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Toward Efficient Continuous Production of Biodiesel from Brown Grease

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Abstract: An increase in energy consumption and the extended use of nonrenewable fossil fuels raises the need to develop alternative fuels as an energy supply that can protect the environment from unwanted emissions of pollutants. One alternative renewable fuel is biodiesel. Currently, most biodiesel feed sources are edible oils, but using them leads to the dilution of global food sources. The present study aims to find an effective method of biodiesel production using food industry fatty wastes called brown grease (BG). BG contains fats, mainly linoleic and oleic free fatty acids (FFAs), that can serve as raw materials for biodiesel production using esterification reactions. The esterification and transesterification reactions for biodiesel production were studied using commercial FFAs, commercial glyceryl trilinoleate (trilinolein), soybean oil, and BG. The reactions were carried out under ultrasonic activation using BF_3 and $AlCl_3$ Lewis acids as catalysts in both free and immobilized forms when immobilization was performed in silica matrices using the sol-gel synthesis route. Biodiesel production was examined in batch and continuous flow reactors. The BF_3 catalyst was more efficient at the initial stages of the continuous operation, reaching a maximum conversion of 90%, with a gradual decrease in efficiency after 15 h of the process. The $AlCl_3$ catalyst showed better stability, reaching maximum yields of 97% and maintaining efficiency until the end of the experiment. The proposed method offers an efficient and easy way to produce biodiesel from a variety of lipids sources, including fatty wastes (BG).

Keywords: biodiesel; brown grease; trilinolein; free fatty acids; soybean oil; Lewis acids; ultrasonic activation; sol-gel; continuous flow reactor

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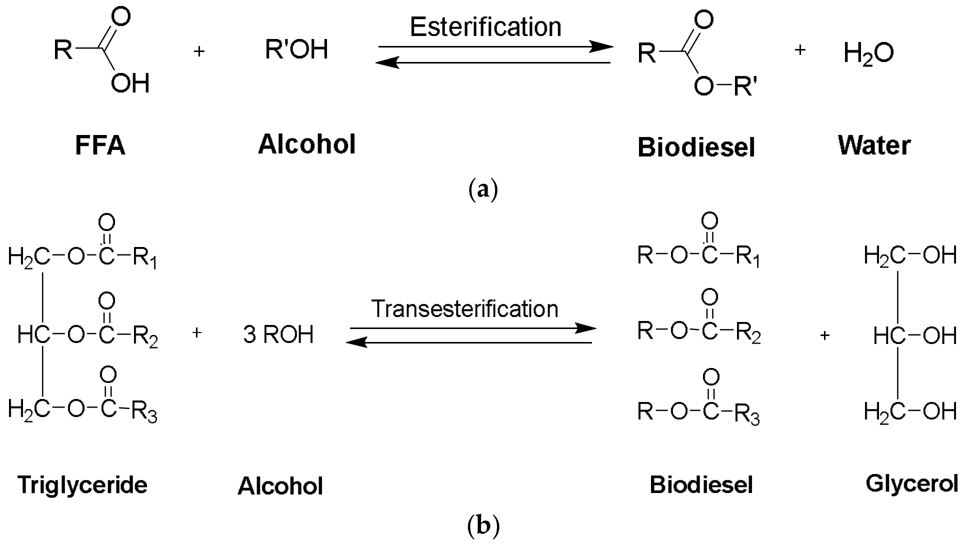
1. Introduction

There is an urgent need to advance sustainable energy due to disturbing trends in global energy consumption, a rise in oil prices, the depletion of fossil resources, a requirement to reduce greenhouse gas emissions, and climate change [1]. For these reasons, the development of sustainable and renewable biofuels has been gaining momentum in recent years. Bioenergy in general and renewable biofuels, in particular, are attracting increasing attention as part of developing a sustainable and environmentally friendly economy [2]. To answer the increasing demand for energy while reducing CO_2 emissions, the world needs to have more efficient and sustainable energy sources [3]. Developing an efficient and economical process for biodiesel production can become a genuine alternative to conventional fossil fuels.

Biodiesel is a biofuel produced from natural components and contains long-chain fatty acid alkyl esters originating from vegetable oils or animal fats (mainly soybean, canola, coconut, corn, peanut, palm oil, etc.) [4]. Global biodiesel production more than doubled between 2010 and 2020 [5]. In 2016, world biodiesel production was 32.8 million tons, with 43% of production coming from Europe, while China produces 336,000 tons of biodiesel annually [6].

Major plant triglycerides and fatty acids are produced in plant cells; therefore, they are regarded as renewable oil sources [4]. Conventional biodiesel production is based on edible and non-edible vegetable oils as raw materials, which amount to approx. 70–95% of the production cost. Another feedstock is grease from wastes, called brown grease (BG). Its prevalence and low cost make it a promising source for biodiesel production. BG is captured in grease traps installed in food service establishments such as restaurants, event halls, and wastewater treatment plants. The annual amount of brown grease production is usually estimated at about 6 kg of FOG (fat, oil, and grease) per year per person [7]. BG disposal into a sewage system is considered illegal in many countries since BG may cause fouling on pipe walls and form hard sediments, which are detrimental to the proper functioning of sewage systems [8]. Usually, the BG collected by sewage suction trucks is landfilled or combusted, which may cause environmental pollution. BG is a good and cost-effective alternative feedstock for biodiesel production that meets the demand for a sustainable and clean energy supply [9].

BG contains high concentrations of free fatty acids (FFAs), which can be used as a feedstock in biodiesel production. Biodiesel can be produced by the esterification of free fatty acids (FFAs) or transesterification of triglycerides using alcohol (usually methanol) in the presence of a catalyst (Figure 1). In the esterification reaction, the acid catalyst first protonates the carbonyl group's oxygen, creating a cationic complex. The carbon in the complex's carbonyl group is subsequently attacked by the oxygen in the alcohol via a nucleophilic attack [10,11]. Finally, water and a fatty acid methyl ester (FAME) molecule are created when hydrogen binds with the acid's hydroxyl group (Figure 1a). In the case of transesterification, a triglyceride first interacts with alcohol to produce a fatty acid methyl ester and a diglyceride molecule [12,13]. The diglyceride then reacts with a second molecule of alcohol to create a monoglyceride and a second molecule of fatty acid methyl ester. Then, the process repeats with the monoglyceride molecule. Therefore, to create three molecules of FAME and one molecule of glycerol, stoichiometrically, a 3:1 molar ratio of alcohol to triglyceride is needed (Figure 1b). Temperature, the amount of catalyst, and the molar ratio of the alcohol to the triglyceride (or FFA) determine the reaction performance in both processes [14].



(**a**)

(**b**)

Figure 1. General scheme of the esterification reaction of free fatty acids (**a**) and transesterification reaction of triglycerides (**b**) with methanol.

The traditional method for activating esterification and transesterification reactions is heating or thermal activation [15–17]. In our previous work, it was suggested to activate the reactions of biodiesel production by ultrasonic treatment without additional heating [18], and ultrasonic activation of FFA esterification with methanol in the presence of a catalyst was even more efficient than thermal activation, leading to almost 100% yield of methyl esters within 15 min. The yield of the same reaction under thermal activation was about 95% [18]. This method of activation by ultrasonic waves in the frequency range of 20–100 kHz can be a powerful method for the efficient production of biodiesel in mild operating conditions.

The use of ultrasound in biodiesel synthesis ensures the formation of a fine emulsion between immiscible reactants. In this case, the area of the interfacial surface increases significantly, leading to an acceleration of the reaction. In addition, ultrasonic cavitation provides the energy to initiate the reaction and leads to an increase in the surface temperature between the reagent phases, which can also increase the esterification rate [19,20]. However, the use of sonication in a batch reactor is limited to a small reactor volume. Efficient ultrasonic activation of large volumes of reagents requires high energy consumption and may significantly increase the cost of the process [21]. Therefore, in recent years, attention has mainly been paid to the development of a continuous process for the ultrasonic synthesis of biodiesel, which allows for the processing of large amounts of reagents in a relatively small reactor volume. Good results in continuous esterification and transesterification have been achieved in ultrasonic reactors using homogeneous catalysts [21–28]. In these works, for the esterification of fatty acids [23,25,26,28] and the transesterification of glycerides [21–25,27,28] with methanol [21,22,24–28] or ethanol [23], free alkaline [21,22,24,27,28], acid [26,28], or their combination [23,25] catalysts were used. Under the activation of the process by ultrasound with 20 [21–24,26–28], 50 [21], and other [25] kHz frequencies, 90–100% efficiency was achieved [21–28]. However, the complexity of separation and purification and the infeasibility of reusing the catalyst increase the cost of biodiesel production. Using heterogeneous catalysts looks more promising, as it can overcome the above disadvantages [29–31]. However, ultrasonic methods are less efficient when working with heterogeneous catalysts due to high resistance to mass transfer, as well as due to the inhomogeneity of the catalyst dispersion in the reaction solution [19,20]. In addition, the deactivation of heterogeneous catalysts after several hours of continuous operation and the problem of catalyst regeneration have been reported [32]. Successful results in the esterification of FFA tobacco and canola oil by ultrasonic activation were achieved using Amberlyst acid ion exchange resin as a heterogeneous catalyst [33]; however, these experiments were carried out in a batch reactor. Another heterogeneous catalyst, KI/ZnO, was also effective in the ultrasonic production of biodiesel from non-edible oils [31]. In this case, the reaction took place in a batch reactor as well, but the possibility of reusing the catalyst in five cycles of the transesterification reaction was checked. Here, a decrease in the catalytic activity of the catalyst was noted in each subsequent cycle; after five consecutive reaction cycles, the catalyst lost ∼50% of its initial activity [31].

In our previous works, the development of a continuous process for bio-diesel production based on ultrasonic activation was reported [34]. In this process, the esterification of oleic acid with methanol was studied, when Lewis acids that were incorporated into silica matrices by the sol-gel synthesis route were used as heterogeneous catalysts. Broadening the scope of this publication, the goal of the current study is to examine the efficiency of the process while using BG collected from the campus cafeteria. In addition, we aimed to examine whether the developed catalytic process can also be implemented to produce biodiesel from vegetable oil.

Esterification and transesterification reactions can be accelerated by basic, acidic, or enzymatic catalysts [18,35,36]. Basic catalysts are the most convenient but are unsuitable for BG esterification and transesterification due to their sensitivity to water and to the high content of FFAs in BG. FFAs react with alkaline catalysts in an esterification reaction, producing soap and water, resulting in catalyst consumption and emulsion formation due to the presence of soap [35,37,38].

Acidic catalysts seem to be more suitable for FFA esterification in BG, but the reaction conditions are rather extreme, requiring higher temperatures and larger amounts of catalysts to achieve the same degree of conversion as in the case of basic catalysis [39,40].

Acidic catalysis is usually performed by mineral acids such as sulfuric acid, which are less sensitive to the presence of water, although this catalysis type is less applicable due to a relatively low reaction rate compared to other catalytic methods [35,41,42]. Drawbacks of enzymatic catalysts include the following: they are expensive, provide a slow reaction rate, and may lose activity as a result of poisoning by contaminations in BG [40,43–45].

All three types of catalysts can be used in both homogeneous and heterogeneous forms [37]. Homogeneous catalysis is more effective than heterogeneous, but it is difficult to separate homogeneous catalysts from the reaction mixture after the end of the process [6,46]. Therefore, it is important to develop heterogeneous catalysts since it is easier to separate them, they are more environmentally friendly, and they can be reused or used in a continuous mode [47,48].

In the current study, Lewis acid-type catalysts were selected since they require less extreme conditions compared to other catalysts [49] and can be used in homogeneous or heterogeneous forms [49,50]. Lewis acids function as electron acceptors and play an important role in organic synthesis [51,52]. In the case of esterification and transesterification reactions, protonation of a carbonyl group causes a nucleophilic attack of alcohol molecules, giving a tetrahedral intermediate product, which is further converted into an ester [53].

This study aims to develop a continuous process for producing biodiesel from oils and fats from different sources, including fatty wastes, using Lewis acid catalysts immobilized in sol-gel matrices.

2. Materials and Methods

2.1. Materials

BF_3 was purchased from Merck, Germany; $AlCl_3$ was purchased from Fluorochem, UK; tetraethoxysilane (TEOS) was purchased from Merck, Darmstadt, Germany; ethanol, methanol, acetonitrile, and n-hexane were purchased from Bio Lab, Jerusalem, Israel; oleic acid ($C_{18}H_{34}O_2$, 0.89 g/cm^3) was purchased from Sigma, Ronkonkoma, NY, USA; linoleic acid ($C_{18}H_{32}O_2$, 0.9 g/cm^3), myristic acid ($C_{14}H_{28}O_2$, 0.99 g/cm^3), and stearic acid ($C_{18}H_{36}O_2$, 0.9408 g/cm^3) were purchased from Acros Organics, Morris Plains, NJ, USA; glyceryl trilinoleate (trilinolein) ($C_{57}H_{98}O_6$, 0.925 g/cm^3) was purchased from Larodan, Solna, Sweden; soybean oil was purchased from Oilio, ADM Antwerp NV, Antwerpen, Belgium. The commercial fatty acid methyl esters methyl oleate ($C_{19}H_{36}O_2$, 0.874 g/cm^3), methyl linoleate ($C_{19}H_{34}O_2$, 0.889 g/cm^3), methyl myristate ($C_{15}H_{30}O_2$, 0.855 g/cm^3), and methyl stearate ($C_{19}H_{38}O_2$, 0.9 g/cm^3) were purchased from Alfa Aesar, Heysham, UK. Brown grease was obtained from a grease trap at the Karnaff Cafeteria of Ariel University (Israel).

2.2. Catalyst Immobilization

Lewis acids BF_3 and $AlCl_3$ were immobilized in silica matrices through a sol-gel process. The matrices were prepared by the method previously described by us in [34] using TEOS dissolved in ethanol, where the catalyst concentration was 160 mg/mL for BF_3 and 63.5 mg/mL for $AlCl_3$. Immobilized BF_3 was designated as BSil, and immobilized $AlCl_3$ as AlSil. A blank matrix (BSil) was prepared by the same method but without the addition of any catalyst [34].

2.3. Batch Esterification and Transesterification Reactions under Ultrasonic Activation

Esterification and transesterification reactions in batch mode were performed according to our previously described method [34]. In brief, a mixture of oleic acid (1.26 mmol) with trilinolein (0.414 mmol), soybean oil (0.4 mL), or BG (0.4 mL) was dissolved in 8.1 mL of methanol. BF_3 catalyst was added up to 5.33% (*w*/*w*) in a free form, or 0.296 g/L of BSil. After the addition of 5 mL n-hexane, the mixture was sonicated for 15–300 min at ambient temperature (25 ± 2 °C) in an ultrasonic bath (Elmasonic Part No., Elma, Germany) at 37 kHz and 100% intensity with a working power of 320 W. Samples were taken at certain intervals (15, 30, 60, and 90 min for esterification of FFAs from BG, and 2, 3, 4, and 5 h for transesterification of soybean oil) to monitor the progress of the reaction over time to study reaction kinetics. Mixtures sampled during reactions were cooled on ice to stop the reaction and then treated for phase separation as described in Kolet et al. (2020) [34]. The yield of the esterification product was calculated as the percentage of the peak area of methyl esters relative to the sum of the peak areas of FFAs and methyl esters in the chromatograms.

2.4. Continuous Biodiesel Production from BG under Ultrasonic Activation in a Flow Reactor

As a flow reactor, a U-shaped tube made of borosilicate glass, filled with 150 g of the matrix, was used. The dimensions of the reactor were a length of 33 cm, an internal diameter of 3.15 cm, and an inner volume of 257 mL. The immobilized catalyst was loaded into the reactor manually and retained inside the glass tube by gravity (the flow of the liquid reaction mixture was quite low and did not lead to the washing out of the immobilized catalyst from the reactor). The tube was submerged in the Elmasonic P 70 H ultrasonic bath (Elma, Pforzheim, Germany) filled with distilled water. The reaction mixture was composed of BG, methanol, and hexane applied in a ratio of 1:20:12 (v/v) and flowed through the reactor by means of the ECOLINE VC-MS/CA8-6 multichannel peristaltic pump (Ismatec, Wertheim, Germany) at a total flow rate of 257 mL/h. The ultrasonic bath was operated at ambient temperature (25 ± 2 °C) at the frequency of 37 kHz and 100% intensity. Each hour, the 5 mL samples were collected at the outlet of the reactor and subjected to extraction by 5 mL of distilled water. Phase separation was performed using the JA-25.50 centrifuge (Beckman Coulter, Brea, CA, USA), and the phase composition was analyzed by high-performance liquid chromatography (HPLC) (see Section 2.5).

2.5. HPLC Analysis of Samples

BG and reaction mixtures were analyzed by HPLC on a Sepax Poly PP-100 (5 µm) 4.6 × 250 mm column (Sepax Technologies, Inc., Newark, DE, USA) using 100% acetonitrile as a mobile phase (UHPLC UltiMate, Dionex, Rommerskirchen, Germany) having a Corona Ultra RS detector (Thermo Scientific, Osterode am Harz, Germany), as described in [18].

2.6. Determination of Acid Value

First, to neutralize ethyl alcohol 95%, 75 mL of 95% ethyl alcohol was added along with 2 mL of phenolphthalein as an indicator. After that, the solution was heated to a pre-boiling point, and 0.1 M sodium hydroxide was added dropwise until a faint pink color persisted.

Then, 0.5 g of brown grease was weighed in a 250 mL conical flask, and 50 mL of neutralized hot ethyl alcohol was added, along with 1.0 mL of phenolphthalein. The mixture was heated and mixed in a water bath at 75–80 °C for 15 min. After 15 min, the mixture was titrated while hot with 0.1 M sodium hydroxide. The titration stopped when the solution turned from colorless to light pink.

2.7. Statistical Analysis

The experiments were repeated three times in duplicate and analyzed using single-factor ANOVA. Quantitative results are presented as the mean ± standard deviation (SD).

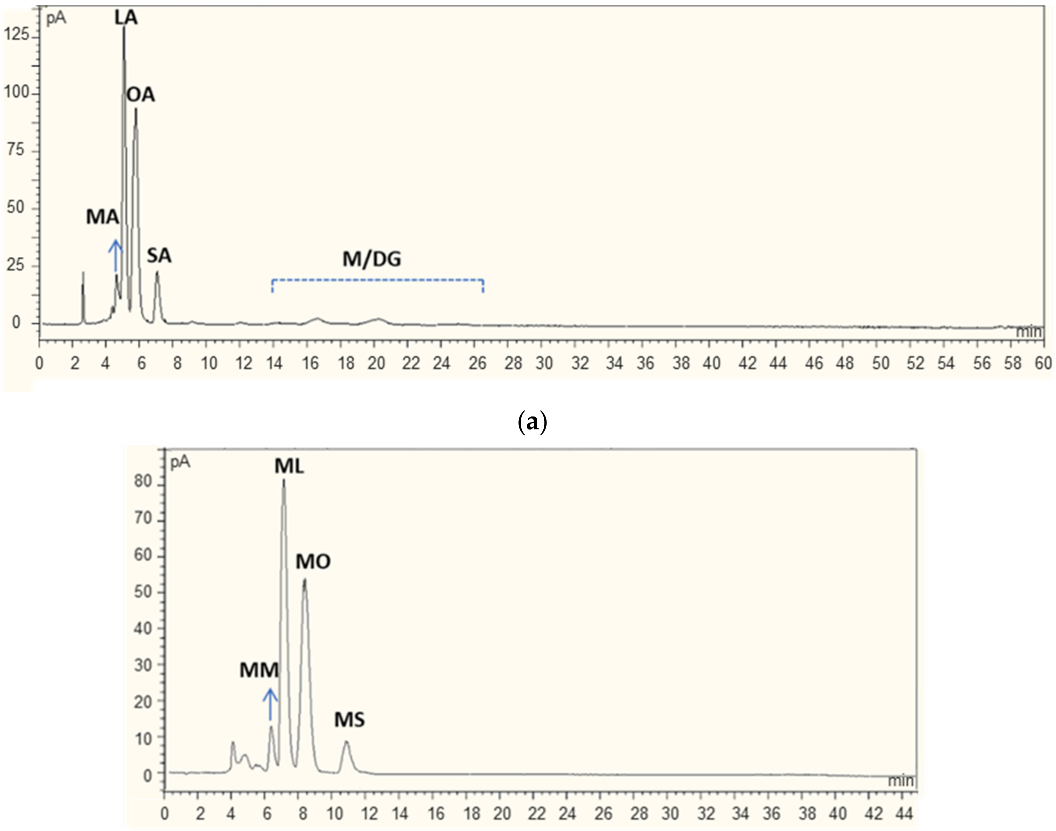
3. Results and Discussion

3.1. Production of Biodiesel from Brown Grease

The production of biodiesel from BG was studied using oil wastes collected from a grease trap of the Ariel University campus cafeteria. Grease trap effluents include three phases: an upper fatty phase, an intermediate aqueous phase, and a lower solid phase. Upon operation of grease traps, the solid phase is removed, and the aqueous phase is outflowed for conventional treatment in a wastewater treatment plant. The upper fatty phase can serve as a source for biodiesel production. Since this phase is still contaminated with components of the aqueous and solid phases due to incomplete separation in a grease trap, the fatty phase should undergo additional separation. In the present work, the procedure previously suggested by us for separating the fatty phase from BG [54] was used. After separation, the composition of the fatty phase was analyzed using HPLC. The chromatograms obtained indicate that the fatty phase of BG contained mainly FFAs, oleic acid (OA), linoleic acid (LA), myristic acid (MA), and stearic acid (SA), in a ratio of about 44:41:6:9, respectively (Table 1), with retention times of 4.6–7.2 min (Figure 2a). The identification of the components was performed using standards of the above-listed FFAs. Unlike soybean oil, BG does not contain triglycerides. This can be seen from the chromatogram of BG, where no peaks with retention times greater than 30 min were observed (Figure 2a). There were small peaks of mono/diglycerides at 14–26 min. Most likely, triglycerides in oil had been hydrolyzed into FFAs and glycerol during cooking and frying, and during the prolonged storage of the fatty phase in grease traps in the presence of water as well as active ingredients such as acids and bases and anaerobic bacteria [55–57]. The acid number of BG was determined as described in Section 2.6 and was 81 ± 1.6 mg NaOH/mg BG.

Table 1. HPLC analysis of BG fatty phase.

	Retention Time, min	**% (*w*/*w*)**
Myristic acid	4.6	6
Linoleic acid	5.2	41
Oleic acid	5.8	44
Stearic acid	7.2	9



(**a**)

(**b**)

Figure 2. Composition of a fatty layer of BG sampled from a cafeteria at Ariel University, Ariel, Israel (**a**) and products of BG esterification by methanol under ultrasonic activation for 60 min using free 5.33% (*w*/*w*) BF_3 as a catalyst (**b**). HPLC chromatograms were obtained on a Sepax Poly PP-100 column with acetonitrile as an eluent.

Esterification of FFAs with methanol under ultrasonic activation was carried out using the separated fatty phase of BG. The first-stage batch experiments were performed by applying the Lewis acid BF_3 as a catalyst. The chromatogram in Figure 2b shows the composition of the reaction mixture after 60 min of ultrasonic activation. By this time, most of the fatty acids, having a retention time of 4.50–7 min (Figure 2a), were already converted into the reaction products, methyl esters, the peaks of which were detected at 7–11 min. The composition of biodiesel was proven by comparing the retention time values of reaction products with those of commercial standards—methyl oleate (MO), methyl linoleate (ML), methyl myristate (MM), and methyl stearate (MS). The peaks of mono/diglycerides with retention times of 14–24 min disappeared as well. This experiment shows that in the case of BG, biodiesel can be produced under ultrasonic activation, which can indeed become a good alternative to thermal activation. Figure 3 presents the change in the reaction components over time. When comparing individual commercial FFAs we used previously [18] with those used here, it appeared that high-yield conversion of FFAs to biodiesel required more time, ca. 60 min, compared to 15 min in the former case. This can probably be explained by the presence of some water in the fatty phase of BG, since the fatty phase was not especially dried after separation. The presence of water in the medium, which is one of the products of the esterification reaction (Figure 1a), shifts the equilibrium of this reversible reaction in the direction of the reactants, reducing the reaction yield. Nevertheless, it is assumed that the suggested approach can be used for biodiesel production from fatty wastes.

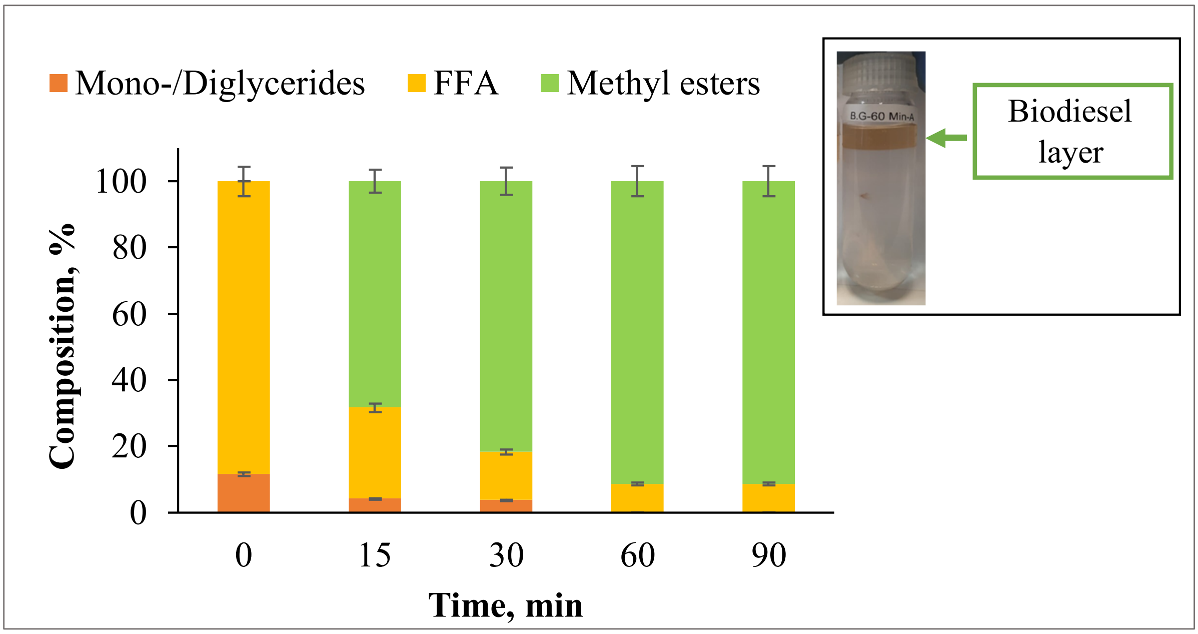


Figure 3. Esterification of FFAs from BG with methanol using a free 5.33% (*w*/*w*) BF_3 catalyst under ultrasonic activation at ambient temperature (25 ± 2 °C). Composition of reaction mixture: FFAs—yellow; methyl esters (biodiesel)—green. Inset: A photograph of the obtained biodiesel layer after phase separation.

Using ultrasonic activation for BG esterification and transesterification is very prospective, as it leads to the formation of a thin emulsion of two nonmixing liquids, thus increasing the contact area and improving the mass transfer between the phases. The result is more efficient, faster, and safer biodiesel production [58–60].

3.2. *Use of Immobilized Catalysts for Biodiesel Production from BG*

In our previous works, we reported on continuous OA esterification with methanol catalyzed by immobilized Lewis acid catalysts under ultrasonic activation [34]. In the present work, we aimed to study the possibility of a continuous process using FFAs from BG. For this purpose, we decided to use the heterogenized version of the catalyst, prepared by the immobilization of BF_3 in a silica matrix. The immobilization of two Lewis acids, BF_3 and $AlCl_3$, by a sol-gel synthetic route to yield BSil and AlSil was reported previously [34]. The immobilized catalysts were characterized by Fourier transform infrared (FTIR), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and a particle sizing counter. When identifying functional groups in the prepared matrices by FTIR spectroscopy, all the characteristic bands of the blank matrix (BlankSil) were also found in the spectra of the catalyst-incorporated matrices, which implies that the entrapment of BSil or AlSil does not alter the internal structure of the matrix. The results of XRD and XPS showed the stability of the matrix during the catalytic experiments [34]. The main challenge in using heterogeneous catalysts is to overcome diffusion restrictions and thus enable higher effectiveness [61,62]. Immobilization of the catalyst allowed its recycling or continuous use, which can increase the profitability of the process.

The reaction was tested first in batch mode using BSil; in comparison to free BF_3, the composition of the reaction mixtures was determined by HPLC. The results are shown in Figure 4. The reaction under catalysis with a free catalyst was more effective and reached a high yield after 15 min, whereas the immobilized catalyst supplied a high yield only after 1.5 h. Results obtained for free catalysts differed significantly from those gained with the immobilized one (p-value 0.043). Despite the longer reaction time, we decided to continue studying the biodiesel production from FFAs from BG using the immobilized catalyst, since it enabled a continuous process.

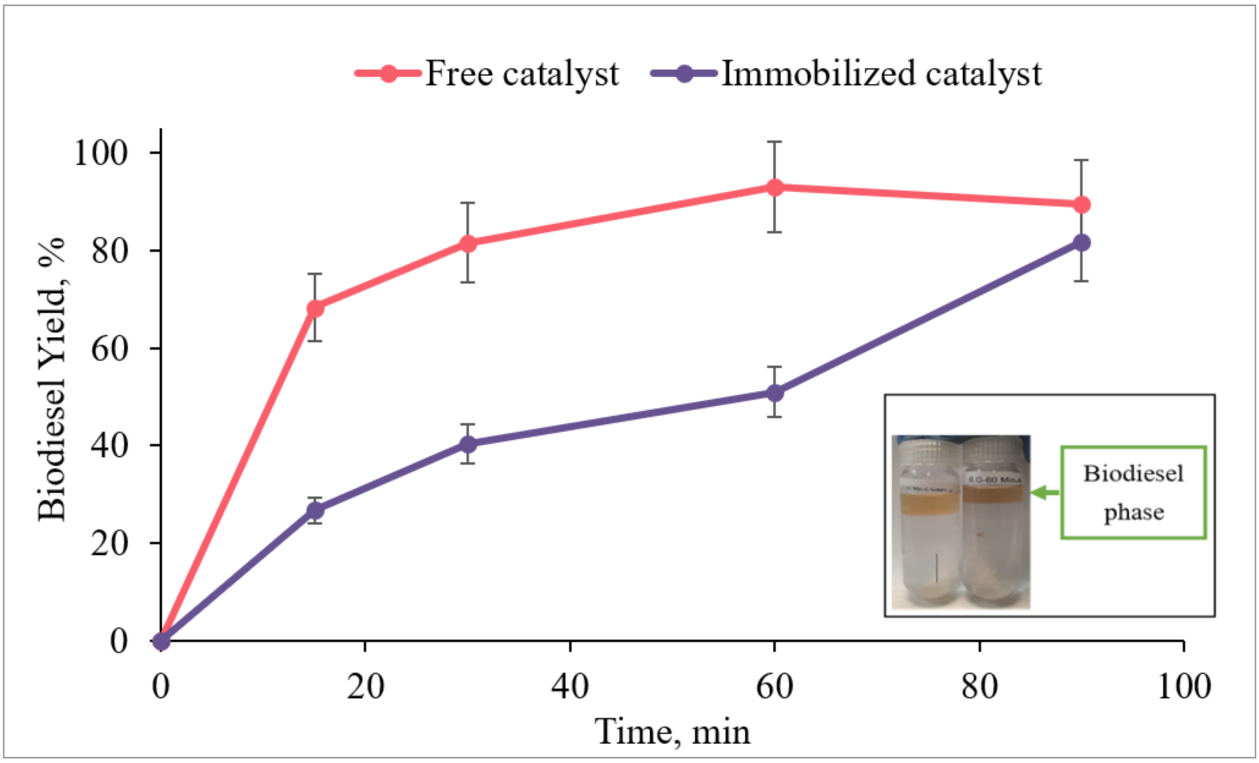
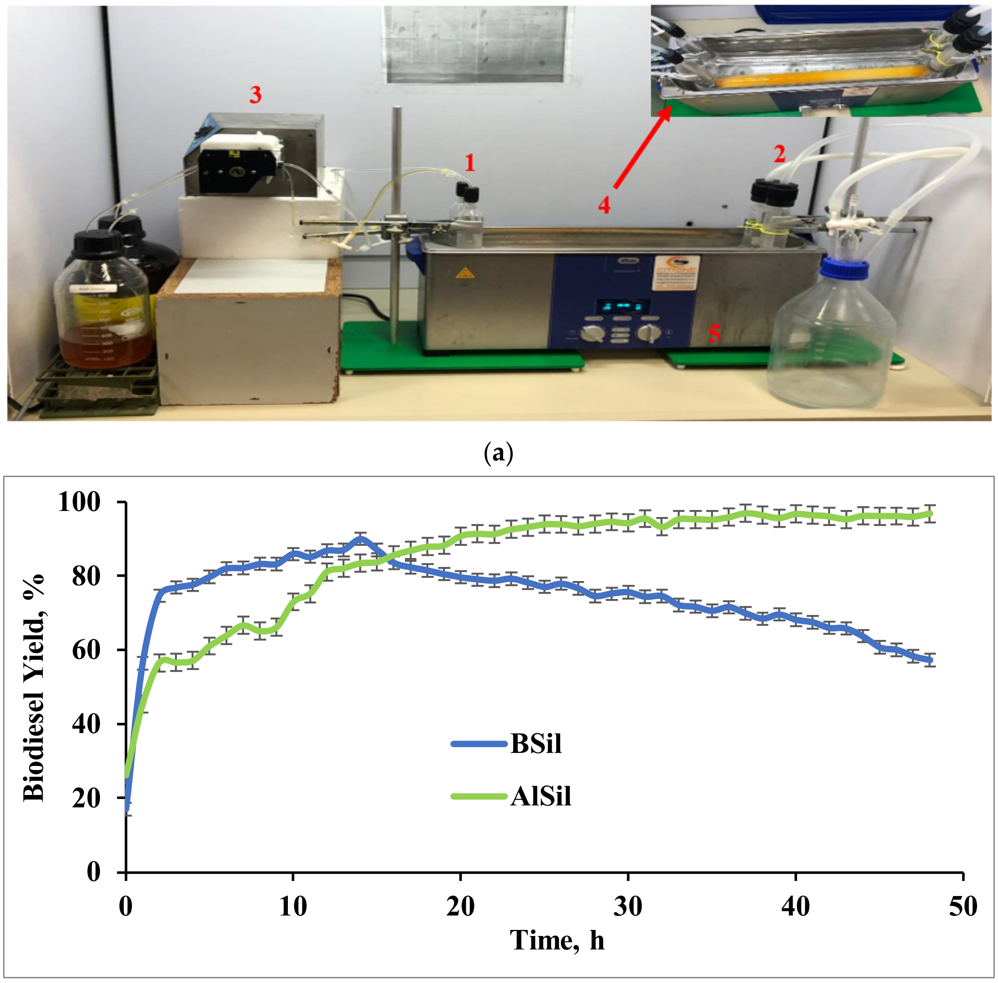


Figure 4. Esterification of FFAs from BG with methanol using catalyst BF_3 immobilized in a sol-gel matrix (immobilized catalyst) and in a free form (free catalyst) under ultrasonic activation at ambient temperature (25 ± 2 °C). Inset: A photograph of the obtained biodiesel layer with immobilized (left) and free (right) catalysts.

The continuous reaction was performed in a flow reactor as described previously [34]. A photograph of the reactor is presented in Figure 5a. The reactor consisted of a glass tube immersed in an ultrasonic bath and filled with an immobilized catalyst, through which the reactants mixture was channeled by means of a multichannel peristaltic pump, while the residence time of the reaction mixture inside the reactor was 1 h. Two types of immobilized catalysts were applied: BSil and AlSil. In both cases, the reactions were continuously run for 48 h. The samples were collected at the outlet of the reactor and analyzed by HPLC. The results are presented in Figure 5b. Before the reaction, the reactor had been filled with solvents only, and in the initial period of the experiment, the reactor operated in a transition state. For this reason, the product at the outlet was very diluted and the product yield was low. After two hours, the efficiency of the reaction reached 56% for AlSil and 75% for BSil, and it continued to rise over time. As can be seen, FFAs from BG were effectively converted to biodiesel, and AlSil demonstrated better stability and enabled high yields to be achieved for a long period. BSil was more effective in the initial stage, but after 15 h, it showed lower yields, probably because of BF_3 leaching from the matrix.



(**a**)

(**b**)

Figure 5. The experimental system for continuous biodiesel production using ultrasonic activation (**a**). (1) Inlet; (2) outlet; (3) multichannel peristaltic pump; (4) glass U-shaped tube filled with matrices, and (5) ultrasonic bath. (**b**) Continuous esterification of FFAs from BG with methanol, catalyzed by BSil at a loading of 160 mg/mL and AlSil at a loading of 127 mg/mL in the matrix under ultrasonic activation.

To determine the catalyst loading effects on the reaction yield, additional continuous experiments were performed using catalysts prepared with different loadings of BF_3 and $AlCl_3$ in the silica matrix, and the reaction yields were measured after 24 h of continuous run. Figure 6 presents the results of this experiment. As can be seen, doubling of BF_3 loading in BSil led to an increase in the yield up to 95%, compared to 78% for the 160 mg/mL loading. In the case of $AlCl_3$, the effect of the loading was even more pronounced, and a decrease in the $AlCl_3$ loading in AlSil led to a decrease in biodiesel yield, from 93% for 127 mg/mL loading to 56% at 63.5 mg/mL loading. Increasing the loadings of catalysts in the matrices enabled almost 100% reaction yield to be achieved, probably due to the increased contact between the catalysts and reactants.

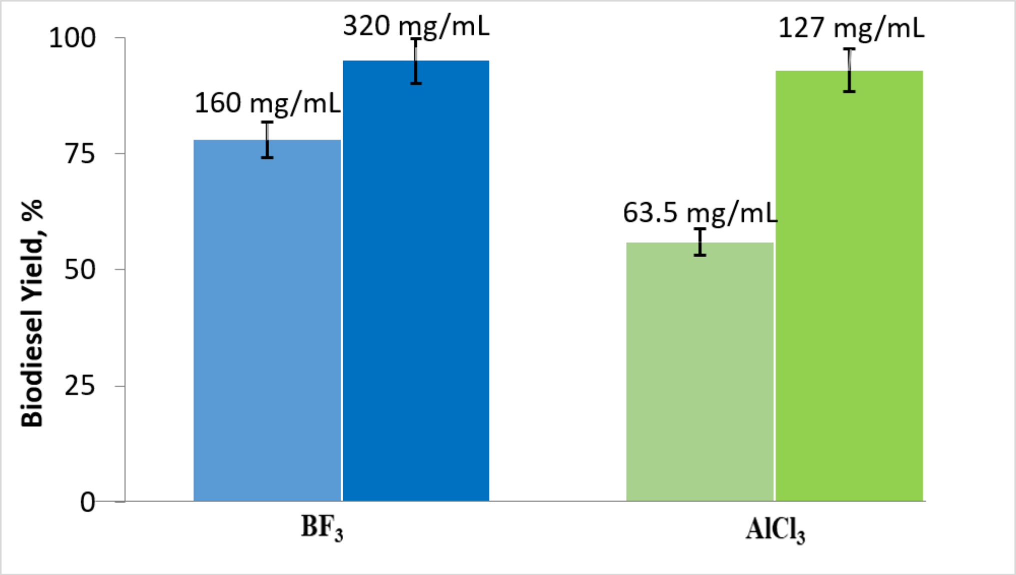


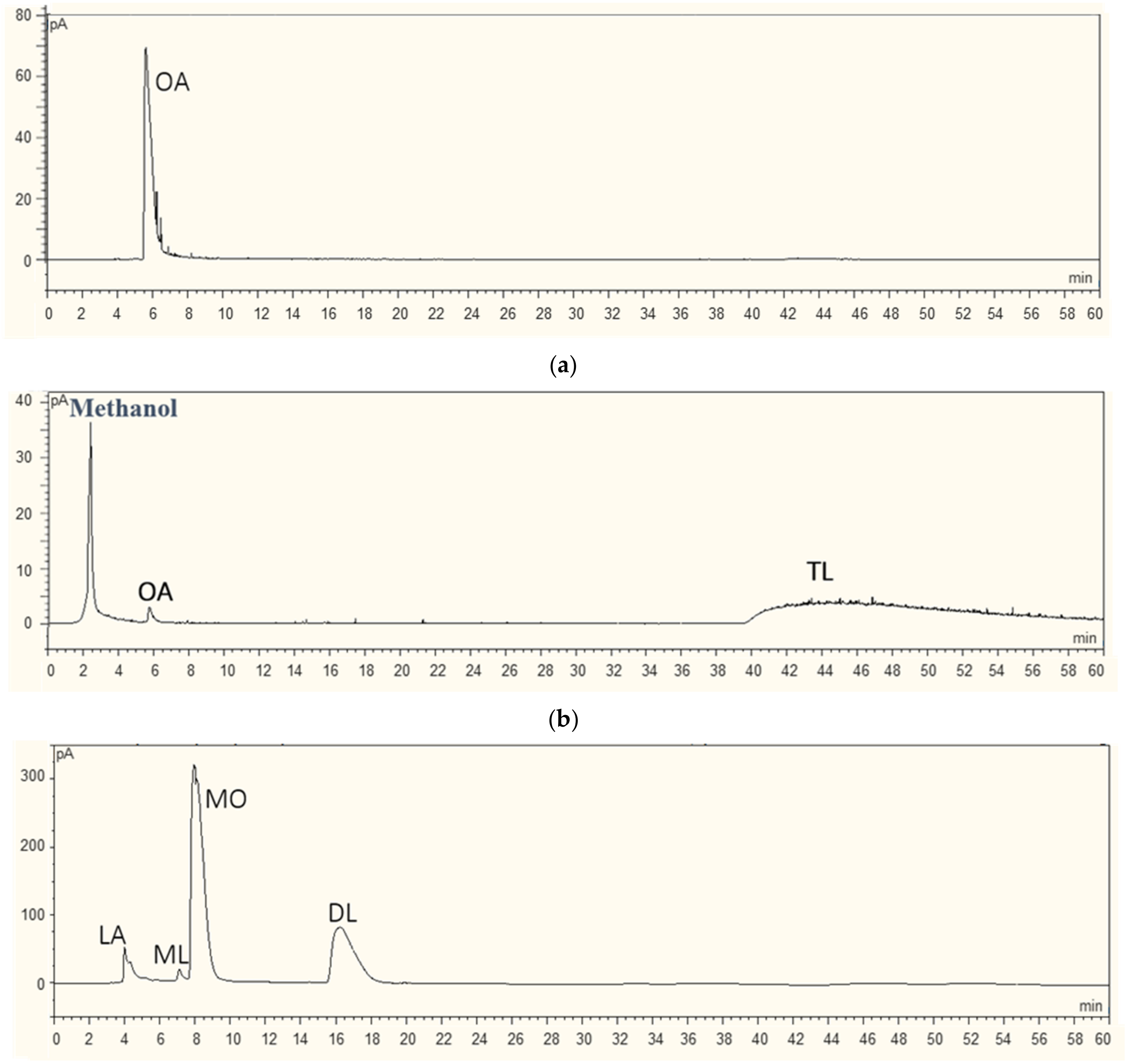
Figure 6. Efficiencies of BG esterification with methanol, catalyzed by Lewis acid catalysts immobilized at different loadings (shown above the appropriate bars) of BSil and AlSil matrices, under ultrasonic activation in continuous operation for 24 h.

3.3. Combined Process of Esterification and Transesterification

In contrast to fatty wastewater that does not contain significant amounts of triglycerides, the feedstock traditionally used for biodiesel production, plant-based oil, contains mainly tri- and di-monoglycerides and has a low amount of FFAs. The development of a process for efficient biodiesel production from oils under ambient conditions could be a broader application of the method developed by us. To that end, a combined process of esterification and transesterification was studied, modeling biodiesel production from a universal feedstock.

The esterification and transesterification reactions were tested using a mixture of triglycerides and FFAs as reactants. Commercial oleic acid (OA) was chosen as a representative FFA, and commercial glyceryl trilinoleate (trilinolein, TL) was chosen as a representative triglyceride. The former lipid was assumed to participate in the esterification reaction, yielding the sole biodiesel product methyl oleate (MO), whereas the latter would participate in the transesterification reaction with the sole biodiesel product methyl linoleate (ML). This approach enabled us to analyze each reaction independently.

The abovementioned mixture was reacted with methanol under ultrasonic activation in the presence of the free BF_3 catalyst and n-hexane, which facilitated the formation of two phases and the separation between triglyceride and biodiesel. The samples from the reaction mixture were separated into two phases, and the composition of each phase during the reaction was determined by HPLC (Figure 7). FFAs and the produced biodiesel were found mainly in the upper n-hexane phase, whereas triglycerides were mainly in the lower methanol phase. As shown in Figure 7, before the reaction, one can see only the reactants OA (Figure 7a,b), methanol (Figure 7b), and TL (Figure 7b). After 30 min of the reaction, the esterification process was completed—the peak of OA disappeared, while a new peak assigned MO was obtained, but the degree of the transesterification was very low. Figure 7c,d shows the content of the upper and lower phases of the reaction mixture, respectively. In the upper phase, the main component was the product of esterification, MO, but the product of transesterification, ML, was at a very low concentration. Two additional peaks were seen—the peak of free LA and the peak of glyceryl dilinoleate or dilinolein (DL), which are the intermediates of the transesterification reaction [59]. The lower phase contained TL and methanol. After one hour of the reaction, the upper phase contained MO and an increased concentration of ML (Figure 7e), but the reaction was not completed, and the intermediate products, LA and DL, were still present at high concentrations (Figure 7e). Additionally, the peak of TL in the lower phase decreased substantially (Figure 7f).



(**a**)

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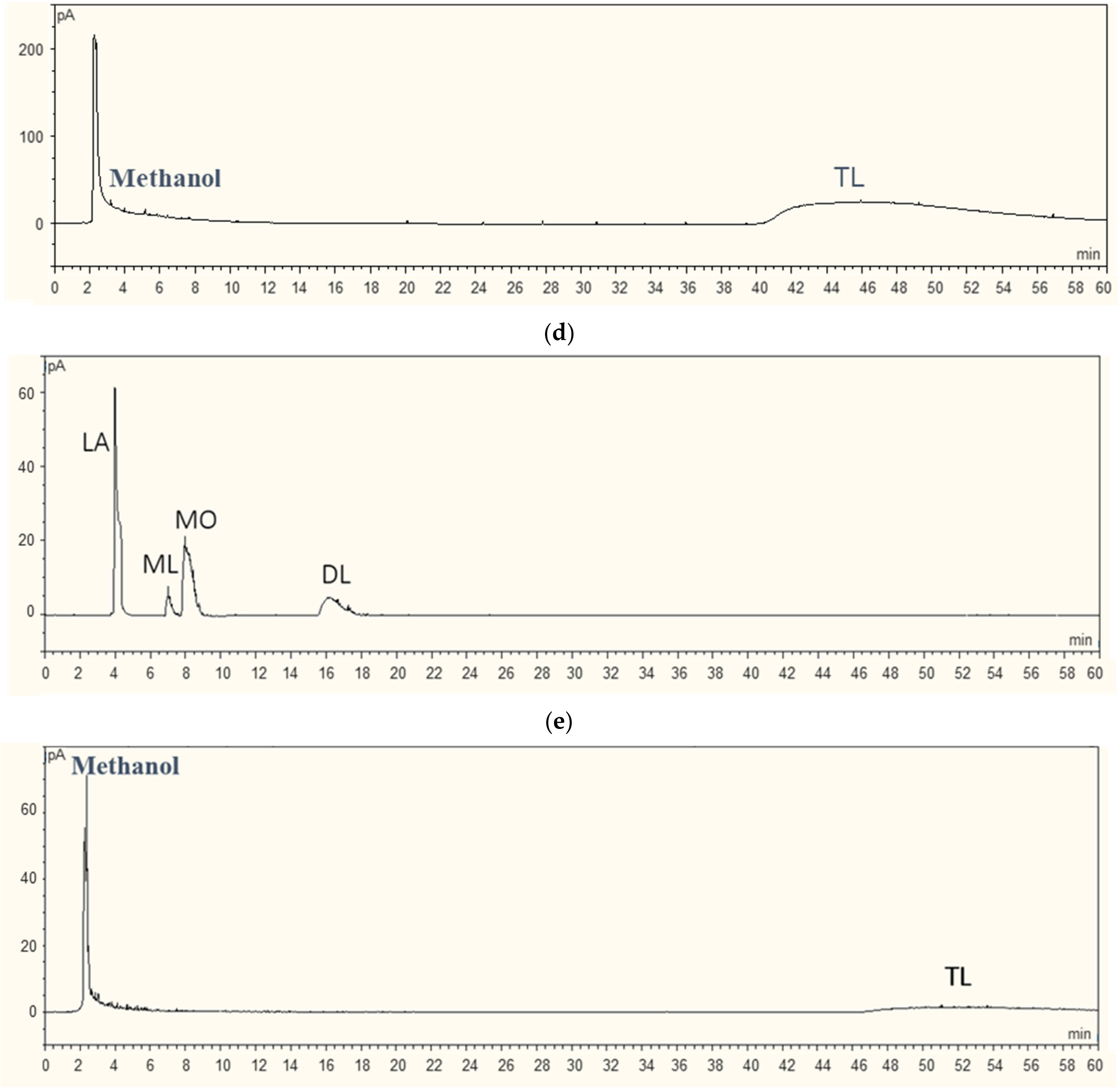
Figure 7. *Cont.*



(**d**)

(**e**)

(**f**)

Figure 7. HPLC chromatograms of the combined esterification and transesterification reactions performed in the presence of 5.33% BF_3 and n-hexane under ultrasonic activation at ambient temperature (25 ± 2 °C) before (**a**,**b**), after 30 min (**c**,**d**), and after 60 min (**e**,**f**) of the reaction. Upper phase (**a**,**c**,**e**) and lower phase (**b**,**d**,**f**). OA and LA—oleic and linoleic acids, MO and ML—methyl oleate and linoleate, DL—dilinolein, TL—trilinolein.

It can be concluded that in the combined system, the esterification process proceeded very rapidly, but the transesterification reaction was very slow and was not completed even after an hour. Since both esterification and transesterification reactions are reversible, it is possible that the fast appearance of MO interfered with the transesterification process. It is also possible that the latter reaction cannot, in principle, be performed with a high yield at ambient temperatures. To understand the applicability of our suggested method to the transesterification process, this process was investigated in closer detail using soybean oil as a source of triglycerides.

3.4. Transesterification of Soybean Oil

To study the transesterification reaction, soybean oil was chosen. Analysis of the oil by HPLC indicated that it contains triglycerides and very low amounts of monoglycerides and diglycerides. The oil composition is shown in Figure 8 (the column at zero time).

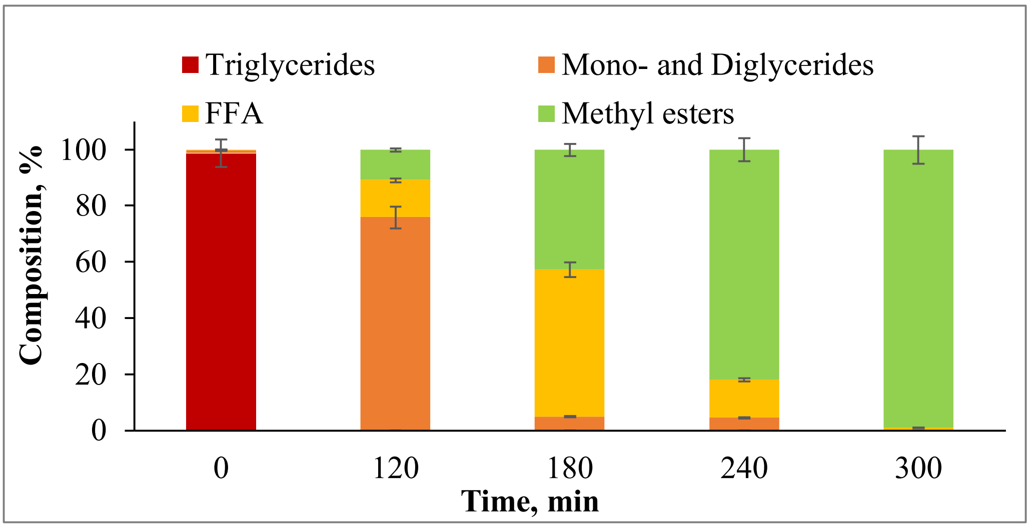


Figure 8. Transesterification of soybean oil with methanol using a free 5.33% (*w*/*w*) BF_3 catalyst under ultrasonic activation at ambient temperature (25 ± 2 °C). The components of the reaction mixture: triglycerides (red), mono- and diglycerides (orange), free fatty acids (yellow), and methyl esters (biodiesel) (green).

Since transesterification reactions require a longer time than esterification [32], the reaction of soybean oil with methanol, using BF_3 as a catalyst, was performed under long sonication for 2–5 h. After the reaction, the samples underwent phase separation, and the composition of the reaction mixture was analyzed. The extent of the reaction and the change in the composition of the reaction mixture over time are shown in Figure 8.

The highest yield of nearly 100% was obtained after 5 h of sonication, whereas after 2 h, the reaction yield was only 10% (Figure 8). As in the previous system (Section 2.3), during the reaction, the triglycerides were first converted into intermediates, di- and monoglycerides, and free acids and then into methyl esters of fatty acids (biodiesel) and glycerol. The triglycerides were totally converted after 3 h of the reaction, and the di- and monoglycerides were completely converted after 5 h.

It can be concluded that our suggested ultrasonic activation of reactions at ambient temperature can be successfully applied to the transesterification of triglycerides in oils, but to achieve high yields of biodiesel, the reaction should be run for several hours.

4. Conclusions

In this study, a method was developed for biodiesel production in batch mode and continuous mode using the fatty phase of fatty wastes from brown grease. Brown grease mainly contains four FFAs, oleic, linoleic, myristic, and stearic acids, which are easily converted into methyl esters by esterification under ultrasonic activation. Due to the inherent challenges in biodiesel production using ultrasonic activation, i.e., high energy consumption for large reaction volumes and lower efficiencies for reactions performed using heterogeneous catalysis, an effective and high-yield continuous and green production process has not yet been developed, and the research in the field is ongoing. Lewis acid catalysts BF_3 and $AlCl_3$ were found to be effective in the esterification and transesterification reactions in either free or immobilized forms, implying the versatility of our developed process. The immobilization of catalysts in a sol-gel matrix allowed them to be used in continuous operation for biodiesel production. The esterification of BG fatty acids with methanol in the presence of immobilized catalysts was carried out continuously for 48 h. The reaction was activated by ultrasound at a frequency of 37 kHz without additional heating. BSil was more efficient at the initial stage, reaching a maximum conversion of 90%, with a gradual decrease in efficiency after 15 h of the process. AlSil showed better stability, reaching maximum yields of 97%, and maintaining efficiency until the end of the experiment. The proposed method offers an efficient and easy way to produce biodiesel from a variety of lipids sources, including fatty wastes (BG).

The use of ultrasound in biodiesel synthesis ensures the formation of a fine emulsion between immiscible reactants. In this case, the area of the interfacial surface increases significantly, leading to an acceleration of the reaction. In addition, ultrasonic cavitation provides the energy to initiate the reaction and leads to an increase in the surface temperature between the reagent phases, which can also increase the esterification rate [19,20]. However, the use of sonication in a batch reactor is limited to a small reactor volume. Efficient ultrasonic activation of large volumes of reagents requires high energy consumption and may significantly increase the cost of the process [21]. Therefore, in recent years, attention has mainly been paid to the development of a continuous process for the ultrasonic synthesis of biodiesel, which allows for the processing of large amounts of reagents in a relatively small reactor volume. Good results in continuous esterification and transesterification have been achieved in ultrasonic reactors using homogeneous catalysts [21–28]. In these works, for the esterification of fatty acids [23,25,26,28] and the transesterification of glycerides [21–25,27,28] with methanol [21,22,24–28] or ethanol [23], free alkaline [21,22,24,27,28], acid [26,28], or their combination [23,25] catalysts were used. Under the activation of the process by ultrasound at 20 kHz [21–24,26–28], 50 kHz [21], and other [25] frequencies, 90–100% efficiency was achieved [21–28]. However, the complexity of separation and purification and the infeasibility of reusing the catalyst increase the cost of biodiesel production. Using heterogeneous catalysts looks more promising, since it can overcome the above disadvantages [29–31]. However, ultrasonic methods are less efficient when working with heterogeneous catalysts due to high resistance to mass transfer, as well as due to the inhomogeneity of the catalyst dispersion in the reaction solution [19,20]. In addition, the deactivation of heterogeneous catalysts after several hours of continuous operation and the problem of catalyst regeneration have been reported [32]. Successful results in the esterification of FFA tobacco and canola oil by ultrasonic activation were achieved using Amberlyst acid ion exchange resin as a heterogeneous catalyst [33]; however, these experiments were carried out in a batch reactor. Another heterogeneous catalyst, KI/ZnO, was also effective in the ultrasonic production of biodiesel from non-edible oils [31]. In this case, the reaction took place in a batch reactor as well, but the possibility of reusing the catalyst in five cycles of the transesterification reaction was checked. Here, a decrease in the catalytic activity of the catalyst was noted in each subsequent cycle; after five consecutive reaction cycles, the catalyst lost ∼50% of its initial activity [31].

5. Patent

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