

**Microwave-assisted biodiesel synthesis employing ammonium-based ionic liquids as catalysts****Síntesis de biodiesel asistida por microondas empleando líquidos iónicos base amonio como catalizadores**

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Abstract

A fast, efficient, and green biodiesel synthesis methodology was developed using ammonium-based ionic liquids catalysts and microwave irradiation as a heating source. All ionic liquids (ILs) probed can act as catalysts, Brønsted acidic ILs containing the $-SO_3H$ group are the most efficient in terms of conversion. In these conditions, biodiesel can be synthesized at 50 °C and 25 minutes of microwave irradiation. According to the results, the new catalysts have great potential for use in environmentally friendly and highly efficient biodiesel synthesis processes.

Keywords: biodiesel, ionic liquids, microwave, catalysts, Brønsted acid.

Resumen

Se desarrolló una metodología para la síntesis rápida, eficiente y ecológica de biodiesel utilizando líquidos iónicos base amonio como catalizadores e irradiación por microondas como fuente de calentamiento. Todos los líquidos iónicos probados pueden actuar como catalizadores, siendo los líquidos iónicos ácidos de Brønsted que contienen el grupo $-SO_3H$ los más eficientes. En estas condiciones, el biodiesel se puede sintetizar en 25 minutos de irradiación en microondas. Por lo tanto, los nuevos catalizadores tienen un gran potencial para su uso en procesos ecológicos y son muy eficientes para la síntesis de biodiesel.

Palabras clave: Biodiesel, líquidos iónicos, microondas, catalizadores, ácidos de Brønsted.

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1 Introduction

Biodiesel is composed of a mixture of fatty acid methyl esters (FAME) obtained from various crude oil feedstocks, such as vegetable oils, animal fats, and waste oils, through transesterification reactions between triglycerides and alcohols (methanol or ethanol).

Biodiesel represents an alternative to replace conventional fossil diesel partially. In addition to being obtained from renewable sources, it is an environmentally friendly fuel due to its biodegradability, non-toxicity, lower particulate emissions, and the possibility of recycling CO₂ (Xie & Li, 2023)

The classic way of obtaining biodiesel is by transesterification of triglycerides from vegetable oils or animal fats with alcohol. The synthesis is carried out in basic homogeneous catalysis (NaOH or KOH catalysts) or acid catalysis (using H₂SO₄ as the catalyst). Generally, the synthesis process is carried out in batch or semi-continuous reactions. Mexican researchers developed a process for continuously synthesizing biodiesel (Evangelista-Flores *et al.*, 2014), and also under supercritical conditions (Aldana-González *et al.*, 2022).

Applying traditional synthetic methods presents environmental issues such as corrosion and emulsion formation. It is often complex to separate the homogeneous catalyst from the biodiesel, and its recuperation leads to toxic discharges linked with these reaction routes (Helwani *et al.*, 2009). Several approaches have been studied to mitigate the previous troubles, involving heterogeneous catalysts, organic bases, supercritical fluids, two-phase and multiphase systems, and enzymatic catalysis (Andreani & Rocha, 2012; Singh *et al.*, 2020).

Currently, ionic liquids (ILs) are achieving extensive acceptance as possible environmentally friendly solvents for their outstanding properties (Martínez-Palou, 2010) and applications in Organic Synthesis (Tierney & Lidström, 2005), catalysis (Olivier-Bourbigou *et al.*, 2010), and biocatalysis (Muginova *et al.*, 2010). ILs are ideal replacements for volatile organic solvents in environmentally friendly technologies (Lei *et al.*, 2017) due to their shallow vapor pressures, thermal and chemical resistance, performance in catalysis, non-flammability, and non-corrosive nature. This reduces workers' occupational exposure risk and atmosphere solvent pollution. Furthermore, it is known that some IL can increase the rate and yield of many organic reactions (Maciejewski, 2021). The biodegradation of ionic liquids by fungi such as *Fusarium sp.* has also been studied (Esquivel-Viveros *et al.*, 2009).

In the recent decades, ILs have been described as

catalysts (Cheng *et al.*, 2022; Han *et al.*, 2022; Lima *et al.*, 2022), solvents (Muhammad *et al.*, 2015a) and media for biocatalysis (Arai *et al.*, 2010; Ruzich & Bassi, 2010; Zhao *et al.*, 2010) in biodiesel synthesis (Muhammad *et al.*, 2015b).

The utility of microwave irradiation (MW) to carry out organic reactions has now become a regular feature, as shown by the increasing number of reviews and books (Kappe *et al.*, 2012; Martínez-Palou, 2006). The non-conventional synthetic route has shown extensive usage as an efficient technique to expedite many organic reactions, providing increased yields, higher selectivity, lower amounts of byproducts, and consequently, easier work-up and purification.

Owing to their ionic character, ILs interact efficaciously with microwaves, and their application in microwave-assisted synthesis is an intense research field (Martínez-Palou, 2010). Facile and efficient biodiesel syntheses centered on microwave irradiation have been reported in many papers (Khedri *et al.*, 2019) including a technique for a continuous flow, circulating microwave system (Choedkiatsakul *et al.*, 2015; Groisman & Gedanken, 2008; Hernando *et al.*, 2007).

Although basic catalyzed transesterification is more generalized and straightforward, the present work uses acid catalysts because alkaline transesterification requires oils with low free fatty acids, water, and impurities to ensure good-quality biodiesel. In contrast, acid catalysis is less susceptible to these limitations. On the other hand, one of the essential variables in transesterification to obtain biodiesel is the energy needed to achieve the triglyceride/alcohol interaction in a very efficient way, so there is a great tendency in recent years to use non-conventional heating methods such as microwaves, ultrasound, and infrared radiation or a combination of them (Kodgire *et al.*, 2023; Sebayang *et al.*, 2023).

Herein, biodiesel synthesis is presented using novel non-symmetric ammonium-based ILs as catalysts under microwave irradiation. Eight ionic liquids were synthesized and evaluated as catalysts for obtaining biodiesel. Although there are many precedents in the use of ionic liquids as catalysts for biodiesel synthesis as cocatalysts using nanocatalysts (Baskar *et al.*, 2022), acidic imidazolium ionic liquids (Ding *et al.*, 2018), acid ionic liquid catalyzed using combined ultrasonic-microwave energy (Yan *et al.*, 2020), etc. To our knowledge, the ionic liquids proposed in this study have not been previously described for this application with or without combination with microwave dielectric heating. The ionic liquids studied in this work are relatively inexpensive compared to imidazolium cation based (the most explored for biodiesel catalysis) and stable, allowing their use under more severe reaction conditions and in large-scale processes and the

catalyst's reutilization. On the other hand, taking advantage of the ionic liquid/microwave dielectric heating synergy allows high yields in short reaction times.

According to the methodology in the present work, biodiesel can be produced quickly and with high purity employing ammonium based ILs. Applying microwave dielectric heating with IL-catalyst decreases reaction time considerably, providing an environmentally friendly process for biodiesel production.

2 Methodology

2.1 General

Biodiesel was synthesized from commercial corn oil and methanol (99%, Merk). Dimethylethylamine (98%, Merk), chloromethyl methylether (99%, Merk), chloromethyl ethylether (99%, Merk), silver acetate (99%, Merk), sodium dicyanamide (99%, Merk), 1,3-propane sultone (97%, Merk), Pyridine (99%, Merck) and 1,4-butane sultone (98%, Merk). All reagents were used without any further purification. ^1H Nuclear Magnetic Resonance (NMR) spectra were acquired at 25 °C on a 300 MHz (Jeol-Eclipse) spectrometer, the chemical shifts (in parts per million) being referenced to the residual peaks of tetramethylsilane using deuterated-chloroform (CDCl_3) or deuterium oxide (D_2O) as solvent. Microwave reactions were performed in a monomode microwave unit (Discover - Microwave Synthesizer, 2023).

2.2 Procedures for the synthesis of ionic liquids

N-(methoxymethyl)-N,N-dimethylethanamonium chloride (entry 1, Table 1). Dimethylethylamine (7.0 g, 96 mmol) and chloromethyl methylether (8.0 g, 0.1 mol) were mixed in chloroform at 0 °C in a cooling bath and then left to rise to room temperature. The reaction was continuously stirred for 18 h. After separating the two phases, the lower phase was cleaned twice using anhydrous ether (50 mL), and the product was dried in a vacuum for 8 h at 50 °C to obtain a yellowish liquid (91%). δ_{H} (D_2O) 1.34 (tt, J = 7.4, 0.8 Hz, 3H), 3.00 (s, 6H), 3.38 (q, J = 7.1 Hz, 2H), 3.69 (s, 3H), 4.60 (s, 2H). δ_{C} (D_2O) 7.5, 57.2, 46.9, 61.2, 91.8.

N-(ethoxymethyl)-N,N-dimethylethanamonium chloride (entry 2, Table 1). Dimethylethylamine (7.0 g, 96 mmol) and chloromethyl ethylether (9.4 g, 0.1 mol) were stirred in chloroform at 0 °C and then left to rise to room temperature. The reaction was stirred for 18 h. After separating the two phases, the lower phase was cleaned twice with anhydrous ether (50

mL), vacuum-dried for 8 h at 50 °C and yellowish liquid was obtained (89%). δ_{H} (D_2O) 1.23 (t, J = 7.1 Hz, 3H), 1.31(t, J = 7.1 Hz 3H), 2.96 (s, 6H), 3.33 (q, J = 7.41 Hz, 2H), 3.88 (q, J = 7.1 Hz, 2H), 4.60 (s, 2H). δ_{C} (D_2O) 7.3, 14.6, 46.7, 56.9, 70.2, 90.3.

N-(methoxymethyl)-N,N-dimethylethanamonium acetate (entry 3, Table 1). N-(methoxymethyl)-N,N-dimethylethanamonium chloride (1.47 g, 0.01 mol) was diluted in 50 ml of acetonitrile, and 1.70 g (0.01 mol) of silver acetate was slowly placed. After 24 h of stirring at 60 °C, the silver chloride was filtered off and vacuum-dried for 2 h at 50 °C. A yellowish liquid was achieved (82%). δ_{H} (D_2O) 1.27 (t, J = 7.14 Hz, 3H), 1.98 (s, 3H), 2.93 (s, 6H), 3.31 (q, J = 7.4 Hz, 2H), 3.61 (s, 3H), 4.52 (s, 2H). δ_{C} (D_2O) 7.4, 21.31, 46.74, 57.03, 61.1, 91.7, 177.6.

N-(ethoxymethyl)-N,N-dimethylethanamonium acetate (entry 4, Table 1). N-(ethoxymethyl)-N,N-dimethylethanamonium chloride (1.59 g, 0.01 mol) was diluted in 50 ml of acetonitrile, and 1.70 g (0.01 mol) of silver acetate was added slowly. After 24 h of stirring at 60 °C, the silver chloride was filtered off and dried. The compound was vacuum-dried 2 h at 50 °C. A yellowish liquid was obtained (82%). δ_{H} (D_2O) 1.23 (t, J = 7.1 Hz, 3H), 1.29 (t, J = 7.1 Hz, 3H), 2.0 (s, 3H), 2.9 (s, 6H), 3.33 (q, J = 7.4 Hz, 2H), 3.88 (q, J = 7.14 Hz, 2H), 4.6 (s, 2H). δ_{C} (D_2O) 7.41, 14.64, 21.53, 46.76, 57.0, 70.9, 90.3, 177.3.

N-(methoxymethyl)-N,N-dimethylethanamonium dicyanamide (entry 5, Table 1). Sodium dicyanamide (0.89 g, 0.01 mol) and N-(methoxymethyl)-N,N-dimethylethanamonium chloride (1.47 g, 0.01 mol) were dissolved in water (50 mL) and heated (50 °C) and stirred for 6 h. The water was eliminated by vacuum. Metathesis produced a colorless liquid (80%). δ_{H} (D_2O) 1.36 (tt, J = 7.4, 0.8 Hz, 3H), 3.0 (s, 6H), 3.39 (q, J = 7.4 Hz, 2H), 3.7 (s, 3H), 4.6 (s, 2H). δ_{C} (D_2O) 7.55, 46.9, 57.2, 61.2, 91.8, 120.3.

N-(ethoxymethyl)-N,N-dimethylethanamonium dicyanamide (entry 6, Table 1). Sodium dicyanamide (0.89 g, 0.01 mol) and N-(ethoxymethyl)-N,N-dimethylethanaminium chloride (1.59 g, 10 mmol), and sodium dicyanamide (1.11 g, 12 mmol), were dissolved in water (20 mL) and heated (50 °C) and stirred for 6 h. The water was eliminated by vacuum to obtain a colorless liquid (85%). δ_{H} (D_2O) 1.28 (t, J = 7.14 Hz, 3H), 1.31 (t, J = 7.4 Hz, 3H), 3.00 (s, 6H), 3.37 (q, J = 7.4 Hz, 2H), 3.91(q, J = 7.91 Hz, 2H), 4.63 (s, 2H). δ_{C} (D_2O) 7.4, 14.7, 46.7, 57.0, 70.2, 90.3, 120.3.

N-(Propyl-3-sulphonyl)-N,N-Dimethylethanamonium p-toluenesulfonate (entry 7, Table 2) and N-(Butyl-3-sulphonyl)-N,N-Dimethylethanamonium p-toluenesulfonate (entry 8, Table 1) were synthesized by reaction dimethylethylamine (0.70 g, 9.6 mmol) with 1,3-propane- or 1,4-butane sultone (1.2 mol), respectively, at 40 °C during 24 hours, to obtain the

requisite zwitterions in quantitative yields, which were washed three times using toluene (20 mL). In the second step, the zwitterions acidification was accomplished by combining a stoichiometric amount of p-toluenesulfonic acid, and the mixture was stirred at 40 °C for 3 days. The ionic liquids were washed repeatedly with toluene (20 mL) and ether (20 mL) and dried under vacuum. IL15 was obtained as a colorless liquid (88%). δ_H (D₂O) 1.10 (t, J = 7.4 Hz, 3H), 1.81-2.00 (m, 2H), 2.19 (s, 3H), 2.65 (s, 6H), 2.94 (q, J = 7.1 Hz, 2H), 3.02 (s, 6H), 4.22 (t, J = 7.1 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 7.53 (d, J = 8.0 Hz, 2H). δ_C (D₂O) 9.2, 18.4, 20.7, 28.3, 42.2, 53.3, 60.0, 125.6, 129.9, 140.2, 142.4. IL16 was obtained as a colorless liquid (83%). δ_H (D₂O) 1.10 (t, J = 7.4 Hz, 3H), 1.69-1.76 (m, 2H), 1.97-2.02 (m, 2H), 2.20 (s, 3H), 2.65 (s, 6H), 2.91 (t, J = 7.7 Hz, 2H), 2.94 (q, J = 7.1 Hz, 2H), 4.22 (t, J = 7.0 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 7.53 (d, J = 8.0 Hz, 2H). δ_C (D₂O) 8.0, 19.3, 20.6, 22.0, 50.2, 57.3, 60.0, 63.5, 129.6, 136.2, 140.0, 142.5.

1-(4-sulfonic acid)butylpyridinium hydrogensulfate (BIL) was synthesized as described before (Wu *et al.*, 2007).

2.3 Microwave-promoted synthesis of biodiesel

In a sealed tube (10 mL) equipped with a stirring bar were added corn oil (1.0 g), methanol (5.0 g), and the IL catalyst (0.10 g). The reaction mixture was placed into the microwave cavity and heated from room temperature up to 50 °C with simultaneous cooling of the reaction tube using airflow (20 psi) to favor continued microwave irradiation with an initial power of 200 W. The irradiation time was 5, 10, 20, and 25 minutes and samples of the product were taken and dissolved in D₂O or CDCl₃. Two relevant signals of ¹H RMN were chosen for integration to monitor the advance of biodiesel reaction. Methoxy groups in FAME (3.62 ppm, singlet) and the R-methylene protons found in every triglyceride compound (2.28 ppm, triplet) of the corn oil (Gelbard *et al.*, 1995). The conversion was estimated from these signals' integrated areas (A) using Equation 1.

$$\%Conversion = \frac{2 * A_{CH_3O}^{3.6ppm}}{3 * A_{CH_2CO}^{2.3ppm}} \times 100 \quad (1)$$

3 Results and discussion

3.1 Selection and synthesis of ionic liquids

Ammonium base ILs derivatives from dimethylethylamine were selected for being evaluated as catalysts for biodiesel synthesis because these ILs are

easy to obtain and cheaper than those consisting of heterocycles (i.e., imidazolium, pyridinium, isoquinolonium, pyrazolium). The unsymmetrical ethyldimethylamine was selected as raw material to favor liquid product formation, which can interact more effectively with the reagents (better mass transfer).

Eight ionic liquids were synthesized under microwave irradiation to accelerate the synthesis of these compounds, increase purity and yields, and avoid using volatile and toxic organic solvents.

3.2 Biodiesel synthesis

Corn oil was chosen as the feedstock for biodiesel synthesis. The choice was made based on the availability of the biomaterial, and it has a relatively low production cost in Mexico.

The transesterification reaction for biodiesel preparation using ionic liquids as catalysts and the protons employed for monitoring the reaction are shown in Figure 1.

In addition, methanol is a suitable microwave adsorbent, and ILs interact very efficiently with microwaves due to their ionic character. For this reason, a high increase in reaction temperature and pressure profile is observed in all reactions.

This work was carried out on a small scale because the microwave used only has small capacity vessels (10 mL), however, from the background of the subject it is predictable that the reaction of both ILs synthesis and transesterification can be scaled up without major inconvenience, even the use of microwaves for a continuous transesterification process has been previously described (Motasemi & Ani, 2012).

3.3 Ionic liquids screening

First screening reactions were run in a monomode microwave reactor in closed tubes with 1 mL of corn oil, methanol, and 1-(4-sulfonic acid) butylpyridinium hydrogensulfate (BIL) as a catalyst to optimize oil/methanol and oil/IL ratio. BIL was employed because it was reported as an excellent catalyst for diesel synthesis under conventional heating (Gelbard *et al.*, 1995) and established temperature at 50 °C during three minutes of MW irradiation as a mild condition with an initial power of 100 W, which decreased as the reaction progressed. Due to the rapid increase in reaction temperature, simultaneous cooling of the reaction tube was applied by airflow (20 psi) to favor continuous irradiation. After screening reaction conditions, the best results were obtained at oil/methanol ratio (w/w) = 1:5 and oil/IL ratio (w/w) = 0.10. The reaction above conditions was also established for the ammonium-based ionic liquids screening.

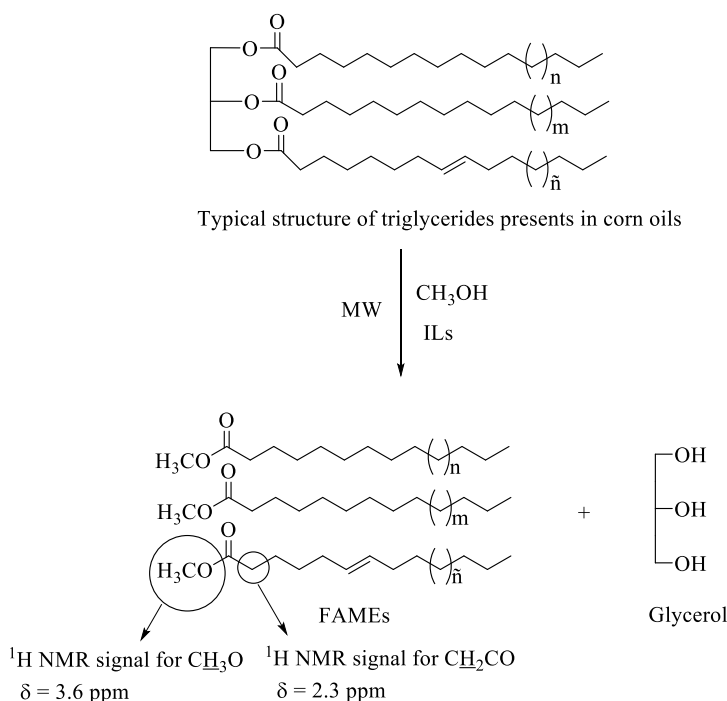


Figure 1. Transesterification reaction to obtain FAMES and protons for ¹H NMR monitored.

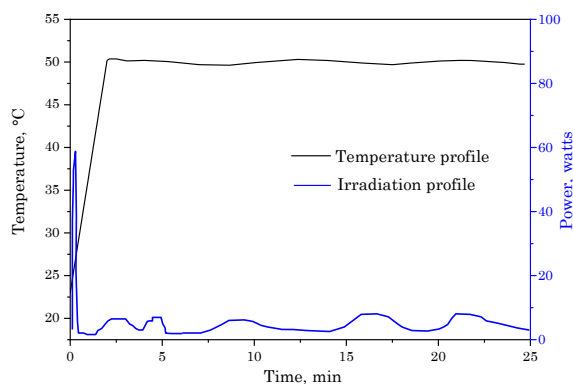


Figure 2. Temperature and irradiation profiles during the microwave-assisted biodiesel synthesis for entry 6.

Interestingly, the ratio of oil/methanol and oil/IL is lower than those commonly reported for reaction under conventional heating and catalyst, and the reaction time was dramatically diminished. Using the same catalyst, the optimum conditions for a quantitative product formation under conventional heating were a molar ratio IL/oil of 0.057 and an oil/methanol ratio of 1:5 at 170 °C for 5 hours.

A screening of the ammonium-based ionic liquids catalysts at different reaction times with an initial power of 100 W is presented in Table 1. As shown in Figure 2, the working temperature was reached in less than 2 minutes because of the high polarity of the medium and was kept constant ($\pm 1^\circ\text{C}$) for the remainder of the reaction time. The irradiation profile is subject to the reaction temperature, so at the

beginning, the irradiation was up to 39 W for a few seconds. From that moment on, the irradiation is much lower, achieving some maximum peaks of 20 W.

Figure 3 shows the kinetic curves with standard deviations of the conversion of corn oil when the eight ILs were used as catalysts to obtain biodiesel. The results are the average of three experimental replicates of each reaction, and the standard deviation of each value is shown in Table 1. Figure 3 shows that when using the ionic liquids of inputs 7 and 8, the highest conversions were obtained at 95.3 and 98.0 %. However, for the IL of input 6, the conversion obtained is not significantly different from that of input 7. The remaining reactions (entries 1-5) achieve conversions above 80% up to 25 min of reaction. Another essential aspect observed in the kinetic curves is that the reactions in which the ILs of inputs 1-4 were used reached the equilibrium conversions after 13 min. On the other hand, in the reactions of inputs 7 and 8, the equilibrium conversions are reached after 20 min, and a tendency to get conversions close to 100 % is observed shortly after 25 min.

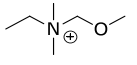
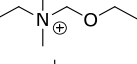
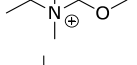
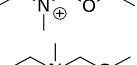
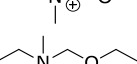
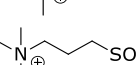

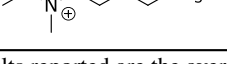
The best results were obtained with the ILs 7 and 8 with an almost quantitative biodiesel formation after 20 minutes of microwave irradiation due to the high Brønsted acidity of the -SO₃H group. The fundamental property that distinguishes ILs from entries 7 and 8 from others is the proton transfer from the acid to the base, giving rise to proton-donor and -acceptor sites that may be available to construct a hydrogen-bonded network as shown in the proposed reaction mechanism for the transesterification process (Figure 4).

Among these ILs, the compound from entry 8 may perform better because a large carbon chain dissociates H⁺ ions efficiently, giving rise to a more robust Brønsted acidity.

The microwave equipment consists of a continuous focalized microwave power delivery system with a power output from 0 to 300 W. Reactions were conducted in a 10 mL sealed tube. An IR sensor underneath the reaction vessel recorded the

temperature in the vessel's chamber. Continuous flow air was injected outside the reaction tube to avoid the accelerated temperature increase and favor a continuous microwave irradiation to the reaction mixture. Temperature, pressure, and power profiles were monitored using commercially available software provided by the microwave manufacturer (Figure 2).

Table 1. Evaluation of ILs as catalysts for biodiesel synthesis under microwave irradiation.

Entry	IL structure		Conversion (%) after MW irradiation time (min) ^a			
	Cation	Anion	5	10	20	25
1		Cl ⁻	49.7±1.5	60.7±1.5	77.0±2.0	80.3±2.1
2		Cl ⁻	48.7±1.5	60.0±1.0	73.7±1.5	85.0±2.0
3		CH ₃ COO ⁻	60.3±1.5	72.7±1.5	81.3±2.1	89.3±1.5
4		CH ₃ COO ⁻	60.7±2.3	76.3±1.5	79.7±1.5	88.3±1.5
5		N ⁻ (CN) ₂	60.7±2.5	82.0±2.0	90.7±2.1	94.0±1.0
6		N ⁻ (CN) ₂	59.0±2.0	79.7±1.5	90.0±2.0	95.0±1.0
7		<i>p</i> -CH ₃ C ₆ H ₄ SO ₃ ⁻	39.7±1.5	64.3±1.5	91.3±1.5	95.3±2.1
8		<i>p</i> -CH ₃ C ₆ H ₄ SO ₃ ⁻	40.0±2.0	66.0±1.0	94.7±1.5	98.0±1.0

^aThe results reported are the average of three replicates of each experiment.

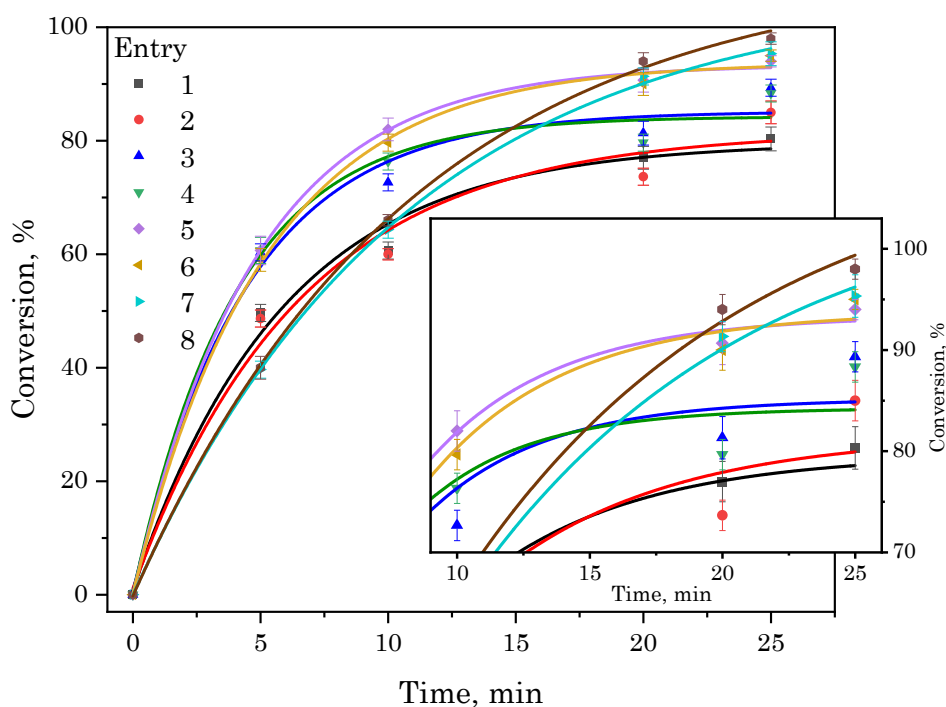


Figure 3. Kinetic curves for obtaining biodiesel using IL as catalysts.

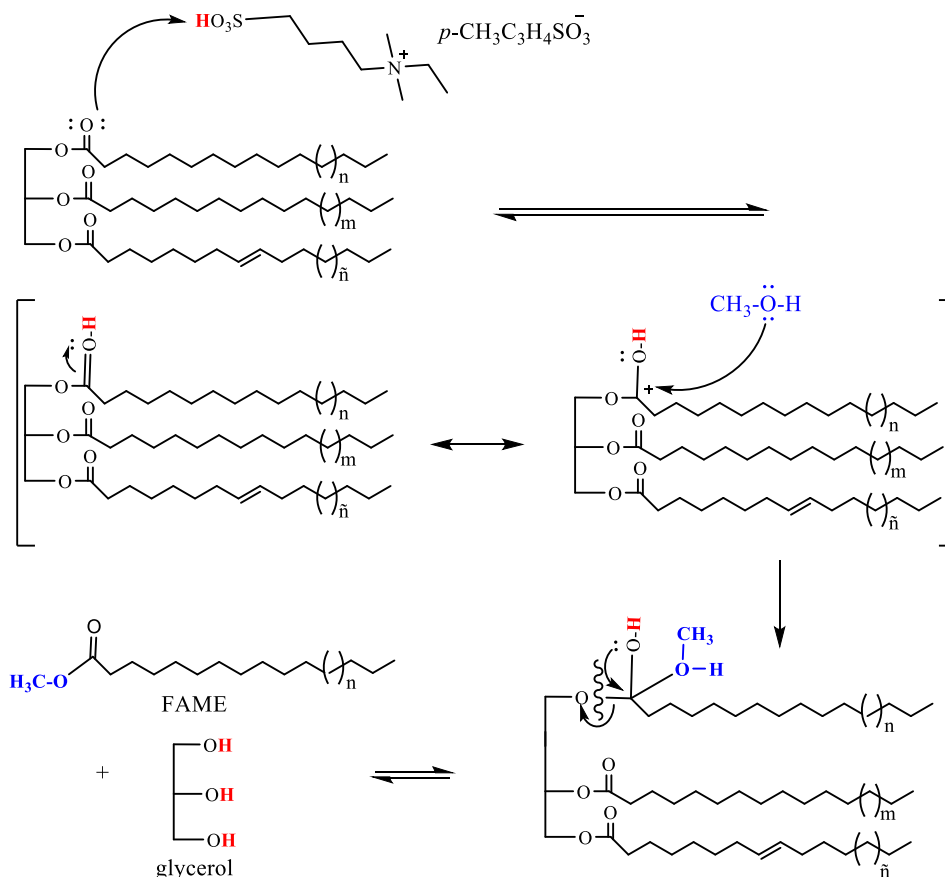


Figure 4. Proposed reaction mechanism for the transesterification process with ILs.

3.4 Microwave-assisted reaction scaling

After the above results were obtained with 6 grams of reagents under closed vessel conditions, a scale-up of the reaction using 30 g of reagents in an open vessel was performed. The reaction was run using the optimal conditions for closed vessel experiments ($T = 25\text{--}50\text{ }^{\circ}\text{C}$, ratio methanol/oil ratio: 1:5 and 0.10% w/w of catalyst IL8). The reactions were conducted using a round-bottom flask provided with a reflux condenser and magnetic stirring bar, and the mixture was heated from room temperature to $50\text{ }^{\circ}\text{C}$ and held at this temperature for 30 minutes. NMR analysis of the reaction products showed a quantitative conversion to biodiesel.

The ILs from entries 7 and 8 in Table 1 were insoluble in the organic phase and water and temperature resistance, making the catalysts' recovery and recycling very convenient. The scaled-up and transfer of the microwave process from batch to stop-flow and continuous flow process for the biodiesel preparation for being converted into a production method have been demonstrated by other authors system (Choedkiatsakul *et al.*, 2015; Groisman & Gedanken, 2008; Hernando *et al.*, 2007).

Conclusions

Eight ILs were synthesized and evaluated as catalysts of biodiesel synthesis under microwave irradiation. All ILs probed can act as catalysts under microwave irradiation. Brønsted acidic ILs containing the -SO₃H group were the most efficient, obtaining 98% conversion. In these conditions, biodiesel can be synthesized in 25 minutes under microwave irradiation. Therefore, IL 8 can act as a novel catalyst and have great potential for use in green and very efficient processes for biodiesel synthesis.

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