

# Biodiesel production from vegetable oil

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## 1 INTRODUCTION

In Germany, biodiesel is the most widely used biofuel, derived from various sources such as vegetable oils and used cooking oils. In 2023, biodiesel production exceeded 2.5 million tons, accounting for more than two-thirds of the nation's biofuel sales volume. It is primarily used as an additive to conventional diesel fuel. Current regulations permit blending biodiesel with diesel at concentrations of up to 7% (B7), provided it meets the DIN EN 590 standard. Importantly, B7 is compatible with existing vehicles, requiring no special technical modifications. Gas station pumps are labeled with a B7 sticker to indicate the biodiesel proportion. To further promote sustainable fuel options, the German government has established a legal framework for a 10% biodiesel blend (B10). Although B10 offers enhanced sustainability, it may require vehicles to be compatible with higher biodiesel content. Key aspects of biodiesel production and usage are summarized in Fig. 1. Biodiesel has gained increased attention due to its environmental benefits and reliance on renewable resources. However, high production costs remain a significant barrier to its widespread commercialization. Biodiesel can be produced using four primary methods: direct use and blending, microemulsions, thermal cracking (pyrolysis), and transesterification. In this study, we focus on producing biodiesel from vegetable oil via transesterification. The process steps are outlined, and the final product is evaluated against current standards for commercial application [1, 2, 3].

Raw materials	Rapeseed and other vegetable oils, animal fats
Annual yield per hectare	3.5 tons of rapeseed produce approx. 1,500 liters of biodiesel (as well as 2 tons of animal feed and 130 kg of glycerine)
Fuel equivalent	1 L biodiesel replaces approx. 0.91 L diesel
Green House Gas emissions (GHG)	52 g CO <sub>2</sub> -eq/MJ biodiesel from rapeseed oil (comparative fuel diesel: 83.8 g CO <sub>2</sub> -eq/MJ), GHG reduction: 38%
Technical information	Biodiesel in pure form: manufacturer's approval required; can be used in blends up to 7% without adapting the engine (DIN 14214)

Fig. 1 | Biodiesel fact sheet. Based on [2].

## 2 TRANSESTERIFICATION

Transesterification is a chemical process used to convert carboxylic acid esters, such as those found in triglycerides, into different carboxylic acid esters through a reaction with an alcohol, typically in the presence of a catalyst. Triglycerides, the primary components of most animal fats and vegetable oils, consist of a glycerol molecule, a trihydric alcohol – a compound that contains 3 hydroxyl groups (Fig. 3a) – esterified with three long-chain fatty acids. Prolonged use or heating of these fats can lead to hydrolysis of triglycerides, releasing free fatty acids (FFAs), which are fatty acids not bound to glycerol. Fatty acids, usually containing an even number of carbon atoms, due to the way they are synthesized in living organisms can be categorized into saturated and unsaturated acids, the latter containing at least one cis double bond between two carbon atoms making them more prone to oxidation and rancidity. Common saturated fatty acids are for instance stearic acid (Fig. 3a) or palmitic acid (Fig. 3a). A common unsaturated fatty acid is oleic acid (Fig. 3a). In the context of biodiesel production, transesterification is a critical step where lipids, including triacylglycerols (TAGs) and FFAs, are reacted with alcohols like methanol or ethanol to form fatty acid methyl or ethyl esters. This reaction can be catalyzed by acids, alkalis, or enzymes. The process is especially relevant for converting non-polar lipids from sources such as vegetable oils, animal fats, and

microalgae oils into biodiesel, a renewable energy source. The general chemical reaction is outlined in Fig. 2 [3].

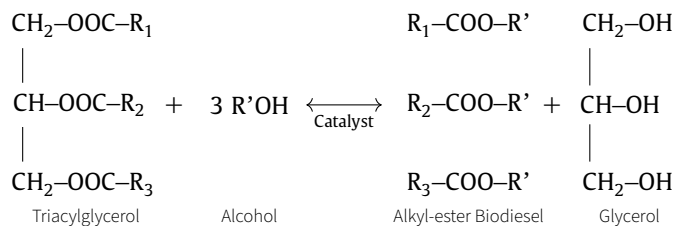


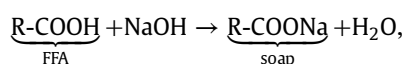
Fig. 2 | Transesterification reaction. Typically, Methanol and Ethanol are used as the Alcohol.

Methyl esters are preferred over ethyl esters in biodiesel production due to several advantages. Methanol, used to produce methyl esters, is cheaper and more readily available than ethanol, as it is typically derived from natural gas, making it more economical for large-scale production. The transesterification reaction with methanol is faster and more efficient than with ethanol because methanol has a smaller molecular size and higher polarity, facilitating better mixing with triglycerides and catalysts. Additionally, methanol is more compatible with commonly used alkaline catalysts like sodium hydroxide or potassium hydroxide, leading to enhanced reaction rates and higher yields. Methyl esters also allow for a simpler separation process, as ethanol can form water during transesterification, which may cause soap formation and reduce biodiesel yield—a problem less pronounced with methanol. In terms of fuel properties, methyl esters generally exhibit lower viscosity and better cold-flow performance, making them more suitable for use in colder climates. Furthermore, industrial processes and regulatory standards have been widely established for methyl ester production, streamlining their integration into existing systems. These combined factors make methyl esters the dominant choice in biodiesel production, although ethyl esters remain a viable option in regions where ethanol is more economical or readily available [4, 5].

### 3 FABRICATION OF BIODIESEL

In the following, we will outline the process steps undertaken in fabricating biodiesel from vegetable oil by usage of methanol.

**Quantification of free fatty acids** For the transesterification of our oil we use sodium hydroxide (NaOH) as catalyst. NaOH is a widely used catalyst since it is a strong base that ensures high reaction rates and good yields. Moreover, it is inexpensive and widely available. However, it has its limits for oils that have high FFA content [6, 7]. FFAs contained in the vegetable oil can react with NaOH to form soap instead of participating in the transesterification reaction. This so called saponification process, is a side reaction that consumes NaOH and reduces its availability to catalyze the desired transesterification process:



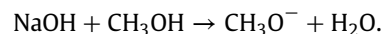
Therefore, the amount of FFAs inside the oil has to be determined such that an appropriate amount of extra NaOH can be added to the transesterification solution later. This is achieved using an acid-base titration method with NaOH. As NaOH neutralizes the FFAs, their concentration can be quantified by tracking the pH of

the solution and the volume of NaOH added. The procedure involves dissolving 1 mL of vegetable oil in 10 mL of isopropanol, which allows the FFAs to react with the base. Three drops of phenolphthalein indicator are added to the mixture, and a 0.025 mol/L NaOH solution is added drop by drop until the solution exhibits a persistent pink coloration lasting at least 30 seconds, indicating the neutralization of all FFAs. During the titration, the mixture is continuously stirred with a magnetic stirrer to ensure thorough reaction between the NaOH and the FFAs. Since FFAs react with NaOH in a 1:1 molar ratio, their concentration is typically expressed as a percentage of the oil's weight and can be calculated using the formula:

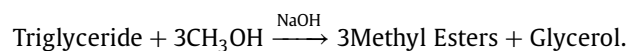
$$\text{FFA (\%)} = \frac{V_{\text{NaOH}} N_{\text{NaOH}} M_{\text{FFA}}}{m_{\text{oil}}} \times 100,$$

where  $V_{\text{NaOH}}$  is the volume of NaOH added,  $N_{\text{NaOH}}$  is the normality (equivalent concentration) of the NaOH solution,  $M_{\text{FFA}}$  is the molar mass of the FFAs, and  $m_{\text{oil}}$  is the mass of the oil used. For practical purposes, an approximate estimation suffices. A common rule of thumb is that for every 1 mL of NaOH consumed (equivalent to 1 mg of NaOH per mL of oil), 0.1 g of additional NaOH must be included in the transesterification solution. In this experiment, 0.4 mL of NaOH was required to achieve a 30-second lasting coloration of the solution, indicating the presence of FFAs. Therefore, an additional 0.04 g of NaOH was calculated and added to the reaction mixture for the transesterification process.

**Transesterification** To fabricate biodiesel, 120 mL of vegetable oil was heated to 45–55°C in a beaker while stirring for approximately 30 minutes. Methanol was used as the alcohol for the transesterification reaction (see Fig. 2), and NaOH powder, ground from pellets, was dissolved in methanol to form methoxide ions ( $\text{CH}_3\text{O}^-$ ):



Methoxide, a strong nucleophile, attacks the carbonyl carbon of triglycerides, initiating the transesterification reaction. For this process, 25 mL of methanol and 0.6 g of NaOH were used to generate methoxide ions. Additionally, to account for the free fatty acids (FFAs) present in the vegetable oil, 0.04 g of NaOH (calculated from the previously determined FFA content) was added. The dissolution of NaOH in methanol was accelerated using an ultrasonic bath. The prepared NaOH-methanol solution was then added to the heated vegetable oil, and the mixture was stirred at 45–55°C for approximately 60 minutes to facilitate the transesterification reaction. During this process, triglyceride molecules react with three molecules of methanol in the presence of NaOH to produce three molecules of methyl ester (biodiesel) and one molecule of glycerol:



After the reaction, the mixture was transferred to a separating funnel, where the glycerol byproduct was allowed to separate and settle. The biodiesel phase was washed multiple times with distilled water to remove residual NaOH and soap, with the water introduced in atomized form using a spray bottle. This washing step was repeated until the pH of the biodiesel was measured to be within the range of 7 to 8. To remove water residues, four spoons of  $\text{Na}_2\text{SO}_4$  were added to the separating funnel, and the mixture was shaken. Finally, the  $\text{Na}_2\text{SO}_4$  was filtered through a pleated filter, leaving the purified biodiesel ready for use.

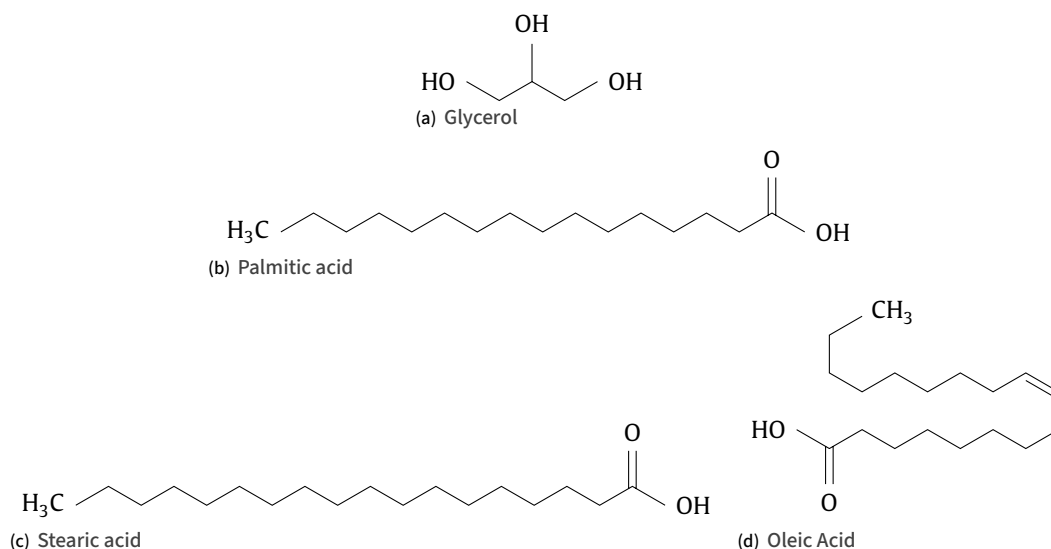


Fig. 3 | Components of typical Triacylglycerol: (a) glycerol, (b) palmitic acid, (c) stearic acid, (d) oleic acid.

## 4 CHARACTERIZATION

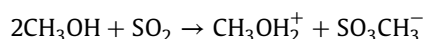
### 4.1 DETERMINING WATER CONTENT

**Oil analysis kit** An oil analysis kit, the “DIGI Water Kit Easy-SHIP” [8], was used to determine the water content in the vegetable oil. The kit operates by measuring the pressure inside a container, which is generated by hydrogen gas produced when the water in the oil reacts with added reagents. This method provides a cost-effective and quick way to assess the water content in oil. However, for very low water contents, the results should be considered approximate. This limitation arises from the need for highly accurate dosing of the oil sample (which, in our case, was done by visual estimation) and the requirement that all water in the oil fully reacts to produce hydrogen gas. For the measurement we obtain a value of < 0.02%.

**Karl Fischer method** The Karl Fischer (KF) method is an analytical technique for determining the water content in various substances relying on a specific chemical reaction between water and the so called Karl Fischer reagent, with the endpoint detected either volumetrically or coulometrically. It is regarded as the standard water content analysis tool especially for oils due to its precision and reliability. The Karl Fischer reagent comprises a solution containing iodine (I) and sulphur dioxide (SO<sub>2</sub>) in a mixture of methanol (CH<sub>3</sub>OH) and a base (RN). Traditionally, pyridine was used as the base, but it has largely been replaced by imidazole due to health and safety concerns. The overall reaction is:



The reactive component in the KF reagent is the monomethylsulfite ion, formed from the reaction between sulfur dioxide and methanol, which is crucial for the titration:



Throughout the titration, water is consumed, allowing the reaction to proceed until all water in the sample is reacted. When no water remains, the added iodine is no longer reduced, leading to the persistence of its brown color, which can be visually detected—typically monitored using a near-infrared (NIR) spectrometer for

precision. Besides visual endpoints, electrometric detection methods, like biamperometry, are often favored for their sensitivity and accuracy. The amount of KF reagent used is directly related to the water content in the sample in the case of volumetric KF. In the coulometric method iodine is generated electrochemically within the titration cell. The amount of electricity (in coulombs) required to produce the iodine needed to react with all the water in the sample is measured, allowing for the calculation of water content [9].

Using the KF Titrand manufactured by Metrohm we determined the water content of the vegetable oil to be 0.03% and the fabricated biodiesel to be 0.18% (volumetric KF).

### 4.2 DETERMINING THE DENSITY

A hydrometer was used to measure the density of the two samples. The hydrometer, shaped like an elongated buoy, is placed into the liquid sample, where it floats at a level determined by the liquid’s density according to Archimedes’ principle. The density is read directly from the scale attached to the hydrometer at the liquid/air interface. The measured density of the vegetable oil was 0.917 g/mL, while the biodiesel’s density was 0.882 g/mL. Theoretically, to account for the water content, the densities of the pure phases for both samples should be calculated using the formula:

$$\rho_{\text{total}} = \frac{m_{\text{total}}}{V_{\text{total}}} = \frac{m_{\text{total}}}{\frac{x_{\text{water}}m_{\text{total}}}{\rho_{\text{water}}} + \frac{(1-x_{\text{water}})m_{\text{total}}}{\rho_{\text{sample}}}}$$

where  $\rho_{\text{total}}$  is the observed density,  $x_{\text{water}}$  is the water fraction, and  $\rho_{\text{sample}}$  represents the density of the pure phase. However, considering the amount of water and the accuracy of our measurement, this would not yield any meaningful insight. The ambient temperature at the time of measurement was recorded to be 15 °C.

### 4.3 DETERMINING THE VISCOSITY

A Gilmont falling ball viscometer was used to measure the viscosity of the samples. The viscometer consists of a glass tube filled

to the brim with the test liquid, and the time it takes for a ball to fall a specified distance within the tube is recorded. Care must be taken during setup to ensure no air bubbles are present in the liquid, as bubbles can adhere to the ball and rise against the direction of its fall, slowing the ball and leading to erroneously high measured times.

The viscosity  $\eta$  is calculated from the measured fall time using the formula:

$$\eta = K(\rho_{\text{ball}} - \rho_{\text{fluid}})\Delta t,$$

where  $K$  is a constant that depends on the geometry of the tube and the ball,  $\rho_{\text{ball}}$  is the density of the ball,  $\rho_{\text{fluid}}$  is the density of the liquid, and  $\Delta t$  is the measured fall time [10].

Using the previously determined fluid densities and averaging two time measurements, made at ambient temperature 15°C, for each fluid, viscosities of  $56.4 \pm 0.4 \text{ mm}^2/\text{s}$  for vegetable oil and  $5.1 \pm 0.3 \text{ mm}^2/\text{s}$  for biodiesel were calculated.

#### 4.4 AGING OF OIL

As mentioned before, the content of free fatty acid molecules is significantly higher in old or previously used oil than in new oil. As soon as the oil comes into contact with oxygen, oxidation also occurs. Due to the reaction with unsaturated fatty acids, this causes the oil to become rancid. Ageing with the addition of air also increases the viscosity. Furthermore, continuous use of the oil leads to the introduction of impurities. The isomerization of the unsaturated fatty acid esters produces carcinogenic trans fatty acids. As a result, the oil cannot be reused indefinitely without posing health risks to the consumer. Transesterification to biodiesel is therefore a cost-effective recycling process [11].

#### 4.5 DISCUSSION OF THE RESULTS

In this experiment, we successfully fabricated methyl ester-based biodiesel from household vegetable oil. The specifications of the initial vegetable oil and the fabricated biodiesel are summarized in Table 1. The water content of the biodiesel was determined to exceed the maximum permissible limits for biodiesel specified by EN 14214 [12]. As expected, the density and viscosity were reduced compared to the initial vegetable oil due to the conversion of triglycerides into fatty acid methyl esters. This reduction occurs because the weaker van der Waals forces between the resulting fatty acid molecules no longer bind them as strongly as in the triglyceride structure. To bring the density and viscosity slightly more within permissible limits, a second round of conversion is necessary to address the remaining triglycerides in the biodiesel. Alternatively, a more cost-effective approach would be to extend the stirring duration during the transesterification reaction, allowing for a more complete conversion. The water content can also be reduced further by repeating the filtration process with  $\text{Na}_2\text{SO}_4$  to improve dehydration. The yield of biodiesel was calculated by comparing the volume of biodiesel produced to the initial 120 mL of vegetable oil used. We obtained a yield of 75.9%, a very good value. It is important to note that the vegetable oil used in this experiment was relatively fresh, with a low free fatty acid (FFA)

	initial Oil	Fabricated Biodiesel	Literature
Water content (Kittwake) [%]	<0.02	N/A	
Water content (Karl-Fischer) [%]	0.03	0.18	$\leq 0.05$
Density [g/mL]	0.917	0.882	0.86-0.9
Viscosity [ $\text{mm}^2/\text{s}$ ]	$56.4 \pm 0.4$	$5.1 \pm 0.3$	3.5-5.0 at 40°C

Tab. 1 | Comparison of the fabricated biodiesel properties against the initial vegetable oil and permissible limits specified by EN 14214 [12].

content. For older or used oils, which typically have higher FFA concentrations, the yield would likely be lower.

## 5 NANOREACTORS

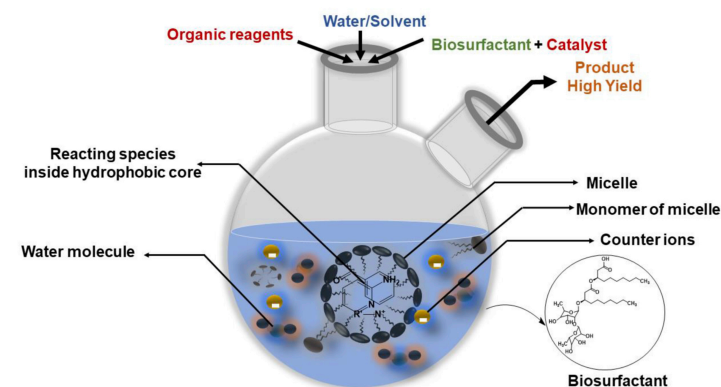


Fig. 4 | Organic reactions for which water is incompatible as solvent can take place inside the hydrophobic environment of micelles acting as nanoreactors. Taken from [13].

Surfactants, characterized by their distinct molecular structures consisting of a hydrophilic head group with a strong affinity for polar solvents and a long hydrophobic tail, known as a hydrophobe or lipophile, which prefers non-polar compounds, are widely recognized for their solubility in polar solvents and effective cleaning properties. These features make them an ideal choice for detergents and other cleaning products. An essential function of surfactants is their ability to reduce interfacial tension by concentrating at the interface of two immiscible liquids, thereby enhancing the solubility of hydrophobic compounds. This is achieved through the formation of micelles, colloidal aggregates that encapsulate the non-polar molecules. Leveraging this property, surfactants have been employed as nanoreactors in organic chemistry, facilitating organic transformations without resorting to toxic solvents. This approach addresses the pressing environmental concerns associated with non-biodegradable and hazardous solvents, which pose significant risks to human health and aquatic ecosystems. Although water is often regarded as an ideal solvent for organic reactions, its incompatibility with many organic reagents restricts its utility. Surfactants create micellar environments that encapsulate organic molecules, providing an effective solution that enables a wide range of organic reactions—including addition, elimination, substitution, and condensation processes—within an aqueous medium (see Fig. 4) [13].

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