



BIODIESEL IN MARINE TRANSPORTATION

Abstract:

Maritime transport remains a cornerstone of global trade and mobility; however, its reliance on conventional marine fuels contributes significantly to greenhouse gas (GHG) emissions and environmental degradation. Biodiesel has emerged as a critical transitional technology to mitigate these impacts as a drop-in solution. Research indicates that biodiesel can reduce carbon dioxide (CO₂) emissions from ships by 25.4% when combined with 80% traditional petroleum fuels. When mixed with 85% petroleum fuels, biodiesel has been shown to reduce nitrogen oxide (NO_x) emissions by 25%. Despite these environmental gains, the widespread adoption of biodiesel is constrained by high production costs and intensive energy requirements. While various biofuel generations offer distinct advantages, current research is increasingly focused on algal biomass as a high-yield feedstock. While 1st and 2nd generation biofuels can only be considered short-term solutions due to their strain on resources, biofuels derived from algae in the 3rd and 4th generations can become long-term solutions in maritime biofuels because of their lipid production capabilities and more reasonable resource requirements. Although promising, the transition to algae-based maritime fuel will likely require advancements in genetic engineering and automated harvesting techniques to achieve long-term economic and energetic viability.

Introduction

Marine transportation plays a significant role in the global economy, from shipments that drive commerce to travel. The maritime sector accounts for approximately 3% of total global greenhouse gas (GHG) emissions [1]. Emissions from maritime usage also contain more negative by-products than those from automotive emissions, such as sulfur and nitrogen oxides, which can result in acid rain and ocean acidification. Acid rain corrodes and weakens construction materials, slowly resulting in the destruction of buildings. Ocean acidification harms wildlife such as coral reefs and therefore plays into issues such as overfishing.

The International Maritime Organization (IMO) adopted a new strategy in 2023, aiming to decarbonize international shipping by 2050 and increase the share of alternative energy sources used by international shipping to 5%, or even up to 10%, by 2030 [2]. An emerging industry that can achieve these goals and meet strict regulations is biofuels, with a specific focus on biodiesels. Biodiesel technologies can mitigate greenhouse gas emissions and reduce other harmful oxides in gas exhaust, while still providing an efficient fuel source for ships. They also come from a renewable source, meaning they can decrease dependence on fossil fuels and can continue to be produced long after oil reserves become too difficult to extract. This paper outlines these technologies, as well as their drawbacks, and highlights future directions for the biodiesel industry.

Biofuel Generations and Stages

There are four generations of biofuels: (1) 1st generation biofuels come from edible plants and seeds. The carbon source comes from sugars, lipids, or starches extracted from a plant. (2) The 2nd generation of biofuels is made up of non-edible plants and seeds, such as trees, as well as animal fats and used cooking oils. (3) 3rd generation biofuels are derived from algae. (4) Finally, the 4th generation consists of genetically modified algae biofuels [3]. Table I demonstrates some

of the different properties of the generations, excluding the 4th generation as it tends to follow with improvements to 3rd generation biofuels.

Although 1st generation biodiesels are currently the most common biofuels used in industry due to their biofuel yield and relatively low lifecycle emissions along with low enough costs, there is resistance to further growth due to the food-vs-fuel debate, as food resources go towards fuel and drive-up global prices. Non-edible plants and seeds have a larger range of yields depending on what plant is being used as a base and the production method, but similarly have other uses in society, and occupy space and water that could be allocated to food production.

Algae have the largest range of production costs and therefore are not yet considered economically viable as they are. Their lifecycle emissions can be considered negative because they consume large amounts of carbon dioxide as they grow, but it often does not counter the emissions required to separate and break down the algae.

Table I. Generation Comparison. Adapted from [9].

Generation	Biofuel Yield (L/kg biomass)	Life Cycle Emissions (gCO ₂ eq/ MJ)	Production Cost (\$/L)
1st	0.15-0.48	16-78	0.86
2nd	0.00086-172100	8.8-50.54	0.304-2.07
3rd	--	-562.8-56.14	0.44-125.08*

*The cost of 3rd generation biofuels varies significantly based on the cultivation system used for the algae. \$125.08/L represents bubble column photobioreactor (PBR), which is the most expensive option for algae cultivation, while the general industry range is considered between \$0.44/L and \$8.76/L for less specialized systems.

The lifecycle of biodiesels generally includes five key stages, which are outlined in Fig. 1: (1) feedstock production, (2) feedstock transportation, (3) fuel production, (4) fuel distribution, and (5) fuel end use, which in the case of this article mainly pertains to marine use.

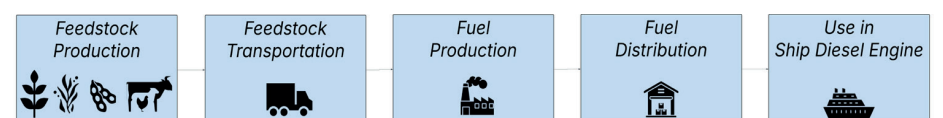


Fig. 1. Biodiesel lifecycle flowchart [4].

The first stage is essential to overall biofuel costs. The price of the feedstock accounts for around 75% of the total cost of biodiesel production, making finding a low-cost, sustainable feed integral to a successful biofuel operation [4]. The 2nd and 4th stages, feedstock transportation and fuel distribution, will contribute to the diesel's overall fossil fuel use, depending on what vehicles are used and how far. The 3rd stage, fuel production, implies a transesterification process, where a long chain of fatty acid methyl/ethyl esters (FAME) is produced from fats or oils.

Finally, the fuel makes it to its destination, a ship where it can be burned in a diesel engine. For the whole biodiesel production process, the output-input energy ratio, also referred to as the energy return on investment (EROI), should be greater than one, meaning the energy gain from the biodiesel should be greater than the fossil energy input in the production process. If this output-

input energy is not achieved, the biodiesel cannot be considered a reasonable alternative fuel. C.Y. Lin [4] outlines recent life cycle assessment studies that have demonstrated that many biofuels, particularly in the 1st and 2nd generations, have an output–input energy ratio that is greater than one, and therefore can be efficiently applied as alternative fuels.

Table II shows the EROI's of some early-generation biodiesels, as well as traditional fuels and algae. Note that the table is not a comprehensive list of all biodiesels. Traditional fuels such as oil, coal, and natural gas still generally obtain the most desirable EROI's, but some biodiesels are near achieving the same output-input energy ratio, meaning they are currently better candidates for immediate implementation. Algae mostly have an EROI below 1, so there is not a positive energy gain, and these fuels are not yet viable solutions.

Table II. EROI comparison of multiple fuel sources.

Fuel	EROI	Reference
Oil, coal, and gas	6*	[10]
Biodiesel from soybean oil	1.5-3.2	[11]
Biodiesel from castor oil	2.0-2.9	[11]
Biodiesel from palm oil	5.08	[11]
Biodiesel from canola oil	2.22	[12]
Biodiesel from algae (Nannochloropsis salina)	0.56-1.03	[13]

*Although the EROI of petroleum is generally indicated around 25, recent data shows it is likely lower due to increasing costs of obtaining the oil and can go as low as 3 [10].

Energy Density, Storage, and Compatibility

Although biodiesels can significantly decrease GHG emissions, including more toxic by-products such as sulfur and nitrogen oxides, they have their drawbacks. One major disadvantage is that the energy density of biodiesel is approximately 10–12% lower than that of conventional marine distillate fuels [5].

A lower energy density means more biodiesel is required to achieve the same effects as fossil fuels. Therefore, more storage is required for biofuels, and costs are higher. Storage proves to be an issue, as biodiesel can generally be stored only 6 to 12 months, compared to regular diesels, which can be stored 12 to 24 months. Furthermore, as the biofuel is derived from vegetable oils or animal fat, it is more susceptible to breakdown due to oxygen exposure [6]. Therefore, storing larger portions of biodiesel needed for longer journeys proves to be an issue as it amplifies the oxidation and infrastructure challenges.

Due to its storage needs and generally lower caloric values, biodiesel cannot stand alone as a separate source of energy. Instead, it must be combined with fossil fuels. Fortunately, biodiesels have essentially the same densities and viscosities as traditional fuels, so they can be combined. In a study on biofuels in marine diesel engines, Sagin et al. [5] found that mixtures ideal for use in engines usually consist of 70-95% petroleum fuel, with the remainder made up of biodiesel.

A fuel mixture containing 5–20% biodiesel fuel can reduce carbon dioxide emissions by 4.1–25.4%. Inherent oxygen in biodiesel molecules improves combustion efficiency, so the more biofuel that is in the fuel mixture, the more carbon dioxide emissions are reduced, which is visually represented in Fig. 2. The payoff is increased storage needs, which is why biodiesel fractions rarely exceed 20%. Furthermore, Sagin found that nitrogen oxides in gas exhaust also decrease.

At mixtures containing 10-15% biofuel, nitrogen oxide emissions can decrease up to 25%, given that the engine is running at 75-85% of rated power, which is ideal for large vessels [5]. By using less biodiesel via mixtures, reasonable storage metrics are possible. Biodiesel can also be refilled at ports, so its continued use is possible for long journeys without spoiling.

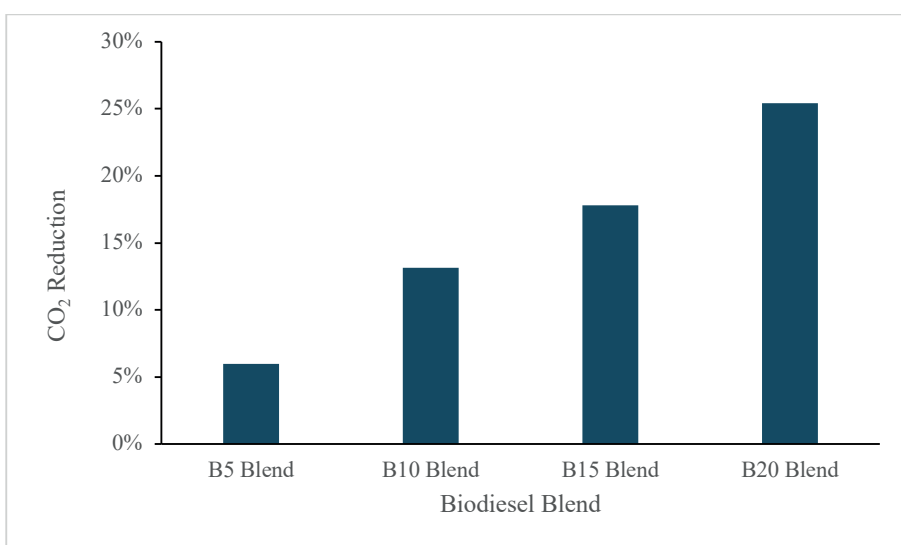


Fig. 2. Carbon dioxide reduction for biodiesel blends. B5 is a biodiesel blend that contains 5% biodiesel combined with regular marine diesel, B10 is a biodiesel blend that contains 10% biodiesel, and so on. All data is for diesel engines with a nominal power of 0.85 [5].

Although biodiesels can be easily combined with traditional marine fuels in engines, another issue that arises with them is that they degrade elastomers, rubbers, and plastic materials, which are

consistently found in fuel feeding systems such as hoses, valves, filters, and seals. Storage tanks made of tin, brass, copper, bronze, and zinc are also vulnerable to biodiesel. An oxidation reaction of these storage materials with biodiesel chemical compounds takes place, and the products of these degradation reactions can lead to clogging within the system.

To avoid these issues, materials that are resistant to degradation reactions with biodiesel must be employed. Rubbers that are compatible with biodiesels are Chemically Resistant Fluoroelastomer, FKM(Viton®), Buna Nitrile, and Expanded Polytetrafluoroethylene (PTFE). Although they all can be used for biofuels, they do experience swelling from reagents in fuel processing, such as methanol. Metals that are compatible with biodiesel include aluminum and stainless-steel, although aluminum can have adverse reactions with catalysts used to produce biodiesels, making stainless-steel the ideal metal in biodiesel systems [7].

Table III lists these issues and their effect on the maintenance of a fuel system, as well as some of the positive effects of biodiesel. The negative impacts are largely for biodiesel mixtures above 20% biodiesel. Although replacements are costly, wear reduction and cleanliness from the biofuels will reduce overall operational costs over time. Similarly, with storage tank replacement, upfront costs of implementing a separate tank for the storage of biodiesel on a ship will be high, but the continued maintenance will not be costly.

Table III. Biodiesel effects on fuel systems. Adapted from [16].

System aspect	Biodiesel impact	Maintenance effect
Hoses and gaskets	Breakdown with use of blends above B20	Replacements needed, usually in vehicles manufactured before 1994
Storage tanks	Oxidation reaction and system-wide clogging	New separate stainless-steel tanks for biodiesel storage
Fuel injector/pump	Easier combustion and better lubricity	Reduced wear and longer life
Fuel system deposits	Solvent effect	Higher initial deposits, then cleaner with less maintenance
Filters	More clogging initially	More frequent filter changes early on, then normal

Algae as the Future of Biofuels

A promising area of development for biofuels is with algae-based fuel, or 3rd generation fuels and onward. An issue with plant and animal-based biofuels is that they take up resources required for food, therefore driving up food prices. Algae, on the other hand, can be produced using land and water that could not otherwise be used for food, such as brackish water, or wastewater, therefore reducing the strain on global resources [14].

Microalgae have more potential for expansion in the biodiesel industry than macroalgae because of comparatively easy cultivation and maintenance. In addition, microalgae show high lipid productivity, which undergoes the transesterification process to produce biodiesel. High lipid productivity results in more energy content in the diesel for a given amount of algae. Another advantage is that algae biodiesels undergo rapid decomposition in marine environments, with around 95% of biodiesel undergoing decomposition within 21 days [1].

This function of algae in biodiesel makes it ideal for maritime transport, as any oil spills made up of algae-derived biodiesel will not have lasting effects on marine environments. These many advantages, which are summarized in Fig. 3, place algae at the forefront of research interest for new innovations to biofuels.

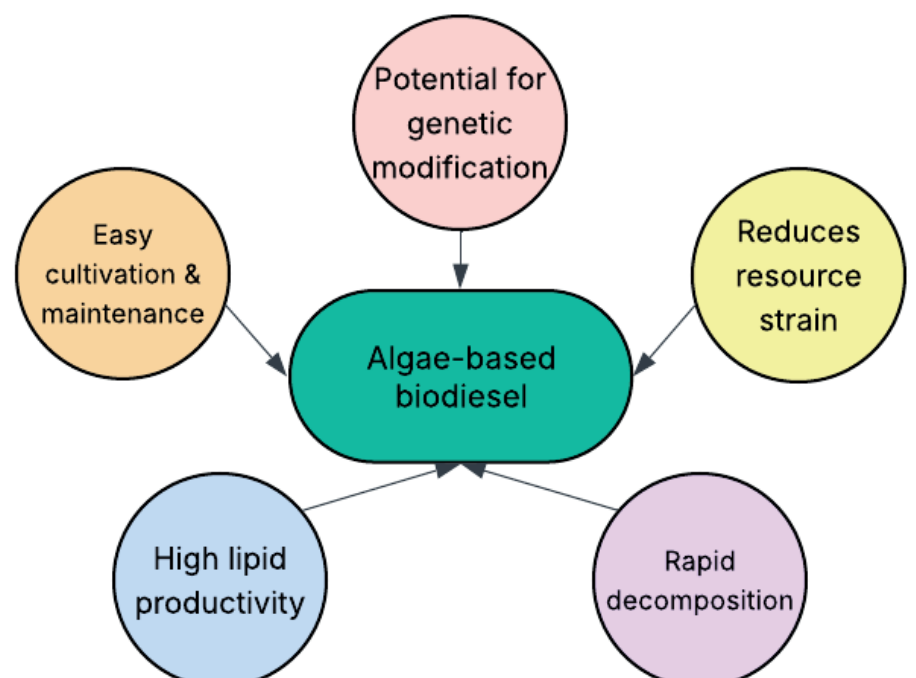


Fig. 3. Summary of advantages pertaining to biodiesels derived from algae [1,14].

Although algae display many advantages for biofuels, they are expensive to cultivate, harvest, and process. Separating algae from water significantly increases capital costs, and the energy required to grow and convert the algae to biodiesel currently results in an output–input energy ratio that

is less than one, as indicated in Table 2 [8]. With an energy ratio that does not break even on the energy required from fossil fuels, algae is not currently a plausible solution. Much research must be done to refine and develop the production of biodiesel from algae sources, so that it can achieve an EROI greater than one and become more cost efficient.

The key areas for improvement in microalgae are the identification of the most ideal algae strains through genetic modification, what culture conditions under which they produce the most lipids, microalgae cultivation, and harvesting.

The genetic modification of algae can allow fewer algae to obtain higher oil productivity and possibly cut down on the amount of water that algae need to grow. Table IV provides a limited list of algal species and how genetic engineering (GE) can affect the algae for biofuel production. The table shows how multiple results can come from genetic modification beyond changes to lipid production, such as improving the algae's resistance to herbicides, or the ability to grow in different environments, as well as improvement in susceptibility to future changes.

Table IV. Strains of algae and their genetic modifications. Adapted from [23].

Algal species	GE technique	Resulting improvement	References
<i>Chlorella vulgaris</i> UTEX395	CRISPR/Cas9	Enhanced editing efficiency	[17]
<i>Tetraselmis</i> sp.	CRISPR-Cas9 RNP	Enhanced lipid production	[18]
<i>Chlamydomonas reinhardtii</i>	CRISPR/Cas9	Herbicide (Sulfometuron methyl) tolerance	[19]
<i>Nannochloropsis oceanica</i> IMET1	CRISPR/Cas9	Normal growth under NH ₄ Cl	[20]
<i>Phaeodactylum tricornutum</i>	TALEN	Improves the molecular toolkit for diatoms	[21]
<i>Synechococcus</i> UTEX 2973	CRISPR/Cpf1	Complex genome modification	[22]

The most common genetic engineering method is currently CRISPR, which impacts different parts of the algae's DNA for varying results. However, genetic engineering technologies such as CRISPR come with restrictions and evolving regulations. The Cartagena Protocol on Biosafety (CPB) is the first international treaty to deal with the production of GMOs. It guides researchers to carry out risk and ecotoxicology studies before releasing GMOs to markets. Also, disputes over the ownership of patents related to CRISPR have created a confusing market landscape, especially in the EU, which could lead to growing disputes among companies [23].

Cultivation is dependent on the light and energy source of the algae. Many algae require carbon dioxide to grow, which can be utilized as a form of carbon sequestration on large enough scales. Phototrophic growth of microalgae, which utilizes sunlight and an inorganic carbon source to form chemical energy via photosynthesis. Open-pond cultivation is a cheap form of phototrophic cultivation, but it yields lower oil productivity.

Photobioreactors could be more effective to grow microalgae by using a favorable light source and reactor configuration, but the reactors are highly costly to build and operate [15]. Ideally, photobioreactor systems could be developed in tandem with a carbon capture plant to maximize efficiency and keep costs as low as possible.

Harvesting must also be improved to make algae a more viable source for biofuel. The most economically feasible harvesting technology currently used is centrifugation, but it can damage cell structure and processing a large amount of culture using centrifugation is time-consuming and costly [15]. Further research must be done on the chemistry and electrochemical properties of algae to determine new directions for harvesting that will enhance the commercial viability of algae-based biofuels.

Conclusion

The transition of international maritime transportation towards sustainable energy sources is a logistical and environmental necessity. Biodiesel presents a viable solution that can be integrated into current systems with minimal disruption, but its widespread adoption is currently hindered by technical and economic factors. The inherent limitations of 1st and 2nd generation biodiesels necessitate a shift toward more advanced feedstocks.

Operationally, the lower energy density (approximately 10% less than conventional marine fuels) and the susceptibility of biodiesels to oxidative degradation and elastomer corrosion require careful management. Current data suggests that fuel blends containing 5–20% biodiesel offer a pragmatic compromise, significantly reducing CO₂ and NO_x emissions without requiring extensive engine modifications or excessive storage volumes.

The future of maritime biofuels likely resides in 3rd and 4th-generation algae-based fuels. Although these sources currently face an unfavorable output–input energy ratio and high cultivation costs, they offer the dual benefits of high lipid productivity and minimal impact on food resources. Continued research into genetic modification and novel cultivation and harvesting processes is essential to achieving widespread use of these biodiesels.

Policies must be implemented that resolve disputes over genetic engineering and make patenting GMO's simpler, so that researchers can focus on developing algal species with high lipid production in low maintenance environments that can easily be converted into biofuels through simpler drying and transesterification. If these economic and energy barriers are overcome, algae-derived biodiesels could serve as a long-term solution to the decarbonized global shipping industry.

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