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ZnO/Ionic Liquid Catalyzed Biodiesel Production from Renewable and Waste Lipids as Feedstocks

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Abstract: A new protocol for biodiesel production is proposed, based on a binary ZnO/TBAI (TBAI = tetrabutylammonium iodide) catalytic system. Zinc oxide acts as a heterogeneous, bifunctional Lewis acid/base catalyst, while TBAI plays the role of phase transfer agent. Being composed by the bulk form powders, the whole catalyst system proved to be easy to use, without requiring nano-structuration or tedious and costly preparation or pre-activation procedures. In addition, due to the amphoteric properties of ZnO, the catalyst can simultaneously promote transesterification and esterification processes, thus becoming applicable to common vegetable oils (e.g., soybean, jatropha, linseed, etc.) and animal fats (lard and fish oil), but also to waste lipids such as cooking oils (WCOs), highly acidic lipids from oil industry processing, and lipid fractions of municipal sewage sludge. Reusability of the catalyst system together with kinetic (*Ea*) and thermodynamic parameters of activation ($\Delta G^{\ddagger}$ and $\Delta H^{\ddagger}$) are also studied for transesterification reaction.

Keywords: biodiesel; zinc oxide; ionic liquid; phase transfer catalyst; transesterification

1. Introduction

In past decades, fossil fuel depletion, energy crises, and greenhouse gas emissions have led to an explosion of interest in the search for sustainable and renewable energy sources such as such wind, hydrothermal, organic, geothermal, solar, and hydrogen, among others. Among renewables, biomass energy shares the largest contribution (9%) and is used as a raw material for the production of heat, power, and transport biofuels [1]. In particular, biomass can be transformed into first generation biofuels such as bioethanol (from sugar cane and corn) and biodiesel (from vegetable oils), through well-established technologies [2], but also into second generation biofuels (from non-edible feedstocks like lignocellulosic biomass, energy crops, algae, and waste materials) by means of emergent methodologies like fast pyrolysis coupled with catalytic hydrodeoxygenation (HDO) [3–6].

In this context, great attention has been received from both the research community and the industry; the production of fatty acid methyl esters (FAMEs) [7–10], namely biodiesel, a well-known renewable, non-toxic, biodegradable fuel, is capable of reducing emissions of carbon monoxide, particulate matter, carcinogenic aromatics, and sulfur in our environment [11,12]. They are ideal substitutes of petro-diesel that can be used without any engine modification and produced via acid or

base-catalyzed transesterification of triglycerides and esterification of free fatty acids present in oils and waste lipids [13–16].

It should be noted that biodiesel production suffers the drawback of threatening food storages due to the exploitation of soils and their potential conversion to industrial use. Therefore, to save food crop sources, the use of nonedible and waste oils became mandatory [17]. Since the rate of base catalyzed transesterification is much higher than that of the analogous process promoted by acids, base catalysis is mainly adopted in the industry. KOH and NaOH are commonly employed, with consequent problems related to equipment corrosion, separation difficulty, competitive saponification side-reaction, and pollutants emission [18].

Among the various alternative catalysts [19,20], zinc oxide received much attention due to its cheap, non-toxic, thermally stable, and amphoteric properties [21–23].

Indeed, ZnO efficiently catalyzes the conversion of a wide range of feedstocks such as palm and soybean oils for biodiesel production [7,24,25], but due to the low transesterification activity of bulk ZnO, most of these protocols require harsh conditions (e.g., $T = 180\ °C$) [26,27]. Alternatively, they must employ composite materials with more basic oxides [26,28–31] (e.g., CaO, MgO, etc.) or nanostructured forms of ZnO [7,23,25,32–34], thus imposing costly, time-consuming, and tedious preparations of catalysts (e.g., calcination, microwave irradiation, etc.). To date, no studies have been reported on the use of ZnO in its commercial bulk form, and very few reports deal with the application of zinc oxide to waste lipids and processes involving the simultaneous esterification and transesterification of highly acidic, unrefined feedstocks [23,29].

In this context, due to our success in the retro-polymerization of waste polycarbonates promoted by ZnO and tetraalkylammonium-based ionic liquids (ILs) [35], in line with our efforts aimed at searching for new green catalytic methods [36,37], we envisioned that such a binary catalyst could be successfully applied to biodiesel production. Exploiting the amphoteric properties of ZnO [28,38], we anticipated that the low catalytic activity of the bulk form could be enhanced using a proper ionic liquid [39], thus enabling transesterification of triglyceride in the mildest of conditions. Being oil and methanol immiscible phases, we predicted that IL should mainly behave as a phase-transfer catalyst (PTC), thus favoring the mass transfer and consequent interaction between the two reagents [40].

We report here the successful application of the cheap and easily recyclable ZnO/TBAI (TBAI = tetrabutylammonium iodide) binary catalytic system to the biodiesel conversion of a series of lipid sources, including edible and non-edible oils, waste cooking oil (WCO), highly acidic unrefined feedstocks, and the lipid component of municipal sewage scum. In these latter cases, the source being mainly composed of free fatty acids (FFAs) and calcium soaps, the catalyst proved to be suitable for the esterification process as well.

2. Results and Discussion

2.1. Optimization of Transesterification Conditions

The optimization of transesterification conditions proved to be important for increasing the biodiesel yields. The concentration of both co-catalysts (ZnO and TBAI), along with the reaction temperature, were very crucial factors for determining the rate and yield of reaction, and thus were varied in a wide range. Catalysis conditions were surveyed on soybean oil as the model substrate, and reaction parameters were calibrated for processing 0.5 mL of oil (0.415 g), 1–6 mL of methanol (2–10 MeOH/oil ratio *v/v*) in the presence of ZnO powder (0–10% *w/w*), and TBAI (0–50% *w/w*). The screened range of temperatures was 40–100 °C.

The effect of the ZnO amount was studied under reaction conditions shown in Figure 1a, from which clearly it emerged that transesterification reached almost complete conversion with 2% of the catalyst. Next, amounts of ZnO up to 10% resulted in a decrease of activity (Figure 1a). Neither the prolonged drying of zinc oxide powder (in an oven at 80 °C for 12 h), nor the reduction of its granulometry proved to affect this trend.

However, by working on up-scaled reactions (more than 10 mL of oil) catalytic efficiency returned to an increased regularity of the ZnO amount and, as expected, the yield values approached a plateau of 100% above 2% of ZnO loading.

A plausible reason for the above behavior could be related to the amount of suspended catalyst powder and reaction volume ratio that unpredictably affects the total surface area and consequently the number of the active sites of the heterogeneous catalyst (see Figure 2).

The dependence of biodiesel production from the ionic liquid (TBAI) dosage followed a more predictable trend (Figure 1b). At first, in the absence of IL, ZnO displayed low activity as expected (10% of yield). Next, an increase of biodiesel yield on increasing the amount of TBAI was observed until reaching a plateau of yield very close to 100% at the value of 30% of quaternary ammonium salt.
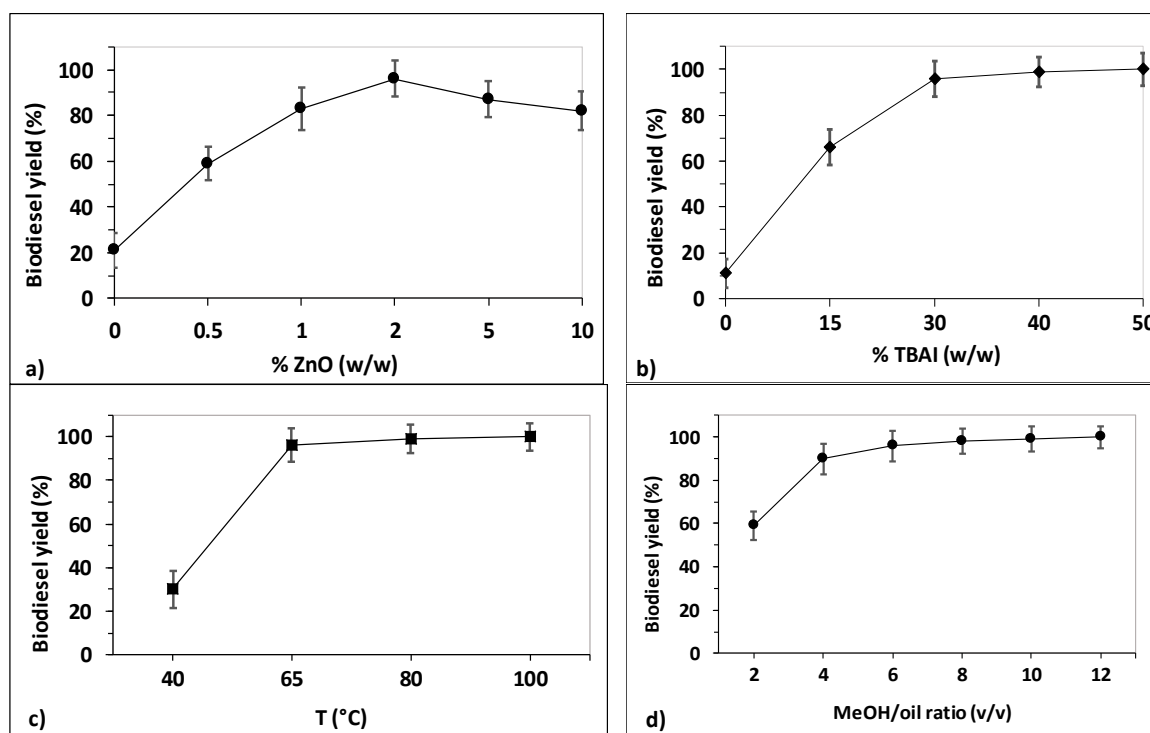

Figure 1. Study of parameters affecting the transesterification of soybean oil (0.5 mL, 0.415 g) with methanol promoted by ZnO/TBAI as catalytic system. (**a**) Effect of ZnO amount: methanol 4 mL, TBAI 123 mg (30% *w/w*), at 65 °C for 7 h; (**b**) Effect of TBAI amount: methanol 4 mL, ZnO 9 mg (2% *w/w*), at 65 °C for 7 h; (**c**) Effect of temperature: methanol 4 mL, ZnO 9 mg (2% *w/w*), TBAI 123 mg (30% *w/w*), reaction time 7 h; (**d**) Effect of oil/MeOH ratio: ZnO 9 mg (2% *w/w*), TBAI 123 mg (30% *w/w*), at 65 °C for 7 h.

Remarkably, although the latter is highly soluble in the methanolic phase, it was completely recovered from the reaction mixture by evaporation of MeOH and successive precipitation with ethyl acetate (see experimental section).

A similar trend was found for the dependence of transesterification from temperature (Figure 1c). A plateau was observed after 65 °C, which was chosen as the optimal temperature value because it enables working under reflux conditions and avoids dangerous increases of pressure in the reactor due to boiling MeOH.

Optimization procedure was completed, investigating the MeOH-to-oil volume ratio. Results in Figure 1d show only a slight effect exerted by this parameter on biodiesel production. Yields were already found above 90% with a MeOH/oil ratio equal to 4:1 (2 mL of methanol). Nevertheless, the use of too-low methanol volumes caused separation problems during the recycling procedure. Therefore, an optimal MeOH/oil ratio of 8:1 (4 mL of methanol) was found to be preferable.

2.2. Influence of the Nature of Ionic Liquid: Mechanistic Insight

The exact role and the synergic effect played by the two components of the binary catalyst ZnO/IL can be highlighted based on the mechanistic hypothesis represented in Figure 2. ZnO exerts the role of a heterogeneous bifunctional Lewis acid/base catalyst, generating CH_3O^- anions through the basic sites represented by oxygen atoms at the surface, but also activating the carbonyl group by means of acid sites represented by Zn atoms. The possibility that the two processes of esterification and transesterification can take place simultaneously is strictly related to these amphoteric properties of this metal oxide [28,38].

At the same time, the ionic liquid assumes the crucial role of phase transfer catalyst (PTC) by carrying methoxide anions into the oil phase [40–42]. In the absence of this component, catalytic action of ZnO becomes disappointing (see Figure 1b).
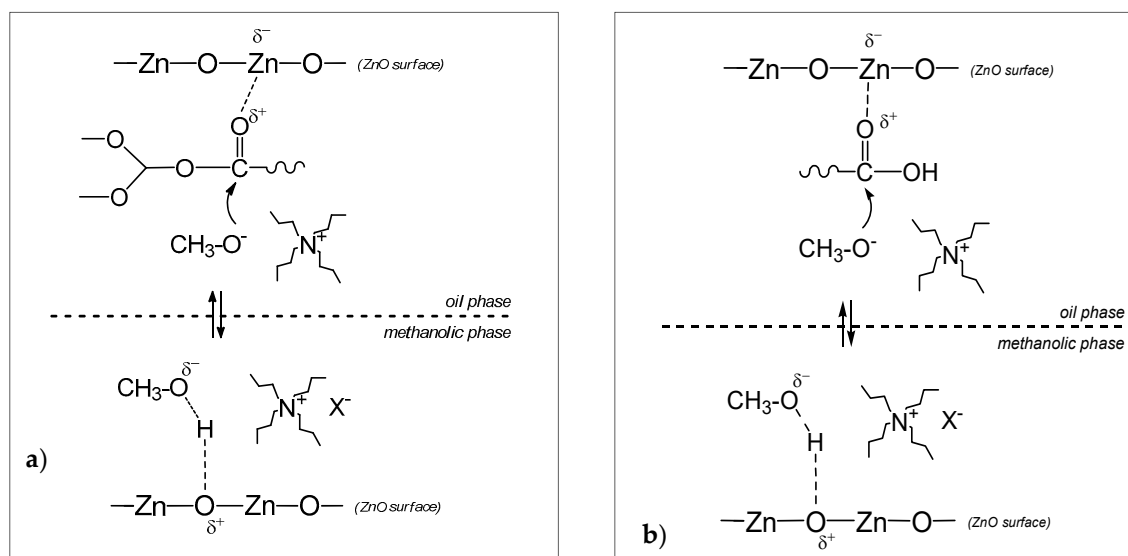

Figure 2. Schematic representation of ZnO/IL catalyst action in (**a**) transesterification of triglycerides and (**b**) esterification of fatty acids.

Since the ionic liquid also plays a key role, the influence of its nature on the catalytic process was studied carefully by comparing the performances of several salts under the optimized conditions established for TBAI. Results (Figure 3) showed that tetraalkylammonium and tetraalkylphosphonium based ILs (TBAI, TBACl, TBAAc, TBPAc etc.) displayed consistently better activity than the imidazolium and pyridinium analogues (BMIM, BDMIM, BMPyCl, etc.).

This behavior could be due to two main reasons: (i) the higher lipophilic properties of the formers, with the consequently higher ability of carrying anions into the oil phase, and (ii) the structure of cations and positive charge shielding.

Indeed, based on our previous findings [43], both the tetrahedral structure and the steric hindrance of alkyl chains of quaternary ammonium (or phosphonium) cations in TBAI, TBACl, TBPAc, etc., shields the positive charge on nitrogen (or phosphorous), leaving counteranion CH_3O^- poorly solvated especially in the oil phase, thus enhancing their nucleophilicity. This phenomenon is less evident in imidazolium and pyridinium analogs (BMIMCl, BDIMCl etc.) due to the planar structure of cations and their stronger interaction with counteranions. Notably, the worse performance of tetrabutylammonium hydroxide (TBAOH) was surely due to its major aptitude in granting the collateral process of saponification.

The influence of the IL anion proved to be of minor importance. With the exception of iodide in TBAI, which displays the best catalytic efficiency, the other anions' activity appeared to be related to their basicity, with acetate ions performing best (e.g., TBAAc and TBPAc). Concerning the halide

anions, the reactivity scale $I^- > Br^- > Cl^-$ observed for the corresponding tetrabutylammonium salts (TBAI > TBABr > TBACl) could be justified based on the electronegativity of anions, which could influence the dissociation of salt in the methanol phase [41].

　　Remarkably, TBAI proved to be not only the best active IL, but also the most easily recoverable co-catalyst due to its very low solubility in ethyl acetate.
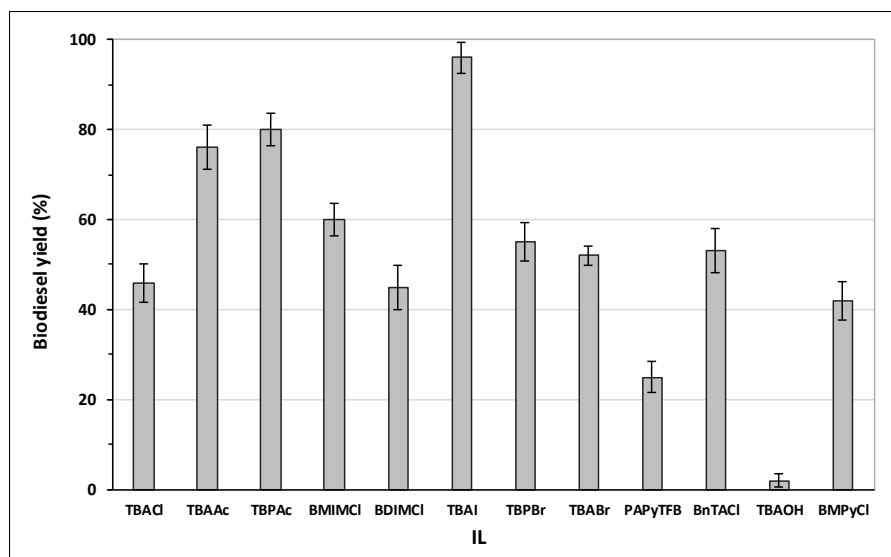

Figure 3. Effect of ionic liquid on the transesterification of soybean oil. Reaction conditions: soybean oil 0.5 mL (0.415 g), methanol 4 mL (MeOH/oil ratio = 8), ZnO 9 mg (2% *w/w*), IL (30% *w/w*), at 65 °C for 7 h. TBACl = Tetrabutylammonium Chloride; TBAAc = Tetrabutylammonium acetate; TBPAc = Tetrabutylphosphonium Acetate; BMIMCl = 1-butyl-3-methylimidazolium Chloride; BDIMCl = 1-butyl-2,3-dimethylimidazolium Chloride; TBAI = Tetrabutylammonium iodide; TBPBr = Tetrabutylphosphonium Bromide; TBABr = Tetrabutylammonium Bromide; PAPyTFB = p-anisylpyridinium Tetrafluoroborate; BnTEACl = Benzyltriethylammonium Chloride; TBAOH = Tetrabutylammonium Hydroxide. BMPyCl = 1-Butyl-4-methylpridinium chloride.

2.3. Kinetic and Thermodynamic Parameters

　　To gain further insight on catalyst performances, kinetic and thermodynamic parameters were additionally evaluated. Transesterification reaction using methanol consists of three-step reactions to convert triglycerides (TG) into biodiesel and glycerol [44,45]. In the first step, triglyceride reacts with one molecule of methanol, producing diglyceride (DG) and one molecule of methyl ester. Thereafter, the molecule of DG reacts with another molecule of methanol to produce monoglyceride (MG) and one molecule of methyl ester. Finally, the reaction between MG and methanol produces methyl ester and glycerol. Thus, the overall transesterification reaction results in the formation of three moles of methyl ester and glycerol as reported in the following:

$$TG + 3CH_3OH \rightleftarrows 3\ FAME + Glycerol$$
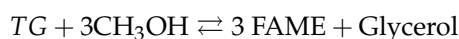
　　In order to simplify the kinetic model, the overall transesterification reaction without intermediate steps can be considered [46–48]. The rate of transesterification can be expressed by Equation (1):

$$r = -\frac{d[TG]}{dt} = k' \cdot [TG] \cdot [ROH]^3 \tag{1}$$

and due to the excess amount of methanol, which can be considered constant, the proposed model of pseudo-first order kinetic [36,41], shall be assumed. Accordingly, the rate equation can be expressed as:

$$r = -\frac{d[TG]}{dt} = k' \cdot [TG] \tag{2}$$

where $k = k' \cdot [ROH]^3$, also

$$r = -\frac{dX_r}{dt} = k \cdot (1 - X_r) \tag{3}$$

where X_r is the conversion of methyl ester $X_r = 1 - [TG]/[TG]_0$, and the integrated equation is:

$$-\ln(1 - X_r) = k \cdot t \tag{4}$$

The plot of $-\ln(1 - X_r)$ against t was used to determine k. For our data, this plot displayed a straight line at all the studied temperatures, indicating that the pseudo-first order model well describes the kinetics of transesterification reactions in the range of temperature explored (Figure 4a).
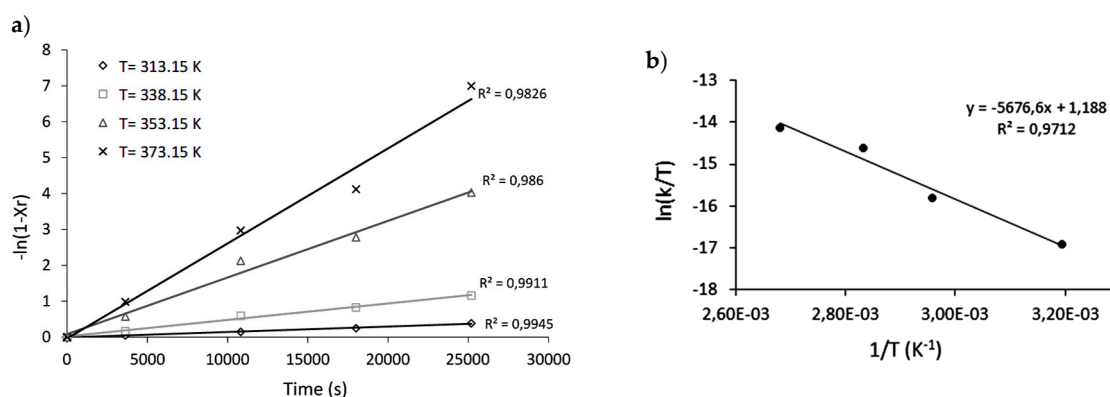

Figure 4. (**a**) Plot of $-\ln(1 - X_r)$ versus reaction time at the studied temperatures (see Figure 1c); (**b**) Erying plot of $\ln(k/T)$ vs. $1/T$ for thermodynamic parameter determination.

Rate constant values (k) at different transesterification temperatures (Table 1) were found in a similar range as compared to the values reported in the literature [49]. They were used to calculate kinetic parameters, activation energy (Ea), and pre-exponential factor (A), through Arrhenius equation (Equation (5)) and from the intercept and slope of the linear correlation resulting of plotting $\ln k$ versus $1/T$ (Equation (6)).

$$k = A\, e^{-Ea/RT} \tag{5}$$

$$\ln k = \ln A - \frac{Ea}{RT} \tag{6}$$

The calculated 48.46 KJ·mol^{-1} Ea value is in agreement with data in the literature, which usually reports for transesterification activation energy values ranging between 26 and 115 KJ mol^{-1} [44,45,49]. From the data it clearly emerged that ZnO/TBAI display a kinetic behavior quite similar to that of many analogous catalytic systems, but without requiring tedious and costly preparations (e.g., calcination, nano-structuration, microwave irradiation, etc.).

Table 1. Kinetic (*Ea*) and thermodynamic parameters of activation ($\Delta G^{\ddagger}$ and $\Delta H^{\ddagger}$) for ZnO/TBAI catalyzed methanol transesterification reaction of soybean oil [1].

T (K)	*k* (s⁻¹)	*Ea* (KJ/mol)	*A* (s⁻¹)	$\Delta G^{\ddagger}$ (KJ/mol)	$\Delta H^{\ddagger}$ (KJ/mol)	$\Delta S^{\ddagger}$ (KJ/mol·K)
313.15	1.4×10^{-5}					
338.15	4.6×10^{-5}	48.46	2.4×10^{3}	72.33 [2]	44.90	−0.081
353.15	1.6×10^{-4}					
373.15	2.7×10^{-4}					

[1] General condition: oil 0.5 mL, methanol 4 mL, ZnO 9 mg (2% *w/w*), TBAI 123 mg (30% *w/w*). [2] at optimal reaction temperature of 338.15 K.

Thermodynamic parameters of activation were calculated by Eyring equation (Equation (7)), a theoretical construction based on a transition state model, which establishes a relationship between constant rate and the Gibbs energy of activation ($\Delta G^{\ddagger}$)

$$k = k^{++} \frac{k_B T}{k} \exp\left(-\frac{\Delta G^{\ddagger}}{RT} \right) \tag{7}$$

where k is the rate constant, k^{++} is the transmission coefficient, which usually takes a value of 1 [50], k_B is the Boltzmann constant (1.38×10^{-23} J·K⁻¹), and h is the Planck constant (6.63×10^{-34} J·s). By substituting the Gibbs free energy equation at constant temperature and pressure ($\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$) in Equation (7) and taking natural logarithms, Equation (8) was obtained, suitable for determining the values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ (Table 1) from the slope and intercept, respectively, of the linear plot of ln (k/T) versus $1/T$ (Figure 4b):

$$\ln\left(\frac{k}{T} \right) = -\frac{\Delta H^{\ddagger}}{R}\left(\frac{1}{T} \right) + \left[\ln(k^{++}) + \ln\left(\frac{k_B}{h} \right) + \frac{\Delta S^{\ddagger}}{R} \right] \tag{8}$$

The positive values $\Delta H^{\ddagger}$ obtained for ZnO/TBAI catalyzed methanol transesterification (Table 1) reveals that heat energy input is required to bring the reactants to a transition state toward the products. Moreover, the negative $\Delta S^{\ddagger}$ value indicates a more ordered transition state compared to the reactants in the ground state as suggested by the catalyst action scheme in Figure 2.

2.4. Recycling Tests

Recycling experiments were carefully conducted to verify complete recovery of the catalyst system ZnO/TBAI and to assure that no residues were released into the biodiesel product during the work-up procedure. Reusability was investigated under the optimized reaction conditions listed in Figure 5. As expected, being insoluble in methanol, zinc oxide was instantly recovered by centrifugation after completion of the reaction.

In the case of the TBAI, which is highly soluble in methanol, complete recovery was due to its very low solubility into ethyl acetate. Indeed, after removal of ZnO and the evaporation of MeOH, the oily reaction mixture was taken up with AcOEt, which induced the complete precipitation of TBAI that was filtered off and promptly reused in a subsequent run. Residues of IL and glycerol were easily removed from biodiesel by water washing, as ascertained by ¹H NMR (see for details experimental part, Section 2.4). After being reused 5 times, the catalyst system proved stable, as the biodiesel yields decreased from 96% to 93% (Figure 5).
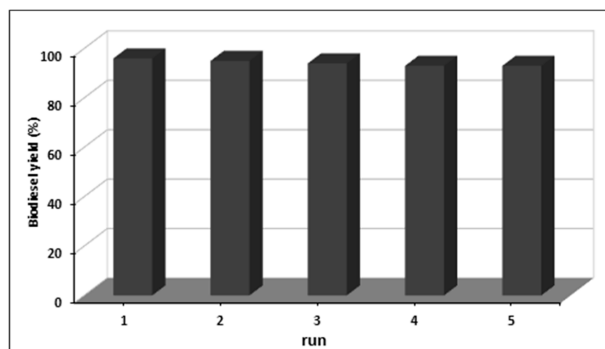
Figure 5. Recycling of the ZnO/TBAI catalyst system in the transesterification of soybean oil. Reaction condition: oil 0.5 mL; MeOH (4 mL), ZnO (2% *w*/*w*), TBAI (30% *w*/*w*), T = 65 °C; 7 h.

To evaluate catalyst life and ascertain that no deactivation process occurred, recycling experiments were further extended and ZnO powder surface was studied by ATR and granulometric analyses (see Supplementary Material, Section S5). As shown in Figure S13, the ATR spectrum of pristine ZnO powder and that obtained after the transesterification experiment were virtually identical, displaying only the large band below 500 cm^{-1} attributed to the Zn-O stretching. Neither bands above 3000 cm^{-1} due to Zn-O-H stretching, nor other absorptions attributable to other species, were detected.

Similarly, the particle size distribution of zinc oxide powder after the catalytic test is virtually the same as that of ZnO recovered after a reaction (Figure S14). Therefore, it can be concluded that zinc oxide lifetime is virtually unlimited, and the slightly lower activity is due to the loss of material during the recycling operations.

2.5. Transesterification/Esterification of Refined and Wasted Lipid Feedstocks

To evaluate the general applicability of the binary ZnO/TBAI catalyst system, the protocol was extended to other refined triglycerides and to unrefined feedstocks coming from waste fats. Among the latter ones, WCO, lipid residues coming from the industrial processing of animal fats (fish oil), or olive oil (olein), and even the lipid component of municipal sewage scum, were investigated as representative examples of waste lipids.

In some of these cases, being the feedstocks composed by random mixtures of triglycerides, free fatty acids (FFAs), and soaps, the catalyst proved to be sufficiently flexible to simultaneously promote esterification and transesterification processes. Lipid composition of the feedstocks used in this screening was ascertained either by standard analyses or furnished by the supplier (see Supplementary Materials for details).

Results listed in Table 2 show that the catalyst worked with the same efficiency on edible (soybean) and non-edible (jatropha and linseed) vegetal oils. The semi-soft white animal fat (lard) was also productively converted, but required higher temperature conditions (100 °C) due to both its viscosity and waxy solid state.

Table 2. ZnO/TBAI catalyzed biodiesel production from refined and waste lipid feedstocks [1].

Feedstock [2]	FFAs (wt.%)	Transesterifiable/ Esterifiable Amount (*w*/*w* %)	Biodiesel Yield (%) [3]
Soybean oil	1	97	96 ± 3
Jatropha oil	<1	99	95 ± 3
Linseed oil	2	98	93 ± 4
Lard (animal fat)	<1	94	95 ± 4 [4]
WCO	1.5	96	95 ± 3
Fish Oil	<1	90	92 ± 5 [4]
Oleic acid	>99	>99	54 ± 4 (99) [5]
Olein residue [6]	76	95	75 ± 5
Municipal sewage scum [7]	32	60	79 ± 4

[1] General reaction conditions: feedstock 0.5 mL, methanol 4 mL, ZnO 9 mg (2% *w*/*w*), TBAI 123 mg (30% *w*/*w*), at 65 °C for 7 h. [2] Properties and composition of these lipid sources are given in Section S2. [3] Isolated yields evaluated based on esterfiable/transesterifiable fraction of feedstock. [4] Reaction carried out at 100 °C. [5] In brackets, yields obtained in autoclave at 70 °C. [6] Highly acidic mixture of lipids coming from oil industry processing. [7] Lipid fraction of municipal sewage scum of Polignano (Italy). Reaction was carried out at 75 °C to allow the reacting mixture to melt.

Notably, even unrefined feedstocks and waste lipids were productively transformed into biodiesel with this protocol. In particular, WCO, coming from domestic use, and fish oil, a raw material derived from recycled by-products of fisheries—both almost entirely composed by triglycerides—were converted in good yields.

Next, the application of the protocol to free fatty acids (FFAs) was assessed. Pure oleic acid was initially investigated as model substrate, verifying its complete esterification into methyl oleate even if slightly harsher conditions were necessary to reach the maximum yield (reaction carried out in autoclave at 70 °C).

Similarly, highly acidic mixtures coming from oil industry processing (olein residue), was converted into FAMEs with 75% yield. Finally, the ZnO/TBAI catalyst proved to be efficient also in converting, with a 79% yield, the lipid fraction of municipal wet sewage scum, that is mainly composed by fatty acids and calcium soaps (see Section 2.2) [38], indicative of the flexibility of the catalyst in promoting simultaneously esterification and transesterification reactions.

Finally, as the protocol provides products not contaminated by the acid or base catalysts, nor by unreacted free fatty acids, the recovery of glycerol in high purity was attempted in order to demonstrate the added value of this methodology. At this end, an up-scaled transesterification (by 20 times) was performed on 10 g of soybean oil, with 2% *w/w* (200 mg) of ZnO, 30% *w/w* (3 g) of TBAI and 40 mL of methanol, under reflux and stirring at 70 °C for 8 h. Results showed 80% of biodiesel and 650 mg (88%) of isolated highly pure glycerol as ascertained by ^{1}HNMR (Figure S3).

3. Materials and Methods

3.1. Materials

Chemicals, solvents, and ionic liquids were purchased from Aldrich or Fluka. ZnO was a Carlo Erba product and were all used as received. Commercial soybean oil (Valsoia S.p.A. Bologna, Italy) was employed for optimization condition experiments. Jatropha oil was furnished by Agroils TECHNOLOGY S.p.A. (Sesto Fiorentino, Italy). Linseed oil and oleic acid (>99%) were from Sigma Aldrich (Milan, Italy). Waste cooking oil was a domestic source and olein residue was furnished by an Apulian oil company. Municipal sewage scum was sampled from the municipal wastewater treatment plant of Polignano (Bari, Italy). Fish oil, a gift of Greenswitch Biorefinery (Ferrandina, Italy), and lard (commercial animal fat by COOP, Casalecchio di Reno, Italy) were used as received. General properties and fatty acid composition of all of these feedstocks are reported in Tables S1 and S2 of Supplementary Materials.

NMR spectra were recorded on an Agilent Technologies 500 MHz spectrometer; the ^{1}H resonance signals were referenced to residual isotopic impurity of $CDCl_3$ (7.26 ppm). Qualitative and quantitative analyses were carried out on an Agilent 6850/MSD 5975C GC-MS (Santa Clara, CA, USA) and Varian 3800 GC-FID instruments (Palo Alto, CA, USA), respectively. FAMEs products were identified by comparison of their MS spectral data with the literature, or with the aid of authentic samples (details of analytic methods are reported into the Supplementary Materials). Catalytic tests were carried out in 10 mL glass vials equipped with a magnetic bar and sealed with a screw cap. Alternatively, reactions were conducted in a 50 mL stainless steel autoclave.

ATR spectra were recorded on a PerkinElmer Spectrum Version 10.4.3 instrument (Waltham, MA, USA), while granulometric analyses were carried out on a HELOS (H3599) & RODOS/M, R1 instruments with elaborated by PAQXOS 2.2.2 software (ver. 2.2.2, SYMPATEC GmbH Clausthal-Zellerfeld, Germany, 2017).

3.2. Lipids Characterization of Real Sewage Scum

A real sample of sewage scum was taken from the municipal wastewater treatment plant of Polignano (Municipality of Polignano, Bari, Italy and was pre-treated with the aim of isolating the lipid fraction suitable for biodiesel conversion as follows: about 30 g of wet sewage scum was placed in a tube of 50 mL and heated in a thermostatic bath at 353 K for 2 h. Then, the tube was rapidly centrifuged at 4000 rpm for 2 min by a three-phasic system where (i) an upper brown oily phase, liquid

at 353 K, but solid at room temperature, were easily pipetted away as the lipid fraction and separated by (ii) an aqueous intermediate phase and (iii) a lower phase of wet solid residues [51,52].

This lipid phase was found to be constituted by a saponifiable fraction for only around 60%wt (with acids having a molecular average weight of 270 uma, calculated by FAs profile). In detail, 32% of this lipid were FFAs, while 28% were calcium soaps. FAs profile (myristic, palmitoleic, palmitic, oleic and stearic acids were found to be respectively 5%, 3%, 34%, 48.5% and 9%) was assured by adopting well-known analytical procedures. Mono-, di- and tri-glycerides were detected only in traces. The remaining part was found to be oily compounds not promptly convertible into FAMEs.

3.3. Transesterification Experiments

In a typical experiment, a 10 mL glass vial equipped with a magnetic bar was charged with Methanol (4 mL), 0.5 mL of commercial soybean oil (415 mg at 25 °C), TBAI (123 mg, 30% *w/w*), and ZnO (9 mg, 2% *w/w*). The vial was then sealed, heated at 65 °C under stirring, and left to react for the proper time. Next, reaction mixture was cooled to room temperature, transferred into a centrifuge tube, and subjected to 3500 rpm for 15 min. A white solid ZnO layered at the bottom; a residual oily phase above (which was absent in the case of complete conversion), and an upper methanolic phase were commonly visible after centrifugation (Figure 6).
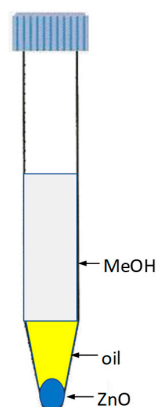

Figure 6. Schematic of the layered phases of reaction mixture after centrifugation.

The supernatant methanolic solution (containing FAMEs, glycerol and TBAI co-catalyst) was roughly separated by means of a Pasteur pipette. The lower biphasic residue (ZnO + unreacted oil) was washed twice with 2 mL of fresh methanol to remove traces of biodiesel and TBAI (by stirring and centrifugating the mixture after each addition of MeOH). The combined methanolic phases (washing fractions and post-reaction solution) were subjected to the separation step of TBAI and glycerol, followed by FAMEs, qualitative, and quantitative analyses (*vide infra*).

Biphasic residue (ZnO + unreacted oil), after washing with MeOH, was treated twice with ethyl acetate (2 mL) and centrifugated. The combined supernatants were evaporated, and the oil residue weighed for determining the conversion (alternatively, conversion was evaluated by ^{1}HNMR as reported in Section S3). The remaining solid ZnO was washed with acetone, filtered and dried in an oven at 80 °C for 4 h, ready to be reused.

For FAMEs analyses, the methanolic phase (FAMEs + glycerol + TBAI) was added to 50 mg of methyl heptadecanoate as an internal standard, evaporated to small volume, and suspended in 10 mL of ethyl acetate. This caused the precipitation of TBAI, which was filtered off and totally recovered in high purity (ascertained by ^{1}HNMR; see Section S3 of Supplementary Materials). The ethyl acetate solution was evaporated to small volume with separation of small drops of a viscous phase due to glycerol, which was removed by washing with water. After drying, the ethyl acetate solution was subjected to qualitative and quantitative analyses (by GC-MS and GC-FID techniques, respectively) to identify FAMEs and determine composition of the biodiesel product (see Section S3 of Supplementary Materials).

3.4. Procedure for Catalyst Recycling

A series of recycling experiments (Figure 5) were carried out to assess the reusability of the ZnO/TBAI catalyst system under optimized conditions established in Figure 1. After completion of the reaction (7 h), the mixture was transferred into a centrifuge tube and subjected to 3500 rpm for 15 min. The supernatant methanol solution was recovered by means of a Pasteur pipette, while ZnO was washed twice with 2 mL of fresh methanol to remove traces of biodiesel and TBAI (by stirring and centrifugating the mixture after each addition of MeOH).

ZnO was washed twice with acetone, filtered, and dried in an oven at 80 °C for 4 h. The solid proved to be recovered for almost 99% and then was promptly reused in the next run.

To recover the ionic liquid, the washing methanol was combined with the starting solution and evaporated under vacuum by rotavapor. The oily residue was suspended in 10 mL of ethyl acetate, thus determining the precipitation of TBAI that was filtered off and completely recovered in high purity (ascertained by ^{1}HNMR Section S3) to be promptly reused. The homogeneous organic phase was evaporated to a small volume with separation of small drops of a viscous phase due to glycerol that was removed by washing with water. After drying and evaporation of ethyl acetate, FAMEs were obtained in high yields and purity as reported in Figure 3.

4. Conclusions

Low-cost ZnO/quaternary ammonium ionic liquid (TBAI) can catalyze simultaneous esterification and transesterification reactions of several refined and unrefined high-acid value feedstocks with good catalytic activity. A maximum yield of 96% was achieved for soybean oil at 65 °C for 7 h, and the catalyst could be separated and reused for five cycles without significant decrease of activity. A ZnO/TBAI catalyst system is composed of bulk powders and displays a kinetic behavior quite similar to that of many analogous catalysts without requiring tedious and costly preparations (e.g., calcination, nano-structuration, microwave irradiation, etc.). Therefore, it is easy to use and shows good potential to be a commercial catalyst for one-step biodiesel production from massive amounts of WCO and waste lipids as an alternative low-cost feedstock.

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