

Biodiesel: An Overview II

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The crescent number of scientific articles published *per* year shows that research on biodiesel continues to play an important role to support the growing demand for this biofuel. The second edition of *Biodiesel: An Overview* presents the worldwide research in the last 15 years. Microalgae biomass is the most studied raw material alternative in this period and several studies have been carried out to develop basic heterogeneous catalysts for biodiesel production. Concerning to production technologies, supercritical conditions and intensification process have been extensively investigated. The development of new antioxidants additives has focused mainly on biomass-derived formulations and there are few studies on biocide candidates. In terms of pollutant emissions, in general, the studies showed that the addition of biodiesel generates lower concentrations of polycyclic aromatic hydrocarbons (PAH), CO and *n*-alkanes pollutants, but carbonyl compounds, major ions and NO_x are emitted in a higher concentration compared to pure diesel.

Keywords: additives, biodiesel, catalysts, emission, feedstocks, review

1. Introduction

Biodiesel plays an increasingly important role in the energy matrix of several countries in the world and its demand is increasing every year. Accordingly, the associated research, development and innovation (R&D&I) on biodiesel is also advancing to the same extent. This could be clearly observed by the growing number of publications in scientific search databases. A bibliographic

search was carried out in the Scopus (Elsevier) database in October 2020 looking for publications that contain the word “biodiesel” in the title, abstract or keywords. A total of 40,492 references were found, and from those, 39,602 papers (98% of them) were published in the last 15 years (2005-2020). Figure 1a shows the number of publications by year.

In turn, the search for publications containing the words “biodiesel” and “review” (or “overview”) in the title, abstract or keywords provided a total of 3,411 references. The search was done again in order to ensure that the

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This paper is dedicated, *in memoriam*, to Professor Angelo da Cunha Pinto.

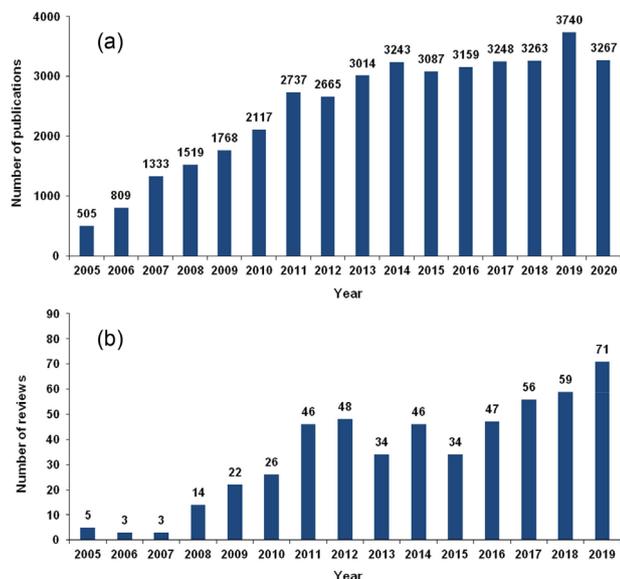


Figure 1. Quantitative of publications (a) and reviews (b) about biodiesel, from 2005 to 2020. Source: Scopus database (October, 2020).

publications are really review articles, now using the same words only in the title. The number was reduced to 583 references. From these, 579 were published between 2005 and 2020. Figure 1b shows the number of review articles by year and Table 1 exhibits the top 20 references with the highest number of citations.

Table 1. Ranking of review articles about biodiesel with the highest number of citations in the Scopus database

Reference	No. citations
1	4,051
2	3,249
3	2,271
4	1,448
5	1,083
6	960
7	913
8	834
9	822
10	774
11	742
12	736
13	596
14	589
15	569
16	543
17	518
18	494
19	459
20	450

Those reviews approach different aspects about biodiesel. Some of them focus on just one topic, such as new sources of raw material,⁹ analytical methods for

biodiesel characterization²¹ and stability of biodiesel.²² Others are even more specific by discussing about a type of a specific feedstock,²³ a specific catalyst aspect²⁴ or regarding the oxidative stability of a given type of biodiesel in particular,²⁵ just to name few examples. There are also some authors who chose to address the key points and/or news of several topics. In 2005, we published one of the five reviews on biodiesel that year, which is among the 20 most cited in the world. The present article provides an overview of research on biodiesel in the last 15 years, including a brief summary about the evolution of biodiesel regulation in Brazil within the period. In the present paper we also discussed about the use of biodiesel by G20 countries, the recent feedstocks and catalysts for biodiesel production, as well as new technologies. Additionally, the use of additives as an alternative to solve some storage problems and emissions are also discussed.

1.1. Implementation of biodiesel in Brazil

Three events were decisive for the implementation of biodiesel in the Brazilian energy matrix: (i) the oil crisis of the 1970s, (ii) the “green revolution” in Brazil that encouraged the Brazilian agribusiness, producing a surplus of vegetable oil, and (iii) the ECO-92 Conference of the United Nations Environment Program.²⁶ The ECO-92 took place in Rio de Janeiro, in which there was the recognition of the potential of biofuels as allies in order to achieve the targets set for reducing carbon emissions.²⁷

Considering the favorable conditions for implementation of biodiesel as an alternative fuel in the Brazilian energy matrix, in 2002 the Ministry of Science and Technology introduced the ProBiodiesel.²⁸ Back then, the ProBiodiesel was a network for research and technological development of biodiesel. This took place by the ordinance No. 702 of the 30th October 2002,²⁸ aiming both partial and gradual replacement of fossil diesel by biodiesel. After the ProBiodiesel, an Interministerial Executive Committee for Biodiesel (CEIB) was created in 2003, with the purpose of conducting studies about the economic, social and environmental viabilities of a prospective biodiesel industry in Brazil.^{26,29} Based on the studies done by CEIB, in December 2004 the President of Brazil officially launched the Brazilian Program for the Production and Use of Biodiesel (PNPB).³⁰ At that time, the Program envisaged different raw materials for biodiesel production, within the context of social inclusion and regional development. Hence, castor oil was initially considered in the pool of feedstocks, but it was proved to be technically unfeasible due to its composition, rich in ricinoleic acid, yielding a biodiesel that does not meet specifications. In addition,

the economic benefits were also not clear, since the unique composition of castor oil makes it highly valuable for cosmetics and pharmaceuticals. Indeed, after all these years, the major raw materials for the production of biodiesel in Brazil are soybean and tallow (data on section 2). Indeed, both soybean and tallow were agrobusiness activities which already existed at the time the PNPB was launched. These facts highlight some economical barriers for implementing other crops in the pool of biodiesel feedstocks to replace the traditional ones. In January 2005, the law No. 11,097 was published,³¹ which officially establishes the compulsory implementation of biodiesel in the Brazilian energy matrix. This law also determined the ANP (National Agency of Petroleum, Natural Gas and Biofuels) to define acceptable limits of percentage variations of biodiesel in fossil diesel.^{26,29,32} In 2008 the addition of 2% (v v⁻¹) biodiesel in diesel (B2) became mandatory in the country.³³ From there to the present day, the biodiesel amount added to fossil diesel was risen gradually. The evolution of the biodiesel percentage increase to mineral diesel is presented in Figure 2.

1.2. Overview of the biodiesel scenario in G20 countries

The group of the twenty countries (the G20) is formed by finance ministers and central bank governors of the world's 19 largest economies. Indeed, the G20 is composed

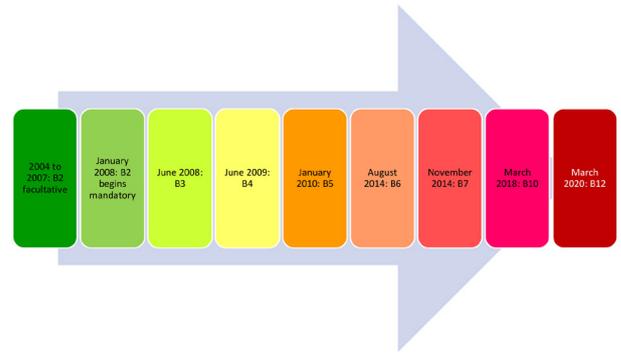


Figure 2. Evolution of the increase in the biodiesel added to mineral diesel in Brazil through the time, up to nowadays (adapted from reference 33).

by Argentina, Australia, Brazil, Canada, China, France, Germany, India, Indonesia, Italy, Japan, the Republic of Korea, Mexico, the Russian Federation, Saudi Arabia, South Africa, Turkey, the United Kingdom, the United States and the European Union.³⁴ G20 reflects the wider interests of both developed and emerging economies. The role of the G20 is “to coordinate policies and to make globalization a smoother, more harmonious, and sustainable process.”³⁵ In this way, international negotiation is favored, integrating the principle of an extended dialogue.³⁵ Table 2 shows a brief summary of studies or actions in progress, or already concluded, regarding the biodiesel inclusion in the G20 countries energy matrices.

Table 2. Summary of actions and feedstocks used to introduce biodiesel in the G20 countries energy matrices

Country	History of actions and current situation	Feedstocks
Germany	addition of 5% (v v ⁻¹) of biodiesel in fossil diesel was allowed in 2004 without labelling; higher blends, except for 100% biodiesel, could be sold, as long as they were labelled; ^{36,37} since 2015, there is a 6% greenhouse-gas-emission-reduction target set for transportation fuel, which should be reached until 2020; ^{36,37} fuel companies that fail to fulfill the new biofuel rules will have to pay the penalty of €470 <i>per t</i> O ₂ eq ^{38,39}	rapeseed (most used), palm, coconut and soybean oils ⁴⁰
France	article No. 2 Ordinance 2011-1105 from 14 th September 2011 is the legal basis regulating the French targets; ⁴¹ in 2015, fuel suppliers were subjected to add 7% biofuel to gasoline and 7.7% biofuel to diesel (in energy content); fuel suppliers who do not comply with the addition rules pay the pollution tax (Taxe Générale sur les Activités Polluantes (TGAP)) ⁴²	soybean, palm and sunflower oils ⁴²
Italy	in 2015, fuel suppliers were subjected to the addition of at least 5% biofuel to conventional automotive fuels (in energy content); ⁴² the following schedule for the mandatory biofuel addition were 5.5% in 2016, 6.5% in 2017, 7.5% in 2018, 9% in 2019 and 10% from 2020 on; fuel suppliers who fail to comply with the mandatory quota have to pay €750 as penalty for every missing biofuel certificate (10 Gcal) ³⁸	soybean and palm oils ⁴²
Russia	the technical standard in Russia allows adding 5% biodiesel to conventional fuel since 2005 (GOST R 52368-2005); ⁴³ however, this addition is not mandatory in the country ⁴⁴	sunflower, rapeseed and soybean oils ⁴⁴
United Kingdom	since 2015, fuel suppliers have been forced to add at least 4.75% biofuel (by volume) to conventional automotive fuels; ⁴⁵ in 2018, the biofuel addition target increased to 7.25%, besides being expected to be risen to 12.4% up to 2032 ⁴⁵	used cooking oil (UCO) ⁴⁵

Table 2. Summary of actions and feedstocks used to introduce biodiesel in the G20 countries energy matrices (cont.)

Country	History of actions and current situation	Feedstocks
South Korea	<p>since 2002, biodiesel has been using in public vehicles;^{46,47} between 2006 and 2007, 0.5% biodiesel was introduced in commercial diesel across the country; the blend percentage was expected to increase by 0.5% every year, so that automotive diesel would be added with 2.0% biodiesel from 2010 on;^{46,47} in 2015, the 2.5% biodiesel addition became law from the RFS (Renewable Fuel Standard) program;^{46,47} between 2018 and 2020, the percentage was expected to increase to 3.0%⁴⁸</p>	soybean and palm oils ⁴⁸
South Africa	<p>in 2012, it was determined the addition of 5% of biodiesel in diesel;^{49,50} the mandatory biofuel addition was supposed to start on 2015;⁴⁹ but lack of pricing and a final approach about how to apply for subsidies, made the government miss its 2015 deadline for mandatory blending;⁵⁰ costs with UCO have increased in recent years in response to growing local and global demands; biodiesel producers pay between 7 and 8 rand <i>per</i> liter for UCO; this fact made it unfeasible to promote biofuel use so far⁵¹</p>	used cooking oil (UCO) ⁵¹
Argentina	<p>resolution No. 37 of the Ministry of Energy, from 2006,⁵² established that diesel had to be mixed with at least 10% biodiesel; in 2007, it was set the initial 5% biodiesel addition to diesel;⁵² currently, the biodiesel market in Argentina is going through one of the worst phases, as official data show exports interruption has led to a fall of more than one third of the biodiesel production activities since 2019^{53,54}</p>	soybean oil ⁵⁵
Canada	<p>British Columbia, Alberta, Saskatchewan, Manitoba and Ontario established from 2 to 4% biodiesel addition to diesel between 2006 and 2010;⁵⁶ the 2020 map featured nine biodiesel plants in Canada with nearly 598 million liters of capacity; in addition, plants with production capacity of over 126 million liters are either under construction or expansion⁵⁶</p>	canola, animal fat and recycled oils ⁵⁷
United States	<p>most biodiesel users have the B20 blend available;⁵⁸ government incentives facilitate biofuel diffusion since regulated fleet using B20 or more, qualify for biodiesel use credits under the Energy Policy Act of 1992;⁵⁹ B100 and other high-level biodiesel/diesel blends are less common than B20, as well as there also are the lower blends; this is due to lack of regulatory incentives and pricing;⁵⁸ in 2020, 134 million gallons of biodiesel were produced, which means 1 million gallons extra when compared to 2019⁶⁰</p>	soybean oil ⁶⁰
China	<p>there is no mandate for biodiesel addition, except for a small trial in two counties from the Hainan province;⁶¹ most of the produced biofuel is used by industries, only about 30% of it is used for transportation purposes;⁶¹ oil companies own 90% of gas stations and they have not encouraged biodiesel use⁶¹</p>	used cooking oil (UCO) ⁶¹
Japan	<p>B5 is used in cars, buses and trucks;⁶² the Ministry of Economy, Trade and Industry (METI) issues licenses for operators to use biodiesel at rates higher than 5% in trucks and buses;⁶² the use of biodiesel by small-scale power plants and large-scale oil-fired power plants increased from 2016 on⁶²</p>	used cooking oil (UCO) ⁶²
India	<p>the biodiesel distribution in the market remains minimal; the biodiesel share in domestic market will probably grow if a commercially viable support strategy would be developed to boost a sustainable biodiesel industry;⁶³ the National Biodiesel Mission (NBM) identified jatropha (<i>Jatropha curcas</i>) as the least edible oilseed to be applied in order to reach the 20% biodiesel-addition target set in 2017; however, the target was not reached due to agronomic and economic issues;⁶³ currently, the policy Biofuels-2018 approved by the government envisages an indicative target of 5% biodiesel in diesel by 2030⁶⁴</p>	used cooking oil (UCO), unusable oil fractions, animal fats and inedible oils ⁶³
Indonesia	<p>the success in the Indonesian biodiesel blending industry is derived from the biodiesel support program; this was financed by a charge on exports of palm oil and its by-products;⁶⁵ the Oil Palm Estate Fund (BPDPKS) was launched by presidential ordinance 61/2015 and it is responsible for managing the funding;⁶⁵ the government plans to expand biodiesel subsidies in order to cover the palm oil-blended fuel consumption by the mining sector;⁶⁶ in 2019, Indonesia adopted the B30 programme, which has been expanded from a previous one with 20% bio-content; the government aims start testing for 40% bio-content in the fuel soon⁶⁷</p>	palm oil ⁶⁸

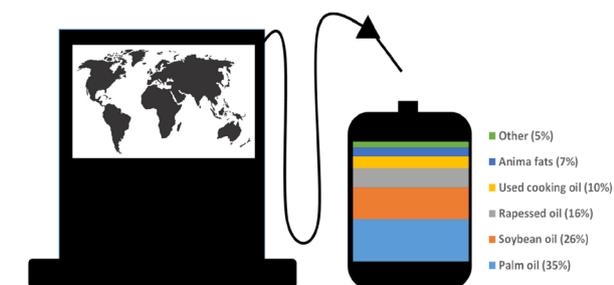
Table 2. Summary of actions and feedstocks used to introduce biodiesel in the G20 countries energy matrices (cont.)

Country	History of actions and current situation	Feedstocks
Saudi Arabia	the economy depends exclusively on its oil sources; therefore, there is no biodiesel production in the country ⁶⁹	–
Turkey	between 2003 and 2006, many biodiesel production facilities were launched in the country; ⁷⁰ the Turkish Energy Regulatory Agency (EMRA) announced in 2011 biodiesel addition (1%) would be mandatory from 2013 and 2014; ⁷⁰ however, the Turkish government did not specify any criteria to the initial stages of the biofuel-sector establishment; there also are no incentive programs for encouraging new investments in biodiesel facilities ⁷⁰	vegetable oil waste ⁷⁰
Mexico	the first law on the Promotion and Development of Bioenergetics was put in force in 2008; ⁷¹⁻⁷³ in 2015, the Law Reform Initiative for the Promotion, Development and Introduction of Renewable Biofuels was issued; it determined the compulsory production and use of biofuels throughout the country; ⁷¹⁻⁷³ after 2018, all gasoline and diesel sold in gas stations should be added with 5.8% (v v ⁻¹) bioethanol and biodiesel, respectively; ⁷¹⁻⁷³ biofuel additions are expected to increase to E10 and B10 by 2021 ⁷¹⁻⁷³	UCO generated by the food industry ⁷⁴
Australia	B5 is the most common biofuel blend used in Australia; ⁷⁵ in turn, B20 biodiesel is often sold for commercial operations; however, biodiesel-use mandates do not cover the country as whole ⁷⁵	animal fats (tallow) and used cooking oil ⁷⁵

2. Feedstocks for Biodiesel Production

In general, vegetable and animal raw materials rich in oils and fats can be used to produce biodiesel. However, it is not easy to find an ideal feedstock for the production of biofuel for internal combustion engines. In regard to economic viability, critical factors such as acreages planted, energy consumption, water quality/quantity⁷⁶ and the possible competition with food and/or pharmaceutical industries, among other possibilities, should be considered carefully. A typical example is the use of jatropha oil for the production of biodiesel in African countries and India. The plant grows in semi-arid regions and has been acclaimed for its alleged ability to resist pests. On the other hand, a large amount of water is needed for irrigation and a large cultivation area is required, creating a potential conflict with food production.⁷⁷

Vegetable oils are a fundamental raw material for biodiesel production. Globally, the most important feedstocks for biodiesel production are palm oil (35%), soybean oil (26%) and rapeseed oil (16%).⁷⁸ Figure 3 shows the percentage distribution of feedstocks used in the biodiesel production throughout the world. In Brazil, the

**Figure 3.** Feedstocks most utilized in the world for biodiesel production.

major source for biodiesel production during 2010-2019 were soybean oil and animal fats (Table 3).⁷⁹

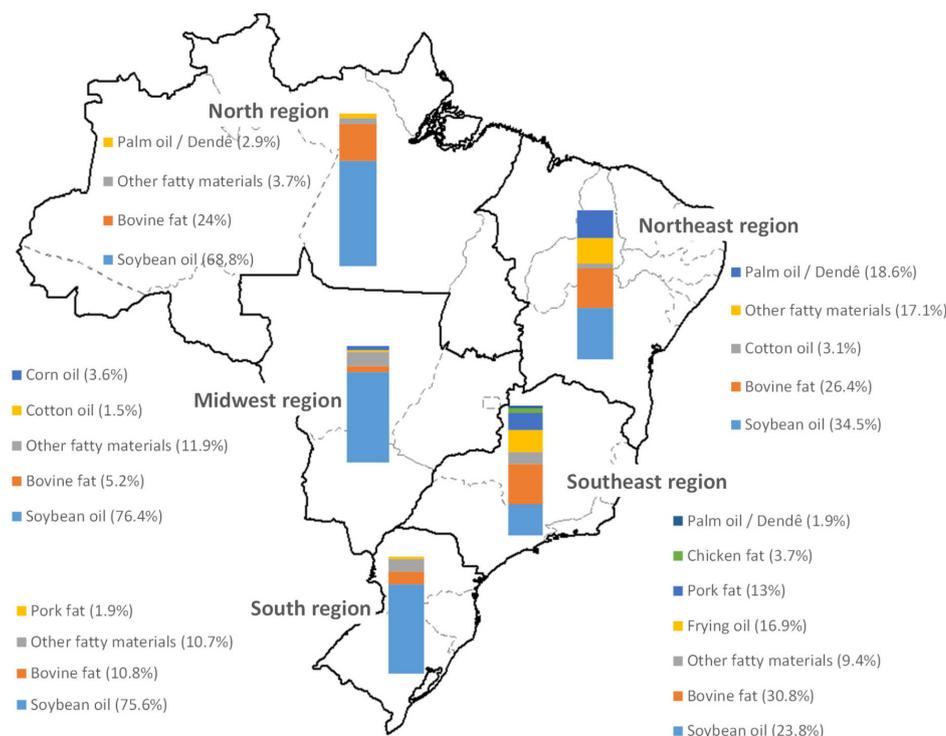
In turn, the map below (Figure 4) shows the main raw materials used in the biodiesel production, distributed according to the Brazilian regions, in 2019. Soybean oil has been the main feedstock for production of biodiesel in all regions of Brazil.⁸⁰ Table 4 shows that soybean oil was the main raw material during all months in 2019, while bovine fat and other fatty materials took turns between the second and third sources of biodiesel production.⁸⁰ Even though soybean does not have the highest oil content (among those feedstocks), this commodity has well-established crops traditionally used in the Brazilian food industry. From Table 4 it also is observed Brazil follows a general trend of reusing urban waste, such as the employment of cooking oil for biodiesel production.⁸¹

Since our last review in 2005,¹⁵ several other oil and fat sources have been investigated for biodiesel production, such as amaranth seeds (*Amaranthus palmeri* L.),⁸² apricot (*Prunus armeniaca* L.),⁸³ papaya seed oil and stone fruit kernel oil,⁸⁴ safflower (*Carthamus tinctorius* L.) oil,⁸⁵ *Moringa oleifera*,⁸⁶ *Calophyllum inophyllum*,⁸⁷ *Styrax officinalis* L. seed,⁸⁸ broiler chicken waste,⁸⁹ duck tallow,⁹⁰ macroalgae,⁹¹ microalgae (*Aurantiochytrium* sp. KRS101,⁹² *Auxenochlorella protothecoides*,⁹³ *Botryococcus braunii*,⁹⁴ *Botryococcus* sp.,⁹⁵ *Chlorella protothecoides*,⁹⁶ *Chlorella pyrenoidosa*,⁹⁷ *Chlorella* sp.,⁹⁸ *Chlorella* sp. KR-1,⁹⁹ *Dunaliella tertiolecta*,¹⁰⁰ *Enteromorpha compressa*,¹⁰¹ *Euglena sanguinea*,¹⁰² *Haematococcus pluvialis*,¹⁰³ *Isochrysis* sp.,¹⁰⁰ *Micractinium reisseri* SIT04,¹⁰⁴ *Nannochloopsis*,¹⁰³ *Nannochloropsis gaditana*,¹⁰⁵ *Nannochloropsis* sp.,¹⁰⁶ *Phaeodactylum tricornutum*,¹⁰⁷ *Phormidium autumnale*,¹⁰⁸

Table 3. Feedstocks for biodiesel production in Brazil (2010-2019), in volume

Feedstock	Volume / m ³				
	2010	2011	2012	2013	2014
Total	2,387,639	2,672,771	2,719,897	2,921,006	3,415,467
Soybean oil	1,980,346	2,171,113	2,105,334	2,231,464	2,625,558
Animal fat ^a	302,459	358,686	458,022	578,427	675,861
Cotton oil	57,054	98,230	116,736	64,359	76,792
Other fatty materials ^b	47,781	44,742	39,805	46,756	37,255
	2015	2016	2017	2018	2019
Total	3,938,873	3,817,055	4,289,351	5,303,632	5,908,237
Soybean oil	3,061,027	3,020,819	3,072,446	3,703,066	4,037,087
Animal fat ^a	738,920	622,311	720,935	860,194	830,761
Cotton oil	78,840	39,628	12,426	49,175	66,577
Other fatty materials ^b	60,086	134,297	483,544	691,197	973,813

^aIncludes bovine, chicken and pork fat; ^bincludes palm oil, peanut oil, turnip oil, sunflower oil, castor oil, sesame oil, canola oil, used cooking oil and other fatty materials. Data from ANP.⁷⁹

**Figure 4.** Major biodiesel sources according to Brazilian regions in 2019. Note: only raw materials above 1% are represented. Data from ANP.⁸⁰

Scenedesmus obliquus,¹⁰⁹ *Scenedesmus obliquus* SIT06,¹⁰⁴ *Scenedesmus* sp.,¹¹⁰ *Schizochytrium limacinum*,¹¹¹ *Spirulina maxima*,^{112,113} *Spirulina* sp.,¹¹⁴ *Teraselmis* sp.,¹⁰⁰ *Thalassiosira pseudonana*,¹⁰⁷ *Tribonema minus*,¹¹⁵ mustard oil,¹¹⁶ mutton fat,¹¹⁷ peanut oil,¹¹⁸ pine and kapok oil,¹¹⁹ pumpkin seed (*Cucurbita pepo* L.),¹²⁰ *Sapindus mukorossi*,¹²¹ soapnut oil,¹²² spent coffee grounds,^{123,124} turnip oil (*Raphanus sativus* L.),¹²⁵ waste fish oil,¹²⁶ waste sewage sludge,¹²⁷ chicken fat,¹²⁸ insects¹²⁹ and yeasts,¹³⁰⁻¹³² among other materials.

Microalgae biomasses, named as third generation energy, are one of the most important raw material alternatives for biodiesel production.¹³³ Many microalgae have advantages over conventional terrestrial crops, such as the possibility of establishing companies at low commercial value lands or devastated areas, the continuous crop production, and possibility of using wastewater.¹³⁴ In the literature there are several strategies suggested for increasing the potential microalgae use as a feedstock for biodiesel production.^{104,135-146} Although it is a promising

Table 4. Feedstocks for biodiesel production in Brazil (2019)

Feedstock	January	March	May	July	September	November
Soybean oil / %	67.00	68.30	73.25	73.13	66.71	53.7
Bovine fat / %	12.47	12.99	10.73	8.12	12.11	8.84
Other fatty materials / %	12.55	12.82	10.52	12.50	12.79	30.85
Palm oil/dendê / %	3.17	1.31	2.13	1.80	2.14	2.03
Pork fat / %	2.00	2.05	1.52	2.04	1.94	1.51
Frying oil / %	1.88	1.46	0.96	1.50	1.48	1.10
Cotton oil / %	0.57	0.62	0.48	0.55	2.20	1.47
Chicken fat / %	0.36	0.45	0.41	0.81	0.63	0.50

Data from ANP.⁸⁰

alternative, it still is at very early stage of development. In addition, the use of conventional microalgae production technologies involves high investments and results in high production costs for biofuel.¹⁴⁷⁻¹⁴⁹

In addition to economic viability in the production of biodiesel, the raw material must be able to synthesize secondary metabolites with appropriate physical-chemical characteristics in order to produce biodiesel with good quality. The viscosity of the biodiesel is directly related to the structural characteristics of some constituents such as fatty acids. Biodiesels mainly produced from saturated and linear chain fatty acids generally have higher melting points and tend to solidify at lower temperatures. On the other hand, biodiesels constituted principally from branched-chain fatty acids are likely to be more fluid.¹⁵⁰ The use of methyl-esters biodiesel by blending it with ethyl esters is a strategy for improving the cold flow properties of biodiesels based on oils with a high content of saturated esters.¹⁵¹ Biodiesel with a high content of unsaturated chains is likely to lead to poor oxidative stability. For example, although the microalgae *Dunaliella tertioleta* has high growth rate and the ability to grow in a brackish environment being a good candidate for biofuel production, a high content of linolenic acid (C18:3) may lead to poor oxidative stability.¹⁵²

The percentage of free fatty acids in the biodiesel matrix is another factor should be taken into account. As the triacylglycerides transesterification usually occurs via basic catalysis, if fatty acids are present, emulsification generally occurs, which makes it difficult the biodiesel purification. Additionally, it causes the catalyst consumption.¹⁵³ For instance, castor seeds (*Ricinus communis*), with the presence of highly toxic proteins (such as ricin) and other allergenic compounds,¹⁵⁴ was considered an alternative for biodiesel production.¹⁵⁵ Although it has a high oil content with the seeds usually containing 40-50% vegetable oil, they also contain very high levels (90%) of ricinoleic acid (12-hydroxy C18:1^{Δ9}). Efforts have been made in order to overcome those problems in the biodiesel production in the

presence of free fatty acids.¹⁵⁶ If problems like those ones could be circumvented, raw materials rich in free fatty acids such as castor seeds could have participation in the biodiesel production. This possibility becomes advantageous for less developed Brazilian regions, since this feedstock normally demands less water for its cultivation.¹⁵⁵

2.1. Genetic engineering of feedstocks for biodiesel production

In *Biodiesel: An Overview*¹⁵ we mentioned “It may be possible in the future to improve the properties of biodiesel by means of genetic engineering of the parent oils, which could eventually lead to a fuel enriched with certain fatty acids, possibly oleic acid, that exhibits a combination of improved fuel properties.” in a reference to Knothe’s article,¹⁵⁷ published in the same year. In the future, genetic engineering’s advances will help the production of fatty acids for biodiesel production.

In fact, research over the past few years has led to significant improvements in manipulation of organisms in order to improve biodiesel production. Genetic engineering methods for producing biodiesel from various sources including plants, yeasts, and algae are one of the latest technology that can be a promising alternative for creating truly sustainable, technically viable and cost-competitive biodiesel.¹⁵⁸⁻¹⁶⁰ Two strategies widely used to improve raw materials for biodiesel production are genetic engineering for (i) length-chain fatty acids and (ii) for increasing the production of monounsaturated fatty acids.

2.1.1. Genetic engineering of length-chain fatty acids

Fatty acids are biosynthesized *in vivo* by either a multifunctional fatty acid synthase type I (FAS I) in eukaryotic cells or the discrete fatty acid synthase complex type II (FAS II) in most bacteria.¹⁶¹ In FAS, the acetyl transferase (AT), malonyl-palmitoyl transferase (MPT), keto synthase (KS) and thioesterase (TE) determine the

fatty acyl chain length. Additionally, the acyl-carrier protein (ACP), which carries fatty acyl intermediates from one enzyme active site to another, is also a key chain-length determinant.¹⁶²

In FAS I, the formation of 3-keto-acyl-ACP occurs by the condensation (Claisen reaction) of acetyl-ACP with malonyl-ACP. The 3-keto-acyl-ACP undergoes a series of reactions: stereospecific carbonyl reduction via keto-acyl-ACP reductase (KR), water elimination via hydroxyl-acyl-ACP dehydratase (DH) and stereospecific reduction of the double bond via enoyl-acyl-ACP reductase (ER). The saturated product enters in a sequence of cycles, which each cycle increases two carbons in the carbon chain. For example, for the formation of palmitic acid (C16:0), this cycle is repeated 7 times. When the required chain length is obtained, the fatty acyl chain can be released as an acyl-Coa (fatty acid with coenzyme A as part of a thioester) or free acid (Scheme 1).¹⁶¹⁻¹⁶⁴

Chain length plays an important role for product properties. For example, gasoline-like and diesel-like biofuels require short/medium-chain fatty acids (C8-C14).¹⁶⁵ These compounds have lower viscosity and higher cloud points than long-chain fatty acids (C16-C18).¹⁵⁸ Finding ways to release fatty acyl intermediates of defined lengths as products is one of the main challenges facing metabolic engineers. Both type I and type II FAS have been engineered to increase medium-chain fatty acyl yields.

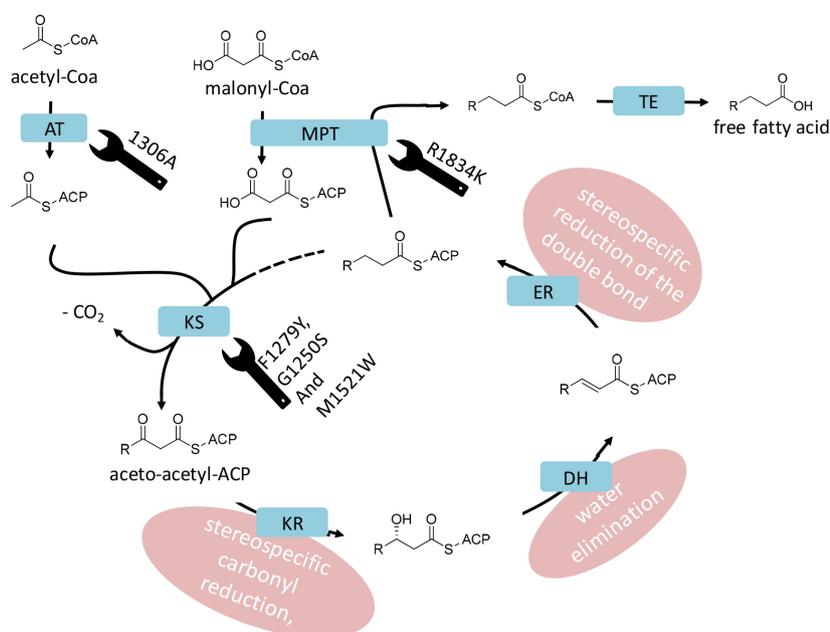
In fungal FAS, the processes of loading of malonyl and unloading of the fully elongated acyl-chain are performed by the MPT domain and the domains KR, DH and ER presumably have no direct influence on chain-length

regulation.¹⁶³ In *Saccharomyces cerevisiae* key active sites of the condensation domain (KS) and the transferase domains (MPT and AT) were rationally engineered. A total of five genes were mutated separately and in several combinations. Three genes of KS (F1279Y, G1250S and M1521W), the domain considered as the most promising target for rewriting chain-length regulation, one gene of MPT domain (R1834K), engineered for reduced malonyl affinity, and one gene of AT(1306A), the domain responsible of loading acetyl in fungal FAS (Scheme 1). The resulting mutated variants of FAS I produced short chain fatty acid, predominantly hexanoic and octanoic, in concentrations which do not occur in the wild type.¹⁶³

2.1.2. Genetic engineering to increase the production of monounsaturated fatty acids

In addition to control the chain length, inexpensive and better quality biodiesel may be produced by changing the level of unsaturation of fatty acids. Blending of a fewer amount of saturated and polyunsaturated fatty acids with a higher amount of monounsaturated fatty acids would potentially yield a better quality biodiesel.¹⁵⁸

Unsaturated fatty acids can arise from more than one synthetic route. In most organisms the mechanism is done by a desaturation of the corresponding saturated fatty acid. Most eukaryotes organisms have an enzyme Δ^9 -desaturase which introduces a double bond with *Z* (*cis*) geometry in the fatty acid. The enzyme can be named in two ways according the position ability of desaturation: from the carboxyl extremity until the unsaturation, designed with the symbol Δ , and from the methyl extremity until the



Scheme 1. Biosynthesis of saturated fatty acids.

unsaturation, which is represented with the symbol ω . The Z-configuration of the double bond introduces a 'bend' into the alkyl chain. This interferes with the close association and aggregation of molecules (possible in saturated structures), which helps to maintain the oils and cellular membranes fluidities.¹⁶⁴

Soybean oil is composed of five fatty acids: palmitic acid (16:0), stearic acid (18:0), oleic acid (18:1), linoleic acid (18:2), and linolenic acid (18:3). The average percentages of these five fatty acids in soybean oil are 10, 4, 18, 55 and 13%, respectively. This fatty acid profile results in low oxidative stability (oxidative breakdown of soybean oil), which results in materials in soybean-derived biodiesel that clogs oil filters. Oxidative instability of soybean oil is due to the relatively high percentages of the polyunsaturated fatty acids, such as linoleic and linolenic acids.¹⁶⁶ In biodiesel a monounsaturated oleic acid (C18:1) is a preferred component as an acyl chain in triacylglycerols, because of its high cetane value, low melting point, and resistance to oxidation.¹⁶⁷

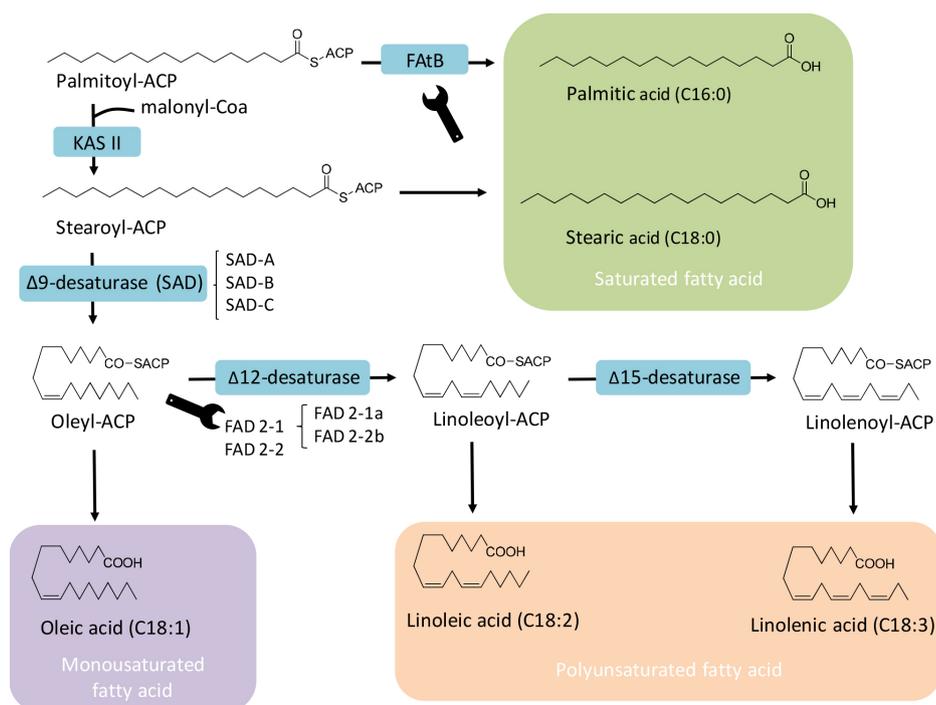
Soybean seeds have thioesterases, which have preference for palmitoyl- and oleoyl-ACPs.¹⁶⁸ Palmitic acid (C16:0) is formed from palmitoyl-ACP by catalytic action of fatty acid thioesterase A (FatB), an acyl-ACP thioesterase enzyme. Towards condensation reaction between palmitoyl-ACP and malonyl-ACP by action of the enzyme β -ketoacyl synthase II (KAS II), stearoyl-ACP is formed. Stearoyl-ACP- $\Delta 9$ -desaturase (SAD) converts stearoyl-ACP in oleyl-ACP. The enzyme $\Delta 12$ -desaturase

produce linoleoyl-ACP from oleyl-ACP toward a single desaturation step. Linolenoyl-ACP is biosynthesized from linoleoyl-ACP by catalytic action of enzyme $\Delta 15$ -desaturase (Scheme 2).^{154,168}

The $\Delta 12$ -desaturase enzyme is encoded by the FAD2 gene. There are two FAD2 gene families in soybean, designated as FAD2-1 and FAD2-2.¹⁶⁹ Two different FAD2-1 genes are present in the soybean genome, designated as FAD2-1a and FAD2-1b. Down regulation of FatB would result in decreased levels of saturated fatty acids, primarily a reduction in palmitate, whereas down-regulation of FAD2-1 results in elevated levels of oleate and a reduction in polyunsaturated fatty acids.¹⁷⁰ The expression of FAD2-1 and FatB was simultaneously down-regulated in a seed-specific fashion, thereby generating soybean oil with a reduced level of palmitic acid content (< 5%) and significantly increased oleic acid content (> 85%) (Scheme 2).¹⁷⁰

These genetic events result simultaneously in the accumulation of oleic acid and a concomitant decrease in polyunsaturated and saturated fatty acids, but not compromised in agronomic performance, including the overall yield, total protein/oil and amino acid profile. Moreover, the biodiesel produced from this extruded oil improved cold flow and enhanced oxidative stability.¹⁷¹

Although several genetic engineering processes to improve biodiesel production have yielded satisfactory results at laboratory scale level, commercialization requires scaling up of these processes. In addition, scaling up should reach very high yields and productivities without



Scheme 2. Biosynthesis of unsaturated fatty acids.

losing performance, which is the greatest challenge in commercialization.¹⁵⁸ From the perspective of sustainability, it would be unwise to rely on a single feedstock source to meet diesel fuel demand, even if supply were sufficient to meet demand. The uncertainties surrounding the production of an oilseed crop, as a result of environmental and biotic imposed stresses, could have a significant impact on yield, and thus on supply, in a very unpredictable manner.¹⁷¹

3. Development of Catalysts for Biodiesel Production

The catalysts can be classified as acid, basic or enzymatic. Yet, they can still be divided into homogeneous or heterogeneous. Figure 5 shows a schematic representation of the various types of catalysts used for biodiesel production with some examples.^{172,173}

Basic homogeneous catalysts usually present higher conversion rate, typically 4,000 times higher than acid

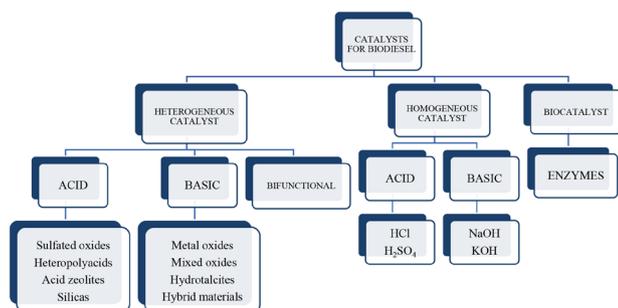


Figure 5. Types of catalysts used in biodiesel production.

Table 5. Types of catalysts used in the production of biodiesel^{12,176-178}

Type of catalyst	Advantages	Disadvantages
Basic and homogeneous	fast reactions and high conversions mild reaction conditions widely available low costs	sensitive to the content of free fatty acids (FFA) formation of soap if the FFA content is greater than 2% difficult purification of the products
Basic and heterogeneous	faster than acid catalysis easy catalyst separation possibility of catalyst reutilization and regeneration reduced purity of the product	sensitive to oils with high levels of FFA formation of soap if the content of FFA is greater than 2% leaching of catalyst active sites
Acid and homogeneous	insensitive to free fatty acid and water content in the oil use of low quality triacylglyceride sources	slower than base catalysis corrosion problems require more severe reaction conditions separation of catalyst from the reaction medium is problematic
Acid and heterogeneous	insensitive to free fatty acid easy separation of the catalyst low quality triacylglyceride sources possibility of catalyst reutilization and regeneration	severe reaction conditions expensive synthesis procedures long reaction times leaching of catalyst active sites
Enzyme	insensitive to free fatty acid and water content in the oil use of low quality triacylglyceride sources low reaction temperatures simple purification steps	long reaction times high cost sensitivity to methanol enzyme deactivation

catalysts, under mild reaction conditions. However, if the free fatty acid content of the feedstock is greater than 2% they cannot be used. The most traditional homogeneous basic catalysts used in the transesterification of oil and fats are NaOH, KOH, CH₃ONa and CH₃OK.¹⁰ Reactions usually occur at temperatures between 40 and 65 °C within 15 and 45 min. On the other hand, homogeneous acid catalysts are insensitive to the presence of free fatty acids in the raw material. Some typical homogeneous acid catalysts are H₂SO₄, HCl and H₃PO₄. However, reactions are slower compared to basic catalysis.²⁴ Some studies^{174,175} have been carried out to develop heterogeneous catalysts for biodiesel production. They allow a number of advantages, such as the possibility of reutilization, regeneration, easy separation of the reaction medium and production of high purity glycerol.^{174,175} Table 5 shows a summary of the different types of catalysts used in the production of biodiesel with their related advantages and drawbacks.

The industrial application of heterogeneous catalysis in biodiesel production is still not viable on a large scale. Most of these catalysts are expensive and show lower catalytic activity when compared to traditional basic homogeneous catalysts. In addition, much of the materials cited in the literature are deactivated due to leaching of the active phase or poisoning of the active sites, caused by impurities present in the raw material or even after exposure of the catalyst to atmospheric air. In some cases, the regeneration of the catalyst can be carried out by heat treatment, when the material withstands high temperatures. In other cases, regeneration is difficult or not effective. Up to now, there

is no promising heterogeneous catalyst for large-scale application. On the other hand, environmental pressures related to waste disposal of the transesterification process, such as washing waters, have motivated studies for the implementation of a heterogeneous catalysis process, and above all, continuous. Solving the problem of leaching and deactivation of heterogeneous catalysts would enable the implementation of continuous processes, with fewer steps of product purification, also including glycerin, which ends up contaminated with most of the homogeneous catalyst.

3.1. Heterogeneous basic catalysts

Alkaline earth oxides, such as CaO, MgO and SrO, hydrotalcites and silica grafted amines are the most common heterogeneous basic catalyst used in the transesterification of oils and fats for biodiesel production.¹⁷⁹ CaO is environmentally friend, non-toxic, low cost and presents low solubility in methanol. In addition, CaO can be derived from natural sources.^{180,181} Roschat *et al.*¹⁸⁰ tested CaO obtained from several sources as a catalyst in the production of biodiesel from palm oil. About 94% yield of biodiesel was obtained with 12:1 molar ratio methanol-to-oil for 5 h at room temperature (30 °C) and 5 wt.% of catalyst loading. Reutilization tests showed the catalyst can be reused for 4 cycles with conversions above 90%. However, conversion was drastically reduced after 9 cycles, which was mostly ascribed to the exposure to the atmosphere, forming Ca(OH)₂ and CaCO₃ upon reaction with moisture and CO₂, respectively.

Mixed oxides of CaO-La₂O₃, with 1 wt.% of lithium, were tested in the transesterification of canola oil and methanol for biodiesel production. The calcination temperature of the catalyst affected the surface area and basicity of the material. Around 96% yield in methyl esters was observed with 15:1 molar ratio methanol-to-oil for 2.5 h at 65 °C and 5 wt.% of catalyst loading. After 4 reaction cycles, the conversion decreased to 85.6%. The authors attributed the deactivation to the poisoning of the active sites by CO₂. Leaching tests

showed conversion of only 4% of biodiesel, indicating that it is a minor factor of deactivation.¹⁸²

Hydrotalcites are anionic clays of general formula $[M^{2+}_{(1-x)}M^{3+}_x(OH)_2]^{x+}[A^{n-}]_{x/n} \cdot yH_2O$, where M²⁺ and M³⁺ are di- (e.g., Ca²⁺, Mg²⁺, Zn²⁺) and trivalent (frequently Al³⁺) cations in octahedral positions, Aⁿ⁻ an anion (e.g., CO₃²⁻, NO₃⁻, Cl⁻) and n is within the 0.1-0.5 range. In the absence of calcination, hydrotalcites do not present significant catalytic activity for biodiesel production. The decomposition of hydrotalcite results in a high surface area material of a mixed oxide that exposes strongly Lewis basic sites.¹⁸³⁻¹⁸⁵ Navajas *et al.*¹⁸⁶ tested hydrotalcites of Mg/Al using a 12:1 molar ratio methanol-to-oil for 8 h at 60 °C and 2 wt.% of catalyst loading. About 50% conversion of sunflower oil was observed at these conditions. Nowicki *et al.*¹⁸⁷ prepared Zr-doped Mg-Al hydrotalcites with different Zr/Mg molar ratios. The catalysts were prepared by the co-precipitation method, calcined at 500 °C for 3 h and tested on the transesterification of rapeseed oil using 12:1 molar ratio methanol-to-oil for 6 h at 100 °C and 8 wt.% catalyst loading. The yield of biodiesel was 99.8%.

Mesoporous materials, such as MCM-41 and SBA-15, are formed by siloxane groups in the interior of the pores and silanols groups on the outer surface, where organic or inorganic groups can be grafted (Figure 6). Mesoporous materials present several applications. Among them, as support of heterogeneous catalysts.¹⁸⁸

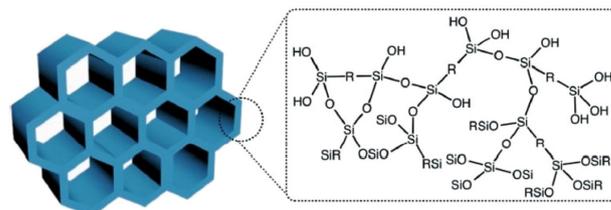


Figure 6. Ordered structure of MCM-41.¹⁷⁸

The amine 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) was anchored on silica MCM-41 (Figure 7) material by the post-synthesis¹⁸⁹ and co-condensation methods.¹⁸⁸ The

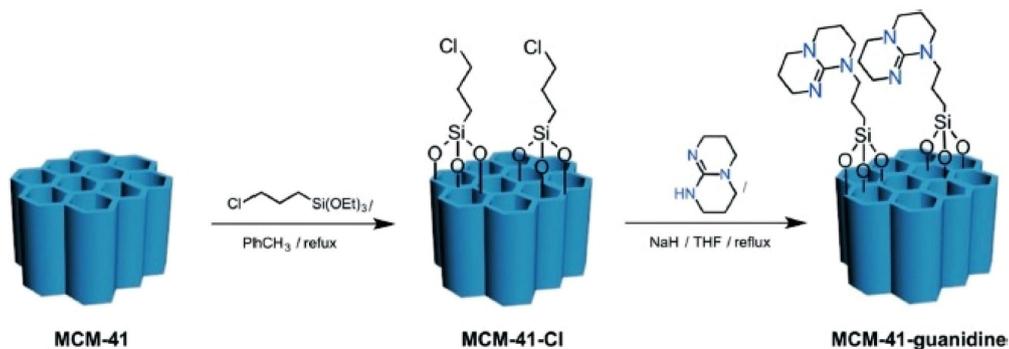


Figure 7. Synthesis of MCM-41-TBD by the post-synthesis methods.¹⁸⁹

post-synthesis method favors the functionalization of the active sites on the external surface and at the entrance of the pores, whereas co-condensation allows a better dispersion of the active sites with more internal functionalization. The materials were tested on the transesterification of soybean oil under mild reaction conditions reaching 99% biodiesel conversions. The loss of catalytic activity during reuse was attributed to some leaching, but mainly to the neutralization of the active sites by the small amount of free fatty acids present in the oil.

SBA-15 materials loaded with calcium were used in the transesterification of sunflower oil with methanol at 200 °C for 8 h. The yield of biodiesel at these conditions was 99.1%. Reutilization tests showed no loss of catalytic activity after 5 reaction cycles. The catalysts were simply removed, washed with methanol and dried for further application. The author suggests that the strong interaction between calcium and SBA-15 support (CaSiO_3) actually occurred.¹⁹⁰

Zeolites are crystalline aluminosilicates with interconnected cavities and channels, forming pores of molecular dimensions. Many ions, such as Na^+ , Ca^{2+} , Mg^{2+} and K^+ can be exchanged on the zeolite structure. This group includes a large number of natural and synthetic minerals that have adsorption capacity, ionic selectivity and are denominated “molecular sieves” because of their crystalline structure. Figure 8 shows some zeolite structures.¹⁹¹⁻¹⁹³

The transesterification of sunflower oil with methanol was carried out with three different zeolites: mordenite, beta and X, impregnated with sodium metal. The reactions were carried out at 60 °C for 7 h, using 6:1 molar ratio methanol-to-oil, 10 wt.% of catalyst loading and stirring rate of 500 rpm. The yield of biodiesel was 95.1% for zeolite X, 65.4% for zeolite beta and 12.7% for mordenite. The higher catalytic activity of zeolite X can be explained by the greater number of strong basic sites.¹⁹⁴ Zeolite X impregnated with sodium was tested in 3 consecutive catalytic cycles and the biodiesel yield decreased from 95.1 to 4.7%. The loss of catalytic activity can be explained by the leaching of the active species, showing that the sodium

species occluded in the zeolite pores are responsible for the high catalytic activity of the catalyst.¹⁹⁴ Table 6 shows some selected studies on the use of heterogeneous basic catalysts in transesterification of vegetable oil with methanol for biodiesel production.

3.2. Heterogeneous acid catalysts

The use of heterogeneous acid catalysts allows the use of low quality raw material, with high levels of fatty acids and water, as well as the easy separation of the catalyst and possibility of reutilization. Various materials can be highlighted, such as sulfated metal oxides, acid zeolites, mesostructured silica materials, heteropolyacids, ionic liquid and solid acid catalysts derived from biomass, such as biochar, activated carbon, biomass residue and refined carbohydrate.^{243,244}

Jiménez-Morales *et al.*²⁴⁵ incorporated aluminum atoms into the structure of SBA-15 by the post-synthesis method. The acidity of the material was linked to the aluminum content and the activation temperature. Transesterification of sunflower oil with methanol at 200 °C for 4 h, using 12:1 molar ratio methanol-to-oil and 600 rpm agitation, yielded 82% of biodiesel. The catalyst was reused in three successive reactions, with no pre-treatment, with a loss of 7% of the catalytic activity. Deactivation was explained in terms of the blocking of the active sites of the catalyst. Chemical analysis did not indicate any loss of aluminum atoms, confirming there was no leaching of the active phase.

Heteropolyacid, such as $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (HPMo) supported on niobia, was tested in the reaction macaw palm oil, with high content of free fatty acids, using 90:1 molar ratio ethanol-to-oil at 210 °C and 20 wt.% of catalysts. The yield of biodiesel was 99.7%. Reutilization tests indicated a decrease of the yield to 11% after 3 reaction cycles, which was ascribed to the decrease in the acidity of the catalyst due to the blocking of the active sites.²⁴⁶

A matrix of mixed titanium and silicon oxides was tested in the transesterification of waste cooking oil using 30:1 molar ratio of methanol to oil for 4 h at 65 °C and

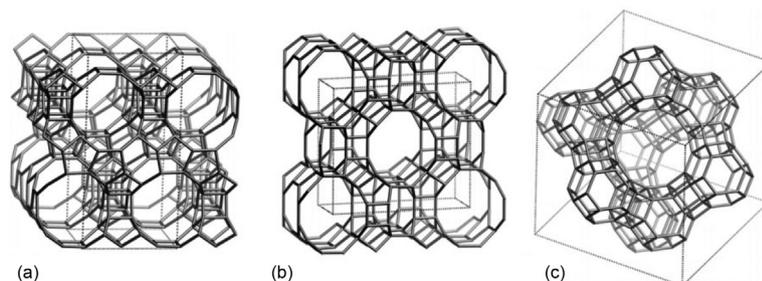


Figure 8. Structure of (a) zeolite beta, (b) zeolite mordenite and (c) zeolite faujasite.

Table 6. Basic heterogeneous catalysts used for biodiesel production

Catalyst	Catalyst loading / wt. %	Vegetable oil	Molar ratio (alcohol:oil)	Temperature / °C	time / h	Yield / %	Reference
CaO	0.4	soybean	14:1	60	2	91	195
CaO	7.5	residual	15:1	65	6	90	196
CaO	5	jatropha	15:1	65	6	89.9	197
SrO	3	palm	9:1	65	1	95.2	198
CaO	6	palm	15:1	65	2	97	199
CaO	8	sunflower	6:1	65	3	95	200
CaO/MgO	3	jatropha	25:1	120	3	90	201
CaO/MgO	2	palm	15:1	60	3	86.6	202
MgO/ZnO	3	jatropha	25:1	120	3	83	203
MgO/ZrO ₂	3	soybean	20:1	150	6	99	204
CaO/La ₂ O ₃	4	jatropha	24:1	60	–	87	205
CaO/MgO	1	soybean	12:1	70	2	98.4	206
CaO/SnO ₂	8	soybean	12:1	70	6	89.3	207
TiO ₂ /MgO	10	residual	50:1	160	6	92.3	208
KBr/CaO	3	residual	12:1	65	1.8	83.6	209
Zr/CaO	15	soybean	15:1	65	3	99	210
CaO/NaY	30	soybean	9:1	65	3	95	211
Ce/HUSY	5	soybean ^a	30:1	200	24	99.8	212
KOH/NaY	10	palm	15:1	60	3	91.1	213
KOH/zeolite	3	palm	7:1	60	2	95.1	214
K/NaX	16	soybean	16:1	60	3	95.2	215
KOH/ZSM5	18	sunflower	12:1	60	24	95	216
K/MgAl	7	palm	30:1	100	6	86.6	217
Na ₂ ZrO ₃	3	soybean	–	65	3	98	218
TMG/SBA-15	5	soybean	15:1	70	12	92	219
MgAl hydrotalcite	4	jatropha	12:1	65	6	75.2	220
MgAl hydrotalcite	2	sunflower	48:1	60	24	96	221
MgAl hydrotalcite	1.5	residual ^b	6:1	80	2.5	95.2	222
MgAl hydrotalcite	2.5	soybean	9:1	65	4	97	223
MgAl hydrotalcite	1	jatropha	4:1	45	1.5	95.2	224
CaFeAl	6	soybean	12:1	60	1	90	225
K/TiO ₂	6	canola	36:1	65	3	81	226
CaO/SiO ₂	5	palm	9:1	65	3	90.2	227
CaO/SiO ₂	5	soybean	16:1	60	8	95.2	228
CaO/MgO/Al ₂ O ₃	12.5	cotton ^a	0.77:1	95	–	94.6	229
KOH/Al ₂ O ₃	15	residual	9:1	70	2	96.8	230
K/γ-Al ₂ O ₃	3	soybean	24:1	60	1	98.5	231
CaO/γ-Al ₂ O ₃	9	palm	15:1	60	3	86.4	232
KOH/ Nd ₂ O ₃	6	soybean	12:1	60	3	89.7	233
KBrO ₃ /Nd ₂ O ₃	6	soybean	12:1	60	3	74.0	233
CaTiO ₃ /CaO	10	sunflower	6:1	60	10	98.1	234
CaSn(OH) ₆	3	sunflower	10:1	65	3	94	235
CaMnO ₃	–	canola	6:1	60	10	92	236
CaO/CoFe ₂ O ₄	1	soybean	15:1	70	5	87.4	237
KNO ₃ /Al ₂ O ₃	6.5	soybean	15:1	65	7	87	238
DCOD /SBA-15	8	soybean	15:1	65	15	93	239
GPMS/silica gel	0.5	soybean	20:1	80	3	99	240
TMPAOH/SBA-15	2.5	soybean	12:1	65	0.5	99	241
TBD/SBA-15	1.05	soybean	–	70	4	100	242

^aReaction with ethanol; ^breaction with both ethanol and methanol. HUSY: zeolite; TMG: 1,1,3,3-tetramethylguanidine; DCOD: 1,3-dicyclohexyl-2-octylguanidine; SBA-15: mesoporous Santa Barbara amorphous-15; GPMS: 3-(*N,N'*-dicyclohexylguanidine)-propyltrimethoxysilane; TMPAOH: tetraalkylammonium hydroxides; TBD: 1,5,7-triazabicyclo[4.4.0]dec-5-ene.

5 wt.% of catalyst loading, yielding 98% of biodiesel. Reutilization tests showed no significant loss of catalytic

activity after 4 successive cycles. Nevertheless, the catalyst needed to be washed, dried and calcined at 700 °C between

the reaction cycles. The loss of catalytic activity in the fifth cycle is due to the leaching of the active species.²⁴⁷

The use of heterogeneous acid catalysts allows the use of raw materials of high free fatty acids (FFA) content, which are cheaper and can be used without the need of additional pre-treatment. It also allows the simultaneous esterification and transesterification of oils with high content of fatty acids.²⁴⁸ Table 7 shows some selected studies on the use of heterogeneous acid catalysts for biodiesel production.

3.3. Enzymatic catalysts

Enzymes, such as lipases, are capable of producing high purity biodiesel at moderate reaction temperatures. However, the reaction rate is slower than acid and basic catalysis and the high cost of the lipases limits its industrial application. In addition, some enzymes deactivate in the presence of methanol. Although it still is an expensive process, the immobilization of enzymes is an interesting alternative. For instance, immobilization of the enzyme in a polymer or resin can make the process less expensive, while allowing the reutilization of the enzyme.²⁶⁹⁻²⁷¹

Enzymatic reactions are insensitive to free fatty acids and water content in the raw material, while demanding lower energy consumption and producing purer glycerol

phase. Notwithstanding, the costs are still high, limiting the process to be used in large scale. Some of the lipases most reported in the literature are: *C. antarctica* (Novozym 435), *Candida* sp. 99-125, *C. rugosa*, *Trichosporon asahii* MSR54, *Yarrowia lipolytica*. Table 8 shows some selected literature on biodiesel production with methanol using enzymatic catalysis.²⁷²⁻²⁷⁴

4. Biodiesel Production Technology

Searching for renewable energy sources to ensure economic development with social inclusion without environmental aggression is a challenge all over the world. Over the years, most of researching related to biodiesel production pursues alternative production routes which maintain the high reaction yields. Furthermore, it is interesting these new production routes decrease the operating cost of the processes, which is one of the main disadvantages for the economic viability of biodiesel production and commercialization. The transesterification process is the main technology to produce biodiesel in industrial units in Brazil. Nowadays, that production occurs mostly on an experimental scale with plants of small capacity.

The biodiesel price to the consumer is lower than fossil diesel. This can be explained by the reduction of governmental taxes.²⁹⁵ The strategy in Brazil is decreasing

Table 7. Acid heterogeneous catalysts used for biodiesel production (with methanol)

Catalyst	Catalyst / wt.%	Vegetable oil	Molar ratio (alcohol:oil)	Temperature / °C	time / h	Yield / %	Reference
TiO ₂ /SO ₄ ²⁻	2	cottonseed	12:1	230	8	90	249
ZrO ₂ /SO ₄ ²⁻	1	palm kernel	6:1	200	1	90.3	250
[CyN _{1,1} PrSO ₃ H][p-TSA]	3	palm	24:1	120	2.5	98.4	251
CS _{2,5} H _{0,5} PW ₁₂ O ₄₀	3	sesame	40:1	260	1	92	252
Sugarcane bagasse-H ₂ SO ₄	1	waste cooking	18:1	66	5	94	253
Cellulose-H ₂ SO ₄	10	waste cooking	20:1	80	3	95	254
Rice husk char-H ₂ SO ₄	5	waste cooking	20:1	110	15	87.5	255
Sulfonated lignin	10	waste vegetable	35:1	65	6	56.8	256
SO ₄ ²⁻ /ZrO ₂ /MCM-41	14.6	sunflower ^a	12:1	200	6	91.5	257
SO ₄ /Fe-Al-TiO ₂	3	waste cooking	10:1	90	2.5	96.0	258
SO ₄ ²⁻ /TiO ₂ -SiO ₂	3	waste cooking	9:1	200	6	92.0	259
Sulfonated carbon	5	corn acid	1:19.95	65	4.5	91.7	260
[BHSO ₃ MIM][HSO ₄]	9.17	palm	11:1	108	6.43	98.9	261
Montmorillonite clay	5	jatropha	6:1	110	2.5	98.0	262
Sulfonated graphene	10	palm	20:1	100	10	98.0	263
Sulfonated carbon	5	waste palm	12:1	65-70	12	92.6	264
CexH _{3,3x} PW ₁₂ O ₄₀	2.2	waste cooking	21:1	65	12	98.0	265
Carbonized coconut	6	palm	30:1	60	6	88.2	266
FeCl ₃ -resin	8	waste cooking	10:1	90	2	92.0	267
KIT-5-PTA	26.5	waste cooking	6:1	70	4	93.0	268

^aReaction with ethanol.TSA: toluene sulphonic acid; MIM: methylimidazole; PTA: phosphotungstic acid.

vehicle emissions, without changes in conventional diesel engines according to the government law.³⁰ The reduction of taxation is very important for biodiesel be used in high proportion.

Biodiesel is mostly produced by the transesterification of triacylglycerides (usually vegetable oils, but it also can be an animal fat or recycled oil). Despite the enormous limitations of homogeneous catalysts, most biodiesel is produced using alkaline and homogeneous catalysis. This is due to the fact it is much faster kinetically than transesterification using solid catalysts and economically viable. Extensive research is being conducted to develop basic heterogeneous catalysts, as discussed on section 3. In addition to the advantages mentioned in the previous section, the use of heterogeneous catalysts does not produce soaps by neutralizing free fatty acids. However, there are still major bottlenecks to be overcome because these processes require expensive refined vegetable oil as a raw material and are sensitive to water and free fatty acid content in the raw material.

In the current process, the triacylglycerides are stored and, after acid correction, it is transferred to the principal reactor. Then, either vegetable oil, animal fat or recycled oil reacts with an alcohol (methanol or ethanol) in the presence of a catalyst (KOH or NaOH) producing a mixture of fatty acid alkyl esters and glycerol.^{296,297} The reaction is completed within 40 min, at temperatures between 30 and 40 °C.

Following, it is necessary a separation step of the biodiesel (main product) from the raw glycerine (secondary product) by decantation or centrifugation. The separation step is one of the most important steps in the biodiesel production, since it is essential for the product specification according to legislation.²⁹⁸ The fuel should have similar characteristics to conventional diesel in terms of their main characteristics. In the case it does not scope the requested specification, it needs to be reprocessed. The type of material, reagents and operational conditions (temperature, catalyst, alcohol-to-oil molar ratio, and reaction time) used in the transesterification influence the biodiesel yield.¹

Generally, alcohol in excess is used in order to increase the biodiesel yielding and to permit its phase separation from the glycerine formed during the transesterification reaction. In turn, the alcohol content in the glycerine can be recovered and reused in the process. Accordingly, glycerine can be purified and utilized, for instance, in the cosmetic and personal care applications, pharmaceutical applications, and paper industry, among others.²⁹⁹

During the transesterification process several steps are required to separate the main product due to the formation of saponified materials. Besides that, another disadvantage of the transesterification process is the raw materials characteristics, which should have low water content and low acidity. In this context, new alternative routes have been researched over the years in order to overcome

Table 8. Enzymatic catalysts used for biodiesel production with methanol

Catalyst	Vegetable oil	Temperature / °C	time / h	Yield / %	Reference
<i>Candida antarctica</i> (Novozym 435)	sunflower oil	45	50	> 99	275
<i>Candida antarctica</i> (Novozym 435)	cotton seed oil	50	7	91.5	276
<i>Candida antarctica</i> (Novozym 435)	palm kernel oil ^a	40	4	63	277
<i>Candida antarctica</i> (Novozym 435)	cotton seed oil	50	24	97	278
<i>Candida antarctica</i> (Novozym 435)	rapeseed oil	35	12	95	279
<i>Candida</i> sp. 99-125	soybean oil	40	24	98.8	280
<i>Pseudomonas fluorescens</i>	sunflower oil	40	48	91	281
<i>Candida antarctica</i> (Novozym 435)	sunflower oil	50	15	97	282
Lipozyme IM-77	soybean oil	36.5	6.3	92.2	283
PS 30 lipase	palm oil ^a	40	8	72.0	284
<i>E. aerogenes</i> lipase	jatropha oil	55	48	94.0	285
<i>P. fluorescens</i> lipase	soybean oil	35	90	80.0	286
<i>IM M. miehei</i> lipase	soybean oil ^a	35	8	95.6	287
<i>IM B. cepacia</i> lipase	palm oil	30	72	100	288
<i>Candida rugosa</i>	soybean oil	35	30	87.0	289
<i>Rhizopus oryzae</i>	jatropha curcas	30	60	80.0	290
<i>Penicillium expansum</i>	corn oil	40	24	86.0	291
<i>Geotrichum</i> sp.	waste cooking oil	50	4	85.0	292
<i>Thermomyces lanuginose</i>	crude palm oil	40	4	96.2	293
<i>R. miehei</i> lipase	sunflower oil	40	48	95.5	294

^aReaction with ethanol.

those disadvantages. For instance, we can refer to the hydro-esterification process, which is a good alternative process for reducing costs related to the separation step. Hydro-esterification is a process that allows the use of any fatty raw material, mainly with high contents of free fatty acids and water. This process is divided in two consecutive steps, hydrolysis followed by esterification. The hydrolysis step consists of chemical reaction between oil and water, producing glycerine and fatty acids. After hydrolysis, the fatty acids are esterified with alcohol (methanol or ethanol), resulting biodiesel in high purity.³⁰⁰ Another alternative is the simultaneous esterification and transesterification of vegetable oils with high content of free fatty acid using heterogeneous acid catalysts. These studies have been mentioned in detail on section 3.

The use of sonication during the transesterification and esterification reactions for producing biodiesel has also been explored. The ultrasound-assisted process not only accelerates the reaction rate but also favors the miscibility between oil and methanol, decreasing the amount of catalyst needed for the reaction. Malek *et al.*³⁰¹ published a review containing a number of studies with this technology. The use of microwave energy is also worth mentioning. The short reaction time is one of its biggest advantages. On the other hand, this technology cannot be easily scaled-up. There are reviews focusing specifically on the microwave-assisted transesterification processes using homogeneous and heterogeneous catalysts for biodiesel production.³⁰² The results achieved from the use of intensification technologies have been well documented in several reviews available in the literature, which also present advantages, disadvantages and the current status of these technologies.³⁰³ Different reactor technologies for biodiesel production are also discussed in detail by Tabatabaei *et al.*³⁰⁴

Another alternative that can be used to produce biodiesel are processes at supercritical conditions. Supercritical fluid has been receiving a special attention in different types of processes due to its unique properties. The change of the fluid properties when within supercritical state is directly related to the density and its high compressibility.³⁰⁵ This difference of density reflects in the fluid coefficient of diffusivity, making the mass transfer easier in the supercritical medium. Besides that, the reaching of gases some properties such as surface tension and low viscosity, promote better dynamic characteristics and greater penetrability for the supercritical fluid.

The use of supercritical conditions in the biodiesel production can occur both in the alcohol used to produce the esters and through the addition of co-solvents in order to reduce significantly the operating conditions. The supercritical alcohol can form a single phase in contrast to

the two-phase of oil/alcohol mixture at ambient condition. This is due to a decrease of the alcohol dielectric constant at supercritical condition. The most commonly used alcohols in conventional biodiesel, methanol (240 °C and 78.7 bar) and ethanol (243 °C and 63.8 bar) production methods have very similar physical characteristics in the supercritical condition.³⁰⁶

The addition of a co-solvent reduces the interfacial tension and promotes better contact between the reactant molecules. Recent studies mainly use water or CO₂ as co-solvent to eliminate the use of the catalyst in the process of biodiesel synthesis.³⁰⁷ Carbon dioxide offers a plenty of advantages as it is inert, non-toxic, non-polar and does not require very high pressure and temperature conditions to reach its supercritical state (31 bar and 73.8 °C). So, it can be used for replacing a non-polar solvent without promoting undesired side reactions of oxy-reductions or breakdown of molecules.³⁰⁸

Recently, Jafari *et al.*³⁰⁹ directly converted wet microalgae biomass impregnated with ethanol in biodiesel using supercritical carbon dioxide. The lipid extraction and the transesterification process occurred simultaneously in a single step.

The use of supercritical medium offers a shorter residence time and higher purity of both products, biodiesel and glycerine, compared to those produced via conventional transesterification or hydro-esterification processes. Nevertheless, the supercritical process requires a higher operating condition. In this process, more robust equipment is necessary to support operating conditions of high pressures. Therefore, the biodiesel production by the supercritical route is still a laboratory condition, economically unfeasible, due to the costs of the process, either by the cost of the equipment to resist high temperatures and pressures, or by the cost of energy.

4.1. Transesterification in supercritical conditions

Transesterification is the traditional biodiesel production process. Therefore, the studies using supercritical conditions are mostly directed towards to this technological route.

According Dermibas,³¹⁰ Saka and Kusdiana³¹¹ and Dermibas,³¹² transesterification with supercritical methanol requires less reaction time to reach high methyl ester conversions, simplifying subsequent product separation steps, since no catalysts were added. The authors have used different sources of vegetable oils for developing both a catalytic transesterification process and a supercritical methanol transesterification process with the same objective of increasing the alcohol solubility in oil. Even though the reactions using supercritical methanol result in a shorter

residence time in the reactor and simplify the separating biodiesel step, it still requires high molar ratios of alcohol-to-oil to achieve good conversions. In addition, the high temperature and pressure conditions bring a high cost of production and high initial investment.³¹²

In order to reduce the operational conditions of the alcohol in supercritical medium, studies³¹³ have added a co-solvent into the process, for achieving smoother critical conditions than it would have by using pure alcohol. Thus, the transesterification reaction can be performed under milder conditions, but still preserving the desired solubility between alcohol and oil. In this context, co-solvents such as carbon dioxide, hexane, propane and nitrogen were tested.³¹³ On the other hand, in the biodiesel production, the addition of supercritical CO₂ to the reaction medium has been highlighted in recent years as the most viable and interesting addition to this process.

Alves²⁹⁹ and Maçaira *et al.*³¹⁴ carried out experiments using heterogeneous catalyst to perform methyl transesterification in the presence of CO₂. The authors obtained a good conversion rate of triacylglycerides to methyl esters. The experiments carried out by Alves²⁹⁹ were in the presence of zinc aluminate as a heterogeneous catalyst. These experiments were conducted with and without supercritical CO₂ in order to evaluate each route separately. The results indicated the best reaction yields were obtained for methyl transesterification with supercritical CO₂ (96.5% with 30 min residence time). Using supercritical CO₂ as co-solvent demonstrated that it is an alternative to overcome solubility and reactional homogeneity problems.

4.2. Esterification in supercritical conditions

The esterification reaction is the second step of the hydrothermal production process. The first reaction step is the hydrolysis. The esterification is commonly conducted when the raw material has a high acidity level, resulted from the presence of free fatty acids in the oil and/or fat. This reaction is responsible for ensuring the predominance of free fatty acids when the raw material is not yet completely converted. As in the transesterification process, esterification can also be conducted in the presence of acidic or alkaline, homogeneous or heterogeneous catalysts, and may or may not be associated with supercritical conditions in the process.³⁰⁶

In recent years, some authors have published the use of supercritical conditions to produce biodiesel via esterification. Alenezi *et al.*³¹⁵ and Koh³¹⁶ performed esterification experiments using supercritical methanol with temperatures ranging from 250 to 320 °C. In both studies,

the authors report the strong influence of temperature and alcohol-to-oil molar ratio, whose increase leads to a better reaction yield. Koh³¹⁶ had also noticed that the quality of the raw material does not influence the process and high conversions are reached in a short time for methanol and ethanol.

Tsai *et al.*³¹⁷ conducted supercritical methanol experiments using carbon dioxide as co-solvent aiming to improve the yield of biodiesel production reactions. Therefore, as in transesterification, it is observed the use of supercritical alcohol modifies the esterification reaction performance. Although eliminating the catalyst separation subsequent steps, this process needs higher temperature and pressure operating conditions and higher amount of alcohol. Within the context of esterification by enzymatic catalysis, the addition of supercritical carbon dioxide also brings considerable improvements in results.³¹⁸

5. Additives for Blended and Unblended Biodiesel

Biodiesel is a renewable fuel which has been proposed as a viable alternative for partial diesel replacement by possibly reducing engine emissions and providing greater lubrication. However, biodiesel has some disadvantages. Among them, we should point the low stability to oxidation and biodegradation as main disadvantages. The maintenance of oxidative stability and the inhibition of microbial growth in biodiesel are extremely important for the biofuel market, both in terms of preserving its quality and the saved costs involved. Oxidative stability has been partly maintained through the addition of synthetic antioxidants originally developed for food products. In addition to increasing the biofuel costs, these products compromise the “green fuel seal”.

Some countries are already adding biocides to biodiesel as well. This is derived from studies³¹⁹ performed for evaluating the degradation of methyl ester mixture caused by microorganisms. However, there are quite a few studies specifically reporting the performance of new compounds acting as biocides. Additionally, biodiesel is hygroscopic and the amount of water absorbed acts directly on the corrosion of the metallic materials which it comes into contact. Regarding that, there also are quite a few studies involving the addition of corrosion inhibitors to this biofuel. Following, we discuss in more detail biodiesel additives.

5.1. Antioxidant additives

A strategy widely discussed in the literature to overcome the biodiesel low oxidative stability is the use of antioxidant additives. Additives are substances added

to the fuel to improve their properties. In the case of the antioxidant additives, they act by preventing or retarding the biodiesel degradation, by donating an electron or hydrogen to the free radicals to neutralize the oxidation reaction. Thus, it avoids the formation of insoluble gums and sediments which increase biodiesel viscosity, may clog fuel filters or make deposits in the fuel injector. This should also be avoided in order to improve engine's functioning.³²⁰

The importance of antioxidant additives is critically discussed in a number of reviews published about this subject from 2005 to 2020. One of the first reviews was published by Dunn in 2008.³²¹ The author summarized the research progress in the development of effective antioxidants for use in biodiesel from soybean oil, rapeseed oil, used cooking oil, tallow and palm oil.³²¹ Several authors have published reviews on the oxidative stability of biodiesel, such as Knothe,³²² Jain and Sharma,²² Bannister *et al.*,³²³ Pullen and Saeed,²⁵ Fattah *et al.*,³²⁴ Yaakob *et al.*,³²⁵ Angelovic *et al.*,³²⁶ Kumar,³²⁷ Agarwal *et al.*³²⁸ and Varatharajan and Pushparani.³²⁰ In addition to the effects of antioxidants on the biodiesel oxidative stability, the most recent reviews also discuss the impact of these additives on performance, combustion and emission of vehicles.³²⁹ The antioxidant additives are divided into two groups: synthetic additives and additives from natural sources. In turn, the synthetic additives are sequentially subdivided into usual synthetic antioxidants, analogues and/or derivatives from the usual synthetic antioxidants and structurally different substances, which do not fall into the two previous classifications.

5.1.1. Usual synthetic antioxidants

The synthetic antioxidants usually added to commercial biodiesel generally are phenolic derivatives that exhibit high antioxidant activity. Those phenolic compounds act by stabilizing the radical generated in the oxidation reactions by the aromatic ring resonance, thus interrupting the free radical propagation reactions. These antioxidants are widely used in vegetable oils sold in the food market.³³⁰ For instance, BHT (butylated hydroxytoluene), TBHQ (*tert*-butylhydroxyquinone), PG (propyl gallate), PY (pyrogallol)

and BHA (butylated hydroxyanisole) are the most used ones. Their chemical structures are presented in Figure 9.

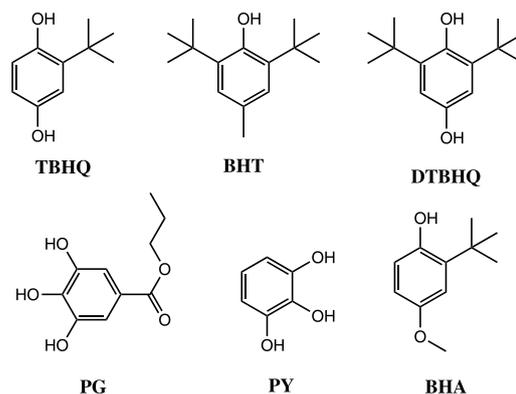


Figure 9. Chemical structures of usual synthetic antioxidant additives.

These antioxidants have been evaluated in several studies on biodiesel from different raw materials. The most commonly used biodiesels were those derived from soybean oil,^{331,332} sunflower oil,³³²⁻³³⁶ and palm oil.^{333,337} The most recent publications have already started to pay attention in evaluating the effect of these antioxidants on the emissions, combustion and performance studies.³³⁸⁻³⁵⁷ In addition to these properties, conventional antioxidants have also been evaluated for antimicrobial activity. Beker *et al.*³⁵⁸ evaluated the effect of BHT and TBHQ antioxidants on the growth of microorganisms in soybean biodiesel. Dodos *et al.*³⁵⁹ evaluated the microbial action of synthetic and natural additives in soybean and olive biodiesels.

5.1.2. Analogues and/or derivatives from usual synthetic antioxidants-phenolic compounds

Most of the new antioxidant candidates are derived from commercially available antioxidant additives. There are commercial products which can be considered derivatives from the usual antioxidants. Two examples are Ionol,^{339,360-364} which is a mixture of phenolic compounds, and Vulkanox or BPH (2,2'-methylenebis(6-*tert*-butyl-4-methylphenol)).^{339,342,365,366} The chemical structures of these components are presented in Figure 10.

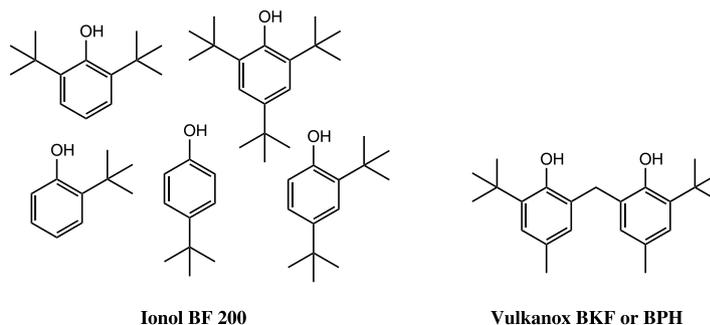


Figure 10. Constituents of the Ionol and BPH products derived from conventional synthetic additives.

Li *et al.*³⁶⁷ synthesized a number of gallic acid-derived esters with different short-chain alcohols. Their antioxidant effects were evaluated in relation to *Jatropha curcas* L. seed oil biodiesel using the Rancimat method. The structures are shown in Figure 11. Singh *et al.*³⁶⁸⁻³⁷⁰ published a sequence of three studies which they synthesized BHT (2,6-di-*tert*-butyl-4-methylphenol) derivatives. The BHT derivatives chemical structures are presented in Figure 12.

Muniz-Wypych *et al.*³⁷¹ proposed new phenolic antioxidant additives derived from alkyl oleates (Figure 13).

This class of compounds is more soluble in biodiesel and showed to be very promising to enhance methyl rapeseed biodiesel oxidative stability.

5.1.3. Unconventional synthetic antioxidants-non-phenolic compounds

The group of so-called structurally different substances (non-conventional synthetic additives) is mainly composed with nitrogen compounds. Among them, the best known species are DPPD (*N'*-phenylbenzene-

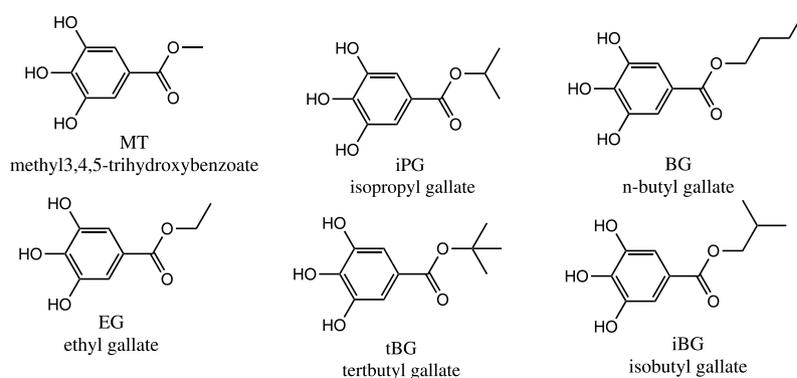


Figure 11. Substances derived from gallic acid.

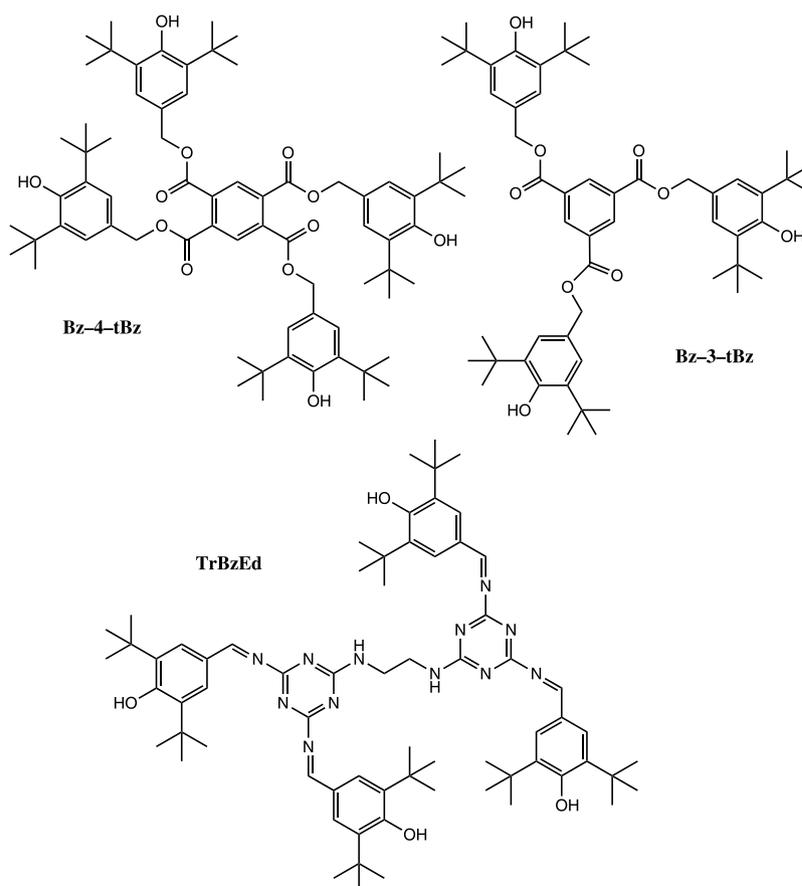


Figure 12. BHT synthetic derivatives.

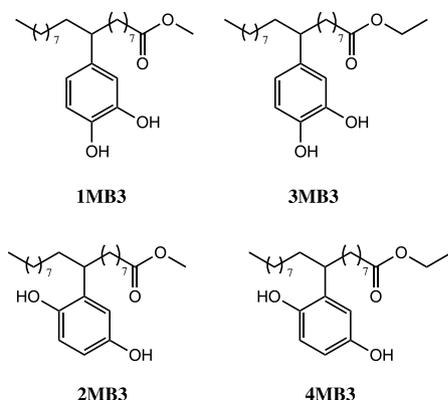


Figure 13. New phenolic derivatives obtained by Muniz-Wypych *et al.*³⁷¹ from the reaction with alkyl oleates.

1,4-diamine),^{332,339,341,372-382} NPPD (*N,N'*-diphenyl-1,4-phenylenediamine),^{341,372,373,378,381,382} succinimide (pyrrolidine-2,5-dione)^{346,373,380} and PDA (*N,N'*-di-*sec*-butylbenzene-1,4-diamine).^{365,383-387} The structures of these compounds are presented on Figure 14. Bär *et al.*^{388,389} studied the antioxidant activity of a series of hydrazide derivatives. Figure 15 presents the hydrazide derivatives evaluated as antioxidants.

Dodson *et al.*³⁹⁰ synthesized new glycerol acetals from aromatic aldehydes (Figure 16), which their antioxidant activities were quantified through a standard procedure using diphenyl-picryl-hydrazine radical (DPPH·) method. The main objective of this study was to investigate a

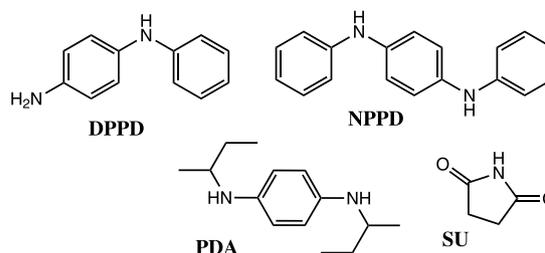


Figure 14. Structures of some non-conventional synthetic additives.

potential application for glycerol, which is a secondary product from biodiesel synthesis.

El-Boulifi *et al.*³⁹¹ obtained kojic acid ricinoleate by lipase-catalyzed esterification in a solvent-free system. The addition of the new kojic acid derivative (Figure 17) improved the rapeseed biodiesel oxidation stability.

Schirmann *et al.*³⁹² synthesized three dimers of 2,6-dimethoxyphenol through laccase-catalyzed oxidative coupling reactions (Figure 18). The product 3,3',5,5'-tetramethoxybiphenyl-4,4'-diol (dimer II) was evaluated as antioxidant candidate for soybean biodiesel and showed an efficacy similar to the commercial antioxidant BHT.³⁹³ Sui and Li³⁹⁴ investigated the antioxidant effect of tetraethylenepentamine on rapeseed biodiesel oxidation resistance at different concentrations. The use of 2.1% of the additive increased the induction time in the Rancimat test by more than 10 times compared to pure biodiesel. Recently, Figueredo *et al.*³⁹⁵ tested the antioxidant activity

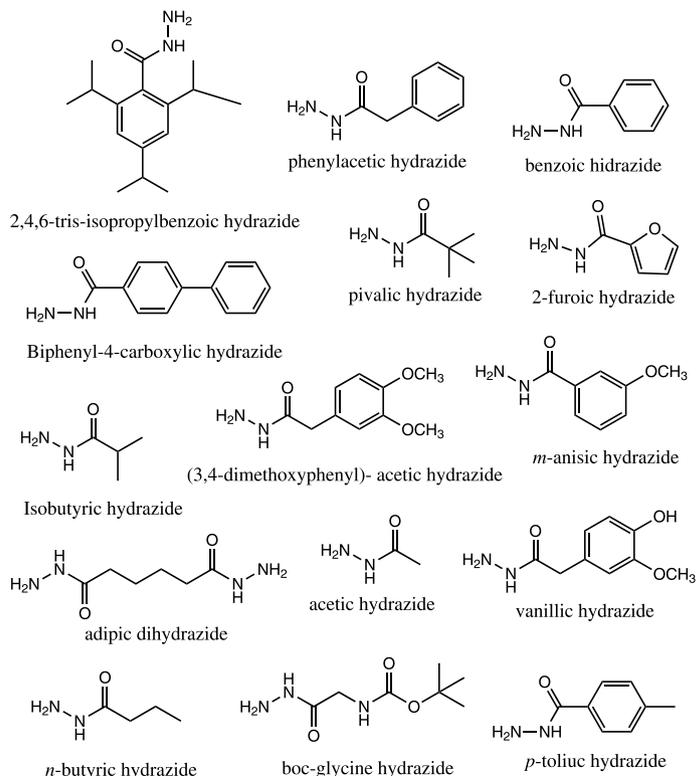


Figure 15. Hydrazide derivatives evaluated as antioxidants.

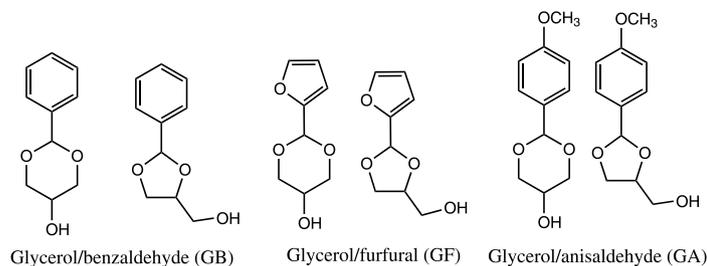


Figure 16. Chemical structure of antioxidant candidates derived from glycerol.

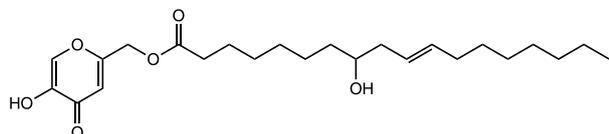


Figure 17. Structure of kojic acid ricinoleate.

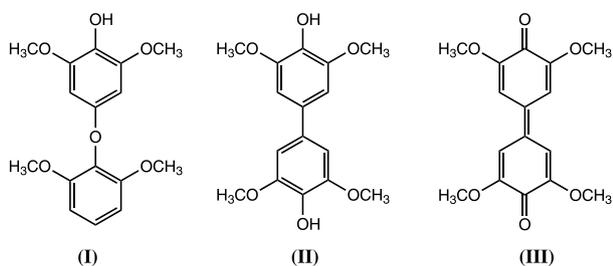


Figure 18. Coupled oxidative products of 2,6-dimethoxyphenol catalyzed by laccase.

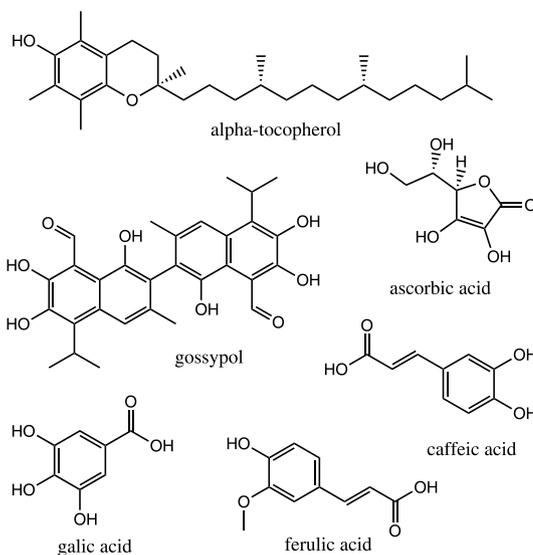


Figure 19. Chemical structures of natural antioxidants.

of *N,N'*-di-sec-butyl-*p*-phenylenediamine in babassu biodiesel by the Rancimat method and differential scanning calorimetry. The results showed a significant improvement in the biodiesel oxidative stability.

5.1.4. Natural antioxidants

Most vegetable oils used to produce biodiesel have in their composition natural antioxidants which are removed during the process of transesterification or esterification. In the literature, there are several studies applying these antioxidants in the exogenous form, as it is the case of α -tocopherol^{384,396-407} and gossypol (substance found in cottonseed oil) (Figure 19).^{399,408} Naturally occurring acids commonly used in the cosmetic industry as antioxidants were also evaluated for their action on biodiesel. In this context, it could be highlighted ascorbic acid,^{374,396,402,403,409-411} caffeic acid,^{359,398,400,412-414} ferulic acid,^{398,400,413} and gallic acid (Figure 19).^{398,415}

Several plant extracts were also used to improve the biodiesel oxidative stability.⁴¹⁶⁻⁴²⁰ The most reported in the literature are the extracts of rosemary leaves,⁴²¹⁻⁴²⁶ basil leaves,^{422,423,427} oregano leaves,^{422,424,425,427} and green tea.^{401,428}

Some authors also have been studying the antioxidant potential of co-products from the pulp industry, the

lignocellulosic bio-oils,⁴²⁹⁻⁴³³ and cashew nut processing industry (cashew nut shell liquid (CNSL)),⁴³⁴⁻⁴³⁷ which is composed by a mixture of alkylphenols.

Regarding to CNSL, its isolated constituents as well as the synthetic derivatives of these alkylphenols have also been evaluated as antioxidant for biodiesel. Rodrigues *et al.*⁴³⁸ evaluated the antioxidant activity of hydrogenated cardanol. In turn, Lomonaco *et al.*⁴³⁹ synthesized and evaluated phosphorylated compounds derived from cardanol. Maia *et al.*⁴⁴⁰ evaluated the antioxidant activity of saturated and unsaturated *tert*-butylated cardanol. dos Santos *et al.*⁴⁴¹ submitted a portion of technical CNSL to an electrolytic process, which resulted in a product with improved antioxidant activity. According to the authors, the electrolysis process may lead to the formation of dimers or oligomers by reaction between phenols in technical CNSL. And these compounds may be the responsible for the observed higher oxidative stability. Liu *et al.*⁴⁴² synthesized cardanol epoxide, being the pioneers in the cardanol alkyl chain transformation. Recently, Costa *et al.*⁴⁴³ evaluated the antioxidant potential and thermal stability of CNSL and cardanols oxygenated derivatives. They synthesized five novel oxygenated derivatives. From those derivatives

the one obtained from the cardanol epoxide hydrolysis increased the commercial biodiesel oxidative stability by three times. Some cardanol synthetic derivatives evaluated as antioxidant are presented in Figure 20.

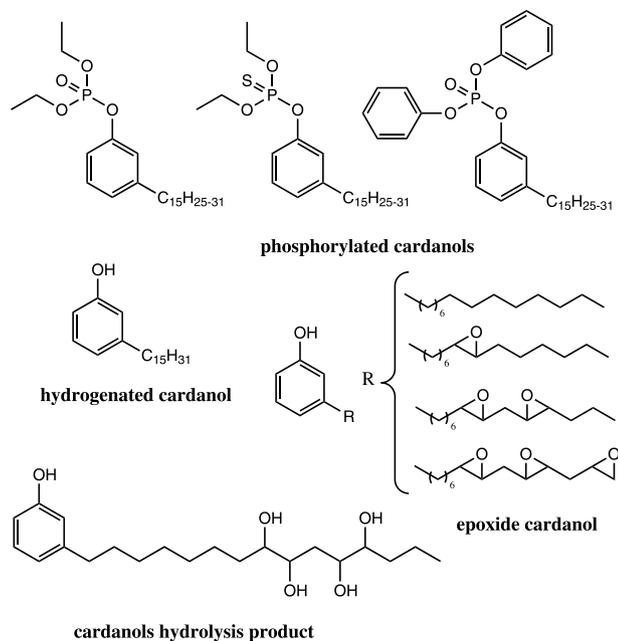


Figure 20. Chemical structures of some cardanol synthetic derivatives evaluated as antioxidants for biodiesel.

5.2. Biocide additives

Microbial contamination is also one of the important problems associated with fuel storage. Indeed, the proliferation of fungi and bacteria are more common in diesel systems.⁴⁴⁴ Microorganisms present in biodiesel/diesel blends are likely to affect the overall fuel quality due to their metabolites, which act accelerating fuel deterioration.³¹⁹ This kind of biomass can damage the engine fuel injection system by clogging pipes and filters as well as by adhering a biofilm onto material surfaces (then forming a type of fouling). In addition, it may lead to storage tanks corrosion, known as microbiologically influenced corrosion (MIC).^{445,446} The fuel, used as a source of nutrients together to its water content, becomes a propitious environment for microbial growth. In this way, a practice of performing periodic drainage of accumulated water at the bottom tanks is an important method of prevention of microbial activity. In addition, the adoption of reduced fuel storage times could also prevent fuel contamination. The literature has been addressing the development of alternative methods for prevention of microbial growth. It has been proposed, for instance, treatment with ultraviolet radiation, safe use of sonication, addition of hydrogen peroxide and biocides.⁴⁴⁷

Since the beginning biodiesel emerged as a renewable fuel and the fact of being biodegradable as one of the main advantages. The biodegradability of fossil diesel increases with the addition of biodiesel, which is a gain in the case of accidental spill of biodiesel/diesel blends.⁴⁴⁸ Accordingly, the use of biodiesel to remediate fuel contaminated areas was considered since the operation is affordable and it does not require high technology.⁴⁴⁹ However, soon after its implementation, what previously was considered an advantage, became a concern. The accumulation of deposits in diesel storage tanks has considerably increased, as well as the need for diesel vehicles maintenance. For instance, the replacement of fuel filters and the cleaning of injection system started to be done at shorter intervals. The main cause why this was happening is the substantial increase of the biomass growth. Furthermore, biodiesel is 30 times more hygroscopic than mineral diesel. Therefore, keeping the water content to a minimum in the biodiesel/diesel blends storage tanks becomes essential. And exercise the water content control in the pure biodiesel (B100) storage tanks is an even more difficult task. Within this context, one plausible strategy to prevent microbial contamination is the addition of biocides to both blended and unblended biodiesel.

In 2013, Passman³¹⁹ provided an excellent survey about microbial contamination and its control in fuels and fuel systems. The review reports about biodeterioration of diesel and biodiesel fuels, factors contributing for microorganism's contamination and proliferation through fuel storage tanks and engine fuel systems, methods of microbial contamination control, and decontamination practices, among others. In the following year, Jakeria *et al.*⁴⁵⁰ reviewed different factors affecting biodiesel stability, including microbial growth. They comment about the degradation mechanism of fatty acid methyl esters by microorganisms, known as cometabolic biodegradation, and the reasons why biodiesel and biodiesel/diesel blends degrade faster than diesel. In our review, we discuss three segments related to microbial growth. The first part presents a brief survey of the microorganisms identified in biodiesel/diesel blends and pure biodiesel storage tanks. The second part describes some studies regarding the evaluation of favorable conditions for microbial growth. This knowledge is important for studying ways to control the growth of these microorganisms. The last part presents products that have been commercially added as biocide in biodiesel/diesel blends and in pure biodiesel, as well as products tested for this purpose.

5.2.1. Identification of microorganisms content in biodiesel and biodiesel/diesel blends storage tanks

Studies have shown, as it happens for diesel, that biodiesel biodegradation is performed by either bacteria,

yeasts and/or fungi. The isolation of the microorganisms present in the sludge from biodiesel and biodiesel/diesel blends requires the use of specific culture media for different microorganisms' growth.⁴⁵¹ For instance, potato dextrin agar is used to detect potential fungi, peptone casein agar and tryptic soy agar usually are employed for detecting bacteria. In addition, malt extract agar is used to detect possible yeasts and anaerobic agar is specifically used to grow anaerobic microorganisms. In turn, the identification of the microorganism species is based on a set of morphological, biochemical, physiological and molecular evidences of the isolates. Table 9 presents some microorganisms isolated in sludge generated from biodiesel/diesel blend or pure biodiesel.

5.2.2. Susceptibility of microorganism growth in biodiesel and biodiesel/diesel blends

Studies involving the evaluation of microbial growth conditions on biodiesel from different raw materials are found in the literature. Some examples are cited on Table 10 and more details are found in their respective references. Some of them used microorganisms isolated from contaminated biodiesel and biodiesel/diesel blends storage systems, as indicated in the table.

5.2.3. Biocide additives for biodiesel and biodiesel/diesel blends

There are three biocides approved and registered by U.S. Military Specification as diesel fuel biocides.⁴⁶⁰

Table 9. Microorganisms isolated in sludge generated from biodiesel/diesel blend or pure biodiesel

Microorganism	Strain or genus	Biodiesel raw material	BX	Reference
Bacteria	<i>Klebsiella oxytoca</i> <i>Klebsiella nov. sp.</i> <i>Staphylococcus epidermidis</i>	canola oil	B5 and B10	451
Bacteria	<i>Pseudomonas</i> , <i>Comamonas</i> , <i>Burkholderia</i> genera, among others	80% soybean oil/ 20% beef tallow	B10	445
Bacteria	<i>Micrococcus luteus</i> <i>Microbacterium sp.</i> <i>Cellulomonas sp.</i> <i>Curtobacterium sp.</i> <i>Bacillus megaterium</i> <i>Bacillus sp.</i> <i>Bacillus pumilus</i>	soybean oil	B100	452
Fungi	<i>Xylariales sp.</i> <i>Penicillium citrinum</i> <i>Penicillium simplicissimum</i> <i>Penicillium corylophilum</i> <i>Hypocreales sp.</i>	soybean oil	B100	452

BX = X% v v⁻¹ of biodiesel in diesel; B100 = pure biodiesel.

Table 10. Data from susceptibility of microorganism growth in biodiesel or biodiesel/diesel blend

Microorganism	Specie, strain or genus	Biodiesel raw material	BX	Reference
Fungi and bacteria	microorganisms from soil	rapeseed oil	B5, B20, B100	453
Fungi and yeasts ^a	<i>Aspergillus fumigatus</i> , <i>Candida silvicola</i> <i>Paecilomyces sp.</i> , <i>Rhodotorula sp.</i>	soybean oil	B5, B10, B20, B100	454
Bacteria ^a	methanogenic bacteria sulfate-reducing bacteria nitrate-reducing bacteria	animal fat	B5, B10, B20, B50, B100	455
Fungus	<i>Pseudallescheria boydii</i>	beef tallow	B100	456
Fungus	<i>Pseudallescheria boydii</i>	linseed, soybean and olive oil	B100	457
Fungus	<i>Pichia anomala</i>	soybean oil and beef tallow	B5, B100	458
Bacteria	<i>Mycobacterium sp.</i>	beef tallow	B5, B100	458
Bacteria	<i>Tepidimonas sp.</i>	soybean oil	B5, B100	458
Fungus	<i>A. niger</i> variety <i>tubingensis</i>	soybean oil, beef tallow 65% soybean/35% beef tallow,	B100	459

^aMicroorganisms isolated from biodiesel or biodiesel/diesel blends storage systems. BX = X% v v⁻¹ of biodiesel in diesel; B100 = pure biodiesel.

The first additive (DOB) consists of 2,2-oxybis-(4,4,6-trimethyl-1,3,2-dioxaborinane) and 2,2-(1-methyl-trimethylenedioxy)-bis-(4-methyl-1,3,2-dioxaborinane). The second biocide formulation (CMIT/MIT) is an isothiazolinone blend (5-chloro-2-methyl-4-isothiazolin-3-one and 2-methyl-4-isothiazolin-3-one) and the third (NBM/ENDM) is a mixture of 4-(2-nitrobutyl)-morpholine and 4,4'-(2-ethyl-2-nitrotrimethylene)-dimorpholine. There is also a fourth product used for microbicidal fuel treatment, 3,3-methylenebis(5-methylloxazolidine), known as MBO.³¹⁹ MBO can be purchased in its pure form or formulated in multifunctional additives which may contain different percentuals of this antimicrobial product. Their chemical structures are presented in Figure 21.

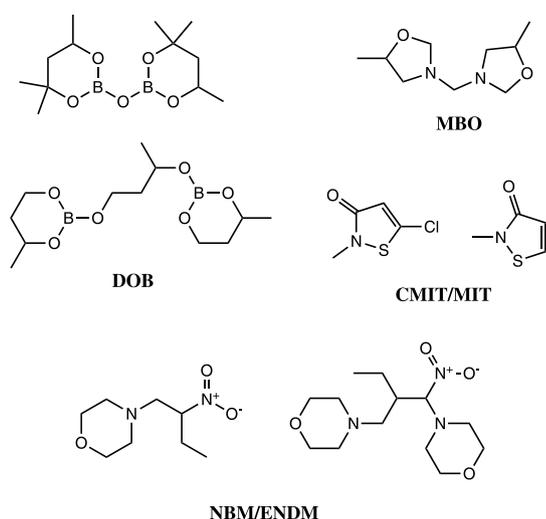


Figure 21. Chemical structures of products used as a fuel-treatment biocide.

In the last years, some of these products have been studied by researchers from the Federal University of Rio Grande do Sul, Brazil. Zimmer *et al.*⁴⁶¹ investigated the effectiveness of MBO, using a multifunctional additive formulation for fuel which contains 50% of this biocide, and MIT/CMIT product, that contains 1.5% of active ingredient, in biodiesel (produced from 60% of soybean oil and 40% of beef tallow), low sulfur conventional diesel, B7 and B10 blends. The efficacy of both biocides was evaluated for 60 days using the fuel phase and two types of aqueous phase (natural bottom-water formed in a biodiesel/diesel blend and synthetic water with low, medium and high levels of contamination). A mix of uncharacterized microbial sludge obtained from different fuels (diesel, biodiesel and biodiesel/diesel blends) was used as inoculum. MIT/CMIT performed better in all conditions tested. The authors suggest the presence of other additives in the formulation is interfering negatively in the action of MBO, since in previous studies pure MBO had performance comparable to MIT/CMIT.

Cazarolli *et al.*⁴⁵⁷ evaluated the efficiency of 100% MBO, 8% MBO, 50% MBO and 100% NBM in the control of *Pseudallescheria boydii* growth using the broth dilution method. According to the values of the minimum inhibitory concentration (MIC) and minimum biocide concentration (MBC), 100% NBM was the most effective in containing growth and presented sporicidal action. The authors did not investigate the effect of the antimicrobial products on a biodiesel or biodiesel/diesel blend system inoculated with fungus. In the same year, Bucker *et al.*⁴⁴⁵ studied the effect of MBO in stored B10 with and without an inoculum derived from diesel sludge. The biodiesel used to prepare B10 blend was originated from soybean oil (80%) and beef tallow (20%). Pure active ingredient (100% MBO) and an additive formulation containing 50% MBO were evaluated. The study revealed microbial growth was effectively controlled with the use of pure MBO in all experiments. The microbial number in the aqueous and oil phases was reduced using the formulation at 50% MBO and the results indicated that 500 ppm of this formulation led to fungistatic activity. The same additive formulation was used by Zimmer *et al.*⁴⁶² to compare the microbial growth in a B10 blend stored under simulated conditions in laboratory scale (250 mL microcosms) and field scale (20 L tanks). They used an uncharacterized microbial sludge obtained from biodiesel/diesel blend as inoculum. The results showed the condition often defined in the laboratory may demand adjustments under real situations.

5.2.4. Evaluation of biocide candidates for pure biodiesel and biodiesel/diesel blends

Despite the need to control microbial growth, there are few studies available in the literature specifically focusing on the development of biocide candidates for use in pure biodiesel and biodiesel/diesel blends. Meanwhile, some researchers have evaluated if antioxidant additives also have biocide action. Beker *et al.*³⁵⁸ evaluated the effect of the commercial antioxidants *tert*-butylhydroquinone (TBHQ) and butylated hydroxytoluene (BHT) on microorganisms isolated from diesel and biodiesel storage tanks (fungi *Paecilomyces variotii*, *Pseudallescheria boydii* and *Candida guilliermondii*, and the bacterium *Bacillus pumilus*). Firstly, the authors evaluated the minimum inhibitory concentration (MIC) of BHT and TBHQ using the broth dilution method. The experiment was also carried out with an uncharacterized inoculum prepared according to ASTM E1259⁴⁶³ using microbiological sludge from a contaminated tank. No antimicrobial effect was observed for BHT in all tested concentrations. In laboratory scale, the uncharacterized inoculum medium was added to soybean biodiesel containing different TBHQ

concentrations. The vials were incubated for 45 days at 30 °C. TBHQ appears to be neither a promoter nor an inhibitor of microbial growth in biodiesel under the conditions tested. Santos *et al.*⁴⁶⁴ tested the growth of the filamentous mold *Paecilomyces variotii* Bainier in presence of biodiesel added with curcumin and pyrocatechol. The study includes biodiesel from various fatty acid sources (waste frying oil, soybean oil, cottonseed oil, sesame oil, macaúba almond oil and microalgae oil). The experiments were carried out in Petri dishes containing solid Sabouraud dextrose agar incubated at 25 °C for 48 h. After this time, the plates were visually inspected for the presence of inhibition zones of fungal growth. The best fungistatic effect was observed in the presence of 0.1 to 0.5% (m m⁻¹) curcumin, depending on the biodiesel sample, and 1% (m m⁻¹) water.

Dodos *et al.*³⁵⁹ evaluated the antimicrobial activity of six synthetic phenolic antioxidants (butylated hydroxyanisole, BHA; butylated hydroxytoluene, BHT; *tert*-butyl hydroquinone, TBHQ; propyl gallate, PG; pyrogallol, PY; and *tert*-butyl catechol, TBC) and four natural phenolic antioxidants (caffeic acid, CFA; gentisic acid, GA; methyl catechol, MCT; and protocatechuic acid, PCA) in B100 and B7 blends from refined pomace olive oil and soybean oil. Initially, the ability of the phenolic additives to inhibit microbial growth was tested against *Bacillus stearothermophilus*, a Gram-positive bacterium, at 64 °C for 3.5 h. TBHQ, PG, MCT and TBC were the most efficient in inhibiting the growth of *Bacillus stearothermophilus* in fatty acid methyl esters (FAME) from both refined pomace olive oil and soybean oil. BHA, BHT, GA and PCA did not show antibacterial activity under the conditions tested. B7 blends were treated with TBHQ, PG, MCT, TBC, PY and CFA. Only TBHQ, PG, MCT and TBC depicted antimicrobial action. In the second part of the study, the authors investigated the antimicrobial activity of the most active phenolic compounds in simulated diesel/biodiesel fuel storage conditions. The inoculum was prepared according to ASTM E1259⁴⁶³ using the aqueous phase of a microbially contaminated commercial diesel. B100 and B7 blends were also treated with the commercially fuel biocide MBO for comparison. As expected, the MBO product practically eliminates the active microbial contamination in FAME from both vegetable oils tested. The microcosm was significantly suppressed in those containing TBHQ and MCT. In both B7 blends microcosms, the two catechol derivatives (MCT and TBC) proved to be more effective antimicrobial additives.

Recently, some studies have evaluated the biocide activity of triacylglyceride derivatives. The objective was to reveal potential additives from chemical modifications in the same raw material used for biodiesel production. Ramalho *et al.*⁴⁶⁵

synthesized an imine product via hydroformylation of the double bonds present in the hydrocarbon chain of soybean fatty acid methyl esters, followed by *n*-butylamine condensation. In other words, the authors synthesized biodiesel-based molecules whose antimicrobial activity was evaluated towards a set of fungi and bacteria commonly present in fuel storage tanks. The addition of 5% of the imine product in soybean biodiesel presented positive antimicrobial activity in both agar diffusion test and antimicrobial susceptibility test, for fungi *Candida krusei*, *Candida parapsilosis*, *Candida albicans*, *Aspergillus niger*, *Aspergillus fumigatus* and *Saccharomyces cerevisiae*, and for bacteria *Escherichia coli*, *Bacillus subtilis* and *Staphylococcus aureus*. Oliveira *et al.*⁴⁶⁶ tested the product of acetylation of epoxidized soybean biodiesel against three fungi species (*Aspergillus fumigatus*, *Trichophyton rubrum* and *Microsporum canis*) and four species of bacteria (*Bacillus subtilis*, *Escherichia coli*, *Pseudomonas aeruginosa* and *Staphylococcus aureus*). The antimicrobial activity was evaluated by agar diffusion test with soybean biodiesel containing 1 to 50% of the biocide candidate. According to the authors, this method is widely used in microbiology laboratories to select substances with potential antimicrobial activity for pharmacological areas. The acetylation product showed fungicidal activity to *Trichophyton rubrum* and *Aspergillus fumigatus*. Costa *et al.*⁴⁶⁷ synthesized nitrated derivatives using soybean oil as starting material. The products were evaluated against fungi and bacteria which have been isolated from biodiesel/diesel blends (fungi *Aspergillus niger*, *Aspergillus fumigatus*, *Candida albicans* and *Saccharomyces cerevisiae*; and bacteria *Bacillus subtilis* and *Acinetobacter baumannii*). None of the products inhibited the bacteria growth. Four nitrated derivatives presented modest fungicidal activity against *A. niger* and *A. fumigatus*. Three products derived from the vegetable oil (Figure 22). The chemical structures are represented

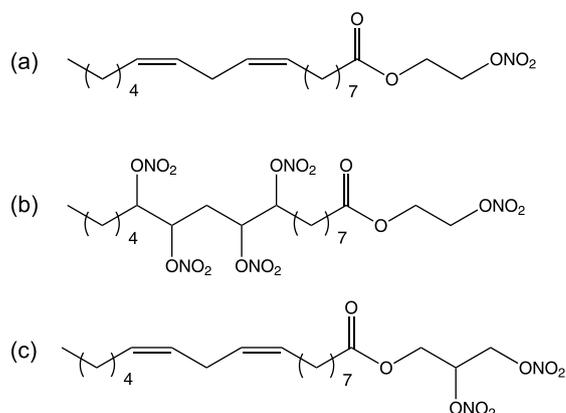


Figure 22. Derivatives from soybean oil with activity against *A. niger* and *A. fumigatus*.

by linoleic chain, which is the major hydrocarbon chain of soybean triacylglycerides, for illustration. The fourth product is the pure nitrate of ethylene glycol linoleate.

6. Emissions

Estimates from the World Health Organization (WHO) state that 4.2 million people die every year due to the exposure to outdoor air pollution and 91% of world's population lives in places where the air quality is inappropriate, according to the WHO's guidelines.⁴⁶⁸ These deaths are mainly linked to chronic diseases, such as pulmonary obstruction, but also lung cancer, cardiovascular diseases and acute respiratory infections in children. According to the WHO's report, worldwide ambient air pollution accounts for 29% of all deaths and disease from lung cancer, 17% of all deaths and disease from acute lower respiratory infection, 24% of all deaths from stroke, 25% of all deaths and disease from ischaemic heart disease and 43% of all deaths and disease from chronic obstructive pulmonary disease.⁴⁶⁸

Pollutants which play an important role for the air quality and public health issues include, amongst others, particulate matter (PM), nitrogen dioxide, ozone and sulfur dioxide. Regarding particulate matter, especially particles with a diameter $\leq 10 \mu\text{m}$ (PM_{10}) and fine particles with a diameter $\leq 2.5 \mu\text{m}$ ($\text{PM}_{2.5}$), it is prone to deeply penetrate in the lungs and bloodstream. Its composition may include, amongst other species, metals, sulfate, nitrates and black carbon, and normally it will play a role in the transportation of different kinds of toxic species adsorbed on its surface, such as organic compounds. In 2013, it was classified by the International Agency for Research on Cancer (IARC) as cause of lung cancer.⁴⁶⁹ According to the WHO,⁴⁶⁸ the effects of PM on health occur at levels of exposure currently present in urban and rural areas and in developed and developing countries. Furthermore, exposures in many fast-developing cities are even much higher than in developed cities of the same size.

Exhaust emissions from diesel burning contain hundreds of compounds, either in the gas or in the particulate phases, which are proved, or suspected to be carcinogenics. Representatives of those exhausted species which may be cited are formaldehyde, acrolein, polycyclic aromatic hydrocarbons (PAHs), nitro-PAHs, benzene, and sulfate, among others. Besides, they also produce large amount of fine particulate matter ($\text{PM}_{2.5}$), which are able to go deep into respiratory systems and may cause different health-related endpoints. As a consequence, the use of alternative fuels is likely to contribute for reducing the health and environmental impacts of diesel emissions, and it has been extensively investigated.

In the last years, several researchers have as main objective the search for solutions which can help to mitigate the emissions of pollutants to the atmosphere. This scenario is not different with respect to emissions from the incomplete combustion process of diesel cycle engines. A lot of technologies have been developed and incorporated in diesel engines, in order to reduce pollutant emissions although there is a special attention in the application of alternative fuels which are not of fossil origin. Biodiesel is the main substitute for the diesel fuel because it does not require modifications to the diesel engine. Besides it may present several benefits, such as reduction of atmospheric pollutants emission and a greater cetane number, among others.

Through a brief research using the keyword "biodiesel emission" in scientific databases, it is possible to map a growing interest on the subject, given the number of papers that aimed at evaluating emissions from biodiesel use. In 2005, when the first article *Biodiesel: An Overview*¹⁵ was published, the number of publications on the subject was already significative. However, more than ten years later, this number has practically increased by 17 times. This demonstrates how significant and effective has been the employment of biodiesel/diesel blends, as a way to mitigate the emission of pollutants from the incomplete combustion of diesel engines.

When the focus of publications is evaluated (Figure 23), it is possible to observe that different parameters are considered in studies as possibly affecting the emissions, such as the use of a third fuel in a ternary mixture, as well as the main types of pollutant emitted, with focus on both regulated and non-regulated pollutants, due to their environment and health impacts. One topic addressed is related to the biodiesel source, since it can be produced either from edible or non-edible parts of different leguminous plants. In order to comply with the current regulations, regarding restrictions on diesel emissions, several technologies have been used. Meanwhile studies have been conducted in order to evaluate the impact of using biodiesel in different combinations to other fuels. Other parameters also evaluated are diesel engines performance (load and power) as well as the use of different types of fuel additives in order to improve fuel lubricity, cetane number, and processes of early oxidation, among others.

Investigations using ternary fuel mixtures containing biodiesel have focused on compounds which do not affect the biodiesel's miscibility in diesel fuel and if they may contribute for reducing pollutant emissions. Short chain alcohols (e.g., ethanol and *n*-butanol),⁴⁷⁰⁻⁴⁷³ ethers (2,5-dimethylfuran)⁴⁷² and kerosene⁴⁷⁴ are examples of compounds which having been added in the fuel blends.

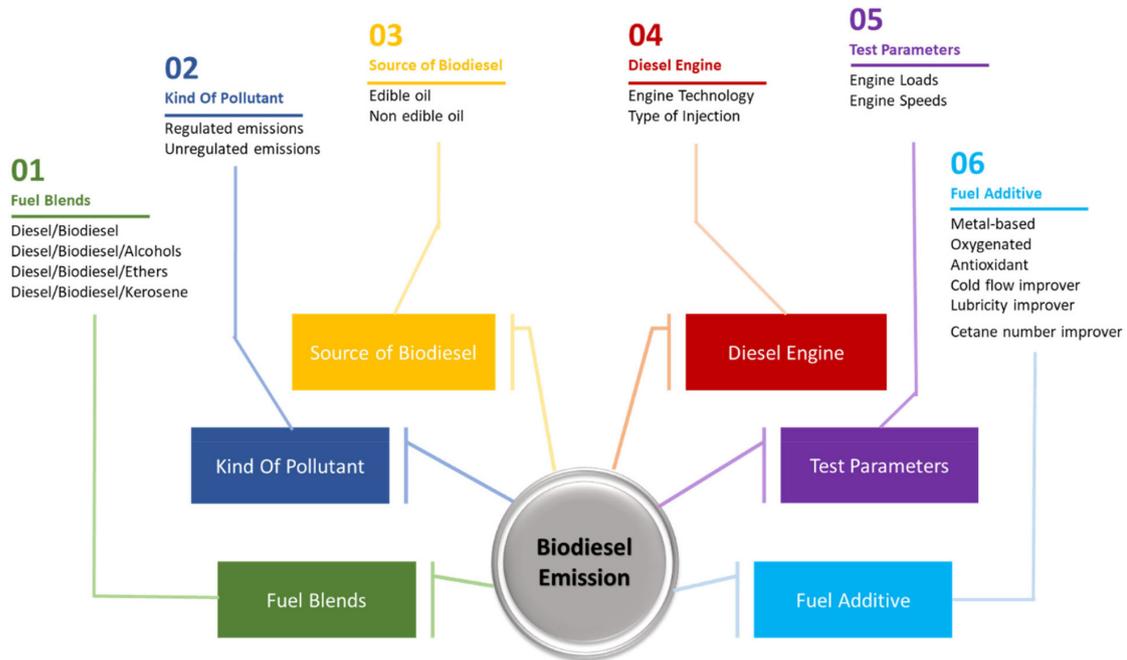


Figure 23. Main subjects related to emission studies with biodiesel, according to databases accessed in the last 15 years.

Several studies are available which evaluate the impacts on the pollutants emission profile from using ternary fuel mixtures. In a review published by Mofijur *et al.*,⁴⁷⁰ the latest studies carried out to evaluate emissions of ternary mixtures with the addition of ethanol were summarized. The fuel blends evaluated had ethanol concentrations added to biodiesel/diesel blends ranging from 2 to 40%.⁴⁷⁵ In general, the addition of ethanol in biodiesel/diesel blends does not cause a clear increasing nor decreasing trend for CO, NO_x and HC emissions (regulated compounds). The emissions depended directly on the test conditions and technologies used.⁴⁷⁰ Meanwhile, there are other studies which state the ethanol addition to diesel/biodiesel/ethanol ternary mixtures could increase CO and HC emissions although they bring contributions by reducing NO_x emissions, particulate matter and particle number concentrations.⁴⁷¹⁻⁴⁷³

Although the vast majority of studies regarding vehicle emissions focused their analysis on regulated pollutants (NO_x, CO, PM, and HC) attention has been given to a large number of non-regulated compounds, which have potential carcinogenic and mutagenic effects. Among them, volatile (VOC) and semivolatile organic compounds (SVOC), such as PAHs, nitro-PAHs, quinones, carbonyl compounds (CC) and others⁴⁷⁶⁻⁴⁸⁴ can be highlighted. The addition of biodiesel in diesel can bring some benefits in reducing the emissions of those compounds. It should be noted, however, that different results can be observed, depending on the applied conditions. For instance, when 10% *n*-butanol was added to biodiesel, the PAH emissions have decreased,

while addition of a larger amount of *n*-butanol has led to the opposite result. Thus, the PAH production is driven not only by the combustion process but also by the fuel origin.⁴⁸⁵ Table 11 shows the main studies about the effect of the use of biodiesel on emissions of both regulated and unregulated pollutants. The complete table, including observed results and details from the use of biodiesel and other fuels, is found in the Supplementary Information section.

In terms of pollutant emissions, the increase of biodiesel added to diesel must be carefully evaluated. In general, there are pollutants emitted in lower concentrations when biodiesel is added (such as HPAs, CO and *n*-alkanes), while other pollutants are emitted in a higher concentration (carbonyl compounds, major ions and NO_x) when compared to pure diesel. In this sense, it is of utmost importance to develop solutions able to mitigate negative impacts caused by emissions from high biodiesel content blends. The use of combustion-enhancing additives could be a viable alternative. In addition, there is a significant number of studies which highlights some carcinogenic compounds emitted during the incomplete combustion process. Those carcinogenic compounds could be regulated by law in a near future, imposing emission limits. The increase in the biodiesel content should consider these contributions.

7. Trends in Biodiesel Patents

In January 2021, a technological prospecting mapping on biodiesel was carried out on the Derwent World Patents

Table 11. Main studies recently published regarding pollutants exhausted through blended or unblended biodiesel fuel

Sampling year	Pollutant	Phase	Fuel tested	Reference
2004	PAH	particulate	B100	486
2004/2005	PAH	particulate	diesel fueled heavy-duty vehicles, diesel burning from ships and smaller boats and dust resuspension through circulation of buses	482
2006/2007	PAH	particulate	diesel	487
2008	PAH, major ions	particulate	B3	481
2008	CC	gaseous	diesel, B2, B5, B10, B20, B50, B75 and B100 from soybean biodiesel and residual oil biodiesel	488
2008	formaldehyde, acetaldehyde, acrolein, acetone, propionaldehyde, butyraldehyde, benzaldehyde	gaseous	diesel, B2, B5, B10 and B20 from castor oil biodiesel	489
2009	CC, CO, CO ₂ , NO _x	gaseous	B5 from soybean biodiesel, castor oil biodiesel and residual oil biodiesel	483
2009	CC	gaseous	diesel and B100 from soybean oil	490
2010	2-nitrobenzanthrone, 3-nitrobenzanthrone	particulate	B4	491
2010	PAH, nitro-PAH, quinones	particulate	B4	478
2010	quinones	particulate	B4	479
2010	low-molecular weight carboxylate, water-soluble inorganic ions	particulate	B5	492
2010	CC	gaseous	B5	484
2011	carbonyl, PAH, nitro-PAH, oxy-PAH	particulate and gaseous	B10, B20 and B30 from fresh and oxidized biodiesel of different source materials	493
2013	CC	particulate	B5	476
2013	water-soluble transition metals, PAH, nitro-PAH, quinones	particulate	B7	477
2014	PAH	particulate	B5, B25, B50 and B100	480
2014	NO _x , CO, HC, CO ₂ , PM	particulate and gaseous	B100, B5 and B5E6	475
2014	NO _x , NH ₃ , N ₂ O	gaseous	low-sulfur diesel, ultra low sulfur diesel and B20 from soybean biodiesel	494
2014	carbonyl	gaseous	diesel, B50 and B100 from animal-fat biodiesel and diesel containing 5% of a tire pyrolysis liquid	495
2015	PAH, nitro-PAHs, petroleum biomarkers	particulate	ultra-low sulfur diesel, swedish low aromatic diesel and neat soybean biodiesel	496
2015	sulfur	gaseous	diesel with different sulfur contents	497
2016	CO, NO _x , saturated hydrocarbon compounds, unsaturated hydrocarbons, aldehydes, alcohols, SO ₂ , formic acid, benzene	gaseous	diesel, B5 and B20 from Karanja oil biodiesel	498
2017	organic carbon, elemental carbon	particulate	B4 from commercial soybean biodiesel. B50 and B100 from waste cooking biodiesel	499
2017	PAH, inorganic ions	particulate	B20 from waste cooking biodiesel	500
2017	CC, unsaturated hydrocarbons, aromatic compounds	particulate and gaseous	diesel, B20, B50, B75 and B100 from waste cooking biodiesel	501
2018	PAH, nitro-PAHs	particulate	B5 and B20 from ultra-low sulfur diesel and soybean biodiesel	502
2019	CO, CO ₂ , O ₂ , total hydrocarbon, NO _x , aldehyde, alkene	gaseous	ultra-low sulfur diesel, B20, B50, B75 and B100 with different oxygen contents from waste cooking biodiesel	503
2019	organic carbon, elemental carbon, PAH, <i>n</i> -alkanes, fatty acids, inorganic ions	particulate	B5, B10 and B20 from waste cooking biodiesel	504
2019	PAH, carbonyls	particulate and gaseous	B80 from palm oil biodiesel, animal fat biodiesel and soybean biodiesel	505
2019	persistent organic pollutants, PAH	particulate	diesel, B20, B40, B60, B80 and B100 from waste cooking biodiesel	506
2020	PAH	particulate	diesel with no oxygen content and a glycerine fuel containing 80% of diesel and 20% of a blend containing waste cooking biodiesel, fatty acid glycerol formal ester and acetals	507

BX = X% v/v of biodiesel in diesel; B100 = pure biodiesel. PAH: polycyclic aromatic hydrocarbons; CC: carbonyl compounds.

require more severe reaction conditions and they also can suffer deactivation. Therefore, more research is needed to overcome these problems, before a commercial process of biodiesel production using heterogeneous catalysts can be implemented. Enzymes are active and selective for biodiesel production. However, the slow reaction rates, together with the associated highly costs, enzymatic catalysis is still far from being commercially used in biodiesel production processes. In parallel with efforts to make the use of heterogeneous catalysis feasible, studies involving the use of intensification technologies have been advancing on laboratory and industrial scales.

Regarding additives for biodiesel, there are still few studies of corrosion inhibitors evaluated under conditions of biodiesel storage. Research on innovative products with biocidal action for biodiesel/diesel blends also deserve more attention. In Brazil, the use of this type of additive needs to be regulated. The search for multifunctional products is certainly the biggest challenge for biodiesel quality assurance and preservation of vehicular metallic materials, transport and storage systems of this biofuel.

Finally, the publications on the effect of biodiesel/diesel blends in emissions of pollutants have been collecting an important set of results on the impact of increasing the biodiesel content in the emission profile. These studies indicated, in terms of pollutants emission, the increment of biodiesel content in diesel should be carefully evaluated since some pollutants (e.g., carbonyl compounds, major ions and NO_x) are emitted in higher concentrations in those conditions.

9. Challenges and Perspectives

The use of biodiesel has been consolidated in the energy matrix of several countries, at the same time some of them are announcing their plans to ban fossil-fuel based vehicles in the following years.⁵⁰⁹ Despite the enormous volume of studies carried out in the last 15 years and the advances achieved, there still are many challenges in this field, which require more investments in research and innovation. We highlight some relevant topics: (i) intensification of genetic researches in oil plants to improve the productivity and yield of oil for biodiesel; (ii) development of sustainable, technically viable and cost-competitive microalgae production technologies; (iii) development of viable heterogeneous catalysts and implementation of a continuous process; (iv) optimization of intensification technologies (such as microwave heating, ultrasonic irradiation, among others) for biodiesel production; (v) development of multifunctional additives in order to guarantee the quality

of both pure biodiesel and biodiesel/diesel blends under storage conditions; (vi) establishment of new uses for glycerin; (vii) evaluation of the impacts on the pollutants emission profile derived from the increasing the biodiesel content in mineral diesel, which could, in turn, contribute to guide decisions in possibly expanding the use of this biofuel; and (viii) development of combustion improver additives as a strategy to mitigate the worsening of some pollutants emission profile when high biodiesel content blends are combusted.

Supplementary Information

Supplementary information associated with this article can be found available free of charge at <http://jbcs.sbq.org.br> as PDF file.

Acknowledgments

The authors would like to thank the Agência Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Serviço Nacional de Treinamento Industrial, Departamento Regional da Bahia (SENAI/CIMATEC) the National Institute of Science and Technology (INCT) for Energy & Environment (INCT E&A, project CNPq No. 465497/2014-4), Project 'Pesquisando Kirimurê: Convergindo Educação, Ciência, Tecnologia e Inovação' (CNPq No. 442187/2018-1) and the Interdisciplinary Center for Energy and Environment (CIEnAm) from Universidade Federal da Bahia. We are also thankful for funding from CAPES (finance code 001). In addition, funding from Fundação de Apoio à Pesquisa do Estado do Rio de Janeiro (FAPERJ) and from Fundação de Apoio à Pesquisa do Estado da Bahia (FAPESB) are also acknowledged.

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Ana Lúcia de Lima received her Bachelor's degree (2011) with Technological Assignments in Chemical Sciences from the Federal University of Uberlândia (UFU), Brazil. She received her MSc degree (2013) and PhD (2017) in Chemistry from the Federal University of Rio de Janeiro (UFRJ), Brazil. Her research work is focused on catalysis, biofuel and synthesis of hybrid materials. She was a post-doctoral (2018) from the same institution, with research focused on the development of hydrogels for advanced oil recovery (EOR). Currently, she is a lecturer at the Department of Analytical Chemistry at UFRJ. Her present research is focused on the synthesis of hybrid materials for CO₂ capture, transformation of biomass and heterogeneous catalysis.



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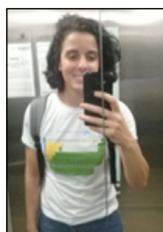


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Submitted: November 30, 2020

Published online: April 8, 2021

