was studied using [mimC$_4$SO$_3$H][SO$_3$CF$_3$] as a catalyst. The yield of fatty acid methyl esters (biodiesel) reached 90% (based on saponifiable lipids) under the following optimised conditions: 10:1 molar ratio of methanol to saponifiable lipids, 7 wt% ionic liquid catalyst (wt%, based on lipids), 100 ºC and 5 h. In addition, the ionic liquid has a good reusability and can be easily separated from the biodiesel. These acidic ionic liquids were found to be efficient catalysts for the synthesis of biodiesel from low-cost and non-edible feedstock like sewage sludge lipids.

Keywords

Ionic liquid, Sewage sludge lipids, Esterification, Biodiesel

1. INTRODUCTION

The need to use alternative renewable fuels, while minimising the environmental impact, is currently increasing due to the rise in oil price, the depletion of sources of fossil fuels and the environmental problems associated with their combustion. Biodiesel is one of the most promising renewable fuels proposed as an alternative to fossil diesel that can be directly used with current engine and refuelling technologies without major modification [1,2]. Biodiesel is generally produced by transesterification of vegetable oils or animal fats with methanol, yielding fatty acids methyl esters (FAMEs) from the lipid fraction. However, the competitive potential of biodiesel is currently limited by the high price of the common lipid feedstocks, which constitutes between 70-85% of the overall biodiesel production cost, strongly influencing the final price of this biofuel [1,3,4]. Furthermore, the cultivation of edible vegetable oils for biofuels raises the concern of food shortage, which competes with fuel production [1]. Therefore, a low-cost and non-edible feedstock is required in order to reduce the production costs and to facilitate competitiveness with petroleum diesel.

Among non-edible feedstocks, municipal sludge lipids are gaining more attention nowadays as a promising lipid source which can make biodiesel production profitable [3-7]. As municipal sewage sludge is a waste, formed during the treatment of wastewater, it is a possible alternative source of lipids for the production of biodiesel, consequently lowering the wastewater treatment plant (WWTP) operation costs.

Nevertheless, the production of biodiesel from sludge lipids as well as from other low-cost feedstock poses significant processing problems in standard biodiesel manufacturing due to the high free fatty acids (FFAs) content, which in the case of the sewage sludge, can account for up to 70% of the lipid content [4,7]. It is well known that the high content of FFAs in lipid feedstocks reduces the biodiesel yield significantly when using a conventional basic catalyst (e.g., NaOH), because of soap formation. This hinders the separation and purification of the by-product. Regarding the sludge lipids with the huge content of FFAs, only soaps would be produced using conventional basic catalyst. Acid catalysts (*e.g.*, H_2SO_4) can be used for simultaneous esterification of FFAs and transesterification of glycerides without any soap formation, however the transesterification of glycerides is much slower and the reaction times are much longer to achieve a high conversion. Homogenous acid and base catalysts are corrosive and difficult to remove after the reaction; a large amount of wastewater is produced due to the separation and purification of products and catalyst [2,8]. In order to overcome these problems, clean and promising new catalysts are required.

Recently, room-temperature ionic liquids (ILs) have been widely recognised as green replacements for volatile organic solvents and a relatively clean and promising catalyst in a variety of applications [8-10]. ILs are defined as salts that are in liquid state at below 100 ºC. They possess important attributes such as a wide liquid range, non-volatility (except at low pressures and high temperature), high catalytic activity, excellent chemical and thermal stability, potential recoverability, design possibilities, and ease of separation of the products from reactants [9-12]. Recent developments have demonstrated that the use of ILs in biodiesel production is a promising alternative for efficient green preparation of biofuels. ILs have a great potential for biodiesel production due to the ease of product isolation from the reaction, the possibility of reusing the catalyst and the low environmental impact [2,8,10]. Several publications have shown that both acidic and basic ionic liquids can function as a good catalyst for transesterification and/or esterification reactions to obtain biodiesel [13-15]. However, in the case of sewage sludge lipids, because of high FFAs content, acidic ILs are preferred. The use of Brønsted acidic ILs as a catalyst for the production of biodiesel from lipid feedstocks with high FFAs content was successfully studied [13,16-19]. Therefore, ILs were shown to have enormous potential for the production of biodiesel from low-cost feedstock as a green replacement for corrosive and volatile acid catalysts. Although extensive studies have been performed in this area, the use of ILs as a catalyst for the esterification of sewage sludge lipids is absent from the biodiesel related literature.

Thus, the purpose of this research was to investigate a possible application of Brønsted acidic ILs with an alkane sulfonic acid functional group for the production of biodiesel from sludge lipids. Six different ILs were prepared and their effects as catalysts on the synthesis of biodiesel from sludge lipids was examined, and compared to conventional acid catalysts. The reaction conditions were optimised and the influence of the ILs on the FAMEs composition of biodiesel was also evaluated.

2. MATERIALS AND METHODS

2.1. Reagents

All reagents used in this study were supplied by Sigma–Aldrich. 1,4-butanesultone (purity ≥99%), 1-methylimidazole (purity ≥99%), trihexylamine (purity 96%), trifluoromethanesulfonic acid (purity 98%), sulphuric acid (purity 99.999%) and lithium(I) bistriflamide (purity ≥99%) were used to synthesise the ILs. The synthesis of biodiesel was carried out using anhydrous methanol (purity 99.8%) and sulfuric acid (purity 99.999%) at the highest purities available. Standards, 37 component FAMEs mix and methyl nonadecanoate (purity ≥99.5%) were used for the identification and quantification of fatty acid methyl esters (FAMEs). Analytical standards of C12:0, C14:0, C15:0, C16:0, C16:1, C18:0, C18:1, and C18:2 were used for free fatty acids (FFAs) determination. Oleic acid, triolein, monoolein, diolein and triolein were the standards used for identification of the lipid classes by TLC. Silica gel matrix TLC aluminium plate without fluorescent indicator was supplied by Sigma–Aldrich. All other solvents and reagents were high performance liquid chromatography grade and analytical reagent grade.

2.2. Synthesis of $NH(SO_2CF_3)_2$

Bis{(trifluoromethyl)sulfonyl}amine, $NH(SO_2CF_3)_2$ was prepared by the addition of sulfuric acid (15.0 g, 145.3 mmol) to lithium(I) bistriflamide (15.0 g, 52.3 mmol) in 60 cm^3 round-bottom tube and connected to a Kugelrohr apparatus. The mixture was heated under vacuum (60 °C, 0.1 mbar) and the product was sublimed out of the reaction vessel. White crystals where obtained (14.05 g, 50.2 mmol, 96 %; T_m = 52-54 °C).

2.3. Synthesis of the catalysts

2.3.1. Brønsted acidic imidazolium-based IL

The imidazolium-based ILs were prepared by the method previously reported in literature [20] with minor modifications. 1-methylimidazole (16.6 g, 0.2 mol) and 1,4-butanesultone (27.2 g, 0.2 mol) were added to a round bottomed flask (250 cm^3) fitted with a condenser and stirred vigorously at 80 ºC in an oil bath for 10 h under nitrogen purge. The synthesis of zwitterion was performed without any solvent. The obtained solid zwitterion was washed with toluene followed by diethyl ether and then dried under vacuum overnight (yield: 92%). Then, a stoichiometric amount of acid (H_2SO_4, CF_3SO_3H, $NH(SO_2CF_3)_2$) was added dropwise to the zwitterion and stirred overnight at 60 ºC in an oil bath under reflux condenser and nitrogen purge. The resultant viscous ILs were dried under vacuum before their characterisation by ^{1}H NMR, ^{13}C NMR and Mass spectra, and before their use as a catalyst.

2.3.2. Brønsted acidic ammonium-based IL

For the preparation of ammonium zwitterion the adapted procedure from [21] was used. Trihexylamine (53.9 g, 0.2 mol) and 1,4-butanesultone (27.2 g, 0.2 mol) were dissolved into acetone in a round bottomed flask (500 cm^3), and the resulting solution was mixed under dry nitrogen gas atmosphere. The obtained solution was stirred for three days at 80 °C in an oil bath under reflux condenser and nitrogen purge. After removal of acetone by evaporation, the residual yellow liquid was repeatedly washed with access amounts of anhydrous diethyl ether, and white paste was obtained. This white paste was dissolved in dichloromethane, and the solution was passed through a column filled with aluminium oxide. Dichloromethane was evaporated and the white solid was obtained. After then, it was washed with ethyl ethanoate, and obtained white powder was freeze dried for 24 h (yield: 60%). The ILs was prepared by adding different acids to the zwitterion, using the same procedure described above (Subsection 2.3.1), increasing only the temperature of the reaction to 80 °C.

2.4. Characterisation of the IL catalysts

Brønsted acidic ILs with an alkane sulfonic acid group ($-SO_3H$) were especially selected for this study due to their much better catalytic activity in esterification and/or transesterification than ILs without the $-SO_3H$ functional group [17,18]. Six different imidazolium and long chain ammonium Brønsted acidic ILs, both with butanesulfonic functional group and with different anions, were synthesised and their chemical structures are depicted as shown in Figure 1. The zwitterions and ILs were characterised by ^{1}H NMR, ^{13}C NMR and Mass spectra (as given below) confirming the structure of the respective ILs.

Zwitterion, [mimC$_4$SO$_3$]; ^{1}H NMR spectrum (400 MHz, d^4-methanol): δ/ppm = 1.81 (p, 2H, C*H*$_2$, *J* = 7), 2.08 (p, 2H, C*H*$_2$, *J* = 7), 2.87 (t, 2H, C*H*$_2$-SO$_3$, *J* = 8), 3.95 (s, 3H, N-C*H*$_3$), 4.29 (t, 2H, N-C*H*$_2$, *J* = 8), 7.59 (t, 1H, C*H*, *J* = 3), 7.68 (s, 1H, C*H*, *J* = 3), 8.97 (s, 1H, N-C*H*-N).
^{13}C NMR spectrum (100 MHz, d^4-methanol): δ/ppm = 22.73 (*C*H$_2$), 29.84 (*C*H$_2$), 36.47 (*C*H$_2$-SO$_3$H), 50.31 (N-*C*H$_3$), 51.41 (N-*C*H$_2$), 123.71 (*C*H), 124.99 (*C*H), 138.06 (N-*C*H-N).

IL 1: 4-(3-methylimidazolium)butanesulfonic acid hydrogensulfate, [mimC$_4$SO$_3$H][HSO$_4$]; ^{1}H NMR spectrum (400 MHz, d^4-methanol): δ/ppm = 1.82 (p, 2H, C*H*$_2$, *J* = 6), 2.09 (p, 2H, C*H*$_2$, *J* = 6), 2.88 (t, 2H, C*H*$_2$-SO$_3$H, *J* = 8), 3.96 (s, 3H, N-C*H*$_3$), 4.30 (t, 2H, N-C*H*$_2$, *J* = 8), 7.59 (t, 1H, C*H*, *J* = 4), 7.67 (s, 1H, C*H*, *J* = 4), 8.97 (s, 1H, N-C*H*-N).

^{13}C NMR spectrum (100 MHz, d^4-methanol): δ/ppm = 22.73 (*C*H$_2$), 29.87 (*C*H$_2$), 36.54 (*C*H$_2$-SO$_3$H), 50.34 (N-*C*H$_3$), 51.46 (N-*C*H$_2$), 123.73 (*C*H), 125.04 (*C*H), 138.07 (N-*C*H-N).

TOF MS ES+ *m/z* (% rel. intensity): [mimC$_4$SO$_3$H]$^+$ 219.0803 (100), 220.0830 (11.0), 221.0780 (5.5). **TOF MS ES-** *m/z* (% rel. intensity): [HSO$_4$]$^-$ 96. 9596 (100), 98.9566 (5.5).

IL 2: 4-(3-methylimidazolium)butanesulfonic acid trifluoromethanesulfonate, [mimC$_4$SO$_3$H][SO$_3$CF$_3$];

^{1}H NMR spectrum (400 MHz, d^4-methanol): δ/ppm = 1.82 (p, 2H, C*H*$_2$, *J* = 6), 2.08 (t, 2H, C*H*$_2$, *J* = 6), 2.90 (t, 2H, C*H*$_2$-SO$_3$H, *J* = 8), 3.95 (s, 3H, N-C*H*$_3$), 4.29 (t, 2H, N-C*H*$_2$, *J* = 6), 7.59 (broad t, 1H, C*H*), 7.67 (broad t, 1H, C*H*), 8.95 (s, 1H, N-C*H*-N).

^{13}C NMR spectrum (100 MHz, d4-methanol): δ/ppm = 22.70 (*C*H$_2$), 29.86 (*C*H$_2$), 36.53 (*C*H$_2$-SO$_3$H), 121.83 (q, *C*F$_3$, *J* = 317), 50.32 (N-*C*H$_3$), 51.49 (N-*C*H$_2$), 123.72 (*C*H), 125.04 (*C*H), 138.04 (N-*C*H-N).

TOF MS ES+ *m/z* (% rel. intensity): $[mimC_4SO_3H]^+$ 219.0803 (100), 220.0830 (11.0), 221.0780 (5.5). **TOF MS ES-** *m/z* (% rel. intensity): $[CF_3SO_3]^-$ 148.9520 (100), 150.9489 (4.96).

IL 3: 4-(3-methylimidazolium)butanesulfonic acid bis{(trifluoromethyl) sulfonyl}amide, $[mimC_4SO_3H][N(SO_2CF_3)_2]$;

^{1}H NMR spectrum (400 MHz, d^4-methanol): δ/ppm = 1.82 (p, 2H; CH_2, J = 8), 2.08 (p, 2H, CH_2, J = 7), 2.90 (t, 2H, CH_2-SO_3H, J = 8), 3.95 (s, 3H, N-CH_3), 4.28 (t, 2H, N-CH_2, J = 7.2), 7.58 (s, 1H, C*H*), 7.66 (s, 1H, C*H*), 8.94 (s, 1H, N-C*H*-N).

^{13}C NMR spectrum (100 MHz, d^4-methanol): δ/ppm = 22.71 (*C*H_2), 29.85 (*C*H_2), 36.53 (*C*H_2-SO_3H), 121.24 (q, *C*F_3, J = 319), 50.34 (N-*C*H_3), 51.48 (N-*C*H_2), 123.71 (*C*H), 125.03 (*C*H), 137.99 (N-*C*H-N).

TOF MS ES+ *m/z* (% rel. intensity): $[mimC_4SO_3H]^+$ 219.0833 (100), 220.0858 (10.6), 221.0815 (7.0). **TOF MS ES-** *m/z* (% rel. intensity): $[N(SO_2CF_3)_2]^-$ 279.9166 (100), 281.9217 (11.82).

Zwitterion, $[N_{6\,6\,6}(C_4SO_3)]$; ^{1}H NMR spectrum (400 MHz, d^1-trichloromethane): δ/ppm = 0.90 (t, 9H, N-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3, J = 8), 1.26-1.43 (m, 18H, 3 N-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3), 1.58-1.70 (m, 6H, N-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3), 1.83-1.98 (m, 4H, N-CH_2-CH_2-CH_2-CH_2-SO_3), 2.88 (t, 2H, N-CH_2-CH_2-CH_2-CH_2-SO_3, J = 8), 3.18 (t, 6H, N-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3, J = 8), 3.46 (t, 2H, N-CH_2-CH_2-CH_2-CH_2-SO_3, J = 8). ^{13}C NMR spectrum: δ/ppm (100 MHz, d^1-trichloromethane): δ/ppm = 13.95 (N-CH_2-CH_2-CH_2-CH_2-CH_2-*C*H_3), 20.94 (N-CH_2-CH_2-*C*H_2-CH_2-SO_3), 22.09 (N-CH_2-CH_2-CH_2-CH_2-*C*H_2-CH_3), 22.50 (N-CH_2-CH_2-CH_2-*C*H_2-CH_2-CH_3), 22.69 (N-CH_2-*C*H_2-CH_2-CH_2-SO_3), 26.17 (N-CH_2-CH_2-*C*H_2-CH_2-CH_2-CH_3), 31.27 (N-CH_2-*C*H_2-CH_2-CH_2-CH_2-CH_3), 50.12 (N-CH_2-CH_2-CH_2-*C*H_2-SO_3), 59.10 (N-*C*H_2-CH_2-CH_2-CH_2-CH_2-CH_3), 59.27 (N-*C*H_2-CH_2-CH_2-CH_2-SO_3).

IL 4: 4-(trihexylammonium)butanesulfonic acid hydrogensulfate, [N$_{6\,6\,6}$(C$_4$SO$_3$H)][HSO$_4$]; ^{1}H NMR spectrum (400 MHz, d^1-trichloromethane): δ/ppm = 0.89 (t, 9H, N-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-C*H*$_3$, *J* = 8), 1.24-1.43 (m, 18H, 3 N-CH$_2$-CH$_2$-C*H*$_2$-C*H*$_2$-C*H*$_2$-CH$_3$), 1.52-1.72 (m, 6H, N-CH$_2$-C*H*$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_3$), 1.81-2.03 (m, 4H, N-CH$_2$-C*H*$_2$-C*H*$_2$-CH$_2$-SO$_3$H), 3.03-3.23 (m, 2H, N-CH$_2$-CH$_2$-CH$_2$-C*H*$_2$-SO$_3$H), 3.23-3.36 (m, 8H, N-C*H*$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_3$, N-*C*H$_2$-CH$_2$-CH$_2$-CH$_2$-SO$_3$H), 12.25 (s, 2H, N-CH$_2$-C*H*$_2$-CH$_2$-CH$_2$-SO$_3$*H*, *H*SO$_4$).

^{13}C NMR spectrum: δ/ppm (100 MHz, d$_1$-trichloromethane): δ/ppm = 13.89 (N-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-*C*H$_3$), 20.39 (N-CH$_2$-CH$_2$-*C*H$_2$-CH$_2$-SO$_3$H), 21.23 (N-CH$_2$-CH$_2$-CH$_2$-CH$_2$-*C*H$_2$-CH$_3$), 21.81 (N-CH$_2$-CH$_2$-CH$_2$-*C*H$_2$-CH$_2$-CH$_3$), 22.29 (N-CH$_2$-*C*H$_2$-CH$_2$-CH$_2$-SO$_3$H), 25.88 (N-CH$_2$-CH$_2$-*C*H$_2$-CH$_2$-CH$_2$-CH$_3$), 31.06 (N-CH$_2$-*C*H$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_3$), 50.33 (N-CH$_2$-CH$_2$-CH$_2$-*C*H$_2$-SO$_3$H), 58.52 (N-*C*H$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_3$), 58.93 (N-*C*H$_2$-CH$_2$-CH$_2$-CH$_2$-SO$_3$H).

TOF MS ES+ *m/z* (% rel. intensity): [N$_{666}$(C$_4$SO$_3$H)]$^+$ 406.3344 (100), 407.3384 (28.78), 408.3322 (9.09), 409.3373 (1.83). **TOF MS ES-** *m/z* (% rel. intensity): [HSO$_4$]$^-$ 96.9596 (100), 98.9566 (5.55).

IL 5: 4-(trihexylammonium)butanesulfonic acid trifluoromethanesulfonate, [N$_{6\,6\,6}$(C$_4$SO$_3$H)][SO$_3$CF$_3$];

^{1}H NMR spectrum (400 MHz, d^1-trichloromethane): δ/ppm = 0.85 (t, 9H, N-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-C*H*$_3$, *J* = 8), 1.19-1.41 (m, 18H, 3 N-CH$_2$-CH$_2$-C*H*$_2$-C*H*$_2$-C*H*$_2$-CH$_3$), 1.46-1.69 (m, 6H, N-CH$_2$-C*H*$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_3$), 1.76-2.00 (m, 4H, N-CH$_2$-C*H*$_2$-C*H*$_2$-CH$_2$-SO$_3$H), 2.97-3.15 (m, 2H, N-CH$_2$-CH$_2$-CH$_2$-C*H*$_2$-SO$_3$H), 3.15-3.32 (m, 8H, N-C*H*$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_3$, N-*C*H$_2$-CH$_2$-CH$_2$-CH$_2$-SO$_3$H), 11.99 (s, 1H, N-CH$_2$-C*H*$_2$-CH$_2$-CH$_2$-SO$_3$*H*).

^{13}C NMR spectrum: δ/ppm (100 MHz, d^1-trichloromethane): δ/ppm = 13.75 (N-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-*C*H$_3$), 20.14 (N-CH$_2$-CH$_2$-*C*H$_2$-CH$_2$-SO$_3$H), 20.77 (N-CH$_2$-CH$_2$-CH$_2$-CH$_2$-*C*H$_2$-CH$_3$), 21.72 (N-CH$_2$-CH$_2$-CH$_2$-*C*H$_2$-CH$_2$-CH$_3$), 22.30 (N-CH$_2$-*C*H$_2$-CH$_2$-CH$_2$-SO$_3$H), 25.79

(N-CH$_2$-CH$_2$-*C*H$_2$-CH$_2$-CH$_2$-CH$_3$), 30.95 (N-CH$_2$-*C*H$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_3$), 50.41 (N-CH$_2$-CH$_2$-CH$_2$-*C*H$_2$-SO$_3$H), 58.21 (N-*C*H$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_3$), 58.94 (N-*C*H$_2$-CH$_2$-CH$_2$-CH$_2$-SO$_3$H), 120.24 (q, *C*F$_3$, *J* = 317.5).

TOF MS ES+ *m/z* (% rel. intensity): [N$_{666}$(C$_4$SO$_3$H)]$^+$ 406.3355 (100), 407.3387 (26.60), 408.3362 (8.72), 406.3373 (1.83). **TOF MS ES-** *m/z* (% rel. intensity): [CF$_3$SO$_3$]$^-$ 148.9520 (100), 150.9489 (5.03).

IL 6: 4-(trihexylammonium)butanesulfonic acid bis{(trifluoromethyl) sulfonyl}amide, [N$_{6\,6\,6}$(C$_4$SO$_3$H)][N(SO$_2$CF$_3$)$_2$];

^{1}H NMR spectrum (400 MHz, d^1-trichloromethane): δ/ppm = 0.88 (t, 9H, N-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-C*H*$_3$, *J* = 6), 1.20-1.43 (m, 18H, 3 N-CH$_2$-CH$_2$-C*H*$_2$-C*H*$_2$-C*H*$_2$-CH$_3$), 1.49-1.71 (m, 6H, N-CH$_2$-C*H*$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_3$), 1.78-1.99 (m, 4H, N-CH$_2$-C*H*$_2$-C*H*$_2$-CH$_2$-SO$_3$H), 3.02-3.17 (m, 2H, N-CH$_2$-CH$_2$-CH$_2$-C*H*$_2$-SO$_3$H), 3.17-3.34 (m, 8H, N-C*H*$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_3$, N-*C*H$_2$-CH$_2$-CH$_2$-CH$_2$-SO$_3$H), 12.63 (s, 1H, N-CH$_2$-C*H*$_2$-CH$_2$-CH$_2$-SO$_3$*H*).

^{13}C NMR spectrum: δ/ppm (100 MHz, d^1-trichloromethane): δ/ppm = 13.77 (N-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-*C*H$_3$), 20.31 (N-CH$_2$-CH$_2$-*C*H$_2$-CH$_2$-SO$_3$H), 21.05 (N-CH$_2$-CH$_2$-CH$_2$-CH$_2$-*C*H$_2$-CH$_3$), 21.77 (N-CH$_2$-CH$_2$-CH$_2$-*C*H$_2$-CH$_2$-CH$_3$), 22.33 (N-CH$_2$-*C*H$_2$-CH$_2$-CH$_2$-SO$_3$H), 25.80 (N-CH$_2$-CH$_2$-*C*H$_2$-CH$_2$-CH$_2$-CH$_3$), 30.99 (N-CH$_2$-*C*H$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_3$), 50.25 (N-CH$_2$-CH$_2$-CH$_2$-*C*H$_2$-SO$_3$H), 58.36 (N-*C*H$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_3$), 58.94 (N-*C*H$_2$-CH$_2$-CH$_2$-CH$_2$-SO$_3$H), 119.89 (q, *C*F$_3$, *J* = 320).

TOF MS ES+ *m/z* (% rel. intensity): [N$_{666}$(C$_4$SO$_3$H)]$^+$ 406.3355 (100), 407.3387 (26.61), 408.3362 (8.26), 409.3373 (1.83). **TOF MS ES-** *m/z* (% rel. intensity): [N(SO$_2$CF$_3$)$_2$]$^-$ 279.9173 (100), 281.9138 (10.09).

2.5. Characterisation of the sewage sludge lipids

Lipids were extracted from municipal primary sludge by direct liquid-liquid extraction with sludge acidification as described previously [4].

Water content in the extracted lipids was determined according to the European standard method EN ISO 8534 [22].

The free fatty acids (FFAs) content in the extracted lipids were analysed according to the method described by [7].

The amount of saponifiable (trans/esterifiable) matter, *i.e.* the total amount of lipids that can be converted into biodiesel (FAMEs), in the extracted lipids was analysed using a modified version of Christi´s method [4], where the lipids were converted into FAMEs using acid catalyst. Then, the FAMEs (biodiesel) produced were determined according to the European standard method EN 14103 [23], using an Agilent gas chromatograph 6890GC with a flame-ionisation detector (GC-FID), equipped with a HP-INNOWax column (19091N-133). The amount of saponifiable lipids was expressed by eqn. (1),

$$\text{Saponifiable}(\%) = \frac{\text{FAMEs}(g)}{\text{Lipid}(g)} \times 100 \qquad (1)$$

where FAMEs is the total FAMEs produced after trans/esterification by the reference method, determined by the GC-FID run, and Lipid is the amount of lipids used for trans/esterification.

The sludge lipids were also analysed by Thin Layer Chromatography (TLC) and by Fourier Transform Infrared (FTIR) spectroscopy to qualitatively understand its composition. The lipids were dissolved in hexane and spotted on a TLC plate which was then developed using a mobile phase of hexane/diethyl ether/acetic acid (60:40:1, v/v/v) [24]. The separated compounds were visualised using iodine vapour and identified by using authentic standards. For the FTIR analysis, the lipid sample was directly scanned using a Fourier Jasco FT/IR-600 Plus spectrometer with a diamond golden gate ATR (GS10542, Specac Ltd) reflectance cell.

2.6. Biodiesel (FAMEs) synthesis and analysis

As only the saponifiable part of the total lipids can be converted into biodiesel, the yield of biodiesel produced was expressed based on saponifiable lipids by eqn. (2),

$$\mathrm{FAMEs\,(\%)} = \frac{\mathrm{FAMEs\,(g)}}{\mathrm{Lipid\,(g)} \times \mathrm{Saponifiable\,(\%)}} \times 100 \qquad (2)$$

where FAMEs is the FAMEs produced after each reaction, determined by the GC-FID run. Lipid is the amount of lipid used for each reaction and Saponifiable is the content of saponifiable in the lipids (the total FAMEs that could yield from the lipid), eqn. (1).

2.6.1. Screening of the ILs

For each experiment 1 g of sludge lipids was first preheated to the designed temperature, followed by the addition of methanol (1 cm^3) and catalyst (0.2 mmol). The reaction was carried out at 40 ºC and 60 ºC in an oil bath for ½ h in a sealed tube (5 ml) under magnetic stirring at 500 rpm. After completion of the reaction, the mixture was cooled to room temperature and was observed to be biphasic with the desired product (biodiesel) remaining mostly in the upper phase, depending on the IL used. Then, the product was washed by adding 4 cm^3 of cool water, followed by further centrifugation of the mixture (5 min, 3600 rpm). The bottom layer contained water, IL and excess methanol and the upper layer contained biodiesel which was collected and analysed according to the European standard method EN 14103 [23] as described in Section 2.5. The yield of biodiesel (FAMEs) produced was calculated by eqn (2).

2.6.2. Optimisation study of different reaction parameters

The optimisation study was performed always using 1 g of sludge lipids preheated to the designed temperature before the addition of a known amount of methanol and $[mimC_4SO_3H][SO_3CF_3]$ catalyst. The reaction was performed under various conditions to study the effect of the amount of methanol (0.5, 1.0, 1.5, 2.0, 2.5, 3.0 and 3.5 cm^3), the amount of catalyst (3, 5, 7, 9 and 12%, based on the mass of lipids), the reaction temperature (25, 40, 60, 80, 100 and 120 ºC) and the reaction time (½, 1, 2, 5 and 10 h). Further procedures were performed as described above, in Subsection 2.6.1.

3. RESULTS AND DISCUSSION

3.1. Characterisation of the sludge lipids

Only the saponifiable part of the total lipids extracted from the sludge can be converted into biodiesel, *i.e.* the fatty acid methyl esters (FAMEs). Thus, it was important to determine the yields of saponifiable lipids and its composition. As shown in Table 1 the sludge lipids contains negligible water content, a very high amount of free fatty acids (65.1%) and 68.6% of saponifiable lipids, which can be converted into biodiesel. The saponifiable lipid fraction consists of 94.9% of FFAs and trace amounts of glycerides, suggesting that the main reaction during the conversion of sludge lipids into biodiesel is the esterification of the FFAs. This composition was confirmed by the FTIR and TLC analyses, presented in Figure 2. As shown in Figure 2(a), the infrared spectrum of the lipids gave the characteristic absorption bands between 2800–3000 cm^{-1} (assigned as the CH_3 and CH_2 stretching vibration in lipid acyl chain) and at 1710 cm^{-1} (assigned as the C=O stretching vibration of the free fatty acids group) while, the peak at 1739 cm^{-1} (assigned as the C=O stretching vibration of the ester glycerides group) [6,25] is scarcely seen, confirming a high content of free fatty acids in the lipids. TLC analysis also demonstrated a low content of glycerides giving a less intensive and smaller spot than for the FFAs, Figure 2(b). Among the glycerides, only the presence of di- and tri-glycerides was confirmed by the TLC analysis. Additionally, besides the other scarcely visible spots on the TLC plate, the lipid sample shows an intensive spot at the top of the developed TLC plate. Apart from the saponifiable lipids (FFAs and glycerides), non-saponifiable lipids (or non-lipids) are also present in the sludge lipids [6,7]. Thus, the intensive spot at the top of the TLC plate could be attributed to non-saponifiable matter (hydrocarbons, wax esters and/or cholesterol esters) as demonstrated by Revellame et al. [26].

3.2. Biodiesel production using different catalysts

3.2.1. Screening of the ILs

Catalytic activity of the six ILs in the esterification of sludge lipids with methanol was tested in comparison to H_2SO_4 as an industrial catalyst. The reaction was conducted at 40 ºC and 60 ºC for ½ h using 1 g of sludge lipids, 1 cm^3 of methanol and 0.2 mmol of catalyst.

As shown in Table 2, for all catalysts tested the FAMEs yield increased with a temperature increase from 40 ºC to 60 ºC, showing that the reaction is temperature-dependent. Irrespective of the reaction temperature, the conventional catalyst, *i.e.* H_2SO_4, gave a higher reaction yield than with the IL catalysts. However, the IL catalysts possess some advantages over the conventional catalyst, such as the facility for product separation from the reaction, the possibility of reusing the catalyst and the lower environmental impact [2,8,10].

The catalytic performances of the ILs containing anions with different acidities of the conjugate acid ($[HSO_4]^-$, $[SO_3CF_3]^-$, $[N(SO_2CF_3)_2]^-$) were compared to select the best performing anion. The IL anion plays a key role in the Brønsted acidic nature of the ILs; the more acidic the conjugate acid of the anion, the stronger the IL's acidity [18,27] however, this does not necessarily result in a higher catalytic activity [27].

Ionic liquids normally demonstrate low nucleophilicity and capability of providing weekly coordinating or non-coordinating environment, such as our chosen ionic liquids. When considering the acidity of a system, the first step is to evaluate from the literature (calculated or experimentally measured) if available, the acidity of the relevant protonic species in the vapour phase at low pressure, as indicated by the proton affinity (PA) values of the conjugate, neutral or anionic bases. With this information as a reference, the acidities of acid/base couples relative to each other in the solvent system can be estimated and, if possible, correlations to the same couples in other solvents can be achieved. Johnson and co-workers [28] calculated proton affinities for various neutral acids and conjugate acids, including those used in this paper (Table 4). The lower the proton affinity of the anion, the more acidic is its conjugate acid, so here the sequence of decreasing acidity is $NH(SO_2CF_3)_2 > CF_3SO_3H > H_2SO_4$, so overall $[N(SO_2CF_3)_2]^-$ ionic liquids are weaker Brønsted-base catalysts than the ones based on the other anions in this paper. However, triflate ionic liquids are much less expensive than their bistriflamide analogues.

As for the proton affinities of the zwitterions used in this paper, the following equation can be applied, and the approach from Aakeröy's paper can be adapted [29]:

$$[\text{zwit}] + H^+ \rightarrow [\text{cat}]^+ \tag{3}$$

The gas-phase proton affinity (ΔH_{PA}) of the zwitterionic species, [zwit], was evaluated as the enthalpy change associated with the addition of a proton (H^+) to the zwitterion, leading to the formation of cation, $[\text{cat}]^+$, according to Equation (1) using calculated values for the enthalpies of formation, $\Delta H_f^0([\text{zwit}])$ and $\Delta H_f^0([\text{cat}]^+)$, and the experimental value for $\Delta H_f^0(H^+)$ (1534.96 kJ mol^{-1}) [30]:

$$\Delta H_{PA} = \Delta H_f^0([\text{zwit}]) + \Delta H_f^0(H^+) - \Delta H_f^0([\text{cat}]^+) \tag{4}$$

The experimental value of $\Delta H_f^0(H^+)$ was chosen because the calculated values [29] are significantly in error for all three methods, 1365.5 kJ mol^{-1} (MNDO), 1316.4 kJ mol^{-1} (AMl) and 1478.0 kJ mol^{-1} (PM3). The values $\Delta H_f^0([\text{cat}]^+)$ and $\Delta H_f^0([\text{zwit}])$ were generated from geometrically optimised structures using Spartan14 Software (Density Functional Theory, B3LYP, 6-31G*) [31]. This yielded values of ΔH_{PA} for $[N_{6\,6\,6}(C_4SO_3)]$ of 2750 kJ mol^{-1}, for $[\text{mimC}_4SO_3]$ of 2588.72 kJ mol^{-1}.

Comparing the FAMEs yields obtained by IL containing anions with different acidities of the conjugate acid, in the case of imidazolium-based ILs, the ILs with the most acidic conjugate acid of the anions gave a higher yield of FAMEs than the weaker inorganic conjugate acid of the anion for both temperatures tested. In general, the catalytic activity of the imidazolium-based ILs for the esterification of sludge lipids increased in the following order: $[mimC_4SO_3H][HSO_4] < [mimC_4SO_3H][N(SO_2CF_3)_2] < [mimC_4SO_3H][SO_3CF_3]$. Although the conjugate acid of the $[N(SO_2CF_3)_2]^-$ anion is slightly more acidic than $[SO_3CF_3]^-$, the IL with $[SO_3CF_3]^-$ anion reached higher FAMEs yield at 40 ºC, but similar at 60 ºC (Table 2).

In the case of ammonium-based ILs, the IL containing the, *i.e.* $[N(SO_2CF_3)_2]^-$ anion, gave the lowest FAMEs yield for both temperatures tested. The IL with $[SO_3CF_3]^-$anion reached the highest FAMEs yield at 40 ºC and it gave equal results to the IL containing $[HSO_4]^-$ anions at 60 ºC reaction temperature. In general, the catalytic activity of the ammonium-based ILs for the esterification of sludge lipids increased in the following order: $[N_{6\,6\,6}(C_4SO_3H)][N(SO_2CF_3)_2] < [N_{6\,6\,6}(C_4SO_3H)][HSO_4] < [N_{6\,6\,6}(C_4SO_3H)][SO_3CF_3]$. These results indicated that for both, imidazolium and ammonium ILs used in this study, the IL containing $[SO_3CF_3]^-$ anion showed the highest catalytic activity, gaining the highest FAMEs yield (Table 2). Additionally, the ILs containing $[SO_3CF_3]^-$ anion are more stable than the others tested [14], which is important for IL recycling. Furthermore, the price of ionic liquids with the $[SO_3CF_3]^-$ anion is much cheaper than $[N(SO_2CF_3)_2]^-$ ones.

Comparing the cation composition of the ILs, with the $[SO_3CF_3]^-$ anion, it can be observed in Table 2, that the catalytic efficiency of the ILs depends on the temperature. At 40 ºC the IL with imidazolium cation achieved slightly higher FAMEs yield than the IL with ammoniumcation, 64.7% and 63.4% respectively. The effect of increasing the reaction temperature to 60 ºC, showed an increase in the FAMEs yield for both ILs and an increase in the activity of $[N_{6\,6\,6}(C_4SO_3H)][SO_3CF_3]$ IL which gave slightly better results than $[mimC_4SO_3H][SO_3CF_3]$, 79.3% and 77.0% respectively. However, $[N_{6\,6\,6}(C_4SO_3H)][SO_3CF_3]$ was not selected for further study due to the presence of other unidentified peaks in the GC chromatograms of the FAMEs produced, as described in Subsection 3.2.2. For that reason, in this study, $[mimC_4SO_3H][SO_3CF_3]$ was selected as the best catalyst for the reaction and was used in the following experiments to optimise different reactions parameters.

3.2.2. Effect of various ILs catalyst on the FAME composition

The influence of IL catalysts on the FAME composition of biodiesel in comparison to a conventional H_2SO_4 catalyst was evaluated and the results are shown in Table 3. The FAME profiles of biodiesel produced by each IL catalyst are very similar to each other and to those of the conventional H_2SO_4 catalyst. The same fatty acid methyl esters were found for all catalysts tested with a predominance of methyl esters from palmitic (38%-40%), oleic (27%) and stearic (15%) acids, showing no influence of the catalyst on the FAME composition. However, an important difference is observed in the content of "others". It was found to be present in a much larger amounts in the three ammonium-based ILs tested as compared to the other catalysts (Table 3). For all imidazolium-based IL catalysts the "others" are exactly the same as for the H_2SO_4 catalyst; the same peaks were obtained in the GC chromatograms. This fraction of "others" mainly consists of hydroxy and oxy fatty acids and branched-chain fatty acid methyl esters [4]. On the other hand, for all the ammonium-based IL catalysts, the percentage of "others" was increased by an unidentified compound; broad peak present only in the chromatograms of the FAMEs produced by the ammonium-based ILs. For that reason, further investigation on trihexylsulfobutaneammonium-based ILs is necessary, not only to improve its synthesis but also to check its stability, physical properties and impurity content.

3.3. Optimisation study of different reaction parameters

The influence of different reaction variables on the biodiesel yield was studied using $[mimC_4SO_3H][SO_3CF_3]$ as a catalyst and the results are shown in Figure 3.

3.3.1. Effect of the amount of methanol

The amount of methanol is a very important factor that affects the yield of biodiesel. Although the stoichiometric molar ratio for esterification and transesterification reaction is 1:1 and 3:1 (methanol to lipids) respectively, it is well known that excess alcohol is required to shift the reaction equilibrium towards the products and produce more FAMEs (this is because the reactions are reversible). Thus, the influence of methanol on the reaction was studied in the range of 0.5 to 3.5 cm^3 which corresponds to approximately 5:1 and 35:1 methanol to saponifiable lipids molar ratio, respectively. The experiments with different amounts of methanol were conducted at 40 ºC for ½ h using 1 g of sludge lipids and 7% (0.2 mmol) of the catalyst, based on the mass of lipids. As shown in Figure 3(a), the FAMEs yield increased considerably from 44% to 65% by increasing the amount of methanol from 0.5 to 1 cm^3. Further increases in the amount of methanol to 2.5 cm^3 showed only a slight increase in the FAMEs yield, giving 68% for 2 and 2.5 cm^3 of methanol. When the amount of methanol was increased beyond 2.5 cm^3, the yield of FAMEs decreased slightly (Figure 3(a)). This concurred with previous findings in literature, because too much methanol was found to cause a dilution in the concentration of IL [13,18,19,27]. Additionally, the use of a larger amount of methanol would not facilitate IL recycling due to the separation of a larger amount of alcohol from the dissolved ILs. Therefore, the slight increase in the FAMEs yield beyond 1 cm^3 of methanol was negligible and 1 cm^3 of methanol (approximately 10:1 methanol to saponifiable lipids molar ratio) was selected as the optimal amount of methanol for the reaction.

3.3.2. Effect of the amount of catalyst

The catalyst amount is also a very important factor that affects the reaction. The number of sulfonic acid group ($-SO_3H$) should be in proportion to the reaction in order to obtain a high conversion. Figure 3(b) shows the effects of various concentrations of [$mimC_4SO_3H$][SO_3CF_3] catalyst (expressed as a percentage based on the mass of lipids) on the esterification of sludge lipids with methanol. The experiments were carried out varying the catalyst concentrations between 3% and 12% while other parameters were fixed at 40 ºC, ½ h using 1 g of sludge lipids and 1 cm^3 of methanol. Figure 3(b) clearly shows that an increase of the amount of catalyst from 3% to 7% resulted in an increase in the FAMEs yield, from 49% to 65%. However, when the amount of catalyst exceeded 7%, no increase in conversion was observed, *e.g.* for 9% and only a slight increase was observed for 12% of catalyst (66% of FAMEs yield). Thus, considering the reaction rate and the cost of the catalyst, the optimum amount of catalyst was found to be 7%.

3.3.3. Effect of reaction temperature

The reaction temperature is another important parameter which influences the reaction and the yield of FAMEs product. As demonstrated in Subsection 3.2.1, a higher reaction temperature gave higher FAMEs yield. Thus, the effect of temperature on the reaction was investigated in the temperature range of 25-120 ºC for a period of ½ h using 1 g of sludge lipids, 1 cm^3 of methanol and 7% of [$mimC_4SO_3H$][SO_3CF_3] catalyst. As shown in Figure 3(c), when the reaction temperature was 25 ºC only 43% of the saponifiable lipid was converted into FAMEs. The FAMEs yield increased sharply with a rise in temperature, reaching 85% at 100 ºC. However, further increases in temperature had no significant effect on the product yield, (86% at 120 ºC). Furthermore, at 120 ºC the reaction system exhibited a very dark brown colour. This suggests that increasing the reaction temperature improves the catalytic activity, but only to a certain extent.

3.3.4. Effect of reaction time at different temperatures

Figure 3(d) shows the effect of the reaction time on the FAMEs yield at different temperatures. The experiments were conducted using the established optimal parameters of 1 g of sludge lipids, 1 cm^3 of methanol, 7% of [$mimC_4SO_3H$][SO_3CF_3] catalyst. As shown in Figure 3(d), the reaction rate and the yield of FAMEs were enhanced with increased reaction temperature. For all temperatures tested, the FAMEs yield increased steadily with reaction time up to 5 h and remains steady afterwards. The reaction moved closer to equilibrium after 5 h, and the product yield did not increase significantly when the reaction time was prolonged to 10 h. The maximum yield of 90% was achieved at 100 ºC for 5 h and 10 h. Therefore, 100 ºC and 5h was selected as the optimum reaction conditions for the esterification of 1g of sludge lipids with 1 cm^3 of methanol catalysed by using 7% of [$mimC_4SO_3H$][SO_3CF_3] ionic liquid.

3.4. Evaluation of the IL as a catalyst for biodiesel production.

The above results demonstrated that the Brønsted acidic IL [$mimC_4SO_3H$][SO_3CF_3] was effective in catalysing the esterification of wastewater sludge lipids with methanol, reaching 90% of biodiesel under the optimum reaction conditions. Therefore, the cheap and non-edible lipid feedstock containing almost only FFAs, *i.e.* sludge lipids, was successfully converted into biodiesel by the green catalyst. The incomplete conversion (90%) was confirmed by the analysis of FFAs in the upper biodiesel phase formed after reaction. Under optimized reaction conditions, 3% of FFAs still left unconverted. The remained unconverted fraction is the glycerides fraction (not confirmed analytically). However, previous studies demonstrated that [$mimC_4SO_3H$][SO_3CF_3] IL have a high potential for catalysing the transesterification of waste cooking oil, lard and glycerides feedstocks, giving 99% of biodiesel yield in both cases, however a much larger amount of methanol and catalyst were used than in this study [14,32]. This clearly demonstrates that the IL is able to efficiently catalyse the conversion of different lipid feedstocks, especially waste feedstock, into biodiesel.

Additionally, one of the reasons that render ILs as green catalysts is their recyclable nature. After completion of the esterification of sludge lipids, the IL is easily separated from the biodiesel product by decantation (Subsection 2.6.1). Then the excess methanol and the water formed during esterification must be removed from the IL by distillation and hence the IL could be reused in further reactions. The catalytic stability of Brønsted acidic ILs with an alkane sulfonic acid group has been widely studied in literature, demonstrating excellent reusability in biodiesel synthesis even up to 10 times [13,17,18,27]. In this study, the IL was reused only once under the optimised reaction conditions determined above, and the yield of biodiesel only slightly decreased from 90% to 89%, suggesting its stability. Additionally, the stability of the recovered IL, after first and second reaction, was also checked by ^{1}H NMR spectroscopy. No additional peaks were found in the ^{1}H NMR spectra of the recovered IL as compared to the initial IL, confirming its stability. The results of the ^{1}H NMR of recovered IL were the same as for IL2, see Section 2.4.

4. CONCLUSIONS

The six Brønsted acidic ILs with an alkane sulfonic acid group tested in this study showed similar catalytic performance for the conversion of sludge lipids into biodiesel. However, the IL containing $[SO_3CF_3]^-$ anion revealed a higher biodiesel yield than the ILs with other anions tested for both imidazolium and ammonium ILs. The imidazolium IL, $[mimC_4SO_3H][SO_3CF_3]$ was selected as the best catalyst due to an easier, less time and energy intensive, synthesis and a purer biodiesel end product than for the equivalent ammonium IL. $[mimC_4SO_3H][SO_3CF_3]$ catalyst was efficient for the synthesis of biodiesel from wastewater sludge lipids, reaching a yield of 90% under the optimum reaction conditions. Compared with conventional sulfuric acid catalyst, the Brønsted acidic IL possesses many advantages such as the facility for product separation from the reaction, catalyst reusability, the possibility of converting different lipid feedstock into biodiesel without the saponification problem and the low environmental impact. Therefore, an efficient catalyst was provided for the green synthesis of biodiesel from low-cost waste feedstocks, such as wastewater sludge lipids or waste cooking oils. Furthermore, the utilisation of sludge lipids, non-edible and low-cost feedstock, for biodiesel production can solve both the economic and environmental problems associated with the biodiesel process and waste management in WWTPs.

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Table 1. Basic properties of primary sludge lipids and its saponifiable matter.

	Composition	wt%
Sludge lipids	Moisture	0.2 ± 0.0
	FFAs	65.1 ± 0.9
	Saponifiable	68.6 ± 2.0
Saponifiable lipids	FFAs	94.9 ± 0.9
	Glycerides*	5.1 ± 0.9

* Estimated by difference

Values are means ± SD, n = 3

Table 2. Effect of ILs and temperature on the FAMEs yield.

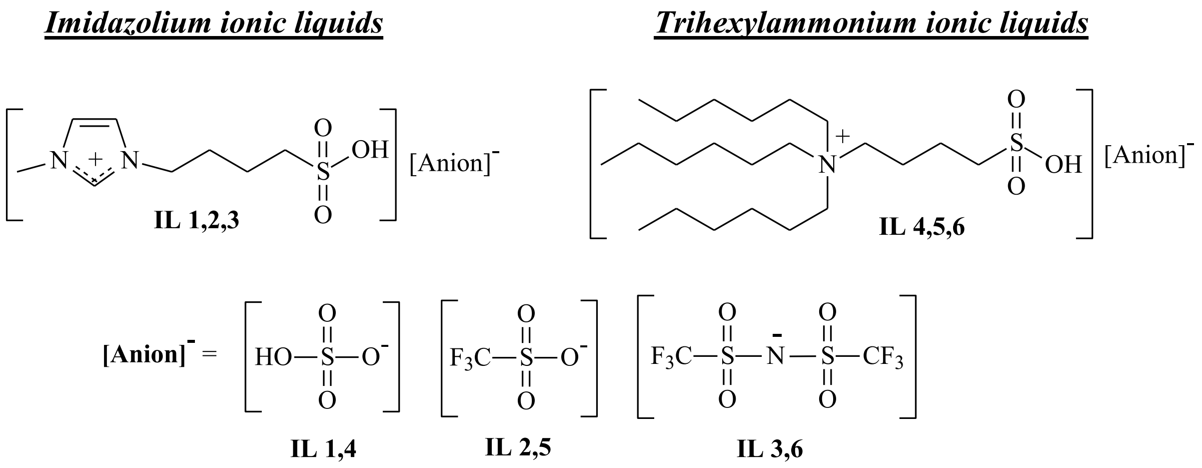
Catalyst	Temperature / ºC	FAMEs yield / %
H_2SO_4	40	66.2
	60	86.1
$[minC_4SO_3H][HSO_4]$	40	59.1
	60	73.1
$[minC_4SO_3H][SO_3CF_3]$	40	64.7
	60	77.0
$[mimC_4SO_3H][N(SO_2CF_3)_2]$	40	63.3
	60	76.5
$[N_{666}(C_4SO_3H)][HSO_4]$	40	61.0
	60	79.0
$[N_{666}(C_4SO_3H)][SO_3CF_3]$	40	63.4
	60	79.3
$[N_{666}(C_4SO_3H)][N(SO_2CF_3)_2]$	40	56.8
	60	76.3

Reaction conditions: sludge lipids 1 g, methanol 1 cm^3, catalyst 0.2 mmol, reaction time ½ h.

Table 3. FAME composition of biodiesel produced from primary sludge lipids by different catalysts (%, w/w).

FAME from fatty acid	H_2SO_4	$[mimC_4SO_3H]$			$[N_{666}(C_4SO_3H)]$		
		$[HSO_4]$	$[SO_3CF_3]$	$[N(SO_2CF_3)_2]$	$[HSO_4]$	$[SO_3CF_3]$	$[N(SO_2CF_3)_2]$
Lauric (C12:0)	1.25 ± 0.01	1.32 ± 0.08	1.32 ± 0.07	1.25 ± 0.4	1.11 ± 0.08	1.21 ± 0.12	1.11 ± 1.25
Myristic (C14:0)	3.59 ± 0.01	3.63 ± 0.06	3.63 ± 0.02	3.65 ± 0.10	3.43 ± 0.13	3.49 ± 0.03	3.42 ± 0.04
Pentadecanoic (C15:0)	0.53 ± 0.01	0.53 ± 0.01	0.54 ± 0.01	0.54 ± 0.01	0.51 ± 0.02	0.52 ± 0.01	0.52 ± 0.01
Palmitic (C16:0)	39.75 ± 0.01	39.57 ± 0.20	39.72 ± 0.29	39.89 ± 0.27	38.07 ± 1.50	37.80 ± 1.60	38.38 ± 0.98
Palmitoleic (C16:1)	1.65 ± 0.01	1.63 ± 0.01	1.64 ± 0006	1.63 ± 0.05	1.56 ± 0.10	1.58 ± 0.05	1.57 ± 0.02
Heptadecanoic (C17:0)	0.40 ± 0.01	0.42 ± 0.04	0.41 ± 0.02	0.41 ± 0.01	0.34 ± 0.02	0.34 ± 0.01	0.35 ± 0.01
Stearic (C18:0)	15.32 ± 0.08	15.06 ± 0.09	15.12 ± 0.08	14.93 ± 0.16	14.52 ± 0.18	14.88 ± 0.35	15.02 ± 0.55
Oleic (C18:1)	27.38 ± 0.52	27.31 ± 0.58	27.27 ± 0.54	27.28 ± 0.19	26.59 ± 0.92	27.12 ± 0.49	26.92 ± 1.14
Linoleic (C18:2)	3.85 ± 0.08	3.90 ± 0.01	3.82 ± 0.05	3.78 ± 0.14	3.65 ± 0.07	3.73 ± 0.01	3.66 ± 0.05
Arachidic (C20:0)	0.53 ± 0.11	0.58 ± 0.11	0.55 ± 0.01	0.53 ± 0.11	0.78 ± 0.14	0.55 ± 0.04	0.57 ± 0.04
Eicosenoic (C20:1)	0.56 ± 0.13	0.50 ± 0.07	0.59 ± 0.09	0.55 ± 0.13	0.68 ± 0.14	0.50 ± 0.12	0.58 ± 0.10
Others	5.19 ± 0.45	5.55 ± 0.06	5.39 ± 0.29	5.57 ± 0.35	8.74 ± 1.31	8.27 ± 1.25	7.92 ± 1.96

Average of the results obtained at 40 ºC and 60 ºC, sludge lipids 1g, methanol 1 cm^3, catalyst 0.2 mmol, reaction time ½ h.



Imidazolium ionic liquids

Trihexylammonium ionic liquids

IL 1,2,3

IL 4,5,6

IL 1,4

IL 2,5

IL 3,6

Figure 1. Structures of ionic liquids prepared and used in this study.

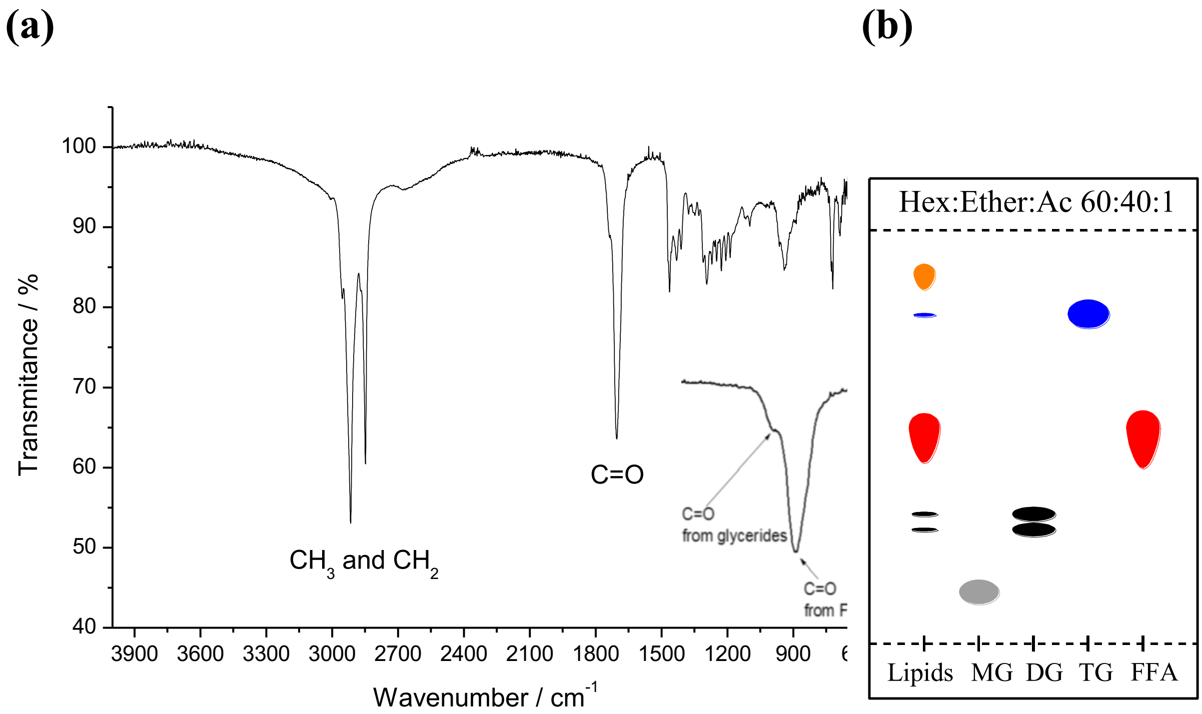


Figure 2. FTIR and TLC analysis of sludge lipids: (a) FTIR spectra of sludge lipids; (b) TLC sludge lipids and standards.

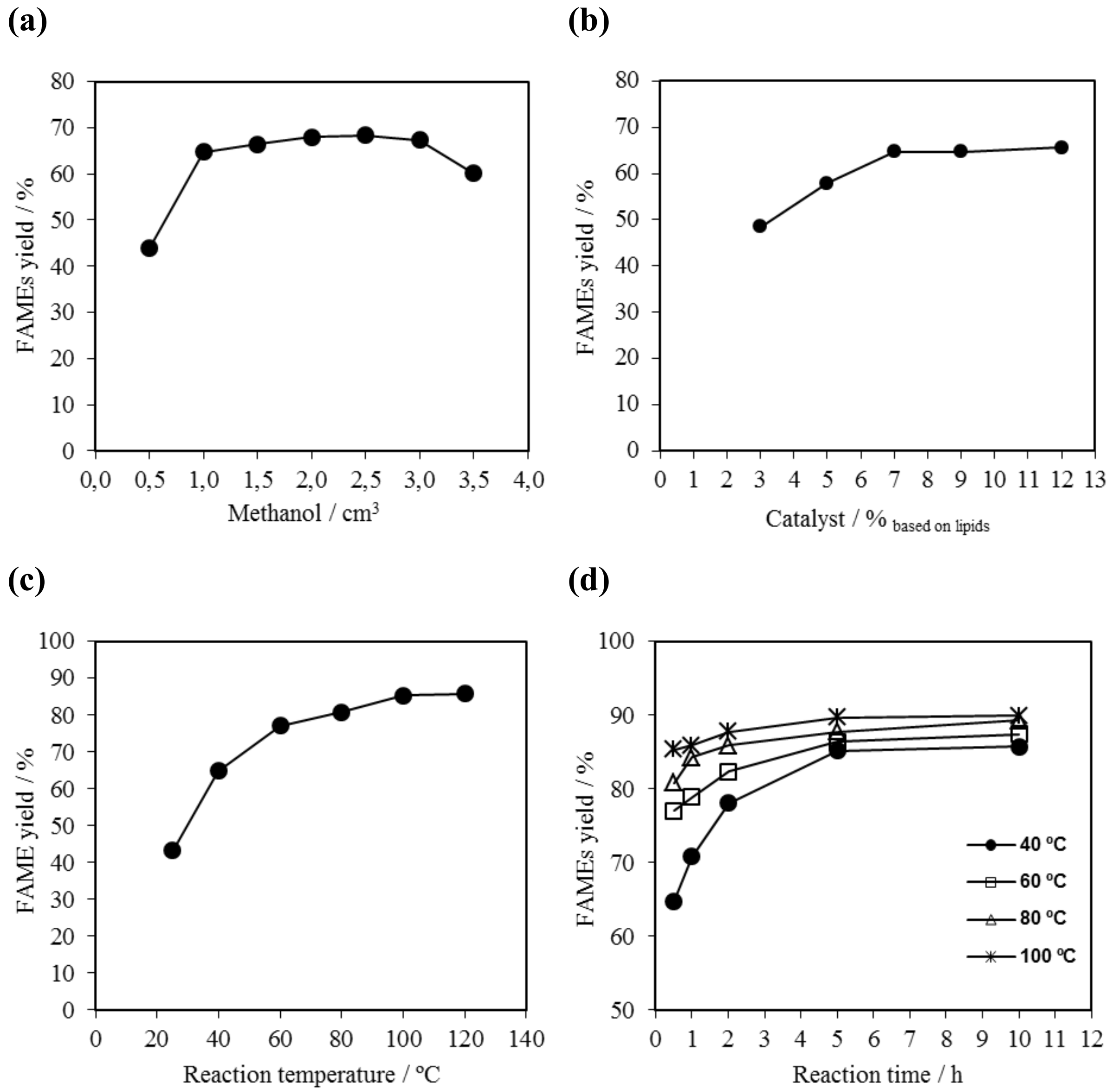


Figure 3. FAMEs (biodiesel) yield *vs.* reaction variables when [mimC$_4$SO$_3$H][SO$_3$CF$_3$] IL was used as a catalyst: **(a)** effect of methanol amount (reaction conditions: sludge lipids 1 g, catalyst 7%, reaction temperature 40ºC, reaction time ½ h); **(b)** effect of catalyst amount (reaction conditions: sludge lipids 1 g, methanol 1 cm^3, reaction temperature 40ºC, reaction time ½ h); **(c)** effect of temperature (reaction conditions: sludge lipids 1 g, methanol 1 cm^3, catalyst 7%, reaction time ½ h); **(d)** effect of time at different temperatures (reaction conditions: sludge lipids 1 g, methanol 1 cm^3, catalyst 7%).