

Article

Biodiesel from Higher Alcohols for Removal of Crude Oil Spills from Coastal Sediments

Mia Gotovuša ¹, Paula Huzjak ¹, Ivana Zadravec ¹, Martina Zadravec ¹, Jelena Parlov Vuković ² and Fabio Faraguna ^{1,*} 

¹ Faculty of Chemical Engineering and Technology, University of Zagreb, Trg Marka Marulića 19, 10000 Zagreb, Croatia

² Ruđer Bošković Institute, Bijenička Cesta 54, 10000 Zagreb, Croatia

* Correspondence: ffaragun@fkit.unizg.hr

Abstract: Throughout the decades, the production, transport, and use of fossil fuels have led to numerous environmental concerns. Crude oil has caused catastrophic accidents after its spillage into the aqueous environment and accumulation on coastal sediments. To tackle this problem in a sustainable manner, researchers have used alternative remediation agents to extract these crude oil spills from the sediments. In this study, the biodiesels fatty acid methyl, ethyl, and butyl esters (FAME, FAEE, and FABE, respectively) were synthesized via transesterification reaction from waste cooking oil and corresponding alcohol in the presence of a catalyst, potassium hydroxide, and used as remediation agents for crude oil extraction. The influence of different experimental conditions on the crude-oil removal efficiency was studied (time of 1, 2, or 4 h; mass ratio of biodiesel to crude oil of 0.5:1, 1:1, or 2:1), with a simulation of coastal effects using a shaker. UV/Vis spectrophotometry was used to determine crude-oil separation efficiency based on the correlation of the residual crude-oil mass fraction and corresponding absorbance. The results show that FAME and FAEE were most effective in the removal of crude oil from sand (removing 88–89%), while FAEE and FABE extracted the most crude oil from gravel (removing 74–77%).

Keywords: crude oil spill; coastal sediments; biodiesel; waste cooking oil; purification



Citation: Gotovuša, M.; Huzjak, P.; Zadravec, I.; Zadravec, M.; Parlov Vuković, J.; Faraguna, F. Biodiesel from Higher Alcohols for Removal of Crude Oil Spills from Coastal Sediments. *Sustainability* **2024**, *16*, 8574. <https://doi.org/10.3390/su16198574>

Academic Editor: Tim Gray

Received: 31 August 2024

Revised: 26 September 2024

Accepted: 28 September 2024

Published: 2 October 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Due to technological progress and man's increasing desire for energy, the intensity of research into and the production, storage, and consumption of crude oil has also increased. Crude oil is a mixture of simple and complex hydrocarbons and, depending on the source, may contain nitrogen, sulfur, and oxygen compounds in smaller concentrations. It usually takes about 10–15 steps to transport crude oil, which includes pipelines, tankers, tank trucks, and rail cars, where a series of accidents and crude oil spills into the environment can occur [1]. Crude oil pollution has a negative impact on the environment and threatens its protection and sustainability. When crude oil spills into the environment, contamination of water, soil, and air can occur, which leads to long-term consequences for animal and plant life. In addition to crude oil, the most common crude oil derivatives whose use and transport results in spills into the environment are diesel, gasoline, kerosene, lubricating oils, fuel oil, heavy oils, and solvents, etc. [2].

In the case of a crude oil spill in water, the impact of the force and speed of the breaking waves can cause crude oil slicks and layers to break up into droplets of various sizes. The size of the crude oil droplet has the greatest influence on the speed of movement of the spilled crude oil through the marine environment [3]. Crude oil can form large patches on the surface, reducing the amount of sunlight reaching the seabed, which in turn reduces the photosynthesis that enables life in aquatic ecosystems. Furthermore, crude oil can harm animals living in and around the sea, such as birds, fish, turtles, and mammals, and disrupt food chains, leading to long-term consequences for the entire ecosystem [2].

In addition to pollution of sea waters, when crude oil is spilled on land, it can also penetrate the soil and contaminate groundwater. Crude oil in the soil can cause changes to the microbial population, the structure and content of organic matter, and the enzymatic activities that take place in it, which hinders the growth and development of plants [1]. Depending on the sediment conditions, such as silt content, sediment particle size, organic matter, and oxygen content, spilled crude oil could reach and easily penetrate to the bottom of the sediments. The penetration of crude oil into the substrate can subsequently lead to crude oil residues in the surface and/or subsurface layers that are difficult to remove. Such residual crude oil in the subsoil can affect the diversity and quantity of marine life, especially benthic organisms [4]. In benthic ecosystems, sea sponges are essential components. In addition to providing other species with a place to live and food, they also regulate the level of nitrogen and ammonia in the water and bioaccumulate heavy metals, which contribute to the maintenance of water quality. However, this system is particularly sensitive to sudden environmental changes, including pollution such as crude oil spills [5]. After the Exxon Valdez disaster in Alaska, it took up to 20 years for benthic communities to recover and return to their original state [4]. There are other negative effects of crude oil pollution as well, such as the impact on human health, jeopardy of fishing activities or tourism in polluted areas, and economic cost [1].

If a crude oil spill occurs, the most important thing is to react in a timely and efficient manner in order to minimize the consequences [6]. Physical, chemical, thermal, and biological remediation methods are available to remediate contaminants from water, including booms, skimmers, adsorbents, surfactants, dispersants, in-situ incineration, and bioremediation [2]. In spills where crude oil floats on the water surface, dispersants are often used to accelerate the process of natural dispersion, i.e., disperse crude oil spots on the surface of the water into tiny crude oil droplets and thereby contribute to crude oil dilution, dissolution, and biodegradation. Therefore, dispersants can reduce the likelihood that crude oil slicks will reach coastal areas and thereby reduce their direct effects on mammals, seabirds, and coastal ecosystems. Dispersants have been used as crude oil spill remediation agents since their first documented use in the 1967 Torrey Canyon disaster in England. During the Deepwater Horizon disaster, record dispersant use was recorded on the surface (1.4 million gallons) and in the wellhead itself (0.77 million gallons) [3].

In the event that crude oil reaches the coast, it is usually cleaned physically, such as washing with hot water and/or under high pressure. For longer-term cleaning, biological treatments are used, which include the application of fertilizers, emulsifiers, enzymes, or the increase of microbial communities. Typically, the primary focus of these cleanup methods is on the rapid removal of the spilled crude oil, often ignoring the recovery of the organisms living there. For example, high-pressure hot water flushing was used in response to the Exxon Valdez spill and effectively removed stranded crude oil on solid surfaces but severely damaged the epibenthos, or bottom sediment-dwelling, organisms [4].

In addition to the most common methods mentioned above for cleaning up coastal pollution caused by crude oil, biodiesel can also be used for this purpose, which is explained in more detail and supported by experiments in the following sections.

Chemically, biodiesel consists of long-chain fatty acid monoalkyl esters and is produced from renewable sources, mostly vegetable oils and animal fats [7–9]. Biodiesel is a clear liquid insoluble in water; its color depends on the type of raw material, but most often it is light to dark yellow [10]. Since it is non-toxic and completely biodegradable, biodiesel poses no danger to the environment and living beings [11].

Biodiesel is the best-known and most widely used biofuel, i.e., a substitute for mineral diesel [7,12]. However, biodiesel can also be used for other purposes, for example for the purpose of obtaining electricity and heat [13]. Waste cooking oil (WCO) is the most suitable feedstock for biodiesel production in terms of cost, availability, energy balance, greenhouse gases, land-use change, and sustainability [12]. Since approximately 70–80% of the total costs of biodiesel production are raw materials, the use of WCO would reduce the cost of production by about 60–70% [14]. The oil used for cooking varies around the

world; some of the oils used include sunflower, coconut, canola, olive, palm, and soybean oils. In biodiesel synthesis, oil reacts with an alcohol via a transesterification reaction. Currently, methanol is mostly used to produce biodiesel due to its low price; however, the use of other alcohols, some of which are ethanol, 1-propanol, and 1-butanol, has been investigated. Today, methanol is primarily obtained from non-renewable sources, i.e., crude oil, which is considered a major drawback. In addition, methanol is toxic, can be adsorbed through the skin, and is miscible with water, which is a big problem if water is contaminated with this alcohol. Because of the above, the possibility of using alcohol that can be produced from renewable raw materials is being investigated [15,16]. Since they are produced from renewable sources, bioalcohols are increasingly used. Bioalcohol is considered as any alcohol that is produced from different types of biomass, including crops, food waste, and lignocellulosic crops or residues. Bioethanol is the most famous bioalcohol that is produced in the largest quantities [14,17]. So far, many biomass sources (sugar, starch, and lignocellulosic biomass) have been studied for bioethanol production [18]. Recently, biobutanol, which is mainly produced from biomass by acetone–butanol–ethanol fermentation, has been increasingly explored. Unlike bioethanol, this bioalcohol is not hygroscopic, does not cause corrosion, and has a higher calorific value [15,19]. Being renewable, the aforementioned bioalcohols can replace methanol in the production of biodiesel, which enables the production of fully renewable biodiesel [15].

Besides being used as fuel, biodiesel can also be an intermediary in the production of long-chain alcohols from vegetable oils that are used in cleaning products. In some cases, biodiesel can replace volatile organic solvents in liquid–liquid extractions. Since esters of vegetable oils have very good dissolving properties, biodiesel can be used as a solvent for cleaning crude oil-contaminated beaches [20]. In the following paragraphs, research on biodiesel as a means of removing pollution is listed.

Pereira et al. [21] proved, by conducting batch experiments, the significant ability of biodiesel to dissolve crude oil. Crude oil-contaminated sediments were sprayed with biodiesel (methyl ester) from soybean oil and subjected to tidal simulation. Microcosm experiments revealed that the highest ratio of biodiesel to crude oil used (2:1) had the best performance in cleaning fine sand. In mesocosm experiments with a ratio of 1:1 (biodiesel/crude oil), it removed 80% of crude oil in fine sand, 50% in coarse sand, and 30% in gravel.

Fernández-Álvarez et al. [22] investigated the effectiveness of different methods on the biodegradation of fuel oil spilled in Spain (2002) from the Prestige tanker. Biodegradation experiments were conducted on sand, rocks, and granite tiles at Sorrizo Beach (A Coruna, Spain). The results showed that the added microorganisms and nutrients did not significantly increase the rate of fuel-oil biodegradation. However, the addition of methyl esters of fatty acids (biodiesel) obtained from sunflower oil accelerated the cleaning of contaminated surfaces and the decomposition of residual crude oil.

So far, biodiesel research for the removal of crude oil pollution has included only methyl esters of fatty acids, while biodiesel synthesized from higher alcohols has not been researched for this purpose. In this paper, the effectiveness of removing crude oil from contaminated coastal sediments (gravel and sand) using three types of synthesized biodiesel (fatty acid methyl, ethyl, and butyl esters) was examined. WCO was used for the synthesis of biodiesel in the presence of potassium hydroxide as a catalyst. The idea of this work was to synthesize a remediation agent for environmental pollution from waste raw materials using a cheap and available catalyst and thereby contribute to environmental protection and the implementation of a circular economy.

2. Materials

WCO, alcohol, and a catalyst were used during the synthesis of the crude oil removing agent, i.e., biodiesel. WCO collected in the student canteen (Student Center in Zagreb) after frying food was used as a raw material for biodiesel synthesis. Sunflower oil is mainly used as a source of the mentioned WCO, with the second oil in the mixture being

rapeseed oil. The most abundant fatty acids in sunflower oil are linoleic (44–75%) and oleic acid (14–43%) [23]. WCO is a waste raw material that may contain unwanted impurities, so it is analyzed before use. Three types of biodiesels were synthesized using different alcohols: methanol (Lach-Ner, Neratovice, Czech Republic), 99.97%), ethanol (Gram-mol d.o.o., Zagreb, Republic of Croatia), min. 99.98%), and 1-butanol (Lach-Ner, Neratovice, Czech Republic), 99.84%). KOH (Lach-Ner (Neratovice, Czech Republic), purity of 89.7%) was used as a catalyst. In order to avoid the saponification reaction due to potentially present water, before the use, KOH was dried in a dryer for 30 min at 100 °C. CPC (Caspian Pipeline Consortium) blend crude oil with 2.76 wt% of sulphur was used as a pollutant, which is a common raw material for processing at the Rijeka Crude Oil Refinery. The density, viscosity, and surface tension of the crude oil were determined prior to its use, since they affect the behavior of crude oil during spills and the success of its removal. The sediments used as crude oil-contaminated materials were sand and gravel. The gravel was collected from the beach at the location of Kvarner Bay and contained residual water, so it was dried in a dryer for 30 min at 100 °C before use. Like sand, the particle size distribution of gravel was determined using sieves. Synthesized biodiesels were used to examine the dependence of crude oil removal efficiency from sediments on the type of biodiesel.

In order to determine the amount of residual crude oil on the sediment after removal, residual crude oil was extracted using dichloromethane (DCM) manufactured by Lach-Ner, with a purity of 99.95%. In addition, DCM was used to dilute the samples before measurement on the UV/Vis spectrophotometer UV-1900i (Shimadzu, Kyoto, Japan).

3. Methods

3.1. Synthesis and Characterization of Crude Oil Removing Agent—Biodiesel

The synthesis of three types of biodiesels was carried out by a transesterification reaction in which triglycerides from oil WCO were reacted with an alcohol in the presence of a catalyst. Synthesis of biodiesel was carried out in reactors with a capacity of 2 L (FAME and FAEE) and 0.5 L (FAEE) heated via a mantle filled with oil, the temperature of which was regulated by a thermostat. First, the desired temperature was set on the thermostat (see Table 1 for temperatures), and, when it was reached, a measure of oil was poured into the reactor, followed by a catalyst solution in alcohol that had previously been homogenized for 24 h on a magnetic stirrer. The mixture was tempered for 5 min, and then the reaction was carried out for 80 (FAME), 60 (FAEE), or 120 min (FAEE). The reaction conversion was determined by ^1H NMR analysis. The samples were dissolved in deuterated chloroform (CDCl_3 , Merck, Darmstadt, Germany), 99.80%). Tetramethylsilane (TMS) was added to the solvent as an internal standard. The analysis was performed on a Bruker Avance 600 spectrometer (magnet 14 T) at room temperature (25 °C).

Table 1. Reaction conditions for the synthesis of FAME, FAEE, and FABE.

Biodiesel	FAME	FAEE	FABE
Temperature (°C)	60	40	60
Time (min)	80	60	120
Molar ratio of alcohol to oil (mol mol^{-1})	6.21:1	12:1	10:1
Mass fraction of KOH (%)	2	1	1

Table 1 shows the reaction conditions for the synthesis of individual biodiesel, optimized according to previous research.

To purify obtained biodiesels, they were washed with a 0.2–0.3% aqueous solution of orthophosphoric acid and bubbled with carbon dioxide to remove glycerol and the catalyst. After that, residual alcohol and water were removed by vacuum drying at different temperatures (FAME at 110 °C, FAEE at 120 °C, and FABE at 135 °C). The purity of the sample was analyzed by ^1H NMR technique.

Synthesized biodiesels (FAME, FAEE, and FABE), crude oil, and water were analyzed for their kinematic viscosity, density, and surface tension. Kinematic viscosity was deter-

mined using a Cannon-Fenske capillary viscometer at 40 °C according to ISO 3104 [24]. The density of crude oil, biodiesel, and water was determined at 15 °C using a DMA 35 Anton-Paar densitometer (Graz, Austria). The surface tension of the samples was measured on a Dataphysics OCA 20 goniometer (Filderstadt, Germany), which continuously dispenses a sample drop of 1.000 µL at a speed of 0.6 µL/s through a needle with a diameter of 1.06 mm. The surface tension of biodiesel, crude oil, and water was measured in order to predict their behavior in the system during crude oil removal experiments.

3.2. Testing the Crude Oil Removal Efficiency of Biodiesel from Coastal Sediments

Sand and gravel were chosen as coastal sediments; therefore, they were contaminated with crude oil, and the efficiency of biodiesel as a crude oil removing agent was tested on them. Ten grams of sediment was weighed into a 100 mL glass beaker, and 1.00 g of crude oil was evenly applied to it with a glass dropper. The crude oil-soaked sediment was left overnight at room temperature. The next day, a certain amount of biodiesel was evenly applied to the crude oil-contaminated sediment with a glass dropper. In order to create coast-like conditions, 10.00 g of water was added to the crude oil-soaked and biodiesel-soaked sand, and the glass beaker was placed on a shaker that operated at 200 revolutions per minute. The conditions that were varied during the implementation of the experiments were the mass ratio of biodiesel/crude oil that was added to the sand (0.5:1, 1:1, and 2:1) and the shaking time (1, 2, and 4 h) at the mass ratio of biodiesel and crude oil of 1:1. After the optimum shaking time was established for the 1:1 ratio, experiments with other ratios were carried out at that time. After a certain time, the glass beaker was taken from the shaker, and water was slowly poured into it up to three-quarters of its volume. All liquid was then carefully decanted. Water was added to the sample for easier decantation of residual crude oil that was removed from the sediment. The mentioned procedure was carried out three times. Sediment and unremoved crude oil remained in the glass. In order to remove residual crude oil and determine its mass fraction, extraction with DCM was performed. A total of 50.00 g of DCM was added to the beaker on three occasions, twice 20.00 g, and finally, another 10.00 g in order to achieve the best possible extraction. Each time, the sample was thoroughly mixed and the liquid was decanted into a 50 mL glass tube. The extracted crude oil sample of 0.5000 g was diluted with 20.0000 g of DCM. Ultraviolet/visible (UV/Vis) spectrophotometry was used to measure the absorbance of residual crude oil on the sediments. With the help of calibration curves, which were also recorded using a UV/Vis spectrophotometer, the efficiency of biodiesel as a crude oil removing agent from coastal sediments was calculated.

The concentration of residual crude oil was measured twice with a Shimadzu UV-1900i UV/Vis Spectrophotometer (Kyoto, Japan). The calibration lines were made from adsorptions at a wavelength of 400 nm. In order to determine the concentration and calculate the efficiency of residual crude oil removal, calibration lines were made by measuring the absorbance at different mass proportions of the biodiesel/crude oil mixture at 0.5:1, 1:1, and 2:1 diluted with DCM. A calibration line of dependence of absorbance on different mass ratios of crude oil was also made.

For comparison, blank experiments were conducted twice as well, without biodiesel, in order to determine how much crude oil is removed by the action of water alone.

4. Results and Discussion

4.1. Synthesis of Biodiesel and Characterization of the Used Materials

Prior to its use in biodiesel synthesis, feedstock (WCO) underwent preliminary property analysis for total acidity according to ASTM D 664 [25] and water content according to HRN EN ISO 12937 [26]. The total acidity of WCO was 1.785 mg KOH g⁻¹, while water content was 510 mg kg⁻¹. According to the work of Bouaid et al. [15], the acid value of the raw material for alkaline transesterification must have a value less than 2 mg KOH g⁻¹. The acid value of the WCO used in this work is 1.785 mg KOH g⁻¹. The share of water in WCO, according to the work of Cvengroš et al. [27], must not be greater than 0.1 wt%,

which is also fulfilled. Since the used oil has a lower acid value and a smaller proportion of water than the permitted value, no pre-treatments were carried out except for filtering, because the WCO contained solid particles.

Three types of biodiesel—FAME, FAEE, and Fabe—were synthesized and used as remediation agents to remove crude oil from coastal sediments. For the synthesis of biodiesel, KOH was used as a catalyst, which is usually used in the industrial process. All biodiesels, after synthesis and purification, were analyzed with the NMR to determine the purity. ^1H NMR analysis (Figure S1, see Supplementary Materials) was used to determine the reaction conversion from the ratio of areas under the signal at the chemical shift of 2.3 ppm and under the signal for the formed fatty acid esters at 3.6 ppm (FAME) and 4.1 ppm (FAEE and Fabe). The signal at the chemical shift of 2.3 ppm belongs to the CH_2 group, which is characteristic of mono-, di- and triglycerides, fatty acid alkyl esters, and free fatty acids [28]. In addition to conversion, NMR analysis also determined the proportion of alcohol in samples.

Integrating the singlet for FAME at 3.6 ppm gave a conversion of around 100.0%. After all the steps of purification and evaporation, the purity was 99.3%, with the methanol content decreasing to 0.7%. By integrating the quartet for FAEE at 4.1 ppm, a conversion of 95.7% after synthesis was obtained, while the after-purification purity was 94.6%, and the ethanol signal could not be quantified, meaning no ethanol was present. By integrating the triplet for Fabe at 4.1 ppm, a conversion of 96.7% was obtained. After the purification, a purity of 97.4% was obtained with no butanol present in the biodiesel. In the cases of FAEE and Fabe, the residual impurity was the original WCO. From the above, it can be concluded that all the biodiesels (remediation agents) were successfully synthesized. In order to determine the properties of the crude oil remediation agents from coastal sediments, in this case biodiesel, their density, viscosity, and surface tension were determined. The density was determined to investigate whether the biodiesel would sink or float in contact with water. In order to determine the behavior of biodiesel when applied to sediments and washed with water, its viscosity was measured, while the surface tension was used to describe the dispersion of biodiesel droplets in water.

Figure 1 shows the results of the average density (three measurements), kinematic viscosity (three measurements), and surface tension (ten measurements) of the synthesized biodiesel, crude oil, and water.

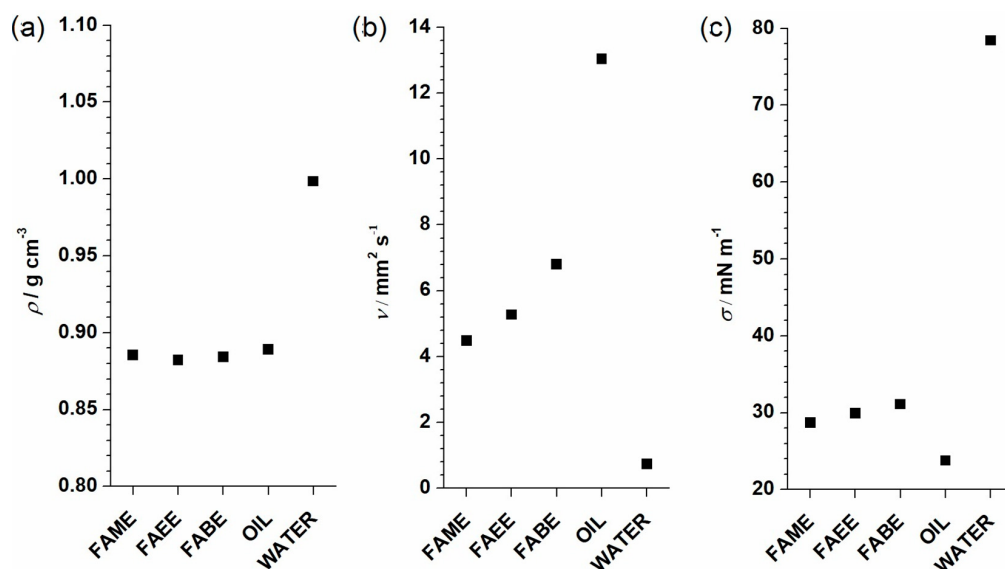


Figure 1. Measured density (a), kinematic viscosity (b), and surface tension (c) results for FAME, FAEE, Fabe, crude oil, and water.

It is observed that the synthesized biodiesels have a small difference in density: FAME with the highest density (0.8854 g cm^{-3}), FAEE with the lowest (0.8822 g cm^{-3}), and FABE in between (0.8841 g cm^{-3}). All biodiesels have a lower density than crude oil (0.8892 g cm^{-3}) and water (0.9985 g cm^{-3}). From the above, it can be concluded that biodiesel and crude oil that did not remain adsorbed to the surface of sand/gravel, when adding water, will float on the water surface.

Furthermore, a trend of increasing kinematic viscosity with increasing chain length of the alcohol part of the ester is visible. Accordingly, FAME has the lowest kinematic viscosity ($4.49 \text{ mm}^2 \text{ s}^{-1}$), followed by FAEE ($5.27 \text{ mm}^2 \text{ s}^{-1}$), while FABE has the highest value of $6.80 \text{ mm}^2 \text{ s}^{-1}$. The results obtained are in accordance with the work of Knothe and Steidley [29]. Compared to the kinematic viscosity of crude oil ($13.04 \text{ mm}^2 \text{ s}^{-1}$), the viscosity value of all used biodiesel is lower than that of crude oil and higher than the viscosity of water ($0.74 \text{ mm}^2 \text{ s}^{-1}$). Lower viscosities imply that biodiesel will be more easily removed from sediments by the action of water compared to crude oil, and that mixing of biodiesel with crude oil will reduce crude oil's kinematic viscosity, therefore making its removal easier.

In terms of surface tension, it can be seen from the graphs that FAME has the lowest surface tension (28.7 mN m^{-1}), followed by FAEE (29.9 mN m^{-1}), and then FABE (31.1 mN m^{-1}). It can be concluded that the surface tension increases with the increase in the chain length of the alcohol component in the fatty acid ester. As the chain length increases, the surface area of the molecule itself increases, which results in stronger intermolecular interactions (cohesive forces), i.e., higher surface tension. The aforementioned characteristic was also observed in the work of Vargas-Ibáñez et al. [30]. Compared to the surface tension of water, which is 78.4 mN m^{-1} , it can be concluded that the surface tension of all biodiesels is significantly lower. Comparing the surface tension of crude oil (23.8 mN m^{-1}), it is evident that the surface tension of all biodiesels is higher. Nevertheless, the difference in surface tension values between biodiesels and crude oil compared to those of crude oil and water is smaller. Therefore, the miscibility of crude oil with biodiesel will be better than with water, allowing the crude oil to be more easily removed from water using biodiesel.

Additionally, materials for contamination (coastal sediments) were also characterized. The graphic representation of the density function of the mass distribution and the visual distribution of particle sizes of sand and gravel can be found in Figure 2. The mass of individual particle sizes in sand and gravel, alongside their mass distribution density function (q_3), are given in Tables S1 and S2 in the Supplementary Materials.

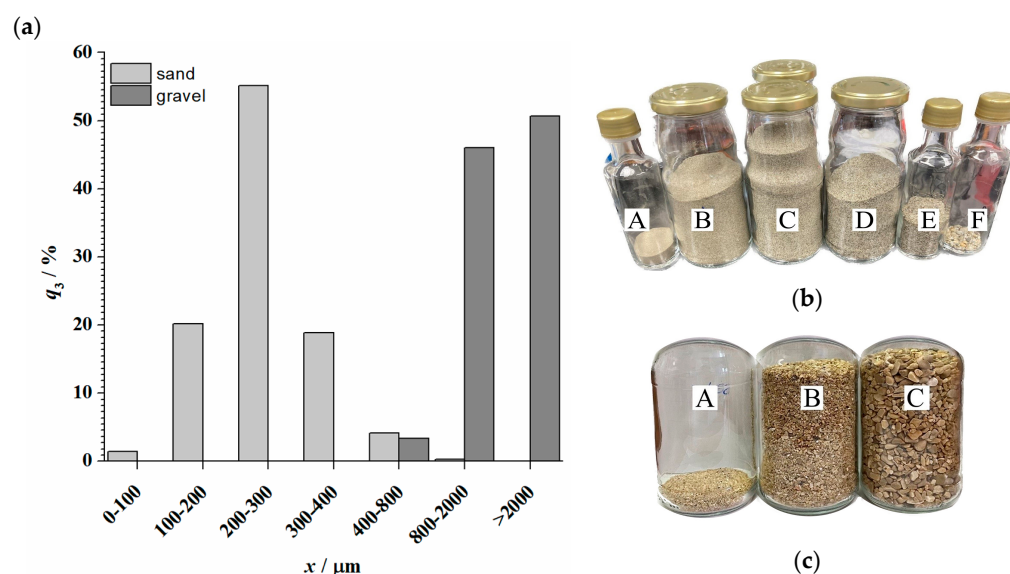


Figure 2. The density mass distribution function for sand and gravel (a); the size distribution of sand particles (b): (A) 0–100 μm ; (B) 100–200 μm ; (C) 200–300 μm ; (D) 300–400 μm ; (E) 400–800 μm ; (F) >800 μm ; and the size distribution of gravel particles (c): (A) 400–800 μm ; (B) 800–2000 μm ; (C) >2000 μm .

According to the particle size distribution (see Supplementary Table S1), sand consists of a larger number of fine particles (100–400 μm), whereas the majority of the particles in gravel are greater than 800 μm . Particle size, as well as the size of pores in between the particles, can affect crude oil diffusion in and out of the sediments. Fine particles alongside larger pores lead to better crude oil removal and dissolution in biodiesel [21].

4.2. Testing the Crude Oil Removal Efficiency of Biodiesel from Coastal Sediments

The efficiency of biodiesel as a crude oil remediation agent was tested on sand and gravel, which were uniformly contaminated with crude oil. The use of UV/Vis spectrophotometers in crude oil removal efficiency determinations is not as common as, for example, using gas chromatography ([31,32]) or gravimetric analysis [33,34]. However, UV/Vis spectroscopy presented itself as a simple and practical method for determining the concentration of the residual crude oil in the sediments. The results obtained using UV/Vis spectrophotometer are given below. Before the measurement, calibration curves were made and used to determine the mass fraction of residual crude oil. The coefficients of determination R^2 , which is an indicator of linearity, are in almost all cases higher than 0.99 (see Supplementary Figure S2).

The biodiesel and water efficiency for the removal of crude oil at different times and at a mass ratio of biodiesel to crude oil of 1:1 from sand and gravel is shown in Figure 3. The test of crude oil removal efficiency from coastal sediments for each condition was carried out twice, in order to check the reproducibility of the results.

Removal of crude oil from sand by the action of water achieved a maximum mean efficiency of 32.43% after 4 h of shaking, and from gravel, 63.52%. In all graphs, when using biodiesel, a general increase in the efficiency of crude oil removal is observed with an increase in the shaking time. The best mean removal efficiency was achieved after 4 h of shaking for all biodiesels (except with gravel and FAME after 2 h); therefore, all further experiments were conducted for 4 h. For sand, with FAME, the maximum mean efficiency after 4 h is 88.41%, with FAEE 88.76%, and with FBE 68.42%. For gravel, with FAME, the maximum mean efficiency is 70.00%, with FAEE 74.01%, and with FBE 76.84%. The results generally show the best efficiency of crude oil removal from sand belongs to FAME, and for gravel, to FBE at a 1:1 biodiesel to oil ratio. In addition, there is also a noticeable correlation between the crude oil removal efficiencies from gravel and the structure of the alcohol used in biodiesel synthesis. The increase in the molar mass of the alcohol, from methanol to butanol, results in an increase in the crude oil removal efficiency. This indicates that biodiesels from higher alcohols are more miscible with crude oil than commercial FAME due to their less polar structure. On the other hand, in the systems where the matrix used was sand, the opposite trend was noticed. The increase in the molecular weight of the alkyl moiety in biodiesel led to a decrease in the crude oil removal efficiency. This can possibly be explained by the increase in kinematic viscosity values from FAME to FBE (Figure 1b), where the diffusion of biodiesel with the lowest viscosity value (FAME) in between the pores of smaller sand particles is the easiest.

Figure 4 shows graphs of the dependence of average crude oil removal from sand and gravel using FAME, FAEE, and FBE during 4 h of the sample shaking depending on the biodiesel to crude oil ratio (0.5:1, 1:1, and 2:1).

From the graph of the efficiency of crude oil removal from sand, depending on the mass ratio of biodiesel to crude oil using FAME, the efficiency decreased with the increase in the mass ratio. The highest value was achieved for the ratio 0.5:1 (94.98%). In all the other cases, the maximum efficiency was achieved at the medium mass ratio of biodiesel to crude oil of 1:1. By removing crude oil using FAEE from sand, the maximum mean efficiency was 88.76%, and from gravel, 74.01%. The use of biodiesel as a crude oil removing agent from gravel shows a lower efficiency than its use for removing crude oil from sand, which is in accordance with the work of Pereira et al. [21]. In the case of using FBE to remove crude oil from sand, the maximum mean efficiency was 68.42%, and from gravel 76.84%. No results are given for the 2:1 ratio because an emulsion of crude oil, water, and biodiesel

was formed after the shaking, which made it impossible to decant the liquid phase from the sand or gravel. This result indicates that too high an amount of biodiesel could act as an emulsifier, making the removal of crude oil more difficult. This is in agreement with other results, where 2:1 has a lower efficiency than a 1:1 ratio.

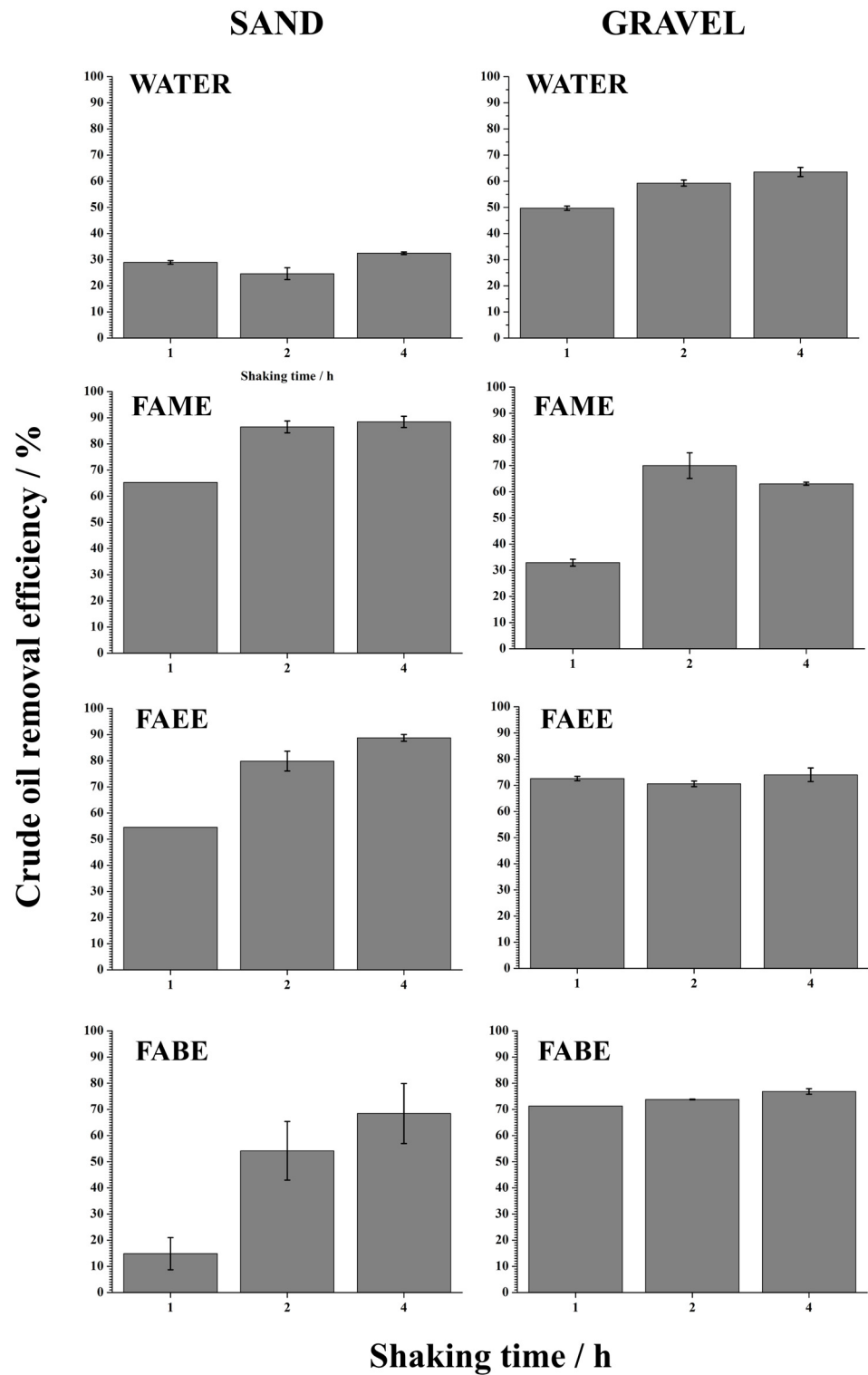


Figure 3. The efficiency of crude oil removal from sand (1st column) and gravel (2nd column) for a water and mixture of FAME/FAEE/FABE to crude oil with the mass ratio of 1:1 at different shaking times.

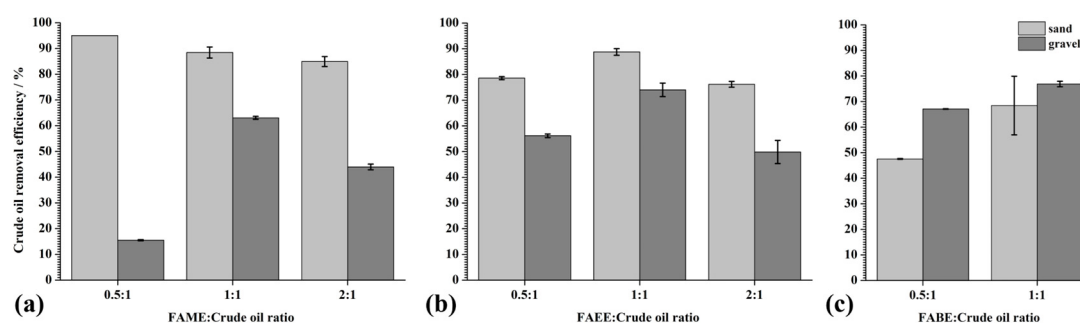


Figure 4. The average efficiency of crude oil removal from sand and gravel: (a) using FAME, (b) FAEE, (c) FBE, depending on the ratio of biodiesel to crude oil during the shaking time of 4 h.

Compared to the results obtained when using other types of nonrenewable agents or extraction solvents, our results are close to those of Wang et al. [35], where the authors investigated the remediation efficiency of crude oil-contaminated soil using different solvent/surfactant systems, i.e., three organic solvents (methanol, acetone, and toluene) with one surfactant (AES-D-OA). Their results suggested that the addition of organic solvents to the surfactant can improve the crude oil removal efficiency from around 73% to around 94%, which is close to the value of 94.98% that we obtained from sand after 4 h using renewable FAME. Another study conducted by Urum et al. [36] researched the application of three different surfactants: Rhamnolipid, Saponin, and sodium dodecyl sulfate in the removal of crude oil from contaminated soil. The results showed that the highest removal efficiency was achieved with the use of synthetic surfactant sodium dodecyl sulfate (46%), followed by biosurfactants Rhamnolipid (44%) and Saponin (only 27%). Similarly, a study by Lee et al. [37] analyzed the remediation of fuel oil-contaminated soil with surfactant-aided soil flushing. After 5 h they observed that hydrogen peroxide had a maximum total petroleum hydrocarbon removal efficiency of 53%, whereas polysorbate Tween 80 had an efficiency of 41%. This clearly indicates how biodiesels as agents obtained in our work can be almost twice as effective in crude oil removal than the investigated surfactants or polysorbates.

The future prospects for upgrading this research may include assessing the crude oil removal efficiency of biodiesels synthesized from other higher bioalcohols (e.g., pentanol, hexanol isomers, or higher) and waste cooking oil in the presence of a possibly renewable catalyst (e.g., biocatalysts produced from waste eggshells).

4.3. The Possibility of Application in a Real System

In order for this research to be applicable in real crude oil spill situations, the procedure for preparing crude oil spill remediation agents, biodiesel, and crude oil removal itself is described below.

In the event of a crude oil spill, coastal sediments contaminated with crude oil would be sprayed with biodiesel and left under the action of waves and natural sea motion, resulting in the removal of crude oil from the sediments to the surface of the water, from which it could be collected by one of the conventional methods. The crude oil thus collected could be used for burning in heat generators, in the production of asphalt, or, depending on the proportion of water and impurities, processed in a refinery [38]. Residual crude oil in sediments would degrade faster due to the presence of residual biodiesel, which serves as an energy source for microorganisms responsible for microbiological degradation [39].

5. Conclusions

In this paper, the application of biodiesel as a crude oil removing agent for crude oil spill remediation from coastal sediments, i.e., sand and gravel, was evaluated. In order to further reduce the impact on the environment, biodiesels were synthesized from WCO. Based on the obtained and presented results, the following can be concluded.

By using environmentally friendly higher bioalcohols (ethanol and 1-butanol), high conversions were obtained for the biodiesel synthesis, as well as by using methanol.

The use of FAME, FAEE, and FBE as crude oil remediation agents from polluted coastal sediments resulted in a more efficient removal of crude oil under almost all conditions compared to removal by water alone. The best average efficiencies were mostly obtained with a mass ratio of biodiesel to crude oil of 1:1 and a sample shaking time of 4 h for all tested biodiesels. Removal of crude oil from sand using FAME (88.41%) and FBE (88.76%) achieved the best results, while using FAEE (74.01%) and FBE (76.84%) was the most efficient when removing crude oil from gravel.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/su16198574/s1>, Figure S1. NMR spectra of different biodiesels: (a) FAME, (b) FAEE, (c) FBE after the synthesis and the last purification step. Figure S2. Calibration lines recorded using a UV/Vis spectrophotometer with different mass fractions: FAME/petroleum (a); FAEE/petroleum (b); FBE/petroleum (c); crude oil (d). Table S1. The mass of individual particle sizes in the sand and their density mass distribution function (q_3). Table S2. The mass of individual particle sizes in the gravel and their density mass distribution function (q_3).

Author Contributions: Conceptualization, F.F.; methodology, F.F.; formal analysis, P.H., I.Z., M.Z. and M.G.; investigation, P.H., I.Z., M.Z., M.G. and J.P.V.; resources, F.F.; data curation, F.F.; writing—original draft preparation, M.G.; writing—review and editing, F.F.; visualization, M.G.; supervision, F.F.; project administration, F.F.; funding acquisition, F.F. All authors have read and agreed to the published version of the manuscript.

Funding: This research was conducted within the Project of the Croatian Science Foundation Development of functional biofuels and (bio)additives and characterization of blends with mineral fuels (FunBioFA, UIP-2019-04-5242).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: No new data were created or analyzed in this study. Data sharing is not applicable to this article.

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

References

1. Michael-Igolima, U.; Abbey, S.J. A systematic review on the effectiveness of remediation methods for oil contaminated soils. *Environ. Adv.* **2022**, *9*, 100319. [CrossRef]
2. Singh, H.; Bhardwaj, N.; Arya, S.K.; Khatri, M. Environmental impacts of oil spills and their remediation by magnetic nanomaterials. *Environ. Nanotechnol. Monit. Manag.* **2020**, *14*, 100305. [CrossRef]
3. Zhu, Z.; Merlin, F.; Yang, M.; Lee, K.; Chen, B.; Liu, B.; Cao, Y.; Song, X.; Ye, X.; Li, Q.K.; et al. Recent advances in chemical and biological degradation of spilled oil: A review of dispersants application in the marine environment. *J. Hazard. Mater.* **2022**, *436*, 129260. [CrossRef]
4. Kim, T.; Lee, C.; Lee, J.; Bae, H.; Noh, J.; Hong, S.; Kwon, B.O.; Kim, J.J.; Yim, U.H.; Chang, G.S.; et al. Best available technique for the recovery of marine benthic communities in a gravel shore after the oil spill: A mesocosm-based sediment triad assessment. *J. Hazard. Mater.* **2022**, *435*, 128945. [CrossRef]
5. Desplat, Y.; Warner, J.F.; Blake, E.J.; Vijayan, N.; Cuvelier, M.; Blackwelder, P.; Lopez, J.V. Morphological and transcriptional effects of crude oil and dispersant exposure on the marine sponge *Cinachyrella allostata*. *Sci. Total Environ.* **2023**, *878*, 162832. [CrossRef]
6. Jeffery, S.; Hannah, L.C.; Herborg, L.; St Germain, C. Oil spill response planning in Pacific Canada: A tool for identifying vulnerable marine biota. *Mar. Policy* **2023**, *148*, 105466. [CrossRef]
7. Mohammadshirazi, A.; Akram, A.; Rafiee, S.; Bagheri Kalhor, E. Energy and cost analyses of biodiesel production from waste cooking oil. *Renew. Sustain. Energy Rev.* **2014**, *33*, 44–49. [CrossRef]
8. Maheshwari, P.; Haider, M.B.; Yusuf, M.; Klemesš, J.J.; Bokhari, A.; Beg, M.; Al-Othman, A.; Kumar, R.; Jaiswal, A.K. A review on latest trends in cleaner biodiesel production: Role of feedstock, production methods, and catalysts. *J. Clean. Prod.* **2022**, *355*, 131588. [CrossRef]
9. Knothe, G.; Steidley, K.R. A comparison of used cooking oils: A very heterogeneous feedstock for biodiesel. *Bioresour. Technol.* **2009**, *100*, 5796–5801. [CrossRef]
10. Yaakob, Z.; Mohammad, M.; Alherbawi, M.; Alam, Z.; Sopian, K. Overview of the production of biodiesel from Waste cooking oil. *Renew. Sustain. Energy Rev.* **2013**, *18*, 184–193. [CrossRef]

11. Demirbaş, A. Biodiesel fuels from vegetable oils via catalytic and non-catalytic supercritical alcohol transesterifications and other methods: A survey. *Energy Convers. Manag.* **2003**, *44*, 2093–2109. [\[CrossRef\]](#)
12. Hajjari, M.; Tabatabaei, M.; Aghbashlo, M.; Ghanavati, H. A review on the prospects of sustainable biodiesel production: A global scenario with an emphasis on waste-oil biodiesel utilization. *Renew. Sustain. Energy Rev.* **2017**, *72*, 445–464. [\[CrossRef\]](#)
13. Viornery-Portillo, E.A.; Bravo-Díaz, B.; Mena-Cervantes, V.Y. Life cycle assessment and emission analysis of waste cooking oil biodiesel blend and fossil diesel used in a power generator. *Fuel* **2020**, *281*, 118739. [\[CrossRef\]](#)
14. Singh, D.; Sharma, D.; Soni, S.L.; Inda, C.S.; Sharma, S.; Sharma, P.K.; Jhalani, A. A comprehensive review of biodiesel production from waste cooking oil and its use as fuel in compression ignition engines: 3rd generation cleaner feedstock. *J. Clean. Prod.* **2021**, *307*, 127299. [\[CrossRef\]](#)
15. Bouaid, A.; El boulifi, N.; Hahati, K.; Martinez, M.; Aracil, J. Biodiesel production from biobutanol. Improvement of cold flow properties. *Chem. Eng. J.* **2014**, *238*, 234–241. [\[CrossRef\]](#)
16. Yusoff, M.F.M.; Xu, X.; Guo, Z. Comparison of Fatty Acid Methyl and Ethyl Esters as Biodiesel Base Stock: A Review on Processing and Production Requirements. *J. Am. Oil Chem. Soc.* **2014**, *91*, 525–531. [\[CrossRef\]](#)
17. Melikoglu, M.; Singh, V.; Leu, S.Y.; Webb, C.; Lin, C.S.K. *Handbook of Biofuels Production*, 2nd ed.; Woodhead Publishing Limited: Cambridge, UK, 2016; pp. 237–258.
18. Zabed, H.; Sahu, J.N.; Suely, A.; Boyce, A.N.; Faruq, G. Bioethanol production from renewable sources: Current perspectives and technological progress. *Renew. Sustain. Energy Rev.* **2017**, *71*, 475–501. [\[CrossRef\]](#)
19. García, V.; Pääkilä, J.; Ojamo, H.; Muurinen, E.; Keiski, R.L. Challenges in biobutanol production: How to improve the efficiency? *Renew. Sustain. Energy Rev.* **2011**, *15*, 964–980. [\[CrossRef\]](#)
20. Singh, D.; Sharma, D.; Soni, S.L.; Sharma, S.; Sharma, P.K.; Jhalani, A. A review on feedstocks, production processes, and yield for different generations of biodiesel. *Fuel* **2020**, *262*, 116553. [\[CrossRef\]](#)
21. Pereira, M.G.; Mudge, S.M. Cleaning oiled shores: Laboratory experiments testing the potential use of vegetable oil biodiesels. *Chemosphere* **2004**, *54*, 297–304. [\[CrossRef\]](#)
22. Fernández-Álvarez, P.; Vila, J.; Garrido-Fernández, J.M.; Grifoll, M.; Lema, J.M. Trials of bioremediation on a beach affected by the heavy oil spill of the Prestige. *J. Hazard. Mater.* **2006**, *137*, 1523–1531. [\[CrossRef\]](#) [\[PubMed\]](#)
23. Akkaya, M.R. Prediction of fatty acid composition of sunflower seeds by near-infrared reflectance spectroscopy. *J. Food Sci. Technol.* **2018**, *55*, 2318–2325. [\[CrossRef\]](#) [\[PubMed\]](#)
24. *EN ISO 3104*; Petroleum products—Transparent and opaque liquids—Determination of kinematic viscosity and calculation of dynamic viscosity. ISO: Geneva, Switzerland, 2020.
25. *ASTM D664-18e2*; Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration. ASTM International: West Conshohocken, PA, USA, 2019.
26. *EN ISO 12937:2000*; Petroleum products—Determination of water—Coulometric Karl Fischer titration method. ISO: London, UK, 2000.
27. Cvengroš, J.; Cvengrošová, Z. Used frying oils and fats and their utilization in the production of methyl esters of higher fatty acids. *Biomass Bioenergy* **2004**, *27*, 173–181. [\[CrossRef\]](#)
28. Parlov Vuković, J. Primjena spektroskopije NMR u analizi biodizela. *Kem. Ind.* **2016**, *65*, 17–24. [\[CrossRef\]](#)
29. Knothe, G.; Steidley, K.R. Kinematic viscosity of biodiesel fuel components and related compounds. Influence of compound structure and comparison to petrodiesel fuel components. *Fuel* **2005**, *84*, 1059–1065. [\[CrossRef\]](#)
30. Vargas-Ibáñez, L.T.; Cano-Gómez, J.J.; Santos-López, I.A.; Iglesias-Silva, G.A.; López-Lázaro, J.d.L.S.; Alcalá-Rodríguez, M.M.; Villarreal-Mendoza, C.; Armendáriz-Ovalle, C. Surface tensions of biodiesel blends with pentanol and octanol isomers at different conditions: Measurement and new correlation. *Fluid Phase Equilibria* **2021**, *540*, 113046. [\[CrossRef\]](#)
31. Miller, N.J.; Mudge, S.M. The effect of biodiesel on the rate of removal and weathering characteristics of crude oil within artificial sand columns. *Spill Sci. Technol. Bull.* **1997**, *4*, 17–33. [\[CrossRef\]](#)
32. Fernández-Álvarez, P.; Vila, J.; Garrido, J.M.; Grifoll, M.; Feijoo, G.; Lema, J.M. Evaluation of biodiesel as bioremediation agent for the treatment of the shore affected by the heavy oil spill of the Prestige. *J. Hazard. Mater.* **2007**, *147*, 914–922. [\[CrossRef\]](#) [\[PubMed\]](#)
33. Mudge, S.M.; Pereira, G. Stimulating the Biodegradation of Crude Oil with Biodiesel Preliminary Results. *Spill Sci. Technol. Bull.* **1999**, *5*, 353–355. [\[CrossRef\]](#)
34. Xia, W.; Xia, Y.; Li, J.; Zhang, D.; Zhou, Q.; Wang, X. Studies on crude oil removal from pebbles by the application of biodiesel. *Mar. Pollut. Bull.* **2015**, *91*, 288–294. [\[CrossRef\]](#)
35. Wanga, M.; Zhang, B.; Lic, G.; Wu, T.; Sun, D. Efficient remediation of crude oil-contaminated soil using a solvent/surfactant system. *RSC Adv.* **2019**, *9*, 2402–2411. Available online: <https://pubs.rsc.org/en/content/articlehtml/2019/ra/c8ra09964b> (accessed on 25 August 2024). [\[CrossRef\]](#) [\[PubMed\]](#)
36. Urum, K.; Grigson, S.; Pekdemir, T.; McMenamy, S. A comparison of the efficiency of different surfactants for removal of crude oil from contaminated soils. *Chemosphere* **2006**, *62*, 1403–1410. [\[CrossRef\]](#) [\[PubMed\]](#)
37. Lee, H.; Lee, Y. Feasibility analysis of the remediation of fuel oil-contaminated soil and groundwater around the railroad station of Y city, Korea with surfactant-aided soil flushing. *Asia-Pac. J. Chem. Eng.* **2013**, *8*, 461–472. [\[CrossRef\]](#)

38. Fingas, M. *Oil Spill Science and Technology—Prevention, Response and Cleanup*; Gulf Professional Publ.: Houston, TX, USA, 2010; pp. 335–336.
39. Ng, Y.F.; Ge, L.; Chan, W.K.; Tan, S.N.; Hong Yong, J.W.; Yang Tan, T.T. An environmentally friendly approach to treat oil spill: Investigating the biodegradation of petrodiesel in the presence of different biodiesels. *Fuel* **2015**, *139*, 523–528. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.