


Perspective

Microalgae Oil-Based Metal Working Fluids for Sustainable Minimum Quantity Lubrication (MQL) Operations—A Perspective

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Abstract: This article presents a perspective on the potential use of microalgae oils in the production of metal working fluids (MWFs) used for minimum quantity lubrication (MQL) operations. The generalities of MQL operations and requirements of MWFs, and current advances in the development of the most promising microalgae oils with high contents of saturated, monounsaturated, and polyunsaturated fatty acids were reviewed and discussed. The analysis of data, discussions, and conclusions of numerous studies published recently and combined with the experience of the multidisciplinary team of authors strongly suggest that microalgae oils do indeed have great potential as sustainable and eco-friendly base oils for producing semi-synthetic MWFs, soluble oils and straight cutting fluids for MQL operations. Additionally, gaps and challenges focused on the use of agro-industry wastewater in microalgae production, green harvesting and oil extraction methods, and replacement of toxic additives in MWFs by green nanoparticles and biopolymers were identified and highlighted for achieving massive microalgae oil-based MWFs production and truly green machining processes.

Keywords: microalgae; cutting fluid; minimum quantity lubrication; green machining



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1. Introduction

Nowadays, the global manufacturing industry is increasingly being pushed to meet developing eco-friendly demands, which have been even more stringent since the last decade. It can be ascribed to the massive increase in the need for consumer goods because of a rising human population and industrialization. As a reference, it has been projected that material extractions for goods production, energy demand, water consumption and greenhouse gas emissions will nearly double in 2050 in comparison to that reported in 2017 [1]. To counteract these problems that could already be seen coming a few decades ago, some manufacturing strategies have been established through extensive research work [2]. Such strategies or techniques are categorized as sustainable or green manufacturing practices, and they should be able to coalesce the research knowledge, technology and industrial skills to preserve resources, energy and the environment [3].

Machining, cutting and material removal processes are among the most critical manufacturing activities in different industrial sectors, which are known to generate high energy consumption, significant environmental affectations, and occupational health risks [4]. The problems are primarily related to high consumption of energy (due to friction and cutting forces), overuse of cutting tools (due to premature failures by wear and rupture) and toxic waste of cutting fluids (via spillage, degradation and evaporation) as a consequence of material removal. Depending on the process, the detachment of swarf and chips,

generation of dusts, mists and volatile organic compounds during machining processes, the treatment and waste of metal working fluids (MWFs) become critical and harmful problems in manufacturing for both environment and human health. Hence, green or sustainable machining processes have been intended to diminish or eradicate these problems. These processes must procure operators' health, environmental friendliness and gaining in economic benefits [5,6]. Up to date, the most followed and accepted green machining techniques in industry are based in dry machining, minimum quantity lubrication (MQL) and cryogenic cooling [7].

MQL is the most popular green alternative for replacing flood cooling/lubrication techniques and solving the deficiencies (short tool life and poor surface quality) of dry machining processes [8]. In other words, MQL looks to address an effective combination between the benefits of conventional flood cooling/lubrication and dry machining. This technique consists of applying a very minute dose of MWF along with air assisted jet, fulfilling the need for cooling and lubrication actions during metal/working processes, as is illustrated in Figure 1. Tiny droplet particles are dispersed in the air jet at high-speed, ensuring the precise amount of oil over the interfaces to keep good lubrication; meanwhile, the cooling and chips removal tasks are carried out by the air jet. Conventional MWFs are emulsions typically made of mineral oils (2–20 wt%) and sodium petroleum sulphonate emulsifiers (10–15 wt%) in water. The oil acts as a lubricant, while water helps to cool down the cutting interface. These MWFs are not readily biodegradable and are one of the most prevalent effluents disposed of in the environment in the manufacturing industry [9]. Their waste is often hazardous [10] because they are vulnerable to bacterial contamination [11], and in many cases, are responsible for some human occupational health disorders, namely, cancers, dermatitis, lung disorders, etc., due to indirect breathing of residual MWF and contact with operator's skin and eyes during operation [12,13].

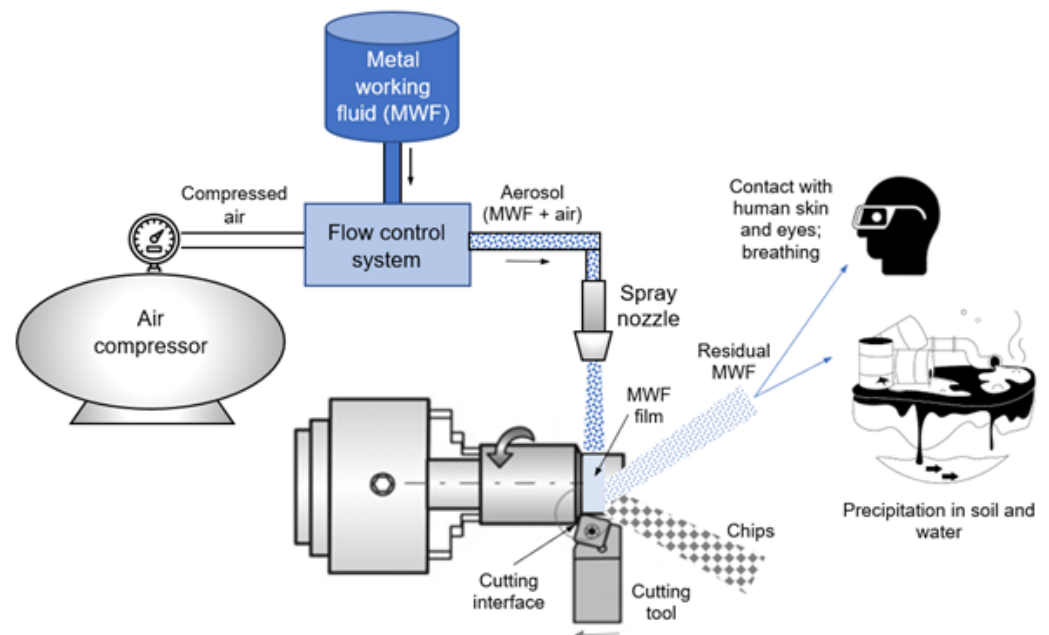


Figure 1. Schematic representation of a MQL process for turning operations.

Due to the abovementioned information, MWFs for green MQL processes should be selected not only based on their cutting performance but also on their biodegradability level. In this sense, the exploration of biodegradable raw materials to be used as straight oils in MQL or in the production of green emulsions in MWFs has been the study topic of many worldwide research groups lately. It has been reflected in a huge amount of the literature reporting on the use and cutting performance of straight vegetable oils or synthetic esters as renewable and biodegradable bio-oils to replace mineral oils in MWFs

for different machining applications, which has been recently (last five years) compiled in many comprehensive review articles [1,4,6,9,14–19]. Those reviews addressed thorough analyses and discussions about state-of-the-art challenges and physicochemical, tribological and cutting performance properties of the most popular and promising bio-oils in MWFs. Overall, it has been stated that the potential of bio-oils is related to their renewability, biodegradability, better lubricity than mineral oils in most cases, nontoxicity, and various agro-economic benefits related to their production [19]. Up to date, the most promising and preferred bio-oils or synthetic ester sources reported for producing MWFs are those obtained from non-edible crops with high content of oil, namely, castor, jojoba, jatropha, neem and calophyllum inophyllum because they do not compete apparently with the production of food crops [20]. Nonetheless, due to the foreseen global demand for MWFs and the land required for getting the crops to produce the necessary quantity of bio-oils, even using inedible bio-oils for MWFs production will cause conflicts for keeping safe the arable lands required for meeting the global food market demand [21]. Thus, although non-edible vegetable oils are biodegradable and exhibit great potential to replace mineral oils in MWFs, they can be unsustainable in the mass production of MWFs.

In order to tackle the above sustainability problem, microalgae have been recently advocated as a developing source of bio-oil that truly meets the sustainable production of lubricants for different applications, including MWFs [22]. As a reference, the differences in biomass oil content and land required for producing biodiesel from microalgae, which involves the use of lipids/oils as lubricants, in comparison to other crops are shown in Figure 2. Microalgae are photosynthetic unicellular micro-organisms that can grow either in marine, freshwater, artificial or wastewater environments offering different advantages: (i) they do not need arable land, (ii) due to their photosynthetic activity, they can consume CO₂, and (iii) they have the capacity to perform the bioremediation waters using nutrients as substrate for growing. They are able to convert nutrients into biomass with different cellular constituents [23] and to produce even other high-value byproducts (e.g., food supplements [24,25], pharmaceuticals [26], cosmetics [27], fuels [28,29], etc.) meeting the intention of algal biorefinery to valorize microalgae biomass and produce different products with minimal waste [30,31]. Although microalgae are an obvious prospective source to produce MWFs due to their potential to produce high amounts of lipids/oil, this application or use has barely been explored and promoted in the scientific and industrial sectors.

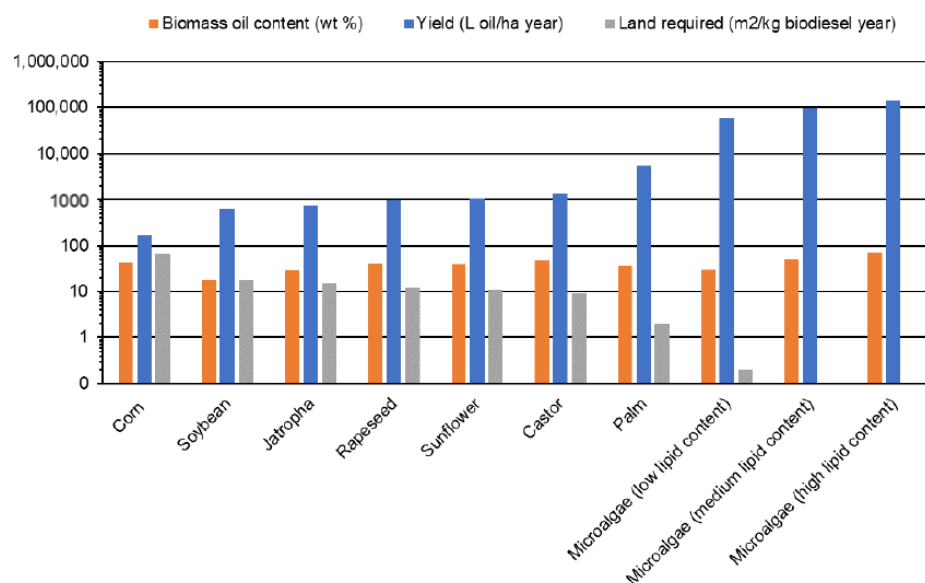


Figure 2. Biomass oil content, oil yield and land required for biodiesel production from different crops and microalgae. Data obtained from [32].

Considering the needs of bio-oil-based MWFs to achieve green machining processes and the sustainability benefits of microalgae, this perspective attempts to display the suitability of microalgae oils for the production of MWFs for MQL operations based on the review and comprehension of the most recent literature. The paper is divided in five sections: Section 1 provides the background, motivation and aim; Section 2 addresses the fundamentals and the current and key considerations of MWFs and MQL processes; Section 3 present a summary of the typical properties and performance of non-edible vegetable oil-based MWFs as reported in the last five years; Section 4 present analyses and discussion of the most suitable microalgae oils reported in the literature with high potential to be used in MWFs for MQL operations; and Section 5 addresses the challenges towards a future effective MWFs production with microalgae oils to achieve greener MQL processes.

2. Considerations of MWFs for MQL Processes

Since the introduction of the MQL concept about 20 years ago [33], MQL techniques have been adjusted and enhanced to increase tool life, surface finish and chip breakability, and reduce cutting forces mainly in processes such as turning [34,35], milling [36,37], drilling [38] and grinding [39]. At present, MQL is applied in conventional machining processes in two different ways: internally or externally, as is illustrated in Figure 3. Internal MQL consists of the application of MWF mist to the interface through tunnels/channels in the cutting tool meanwhile external MQL requires an external nozzle fed by an external MWF supply system. In contrast to flood lubrication systems for cutting processes requiring MWF flow rates between 50 and 1000 L/h [40], the flow rate for MQL should be from 0.01 to 2 L/h to be considered as an appropriate MQL process [41]. For both internal and external processes, MWFs must comply with several requirements to provide effective cooling, lubrication and chips removal functions at the cutting interfaces. Therefore, the requirements of MWFs for MQL focus on thermal conductivity and stability, lubricity, flash point, corrosion inhibition, viscosity, biodegradability and toxicity [42], as disclosed in Figure 4. In contrast to conventional MWFs for flood cooling/lubrication, MWFs for MQL are required to be readily biodegradable because they are spilled or volatilized into the environment once they are misted up. The one-time use of MWFs in MQL reduces the necessity of base oils with high thermal stability. Additionally, the air jet, which acts to remove chips but also to cool down the cutting interface in the MQL, eliminates the need of base oils with high thermal conductivity. In this sense, the use of bio-oils, even those with poor thermal properties, as base oils for producing MWFs becomes very appropriate for MQL operations.

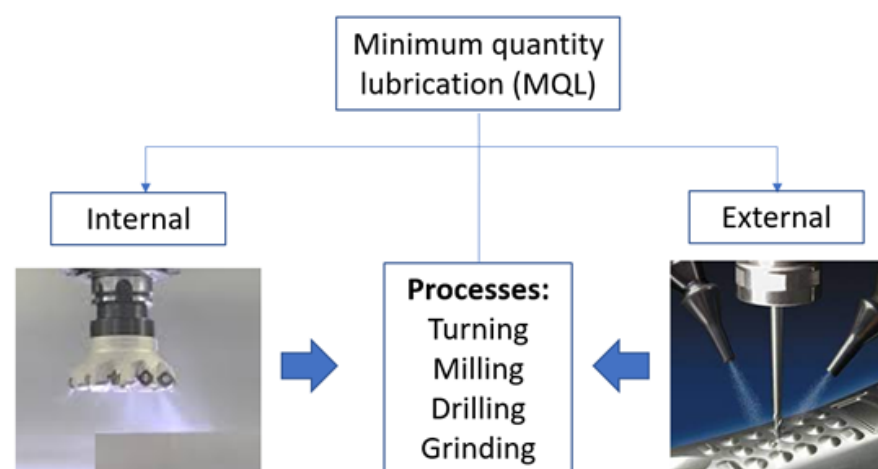


Figure 3. Types of MQL processes.

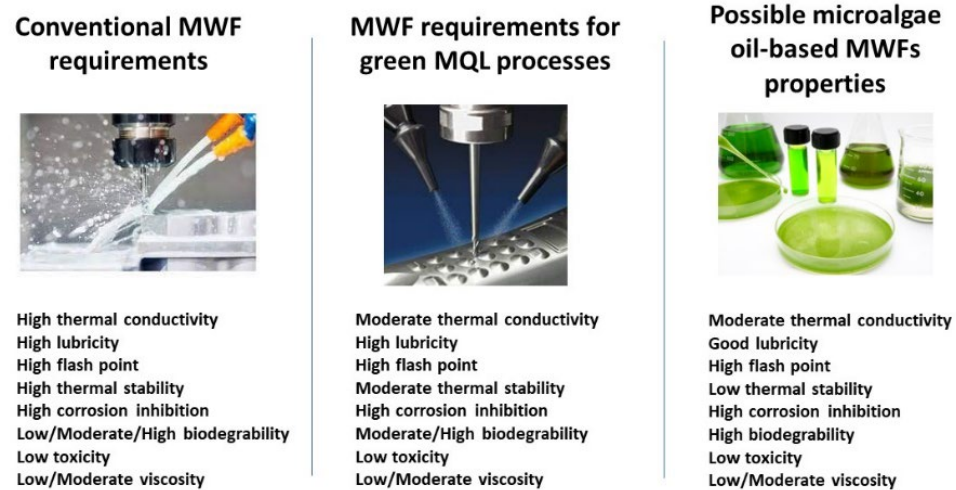


Figure 4. General requirements of metal working fluids (MWFs) for flood lubrication and MQL processes, and their comparison to microalgae oil-based MWFs expected properties.

In general, there are four main types of MWFs for the different machining processes and MQL operations (see Figure 5): synthetic MWFs, semi-synthetic MWFs, soluble oils and straight cutting oils. Synthetic MWFs, also named as oil-free MWFs, are diluted with simple synthetics, organic and inorganic salts or polymeric agents to form a clear solution. They should not contain any type of oil in their formulation and are used to continually dampen machining tools to prevent mist and smoke in grinding processes. Semisynthetic MWFs can contain between 5 and 40% pure oil diluted with water through emulsifiers. They are mainly used to cool and lubricate the tool and work piece in any kind of cutting process. Soluble oils are made to cool and lubricate, particularly in cutting and grinding processes. They contain from 50 to 90% oil with emulsifiers and water dilution and are suitable to prevent welding between the cutting tools and workpiece and reduce the wear of the tool. Finally, straight cutting oils are neat oils (not diluted) blended with different additives (mainly extreme pressure agents) in concentrations below 10%. They are used in heavy-duty machining processes. Hence, according to the above MWF categories, bio-oils, including those microalgae oils, can be effectively used to produce either semi-synthetic MWFs, soluble oils or straight cutting oils.

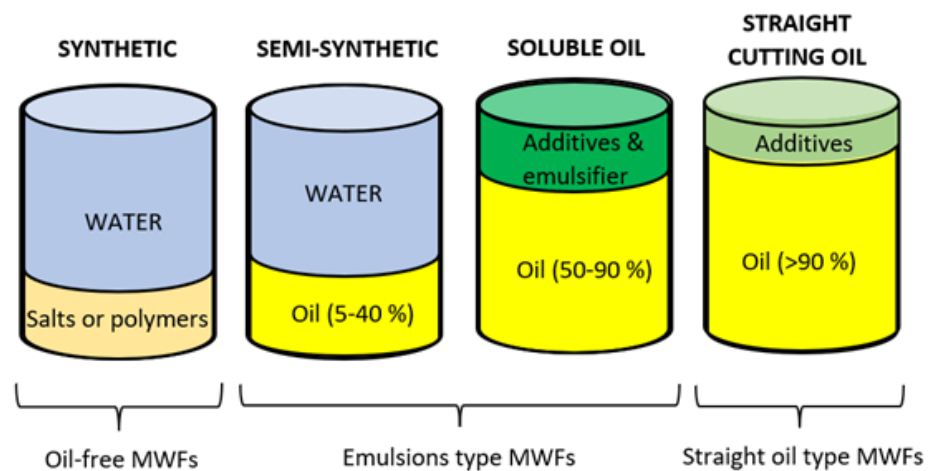


Figure 5. Types and general composition of commercial metal working fluids (MWFs).

One of the most important drawbacks of straight bio-oils for lubrication purposes is the low thermal stability as consequence of their natural composition of 92–98% of triacylglycerol and a variety of fatty acids [43]. It promotes easy/quick aging/degradation/polymerization

(increase in viscosity as main consequence) and loss of lubricity through high temperatures (≥ 60 °C), thermal cycling due to continuous use and long storage periods [22,44]. Microalgae oils like other bio-oils are known to exhibit certain properties (lubricity, viscosity, pour point and oxidation stability) depending on their carbon chain length, saturation degree and polarity [45]. Having long carbon linear chains ($n \geq 9$) and high saturation degree (saturated fatty acids (SFAs), monounsaturated fatty acids (MUFAs) and polyunsaturated fatty acids (PUFAs)) with high polarity are the best for lubrication purposes, including machining processes [22]. Nevertheless, for MQL purposes, even straight bio-oils without having the above desired chemical structure could actually be used as MWFs if they comply with a suitable viscosity (between ≈ 10 to 150 cSt (mm^2/s) at 40 °C for MWF base oils [46]). It is noteworthy that microalgae oils with poor properties, in particular those with low thermal stability, poor lubricity and inappropriate viscosity, could be used after being subjected to some chemical conversion methods, which have been positively demonstrated by numerous research groups lately [45,47,48]. The most effective reported conversion methods are intended to produce estolides [49,50] and fatty esters from straight bio-oils by transesterification [51], partial hydrogenation [52,53] or epoxidation [54,55]. Alternatively, or complementarily, straight or modified bio-oils can be further boosted by incorporating different chemical or physical additives depending on each particular application requirements. In the case of conventional or bio-based MWFs, the most common additives used are antimicrobial pesticides (biocides), antimist agents, antioxidants, corrosion inhibitors, coupling agents, defoamers, dyes, emulsifiers, extreme pressure agents, lubricity additives, metal deactivators, reserve alkalinity boosters (amines) and wetting agents [56]. However, it should be noted that some of the above additives are considered toxic or contaminant according to the current environmental policies, so they can reduce the eco-friendly attributes of the MWFs even those produced with bio-oils. Hence, modern research on green MWFs is being focused on the exploration of different nanoparticles [15] and biopolymers [57] as green additives to replace polluting additives by keeping or improving cutting performance.

3. Typical Physicochemical Properties of Non-Edible Vegetable Oils and Microalgae Oil

In order to provide some of the key typical characteristics of bio-oils used as MWFs and microalgae oil, Table 1 presents a comparison of physicochemical properties and the main machining advantages of non-edible vegetable oils used as MWFs and microalgae oil. For this comparison, oils considered edible were discarded due to the fact that they cannot promote sustainable production of MWFs without affecting production of human feed stocks. According to the viscosity requirement for MWFs, jatropha, jojoba, neem, callophyllum inophyllum and microalgae oil meet with viscosity in the range of (≈ 10 – 150 mm^2/s), so they can be potentially considered for producing MWFs for MQL. The viscosity index is an arbitrary unit that represent the change in viscosity relative to temperature change of a fluid. As a reference, a traditional mineral oil has a viscosity index between 90 to 100. Usually, bio-oils have higher viscosity index than mineral oils. In this case, only jatropha, jojoba and Callophyllum Inophyllum oils have been reported to exhibit higher viscosity index than mineral oil. The viscosity index of microalgae oil was not reported. It is noteworthy that most of the literature on microalgae oils is majorly focused on exploring its properties as biodiesel. So, microalgae oils are chemically modified to produce biodiesel. Therefore, relevant properties for MWFs such as viscosity index, pour point, flash point, etc., of microalgae crude oil are scarce in the literature. The non-edible vegetable oils have higher pour points than mineral oil, which means that they can lose their flow characteristics at low temperatures. Only castor and jatropha oil present pour points below 0 °C. In the case of flash point, all the non-edible oils were reported to present much higher flash point than mineral oil, which is good for MWFs.

Table 1. Comparison of physicochemical properties and advantages of common non-edible vegetable oils used as MWFs.

Oil	Main Physicochemical Properties					Advantages	Reference
	Density (g/mL)	Viscosity at 40 °C (mm ² /s)	Viscosity Index	Pour Point (°C)	Flash Point (°C)		
Mineral oil	0.85	9	90–100	−40	150	-	[58]
Castor oil	0.970	249.8	85	−31	260	In contrast to dry cutting, castor oil achieved better performance in MQL in terms of lubrication, tool life, cooling ability and surface roughness.	[1,59,60]
Jatropha oil	0.917	36.97	186	−3	273	It exhibited excellent lubrication properties as cutting fluids.	[1,61,62]
Jobba oil	0.849	21.8	242	9	295	Applying Jobba oil as machining fluids helped to enhance surface finishing.	[1,63]
Neem oil	0.910	48.32	40	7	250	Neem oil was found to be an effective alternative as mineral oil-based coolant as it provides better results in terms of cutting force reduction, also ensures hazard-free environment at machining area.	[1,17]
Callophyllum Inophyllum oil	0.896	53.136	159.2	8	218.5	It was found to exhibit almost similar cutting forces and chips quality than synthetic ester, crude jatropha oil and refined bleached and deodorized palm olein.	[64,65]
Microalgae oil (<i>Scenedesmus</i> sp. Biocrude Oil)	0.97	70.7–73.8	-	-	-	-	[66]

4. Identification of Suitable Microalgae Oils for Use in MQL Operations

Microalgae oil production consists basically of four stages, namely, cultivation, biomass growth/lipids accumulation, biomass harvesting and oil extraction [22]. Afterwards, the resulting oil (either straight oil or chemically modified oil) can be used to produce MWFs, as illustrated in Figure 6. Although the microalgae oil production process has been widely reported, the production of microalgae oils is still considered not totally feasible at a commercial level due to the lack of commercial and efficient large-scale photobioreactors for biomass cultivation, low-cost, green and more effective methods for harvesting, oil extraction and purification [32]. However, it is expected that the above shortcomings in large-scale production can be accomplished in the coming years according to significant evidence of recent research and efforts by academia–industry linkages, as elucidated in several bibliometric reviews [67–71]. In fact, some companies such as ExxonMobil, PureBiomass In, Helios NRG, etc., are recently investing the development of microalgae-based lubricants and fuels and extensive cultivation technologies, mainly in large scales [70]; For example, ExxonMobil projects the production of 10,000 barrels per day of microalgae-based biofuel for 2025 [72].

The most important stages for achieving the specific type and highest amount of lipids/oil for producing MWFs or other lubricants are cultivation and growth/lipids accumulation. Up to date, it is known that the amount and type of lipids (glycosylglycerides, phosphoglycerides, betaine ether lipids, and most importantly storage lipids as triacylglycerids (TAGs) for lubrication purposes [73]) formed and accumulated in microalgae can be controlled or optimized via several variables during cultivation, namely, microalgae culture selection, type of photobioreactor (open or close), salinity grade, indoors or outdoors conditions, temperature, dissolved oxygen concentration, agitation speed, light/dark cycles, illumination type and amount of nutrients (e.g., C, N and P) [22]. The change of these parameters induces stress to the microalgae causing alterations in the biochemical reactions and rate of growth, and thus TAGs formation/accumulation. In simple words, the largest accumulation of TAGs means the largest amount of suitable and available oil for extraction from microalgae. The increase in TAG concentration in microalgae has been achieved substantially in recent times through different stress strategies based on deprivation of nutrients (N and P) [74,75], oxygen saturation [76], light intensity and illumination/dark

cycles [77–79], salinity [80–82], temperature [77,83] and mutant genes [84], depending on each microalgae strain. Therefore, the existence of a wide variety of microalgae species (more than 150,000 [85]) in the world with a broad range of possibilities in terms of cultivation and growing conditions, which are capable of producing high amounts of lipids/oil, is promising for having different options of sustainable bio-oils with different chemical structure/properties from microalgae that can be used for MWFs. According to a previous review work of microalgae strains capable to producing suitable lubricating oils for different applications [22] (containing fatty acids with long carbon linear chains ($n \geq 16$) and high saturation degree (MUFAs, PUFAs and SFAs)), the most suitable microalgae species reported to date for producing oils under optimized growing conditions with the potential for MWFs were identified and listed in Table 2. The expected properties were predicted in a qualitative way according to the fatty acid contents reported.

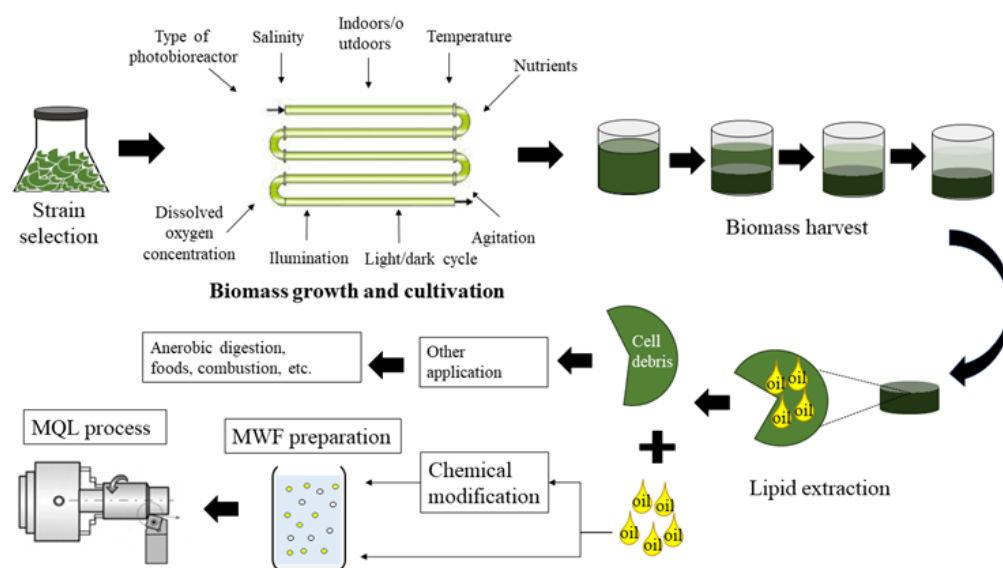


Figure 6. Schematic representation of the production process of microalgae oil-based MWFs.

Table 2. Suitable microalgae strains and expected properties as base oils for MWFs.

Microalgae Strain	Fatty Acids	Main Lubricant Properties *				Reference
		Lubricity	Viscosity	Pour Point	Oxidation Stability	
<i>B. braunii</i> (UTEX LB 572)	MUFA (C:18)	✓✓✓	✓✓	✓	✓✓✓	[86]
<i>B. braunii</i> (IBL-C117)	MUFA (C:22)	✓✓✓	✓✓✓	✓	✓✓✓	[86]
<i>B. terribilis</i> (IBL-C115)	MUFA (C:18)	✓✓✓	✓✓	✓	✓✓✓	[86]
<i>Chlorella</i> sp. 800	MUFA/PUFA (C:18)	✓✓	✓✓	✓✓	✓✓	[86]
<i>Chlorella saccharophila</i> 477	PUFA (C:18)	✓	✓	✓✓✓	✓	[86]
<i>Chlorella minutissima</i> 494	PUFA (C:18)	✓	✓	✓✓✓	✓	[86]
<i>Chlorella</i> sp. 313	PUFA (C:18)	✓	✓	✓✓✓	✓	[86]
<i>Chlorella minutissima</i> 444	PUFA (C:18)	✓	✓	✓✓✓	✓	[86]
<i>Schizochytrium</i> sp.	PUFA (C:22)	✓	✓	✓✓✓	✓	[87,88]

Table 2. Cont.

Microalgae Strain	Fatty Acids	Main Lubricant Properties *				Reference
		Lubricity	Viscosity	Pour Point	Oxidation Stability	
<i>Schizochytrium</i> sp. HX-308	PUFA (C:22)	✓	✓	✓✓✓	✓	[89,90]
<i>Phaeodactylum tricornerutum</i>	PUFA (C:20)	✓	✓	✓✓✓	✓	[91]
<i>Chlorella vulgaris</i>	MUFA (C:16)	✓✓✓	✓✓	✓	✓✓✓	[92]
<i>Dunaliella salina</i>	MUFA (C:18)	✓✓✓	✓✓	✓	✓✓✓	[93]
<i>Nannochloropsis gaditana</i>	SFA (C:18)	✓✓✓	✓✓	✓	✓✓✓	[94]

* ✓Low; ✓✓Regular; ✓✓✓High.

5. Current Challenges and Concluding Remarks

In summary, the use of truly sustainable and readily biodegradable MWFs (with acceptable performance) in green machining practices such as MQL processes is still considered one of the biggest challenges in the present and coming years for the metal working industry. Hence, microalgae are considered the most sustainable source of oil for producing MWFs and even other lubricants. Either with high or low quality in terms of physico-chemical properties, microalgae oils can be a promising green alternative in the production of biodegradable and sustainable MWFs (semi-synthetic, soluble oils or straight cutting oils) for MQL applications and to achieve truly green machining operations. In particular for MQL processes, microalgae oil-based MWFs can be considered very promising due to the characteristics of the MQL technique, which needs biodegradable base oils with no too stringent requirements in terms of physico-chemical properties. Moreover, the modern chemical conversion methods for bio-oils and additives can be deemed effective for improving the possible deficiencies of bio-oils and increasing the MWF performance by keeping eco-friendly demands in green machining processes. However, even considering the sustainability attributes and the well-documented evidence demonstrating the appropriateness of microalgae oils for producing lubricants such as MWFs, the massive production and use of microalgae oils for this purpose brings some other problems which must be anticipated and solved. These problems are mainly related to microalgae production on a large scale and the lack of green methods for cultivation, harvesting, oil extraction and enhancement/refinement.

To achieve an effective and feasible production of microalgae oil-based MWFs, a large-scale microalgae oil production is needed. For this, further developments in design, construction and handling photobioreactors (either open or closed) are required. Effective cultivation and harvesting in reactors with scaling up to 300,000 L is a current obstacle in getting efficient and green oil production processes [67]. The use of clean water and high-quality nutrients sources for microalgae cultivation can cause a sustainability conflict regarding the need of drinking water for human consumption and increasing production costs. Thus, to reduce the cost and decrease even more the environmental impacts and achieve a more sustainable microalgae production, the use of agro-industry wastewater as substrate is a future expectation and research gap for biomass generation [95–97]. Most of the biomass harvesting processes at small, regular or large scales are carried out by flocculation/coagulation, while oil extraction is performed using either organic solvents, the Soxhlet extraction/Bligh and Dyer’s method or ionic liquids, which are all considered to cause grave secondary environmental problems [98]. In this sense, the exploration and optimization of green methods for microalgae harvesting, namely, sedimentation, filtration, etc., and for oil extraction, such as supercritical fluids for massive oil production, are research gaps which are required to be attended to guarantee a cleaner production of microalgae oil. The establishment of green and effective cultivation, biomass harvesting and oil extraction methods are also intended to assure product quality and consistency for massive production.

In addition, the search to upgrade the performance of MWFs in further developments will promote the use of some chemical conversions to microalgae oil or/and the addition of substances as additives. The challenges are the development and implementation of chemical conversion methods which cause minimal environmental problems and the replacement of toxic additives with green nanoparticles and/or biopolymers.

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