



# Article **Production of Biodiesel from Brown Grease**

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**Abstract:** Among the renewable energy sources is biodiesel. This fuel is usually produced by catalytic transesterification of vegetable oils and animal fats under heating and pressure. Brown grease is a mixture of oils, fats, solids and detergents from food industry wastes that is captured in grease traps. Brown grease is classified as waste and must be treated and disposed of appropriately. It contains oils and fats that can be converted into biodiesel. However, the high concentration of free fatty acids in brown grease does not enable the use of conventional biodiesel production schemes. This study proposes a new scheme for biodiesel production from brown grease. In addition, conditions for the effective separation of a fat phase from brown grease were tested, and the composition of a fatty phase was determined for several grease traps. Esterification and transesterification of brown grease lipids were carried out with methanol, where the Lewis acids BF<sub>3</sub> and AlCl<sub>3</sub> were used as catalysts and the reaction was activated by ultrasound. The results show that biodiesel can be obtained from brown at room temperature. These results open prospects for the development of efficient, low-cost and environmentally friendly biodiesel production.

Keywords: biodiesel; brown grease; Lewis acids; ultrasonic activation

# 1. Introduction

In the early 18th century, in Paris, Rudolf Diesel powered a diesel engine on 100% peanut oil. After his death, the engine was changed and operated on different diesel fuels. In the 1930s and 1940s, plant-based oils were used as a replacement for diesel fuel in emergency situations. For example, in 1940, methyl ester fuel was used in buses in Belgium [1,2]. Until the 1980s, research on the development of alternatives to fossil fuels was not a high priority. However, rising oil prices led to widespread experiments on the use of fats and plant oils as alternative fuels. Biodiesel production has been growing steadily since the early nineties, due to increasing demand for fuel for transportation and the environmental benefits of biodiesel [1,3].

As a result of industrialization and modernization, the demand for using petroleum is constantly on the rise. However, serious global environmental problems and climate changes necessitate finding green renewable alternative sources for fuels, where one of them is biodiesel [1,4,5]. Biodiesel is a biofuel produced from natural components and can be used as a full or at least partial substitute for fossil fuels. It can be obtained from a variety of animal fats, vegetable oils, cooking oil wastes and wastewater grease [6,7].

Biodiesel is based on organic hydrocarbon alkyl esters that can comprise an eco-friendly alternative to fossil fuels, since it can be obtained from vegetable oils or animal fats [6,7]. Since major plant fatty acids and triacylglycerols are produced in plant cells through de novo synthesis, they are regarded as a renewable oil source [8–10]. The global need for biodiesel production has been growing at an annual average rate of 29% since 2009 [11]. Biodiesel production is dependent on edible and

non-edible vegetable oils as feedstocks, where the feedstocks comprise ca. 70–95% of the cost of biodiesel production. Growing feedstock plants on farmland increases the price of biodiesel production. Another feedstock, wastewater grease, is cheap and abundant, and may, therefore, become a prospective source for biodiesel production [12].

Brown grease is captured in grease traps that are installed for intercepting grease wastes that originate mainly from foodservice enterprises such as restaurants and event halls or wastewater treatment facilities. In the United States alone, 1,700,000 T of brown grease is collected annually [7]. If brown grease is not trapped in a grease trap, it may cause severe tube fouling and even sewer blockages [7,13]. Brown grease consists of fats, oils and greases (ca. 50–60% w/w), water (about 25–30% w/w) and biosolids (about 15–20% w/w) [14,15]. About 80% of the lipids are free fatty acids (FFAs), mostly oleic, linoleic and palmitic acids [16], obtained as a result of triglyceride decomposition in the course of frying and other cooking processes [7,16,17].

The collected brown grease is usually landfilled or combusted. This may cause environmental pollution [7,13]. Brown grease can also be utilized for conversion to biogas via anaerobic digestion [18,19]. This process is complicated and challenging, since brown grease is far from an ideal substrate for anaerobic digestion [7,13].

At the same time, brown grease is a good alternative source for biodiesel production, since it has a higher FFA content than yellow grease (used vegetable oil) [20]. Yellow grease has a substantial triglyceride content and for this reason, using this source for biodiesel production requires significant energy investment. Brown grease is, therefore, considered as comprising a lower cost feedstock with greater potential for biodiesel production than yellow grease [14,19,21,22].

FFAs can be converted into biodiesel by an esterification reaction in which ethyl esters (biodiesel) are the main product and water is a side product. The alcohols that are frequently used in this process are methanol and ethanol. Methanol is cheaper than ethanol and is usually used in industry. Intrinsically, esterification is accelerated by a catalyst that improves the reaction efficiency and the biodiesel yield. The main types of catalysts are base, acid or enzymatic catalysts that can be applied homogeneously or heterogeneously [23,24].

Base catalysts are active under conditions of moderate temperatures (60–90 °C) and pressure (1.5–4 atm) and are cheaper than acid catalysts. However, their use in the esterification process is very problematic because of a possible side saponification reaction between FFAs and bases [8,14], which may reduce the esterification yield [25,26]. In addition, base catalysts are very sensitive to a water content that exceeds 1% in the FFA feedstocks. Base catalysts are, therefore, not recommended as catalysts in reactions with brown grease [23,24,27].

Contrary to base catalysts, acid catalysts are not too sensitive to the presence of water in the reaction mixture and can catalyze FFA esterification. However, the reaction is very slow (over 12 h) and requires high temperatures (120–250 °C) [25,26]. Acid catalysts include mineral acids such as sulfuric acid, which are commonly used since they are cheap and convenient to use [14,23,28].

Another group of possible acid catalysts is Lewis acids [29]. One example of Lewis acid catalysts in esterification using methanol is  $BF_3$  [30,31]. These catalysts are effective in esterification in both homogeneous and heterogeneous forms [29,32] and are active under mild conditions. An additional advantage of using heterogeneous Lewis acids is reduced corrosion of the reaction facilities [27]. The mechanism of Lewis acid catalysis of an esterification reaction is described in detail in the works of Georgiou and Whiting [33] and Otera and Nishikido [34]. In this reaction, a nucleophilic attack of alcohol molecules occurs after protonation of a carbonyl group, resulting in an intermediate tetrahedral product, which subsequently converts into an ester [35].

Enzymatic catalysts operate under even more moderate conditions than base catalysts. However, they are very expensive, and the benefits of using enzymes in industry are not obvious [26,36,37]. Furthermore, enzymes have poor stability, require a very long reaction time and provide low conversion rates [20,36].

All three types of catalysts can be used in homogeneous and heterogeneous forms [8]. Homogeneous catalysts are more effective than heterogeneous ones, but it is difficult to separate them from the mixture after the reaction has ended [38,39]. Therefore, the main focus is currently on the development and application of heterogeneous catalysts, since they are more environmentally friendly, and it is easier to separate them from the reaction mixture. Heterogeneous catalysts allow their re-use or continuous use [40,41].

Today, the main method for activation of esterification reactions is thermal [42,43]. An alternative approach to activation, using ultrasound, has been developed in recent years [44]. This method is based on the application of ultrasonic waves at a frequency range of 20–100 kHz. Industrial implementation of ultrasound has significantly increased since the 1980s, and ultrasonic waves are currently widely used in impregnation, crystallization, extraction and fragmentation [45,46]. Ultrasonic activation may become a possible way for effective biodiesel production under mild operating conditions without additional heating. We previously reported on effective biodiesel production from commercial FFAs under ultrasonic activation [44].

The aim of the present work was to develop a novel technology of biodiesel production from brown grease under Lewis acid catalysis and ultrasonic activation.

#### 2. Results and Discussion

Brown grease contains components that can be separated into three phases: upper phase—oils; middle phase—aqueous phase; and lower phase—solids. The solid phase obtained after separation is eliminated, and the aqueous phase is evacuated for conventional treatment at the wastewater treatment plant [7,18]. The upper fatty phase contains mostly oils polluted by components of the aqueous phase and should be purified from contaminations. The relative ratio of the fatty phase depends on the waste's origin and on the frequency of the waste's removal from the grease trap.

#### 2.1. Separation of a Fatty Phase from Brown Grease

Sedimentation was compared to centrifugal separation of brown grease from two sources in order to find appropriate conditions for effective separation of the fatty phase. Before separation, the samples were incubated at different temperatures for 15 min. The efficiency of the separation was examined by tracking the thickness of the fatty phase after its stabilization and by gravimetric analysis. Figure 1 shows the mass fraction of the fatty phase obtained after incubation at different temperatures followed by centrifugation or sedimentation.

According to data presented in Figure 1, the yield of the fatty phase achieved by sedimentation at the ambient temperature was only 8%. After heating to 40 °C, the yield increased to 21%, and after incubation at 60 °C, it increased to almost 24%. Heating above 40 °C did not lead to any substantial increase in the weight fraction of the fatty phase. Centrifugation significantly improved the separation at each temperature. The fraction of the fatty phase obtained at the ambient temperature was more than 30%, and at 40 °C it increased to 50%. Increasing the centrifugation speed affected the yield of the fatty phase up to 1500 rpm. However, there was no additional improvement in separation at higher speeds. Centrifugation time affected the separation efficiency up to two min only. Further prolongation of the process did not improve the phase separation.

Tran et al. [12] performed separation of the brown grease fatty phase by extraction with hexane as a solvent added in an equal volume to brown grease (1:1) at 300 rpm for 2 h at the ambient temperature. Spiller et al. [7] also used hexane to extract the FFA by stirring the mixture overnight, followed by centrifugation at an RCF of  $200 \times g$  for 10 min, repeated three times. In both studies, the yield of the fatty phase was the same as in the present study but required a much longer time and additional energy investment for prolonged mixing.



**Figure 1.** Separation of the fatty phase after incubation at various temperatures followed by sedimentation for 15 min or centrifugation for 5 min, 1500 rpm, 25 °C. In the inset—photo of samples before and after separation.

# 2.2. Composition of the Brown Grease Fatty Phase

After the separation, the chemical composition of the brown grease fatty phase was analyzed and identified using High Pressure Liquid Chromatography (HPLC). Figure 2 shows the results of HPLC analysis of the fatty phase from four sources of brown grease compared to four FFA standards. Fatty acids found in the brown grease were typical for edible oils and were identified as myristic (MA), linoleic (LA), oleic (OA) and stearic (SA) acids (Figure 2a–d, respectively) [16]. Chromatograms of the fatty phase obtained from four different sources of brown grease—a cafeteria, a slaughterhouse and two event halls—are presented in Figure 2e–h, respectively. All brown grease sources contained two major components: OA and LA, and two minor FFAs: MA and SA. No triglycerides were found in any of the brown grease samples.

Table 1 summarizes the composition of the brown grease fatty phase from various sources. The FFA content of the brown grease fatty phases was very similar in all cases. OA and LA were the major components of the fatty phase (83–88%), where each FFA comprised from 38% to 47%. The minor components MA and SA were present at amounts from 11% to 16% and each of them comprised from 4% to 10%. Pastore et al. [21] previously reported on a 50% content of FFAs in the brown grease fatty phase. Portilho et al. [16] examined the lipid phases from a grease trap and found a high content of free OA and LA, similarly to our results. The obtained results are not surprising, since OA and LA are the main ingredients of vegetable oil triglycerides commonly used in restaurants: canola oil, soybean, palm oil and others, as well as of animal fats such as butter, beef fats, chicken and fish. It should be noted that triglycerides undergo hydrolysis to FFAs during cooking and during long storage in the presence of water in the grease trap, probably by means of anaerobic bacteria growing in the grease traps and/or catalysis by acids and bases present in the wastewater [7,14,16].



**Figure 2.** HPLC chromatograms of commercial free fatty acid (FFA) standards: (**a**) myristic acid (MA), (**b**) linoleic acid (LA), (**c**) oleic acid (OA) and (**d**) stearic acid (SA), and of the fatty phase of brown grease from four different sources: (**e**) cafeteria, (**f**) slaughterhouse and (**g**,**h**) two event halls.

Brown Grease Source	Composition of the Fatty Phase			
	Oleic Acid, %	Linoleic Acid, %	Myristic Acid, %	Stearic Acid, %
Cafeteria	39.5	43.9	8.1	8.5
Slaughterhouse	46.9	39.2	3.9	10.0
Event Hall 1	44.5	43.8	4.7	7.0
Event Hall 2	45.6	38.6	5.6	10.2
Average $\pm$ SD	$44.1 \pm 3.2$	$41.4 \pm 2.9$	$5.6 \pm 1.8$	$8.9 \pm 2.2$

Table 1. Composition of brown grease fatty phase from various sources.

## 2.3. Production of Biodiesel from Brown Grease

In the next stage of our study, we examined the possibility of biodiesel production from brown grease using the method suggested by us earlier [44]. The reaction was based on esterification of FFAs by methanol under ultrasonic activation, with Lewis acids as catalysts. The main products of the reaction are methyl esters of the FFAs: methyl oleate (MO), methyl linoleate (ML), methyl myristate (MM) and methyl stearate (MS). The results of the brown grease esterification are presented in Figure 3.





The FFA conversion to appropriate monoesters was close to 100%, and the mixture after the reaction (blue line) did not contain any FFAs.

The composition of biodiesel from the brown grease fatty phase was also examined using a more sensitive method of gas chromatography supplied with a mass spectrometry detector (GC-MS). This method enabled finding six FFA methyl esters that comprise the obtained biodiesel: methyl oleate (50.9%, MW 296 g/mol), methyl linoleate (29.8%, MW 294 g/mol), methyl palmitate (11.3%, MW 270 g/mol), methyl stearate (6.0%, MW 298 g/mol), methyl myristate (1.2%, MW 242 g/mol) and the methyl ester of eicosanoic acid (0.8%, MW 326 g/mol). Two of these residues, methyl palmitate and the methyl ester of eicosanoic acid, were not detected by the HPLC analysis of brown grease (Section 2.2 and Figure 3). It should be noted that the composition of the biodiesel originating from the brown grease did not differ from that reported earlier by Portilho et al. [13] and Pastore et al. [18].

Since  $BF_3$  is a gas that dissolves well in methanol at ambient temperatures, it can be assumed that the brown grease esterification proceeds under homogeneous catalysis. Although in this case the reaction efficiency is very high, it is important to separate the catalyst from the reaction mixture for re-reuse, for up scaling the biodiesel production from brown grease, and this is very problematic in a homogeneous system. Another Lewis acid, a solid-stage AlCl<sub>3</sub> proven earlier as a good catalyst of the esterification reaction [44], was, therefore, used for biodiesel production from brown grease.  $AlCl_3$  has low solubility in the reaction mixture and can, therefore, be considered as a heterogeneous catalyst. The catalytic efficiency of  $AlCl_3$  in brown grease esterification was compared to that of  $BF_3$  under the same reaction conditions. Figure 4 shows that the two catalysts were equally efficient. After 15 min, all FFAs of the brown grease were totally converted into biodiesel (Figure 4a,b).



**Figure 4.** Efficiency of brown grease esterification by methanol catalyzed by (**a**) 5.33% BF<sub>3</sub> and (**b**) 43.9 mg/mL AlCl<sub>3</sub> under bath sonication at 37 kHz at the ambient temperature. BG—brown grease. In the insets—photo of samples after the reactions.

In previous studies, Pastore et al. [21] used AlCl<sub>3</sub>·6H<sub>2</sub>O as a catalyst for brown grease esterification by methanol under thermic activation at 47 °C and achieved a 90% yield after 4 h. Using the same catalyst at 72 °C, they gained a yield of 94% after 2 h [47]. Implementation of AlCl<sub>3</sub> hexahydrate as a catalyst was probably problematic because water can interfere with the reaction. This explains the incompleteness of the reaction. Another explanation could be that the reaction temperature was not high enough for effective thermic activation of the brown grease esterification [30].

Bashir et al. [14] carried out brown grease esterification with methanol using  $H_2SO_4$  as a catalyst at 65 °C for 2 h, gaining a yield of 99.7%. Both catalysts used in the present study (BF<sub>3</sub> and AlCl<sub>3</sub>) enabled achieving the same yield as in the work of Bashir et al. [14]. However, in the scheme suggested by us, the reaction occurs 12 times faster and does not require an investment of energy for heating the system. Trentini et al. [48] performed brown grease esterification and triacetin transesterification using methyl acetate and water without any catalyst under supercritical conditions of 300 °C and 20 MPa and reached a yield of almost 60% after 30 min. Wang et al. [49] studied brown grease esterification by methanol in the presence of tetrahydrofuran using ZnO/ZrO<sub>2</sub> as a catalyst and showed a yield of 78% after 2 h at 200 °C under autogenous pressure. The catalysts BF<sub>3</sub> and AlCl<sub>3</sub> applied in the present research enabled much higher yields under moderate conditions without external heating and after a shorter time. Thus, the method suggested by us can be considered as more environmentally friendly and economic.

The catalytic efficiency of BF<sub>3</sub> and AlCl<sub>3</sub> in brown grease esterification was further tested at the ambient temperature using short-term (15 min) activation by additional methods: mechanical mixing and horn sonication. As a control, the reaction mixture was incubated at the ambient temperature without any external activation. Figure 5a,b present the results of this experiment using BF<sub>3</sub> and AlCl<sub>3</sub> as catalysts, respectively. In both cases, horn sonication was less effective than bath sonication, providing a 92% reaction yield for BF<sub>3</sub> and 87% for AlCl<sub>3</sub> compared to 100% yield in the case of bath sonication. The bath ultrasonic device is very easy to manage. The ultrasonic system does not require any cleaning because it does not come into direct contact with the reaction mixture. The reduction in reaction efficiency in the case of horn sonication can probably be explained by the mode of energy distributed in the reaction mixture as in the case of the bath ultrasonic device [50]. Mechanical mixing was least effective, and the biodiesel yields were only 74 and 55% in the case of BF<sub>3</sub> and AlCl<sub>3</sub>, respectively. Incubation of reaction mixtures in the presence of the catalysts without any external activation did not gain biodiesel in the case of both catalysts (Figure 5a,b).



**Figure 5.** Effectiveness of brown grease esterification by methanol for 15 min at ambient temperature under different types of activation catalyzed by (**a**) 5.33% BF<sub>3</sub> and (**b**) 43.9 mg/mL AlCl<sub>3</sub>. Control—incubation of reaction mixture without any external activation.

Ultrasonic activation of chemical reactions is based on a very high frequency of sound waves. Exposure of the liquid solution to such waves causes rapid swirling of the fluid and formation of microscopic bubbles that collapse into themselves almost immediately. The bubble collapse produces instant local heating around the collapsed bubble to high temperatures (4500–5000 K) and very high pressures ( $\approx$ 1000 atm). Unlike thermal activation, there is no need to heat the entire system, and the reaction occurs more quickly and efficiently [51–53].

Sáez-Bastante et al. [54] performed transesterification of *Camelina sativa* oil with methanol under ultrasonic horn activation (20 kHz, 50% amplitude) using KOH as the catalyst. Dange et al. [55] studied esterification of butyric acid with methanol under ultrasonic horn activation (22 kHz, 50% amplitude) applying the catalyst Amberlyst-15. In both cases, horn ultrasonic activation did not lead to a reaction yield that exceeded 90% [54,55]. Poppe et al. [56] studied yellow grease (frying oil wastes) transesterification by ethanol in an ultrasonic bath (40 kHz) and reported a 90% yield achieved after 18 h. Sharma et al. 2020 [57] also performed yellow grease (cotton oil wastes) transesterification with methanol using ultrasonic horn sonication at 20 kHz for 30 min and achieved a 90% yield using two catalysts, KOH and CaO. It should be mentioned that in the case of esterification, application of base catalysis leads to side reactions and is inappropriate for biodiesel production from brown grease.

#### 3. Materials and Methods

## 3.1. Source of Brown Grease

Brown grease was sampled from four grease traps of two local event halls (Jerusalem), a poultry slaughterhouse (Jerusalem) and the Ariel University cafeteria (Ariel) with the owners' permission.

#### 3.2. Separation of the Fatty Phase from Brown Grease

Separation of the fatty phase was performed by two methods. (1) Samples of 40 mL brown grease in 50 mL centrifuge tubes (polypropylene screw, Nalgene, Rochester, NY, USA) were incubated in a water bath at different temperatures (40–60 °C) for 15 min and kept at the ambient temperature for an additional 2 min. (2) The brown grease samples were centrifuged for different time periods (1–5 min) and at different speeds (500–2000 rpm) in a centrifuge (Beckman Coulter, Brea, CA, USA) using a JA-25.50 rotor (Beckman Coulter). In control series, samples were not heated or were not centrifuged. In both methods, the centrifuge tubes were cooled to the ambient temperature before examination. Fatty and aqueous phases were separated and weighed for calculation of the fatty phase content in the brown grease.

## 3.3. Esterification of Brown Grease under Ultrasonic Activation

The esterification reaction was performed according to the method described by us [44]. In brief, brown grease reacted with methanol upon addition of n-hexane. The catalysts were 14% BF<sub>3</sub> in MeOH at a final concentration of 0.67 M or AlCl<sub>3</sub> at a loading of 0.33 mmol/mL. The reaction time was 5–15 min under bath ultrasonic activation at 37 kHz (Elmasonic P 30 H, Elma, Singen, Germany). The reaction was also performed for 15 min under mechanical mixing by magnetic stirring at 800 rpm (MH-6, Fried Electric, Haifa, Israel) at the ambient temperature and using horn sonication. The latter reaction was performed using a horn sonicator Q700 at 20 kHz (QSUNICA, Melville, NY, USA; 700 W) with the help of a flanged horn solid tip in 4650 LV Flocell (644-A, QSUNICA). The sonicator chamber was supplied with a heat exchanger connected to a water bath for providing an ambient temperature. The control reaction was kept in the presence of catalysts for 24 h at the ambient temperature. After the reaction, the reaction tubes were centrifuged for 2 min at 1500 rpm in a J-E centrifuge (Beckman Coulter, Brea, CA, USA) using a JA-25.50 rotor for phase separation. The fatty phase composition was analyzed using HPLC (Section 3.4.).

#### 3.4. HPLC Analysis of Samples

The fatty phase from the four brown grease sources was dissolved in a methanol-acetonitrile mixture (7:5 by volume). Samples of each phase were filtered twice using 0.45  $\mu$ m polytetrafluoroethylene filters (PTFE, Membrane Solutions, North Zhongshan, Shanghai, China) and analyzed by HPLC by the method described by us in Kolet et al. (2020) [44].

## 3.5. GC-MS Analysis of Biodiesel

Samples of the obtained biodiesel were filtered twice using a 0.45  $\mu$ m polytetrafluoroethylene filter (PTFE, Membrane Solutions) and analyzed for methyl ester content by a 9000 Triple Quadrupole GC-MS/MS System (Thermo Scientific, Waltham, MA, USA) using a Rxi<sup>®</sup>-5Sil MS capillary column 30 m, 0.25 mm ID, 0.25  $\mu$ m column (Restek, Bellefonte, PA, USA) in an isocratic regime using 100% helium as the carrier gas (Stanley Works Israel Ltd., Rosh HaAyin, Israel). The eluent flow rate was 1.2 mL/min, the column temperature was 220 °C and the injection volume was 1  $\mu$ L.

#### 3.6. Statistical Analysis

The results were obtained from at least three independent experiments carried out in duplicates and analyzed by single-factor ANOVA analyses. Quantitative results are presented as the mean  $\pm$  standard deviation (SD).

# 4. Conclusions

In this study, a method for biodiesel production from the fatty phase of brown grease is suggested, in which hazardous wastes are utilized for fuel production. The conditions for effective separation of the fatty phase of brown grease were determined, enabling an increase in the productivity of the process. The composition of the fatty phase and the obtained biodiesel was analyzed. The Lewis acids proposed in this work as catalysts for esterification of FFA are more efficient than traditional alkaline and acid catalysts and are less expensive than enzyme catalysts. The ultrasonic activation used in the study increased not only the efficiency but also the safety of the process, compared to the traditional method of thermal activation. Biodiesel can be produced from brown grease by this novel method using the homogeneous catalyst BF<sub>3</sub> or the heterogeneous catalyst AlCl<sub>3</sub> under ultrasonic activation without additional heating with a 100% yield within 15 min.

# 5. Patent

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Conflicts of Interest: The authors declare no conflict of interest.

# Abbreviations

BG	Brown grease	
FFA	Free fatty acid	
GC-MS	Gas chromatography-mass spectrometry	
HPLC	High pressure liquid chromatography	
LA	Linoleic acid	
MA	Myristic acid	
ML	Methyl linoleate	
MM	Methyl myristate	
MO	Methyl oleate	
MS	Methyl stearate	
OA	Oleic acid	
SA	Stearic acid	

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