Chapter

Oleochemical Processing Technology: From Process Engineering and Intensification Techniques to Property Models for the Exploitation of Residual Marine Oils

Alicia Román-Martínez

Abstract

A review of the efforts done in process engineering aspects, such as process optimization and process intensification of residual oils processing, are described and discussed. It should be emphasized that the important characteristics of marine oils be determined for a good process design practice, especially, the quality attributes of the residual oil as a raw material. Finally, some property prediction models that have been proposed are indicated. All these aspects: 1) novel process engineering tools, 2) quality characterization, and 3) property models, are important for sustainable products and processes implementation in a circular economy.

Keywords: lipid processing, lipid characterization, lipid property models

1. Introduction

Lipids are an indispensable part of the diet and participate in numerous important biological functions. Products obtained from lipid sources (e.g., animal, vegetable fats, and oils) have gained relevance in the last two decades as the need for healthier food products or the growing interest in biofuels, among others, have increased. Consequently, the processing of fats and oils has been of vital importance throughout the history of humanity [1]; lipids have been used since time immemorial, mainly for food purposes, although there are other recent applications, such as paints, lubricants, personal care products, and (bio)fuels, as well as in animal feed [2]. The increase in the variety of lipid products and population growth have caused the annual demand for fats and oils to practically double since the end of the 1990s worldwide. The total production volume for the 12 most important oils was around 90.5 million metric tons in the year 2000, while it is currently estimated at 207.5 million tons per year [3].

On the other hand, it is known that food production systems in general represent around 20–30% of the consumption of natural resources worldwide [4]. Therefore, it has become essential to consider a change toward sustainable systems at all stages of the design and implementation of processes, which implies that they have the capacity to meet the present needs of society without compromising those of future generations. As in most human activities, in the oleochemical industry, there is a continuous effort to reduce overall production costs and, more recently, to mitigate environmental impact, meet consumer needs and promote social progress [5].

In order to address these challenges, the concept of circular economy (CE) was developed to transform productive activities from a linear perspective to a circular one, increasing efficiency in the use of resources, as shown in **Figure 1** [6, 7]. Optimal use of available resources prolongs their functionality and value, promotes production patterns with cycle closure, and thus reduces waste generation [8]. This implies, among other activities, the recycling and reuse of biomass sources, and organic waste to generate various products and materials, including food, chemicals, biopolymers, fuels, and bioenergy [9, 10].

In this context, numerous proposals have been made to exploit oil/lipid-based feedstocks that could lead to waste utilization and valuable products [11–13]. Among these, waste from the fishing industry has attracted great interest as it is a source of minerals, proteins, and fats with high potential for use [14]. About 30–40% of the fish is consumed fresh, while the rest is processed for marketing and other purposes [15]. However, not all parts of the fish are consumed, as substantial parts (e.g., fish oil) are often wasted. The processing of these marine oils, in addition to offering the possibility of obtaining biofuels, can be used to extract and refine commercial by-products of high nutraceutical value, such as tocopherols, sterols, and omega-3 (ω-3) fatty acids, particularly eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA) [16].

These polyunsaturated fatty acids (PUFAs) from the omega-3 family have received particular attention due to their unique health benefits. Epidemiological studies conducted in the 1970s indicated a remarkably low incidence of death from ischemic

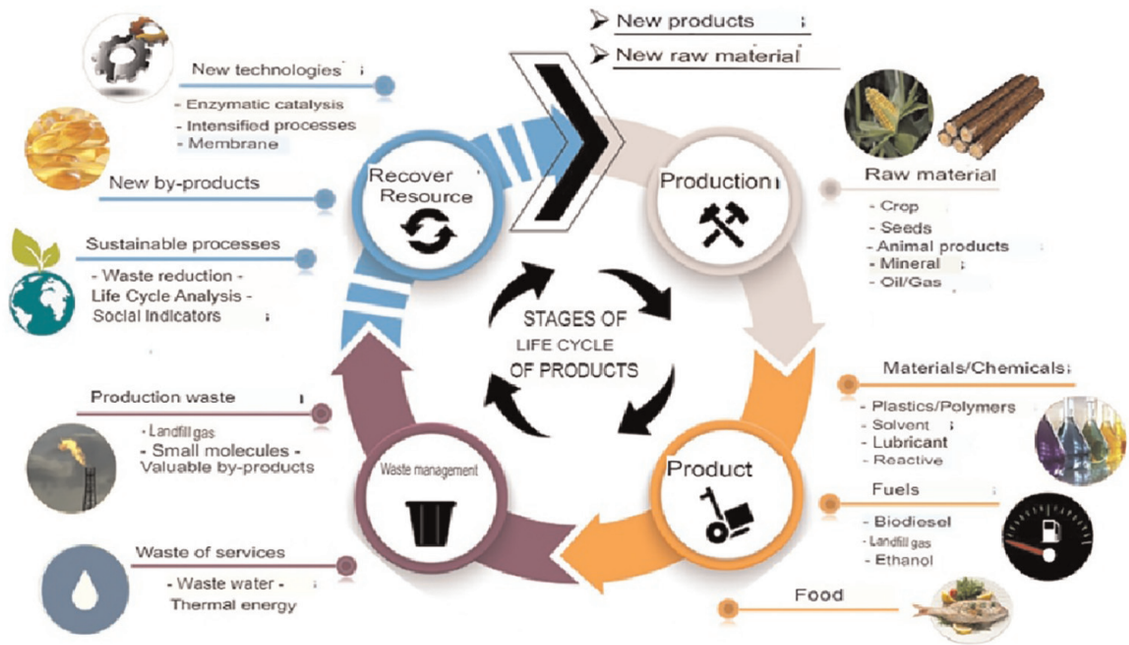

Figure 1.
General diagram of the life cycle of products with a circular economy approach. Adapted from [6].

heart disease in Eskimos from Greenland, as well as in Japanese and Turkish coastal populations with diets rich in fish constituents [17, 18]. Since then, numerous biochemical and biomedical investigations have been published in relation to the effects of these fatty acids, whose consumption is critical for physical and mental health, and playing an important role in infant brain and eye development [19, 20].

To obtain the benefits of this family of lipids, the World Health Organization (WHO) and the North Atlantic Treaty Organization (NATO) recommend a daily intake of 200 to 500 milligrams of EPA and DHA [21]. According to the UK Scientific Advisory Committee on Nutrition Guidelines (2004), and the Dietary Guidelines Advisory Committee Report (2005) published by the Department of Health and Human Services of the United States, it is recommended to consume at least two servings of fish in the diet per week [22].

However, these recommendations are hardly met. In 2010, the global mean intake of ω-3 fats from marine sources was 163 mg/day, with huge regional variations; only in 45 of the 187 countries, the average consumption was greater than 250mg/day, while in 100 countries there is a very low consumption (<100 mg/day), generally in regions of Africa, Asia, and Latin America, representing the 66.8% of the world adult population [23].

This situation has led to the rapid growth of the ω-3 supplement industry from marine oils. At the beginning of the last decade, only about 5% of the world's fish oil production was destined for the extraction of its ω-3 content for use as ingredients and dietary supplements, while the remaining fraction was discarded or used for fish farming or aquaculture (food for raising fish) [19]. Currently, the consumption of marine oils is expanding due to the recognition and dissemination of their beneficial properties, and this demand is expected to continue growing, with the world market for ω-3 reaching around 6955 million dollars for the year 2022 [24]. Therefore, the recovery and transfer of these important nutrients from the sea to the human food chain, within the circular economy approach, is a relevant opportunity to promote economic growth, environmental protection, and human health in general.

In addition to the increase in demand, progress in the investigation of methodologies for the extraction, purification, and stabilization of ω-3 fish oil has made significant progress in recent decades, although its application has not been widely extended on a large scale in the industry due to the challenge it represents. Marine oils are complex mixtures of fatty acids with variable chain lengths and degrees of unsaturation, which makes their separation difficult [25]; in addition to being highly susceptible to deterioration processes, such as thermal oxidation and enzymatic hydrolysis [26].

Additionally, unlike the chemical industry, the development of the oleochemical industry has not had such rapid progress in terms of modeling thermo-physical properties and development of adequate computational tools for the design, analysis, and optimization of processes related to lipids, coupled with the lack of integration of sustainable aspects [27–29]. Marine oil processing involves a variety of stages, from the extraction and recovery of crude oil to the refinement and modification of the final product. Typical unit operations include fluid transport, heat transfer, and separation processes, such as adsorption, phase separation, crystallization, filtration, chemical synthesis (interesterification, hydrogenation), and vacuum steam distillation, among others [25, 30].

Within this context, the decision-making set when designing a plant, also called "process synthesis," must balance the criteria of sustainability and incorporate the circular economy within the design, for which different tools and technologies have been

developed. Among them, process intensification (PI) may be a promising engineering approach. PI is considered as any novel equipment, processing technique, or method that, compared to conventional ones, offers a substantial improvement in the efficiency and/or performance of manufacturing (bio)chemical products [31]. Another complementary definition suggests an optimization of the basic functional principles of chemical processes (momentum, heat, and mass transfer) in the design of operations [32].

A wide range of applications and developments in the oleochemical industry can be considered intensified, as shown in **Table 1**. For example, nano-neutralization seeks to integrate degumming and neutralization operations to reduce the number and size of equipment, as well as the dosage of necessary reagents and the generation of waste [34]. Companies, such as Alfa Laval® or Unilever®, have developed strategies to improve the configuration of the process and the operating parameters in order to optimize the removal of impurities depending on the nature and quality of the oil [33]. Microwave irradiation has been used to improve the efficiency of biodiesel production, reducing reaction time with energy savings of up to 44% [35]. Similarly, ultrasound-assisted transesterification of various vegetable oils has proven to be effective by increasing the contact surface between the alcohol/oil phases, improving mass transfer and reducing the amount of catalyst needed for biodiesel production [36, 54], as well as ethyl esters of fish oil [37].

PI principle applied	PI Technology	Applications in the oleochemical industry	References
Integration of unit operations. Hybrid separations	Special Combi-Mix Alfa Laval® degumming	Degumming and neutralization	[33]
	Nano-neutralization	Degumming and neutralization	[34]
Higher performance for a given process or equipment size. Improvement in the transfer of heat, mass or momentum through alternative energy sources	Microwave/Ultrasound-assisted reactors	Transesterification reactions for the production of biodiesel or ethyl esters	[35–37]
	Membrane technologies	Degumming, neutralization, deodorization, fatty acid concentrate	[38, 39]
	Technology with supercritical fluid (CO_2)	Oil extraction, fatty acid concentrate	[40–43]
Smaller volume of equipment for a given process or output. Improved heat, mass, or momentum transfer	Molecular distillation	Deodorization, fatty acid concentrate, recovery of valuable lipid compounds, such as tocopherols	[44–46]
	Chromatographic methods	Fatty acid concentrate	[47–49]
Less use of ancillary services and/or raw material flows (reagents, solvents, electricity...). Greater yields	Trysil® Silica Adsorbent Hydrogels	Oil washing and bleaching	[50]
	Enzymatic alternatives	Oil extraction, degumming, neutralization, lipid modification (trans/interesterification)	[51–53]

Table 1.
Some process intensification (PI) options with reported applications in the oleochemical industry.

Other strategies include oil extraction or fatty acid separation using supercritical fluids [40], membrane technology for impurity filtration [38], or PUFA concentrate [39, 55], in addition to enzymatic alternatives for different reactions [51, 52].

Evaluating different process alternatives (conventional or intensified) from a sustainable perspective normally requires multi-objective or multi-criteria decision-making that must often consider antagonistic criteria, that is, when deciding to prefer one, the other criteria are affected; consequently, you are forced to make more informed and, therefore, better decisions. In these problems, there is not usually a single optimal solution and it is necessary to use a decision-making methodology to be able to differentiate the alternatives and prioritize the possible solutions.

To achieve this goal, the life cycle analysis (LCA) can be a very helpful tool, since it involves metrics that characterize the environmental impact of a product or process in all its stages, from the extraction of the raw material to the final disposal of waste [56], which obviously allows integrating the concept of circular economy within the process design [57]. There are several studies that demonstrate the potential application of LCA in oleochemical systems [58]. Additionally, the use of mathematical optimization methodologies allows evaluating these multi-criteria indicators in a robust way, as well as implementing of this set of strategies in software or process simulators [59, 60] in order to speed up the decision-making process.

Table 2 presents a synthesis of different studies carried out on the design of processes involving lipids, and the tools or approaches addressed in each one. It is possible to observe that there is rarely a comprehensive vision of the strategies or indicators that would allow achieving an optimal sustainable process (e.g., there are few studies that address the evaluation of social metrics, a pillar of sustainability as important as the economic or the environmental). Therefore, the proposal of systematic methodologies that involve the mathematical evaluation of alternatives through a balance of sustainable indicators is vital for the design of processes in the context of the circular economy. The integration of these approaches together with social aspects, such as risk analysis and the opportunity to mitigate the nutritional deficiencies of vulnerable communities (by valorizing the sources of ω-3), complement a promising strategy that would allow the generation and evaluation of robust alternatives of processing aimed at the development of a more sustainable industry.

2. Marine oil processing

The processing of plant seeds or animal tissues into edible oils can be divided into four sets of operations: extraction, refining, conversion or modification, and stabilization [77, 78]. Oil extraction consists of pressing the material or matrix to separate the crude oil from the protein-rich solids or moderately pressing it with solvent, usually hexane. The defatted solids are known as cake or flour. The oil obtained is considered "crude" because it contains undesirable components, such as pigments, phospholipids, free fatty acids, and unpleasant flavors and odors, so it must be refined to remove these contaminants, and thus obtain a high-quality edible oil. Refined oils consist mainly of triacylglycerides (>98%) that can be subsequently modified through processes, such as hydrogenation, winterization, fractional crystallization, or interesterification, whose objective is to obtain properties different from the original oil, such as the conversion of liquid oil into semi-solid fats or the fatty acid concentrate of interest (e.g., ω-3). The stabilization of the final product to suit the needs of the consumer depends on the use that it will have. Plasticizing and tempering are

Characteristics and references	Approach or tool													
	Process design/ simulation	Process intensification (PI)	Sustainability					Optimization						
			Economic analysis	Environmental impact	Social indicators	Circular economy	Life Cycle Assessment (LCA)	Mono-objective	Multi-objective	Linear Programming (LP) or Non-Linear Programming (NLP)	Mixed-Integer Non-Linear Programming (MINLP)	Superstructure Approach	Stochastic (uncertainties)	Sensitivity analysis
Biodiesel production from palm and rapeseed oils, compared with petroleum-based diesel [61]	•		•	•			•							
Comparison and impact of different methods to produce biodiesel from rapeseed oil [62]	•		•	•	•									
Risk analysis in the design of edible oil refineries [63]	•				•									
Comparison of three alternatives for biodiesel production from discarded oils [64]	•	•		•		•		•						
Biodiesel production from fresh and residual vegetable oils, using a conventional and an intensified method [65]	•	•	•			•								•
Analysis of biodiesel production from oil discarded in a restaurant [66]	•		•	•		•								
Life Cycle Analysis for the production of five vegetable oils [67]				•			•						•	
Design of the solvent-based butter fractionation process using a systematic approach [11]	•		•	•			•							

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	Process design/ simulation	Process intensification (PI)	Sustainability					Optimization							
			Economic analysis	Environmental impact	Social indicators	Circular economy	Life Cycle Assessment (LCA)	Mono-objective	Multi-objective	Linear Programming (LP) or Non-Linear Programming (NLP)	Mixed-Integer Non-Linear Programming (MINLP)	Superstructure Approach	Stochastic (uncertainties)	Sensitivity analysis
Transesterification and separation of oleic acid by reactive distillation [68]	•	•												
Modeling of biodiesel production in a continuous tubular reactor with static mixer [69]	•	•	•											•
Production of glycerol and biodiesel from algal oil [70]	•		•					•		•				•
Systematic analysis of the soybean oil extraction process. Prediction of thermodynamic properties [71]	•							•		•				
Hybrid optimization model for the design of a biorefinery using a sustainable perspective [72]		•	•						•	•		•		
Optimization of a glycerol purification process and solvent crystallization of a vegetable oil [73]	•		•	•				•			•	•	•	
Simulation of a palm oil extraction, refining and fatty acid separation process [74]	•		•	•					•		•	•	•	
Analysis of a biodiesel production process from discarded fish oil [12]			•			•								

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	Process design/ simulation	Process intensification (PI)	Sustainability					Optimization						
			Economic analysis	Environmental impact	Social indicators	Circular economy	Life Cycle Assessment (LCA)	Mono-objective	Multi-objective	Linear Programming (LP) or Non-Linear Programming (NLP)	Mixed-Integer Non-Linear Programming (MINLP)	Superstructure Approach	Stochastic (uncertainties)	Sensitivity analysis
Design of a biorefinery for the production of Omega-3 concentrates from discarded fish oil [42]	•	•	•	•		•								
Comparison of the production of Omega-3, protein and biofuel from algal and fish oil [75].	•			•			•							•
Economic evaluation and simulation of an enzymatic process for the production of biodiesel from rapeseed oil [76]	•	•	•											

Table 2.
Examples of different approaches and tools used in lipid process design.

operations designed to stabilize mixtures used in margarines and shortenings, while nutraceutical oils used as supplements usually undergo encapsulation or microencapsulation processes to prevent deterioration and facilitate their consumption or incorporation into other food products [79].

2.1 Extraction methods

The method chosen for oil extraction depends on the nature of the raw material, as well as the capacity of the industrial plant [80]. Particularly, for fish oil, it is obtained in most cases through the "wet-rendering" process, which consists of heating or "cooking" fresh fish with steam to break the cellular structure, and then pressing to separate the particles, liquid, and solid fractions. The solid fraction is dried to produce fishmeal.

The liquid fraction contains water, oil, and minor amounts of suspended solid material. This liquid is processed using centrifuges and decanters to remove solids and separate the water from the oil, which is stored for later use as crude oil. The water fraction is evaporated and recirculated to the solid fraction before drying [81].

Other traditional methods for its extraction include enzymatic hydrolysis, autolysis, dry rendering, solvent (hexane) extraction, and more recently innovative and ecologically friendly methods, such as supercritical fluid extraction, enzyme extraction, and extraction using ultrasound or microwaves have been used [40].

2.1.1 Storage and preservation of crude oil

It can be considered that the processing of oil starts from the storage tanks since the quality and performance are affected by the conditions in which it is stored. In particular, it is desired to avoid increases in free fatty acids, oxidation products, color changes, and contamination by insoluble impurities.

In general, tanks should store oil at room temperature (<25°C), or cooler when practical and possible. It is recommended to use containers made of stainless steel that presents the least possibility of iron contamination, for example, coated food-grade stainless steel (316). It is critical to have completely sealed tanks, as well as to fill the upper space with nitrogen to displace the air and avoid its contact with the oil since PUFAs in particular are prone to oxidation phenomena, as will be described later [26, 82].

2.2 Oil refining

Refining generally refers to the removal of non-triacylglycerol fatty materials, as well as pretreatment and deacidification or neutralization operations. Consumers typically want mild or neutral-flavored, light-colored, and oxidatively stable oils, so the goal is to remove impurities that may cause the product to have an off-color or off-flavor or cause harmful metabolic effects for human consumption.

Edible oils can be refined through chemical or physical processes. Each method has its own specific advantages, and the use of one or the other depends on quite a bit on the quality and type of oil involved. In chemical or alkaline refining, caustic soda is used to neutralize the free fatty acids in the oil, while in physical refining this stage is skipped, removing these acids (to a lesser extent) by single-stage distillation during the process of deodorization. In general, when the acidity of the oil exceeds approximately 2%, chemical refining is carried out, while for lower values, physical refining is

Method	Characteristics	Applications	Limitations
Refining or physical deacidification	It uses vacuum steam distillation, which removes free fatty acids and aromatic compounds. Requires high temperatures and depends on efficient prior degumming.	Suitable for oils with a high content of free fatty acids. Low capital and operating cost. Higher oil yield. Reduced amount of effluents (does not produce soaps).	Pretreatments are more rigorous. Not suitable for heat-sensitive oils (cotton, fish). Possible thermal polymerization. Controlled rate of elimination of free fatty acids.
Refining and chemical acidification	Industrially, it is the most common method. It is done by adding an alkaline substance (caustic soda) that precipitates free fatty acids as soaps.	Versatile (produces good quality oil from any type of source). Multiple effects; purified, degummed, neutralized and partially bleached. Chemically more stable product.	Excessive loss of neutral oil when there is a high content of free fatty acids. Produces waste (soaps). Oil hydrolysis.
Mixed or miscellaneous refining	More suitable for the integration of an extraction and refining plant, since it combines both processes, mixing a solvent (hexane) that helps to separate impurities during degumming and neutralization.	Lower strength of caustic solution. Higher separation efficiency. Minimal oil occlusion in soap scum. Better color in the final product. Water washout removed.	Higher investment costs. Loss of solvent (requires careful operation and increased maintenance). For efficient operation, the oil concentration in the micelle should be ~50% (two-stage solvent removal).

Table 3.
Industrial oil refining methods. Adapted from [33, 80, 83].

carried out, provided that the quality of the oil allows it [83]. **Table 3** presents the main characteristics, advantages, and disadvantages of these refining approaches.

Regardless of the approach, refining is a set of operations designed in such a way as to minimize the loss of "neutral" oil and maximize the availability of beneficial components. The traditional process [33] includes the stages of degumming, neutralization, bleaching, deodorization, and in some cases, winterization (although the latter is considered a PUFA concentrate method). Each stage is important to remove the different impurities [84].

Evolution in the ω-3 fatty acid market has led to the development of new processes for treating marine oils, designed to preserve these acids, while reducing impurities. In some cases, these processes were initially expensive, but due to the evolution of this market, they are now considered conventional processes [16]. The processing steps and the compounds removed by them can be summarized in **Table 4**.

2.3 PUFA modification and concentrate

Oil modification processes involve a substantial change in their physical behavior and structural properties, unlike the previously discussed refining processes where their effect is aimed at removing impurities and improving organoleptic properties, as well as nutritional value [1]. Chemical modifications offer the possibility of changing the properties of fats and oils within wide ranges, making them suitable for many uses.

Technique or Stage	Purpose
Storage	Insoluble impurities, residual moisture, and some phospholipids precipitate in the tanks.
Degumming	Remove phospholipids, sugars, resins, protein compounds, trace metals, and other materials.
Alkaline refining (Neutralization)	Remove free fatty acids, pigments, phospholipids, water-soluble and insoluble material, and trace metals.
Silica washes/treatment	Soaps are produced during the neutralization stage, oxidation products, and trace metals.
Dying	Moisture reduction.
Adsorbent bleaching and/or carbon treatment	Pigments, oxidation products, trace metals, sulfur compounds, dioxins, furans, and polycyclic aromatic hydrocarbons.
Winterization	High melting point triacylglycerides and waxes. Used to increase unsaturated triacylglycerides.
Deodorization	Eliminates volatile compounds: free fatty acids, mono-diacylglycerides, aldehydes, ketones, chlorinated hydrocarbons, and pigment decomposition products, as well as oxidation. It is usually the final step and results in a mild-tasting oil.
Vacuum extraction, molecular or short distillation.	Removes chlorinated hydrocarbons, fatty acids, PCB oxidation products, and free cholesterol. It can be used to replace deodorization.

Table 4
Stages of oil processing and the main impurities removed in each one [16].

Two main modification technologies are generally considered in the edible oil industry:

i. Hydrogenation or hardening: It consists of the addition of protons (hydrogen atoms) to the unsaturated sites of the hydrocarbon chain of fatty acids, transforming these into saturated bonds. It was originally used to improve the stability of oils with large amounts of PUFAs, such as marine oils, however, the use of this process has been considerably reduced as it has been identified as an important source not only of saturated fats but also of trans fatty acids in the human diet, associated with an increased risk of heart disease [85]. It should also be considered that, by eliminating unsaturation, its nutritional value is lost [1].

ii. Esterification reactions: Two terms are commonly used in the literature to designate a wide variety of ester-ester exchange reaction mechanisms [52]:

   a. Interesterification: General term for reactions between an ester and fatty acid, alcohol, or other esters, although it can only describe ester-ester exchanges or randomization of oils and fats by alkaline or enzymatic catalysis.

   b. Transesterification: Term used for ester-ester exchanges, including acidolysis and alcoholysis. It is mostly used to describe reactions of oils with methanol or ethanol for the production of biodiesel or ethyl esters.

Technique	Description
Interesterification	Re-arrangement of the triacylglycerides in the oil in a particular or more random distribution.
Hydrolysis or esterification	Separation of fatty acids from triacylglycerol molecules, producing free fatty acids or esters with glycerin as a by-product.
Urea complex	By dissolving the fatty acids or esters in methanol or ethanol, adding urea, and reducing the temperature, it is possible to precipitate a complex that traps the saturated and monounsaturated ones, resulting in a PUFA concentrate. Depending on the type of oil, the losses can be significantly large.
Winterization / Dry fractionation	Separation of high melting point (saturated) waxes and triacylglycerides by cooling the oil below their crystallization temperature, and their subsequent separation by filtration.
Molecular distillation	This stage can be used to remove free cholesterol or further concentrate esters or fatty acids.
Extraction with supercritical fluids (SCF)	Purification to obtain >85% pure compounds and remove cholesterol, using fluids at supercritical conditions of temperature and pressure.
Preparative High-Performance Liquid Chromatography (HPLC)	Purification of esters or fatty acids to produce compounds with more than 95% purity. It is a chromatography-based technique and can be very expensive and complicated.
Re-esterification	Conversion of purified fatty acids or esters back to their triacylglycerol form, which is considered more natural and more bioavailable to the body. It is made by a catalytic reaction with excess glycerol.

Table 5.
Techniques for the concentration and purification of omega-3 fatty acids. Adapted from [16, 86].

Once their properties have been modified, there are additional steps that can be used to convert refined marine oils into concentrates and relatively purified esters or fatty acids into ω-3 fractions (**Table 5**).

Many of these processes described above can be adapted, combined, or in some cases improved through the use of enzymes [25, 52]. The use of simple processes based on green chemistry, low pressures, and methods that avoid toxic solvents and high temperatures have been positioned to replace conventional methods for the extraction, purification, and stabilization of marine oils rich in ω-3 fatty acids [19].

3. Analysis of oils and quality parameters

Regardless of where they come from, oils and fats are similar in terms of the effects of the aforementioned impurities on processing and final product quality. Therefore, it is necessary to determine certain key analytical values to be able to modify or establish the process conditions in order to obtain a product of satisfactory quality [1]. Each analysis provides specific information to the manufacturer, as well as to future consumers.

3.1 Analytical characterization

Tests that are important to consider in determining the quality and handling of crude fish oil (or any oil) are as follows:

i. Sampling methodology: The objective of sampling is to obtain a manageable quantity of oil whose properties correspond as closely as possible to those of the original source, as well as to ensure its transport and storage. The considerations according to ISO 5555:2001 [87] must be taken into account.

ii. Determination of percentage of free fatty acids (FFA): Free fatty acids appear with the decomposition of lipids, being indicators of degradation. Their percentage must remain below the standards established for human consumption, so they must be neutralized during the refining of the oil. For its determination, the AOCS Ca 5a-40 methodology [88] is used.

iii. Determination of peroxide index (PI): It is the amount (expressed in milliequivalents of active oxygen per kilogram of fat) that indicates the initial oxidation state of the oil. A maximum value for refined oils of 5 to 10 meq/kg of O2 should be considered. The methodology used is AOCS CD 8b-90 [89].

iv. Determination of the p-anisidine index (AI): The use of the peroxide index is limited to the initial stages of lipid oxidation, so the anisidine index is established as a useful measure of secondary oxidation products to evaluate the past of the oil and predict its stability. Its value must be less than 20meq/kg of O2. The methodology used is AOCS Cd 18–90 [90].

v. Determination of TOTOX (total oxidation) index: Indicates the general state of oxidation of the oil, the lower it is, the better its quality. It is simply calculated by combining the peroxide and p-anisidine values with the formula AI+2PI. It must be less than 26 meq/kg of O2.

vi. Determination of iodine index (II): This is a measure of the unsaturation of fats and oils expressed in terms of the percentage of iodine absorbed per gram of sample. The higher this index, the greater the number of double bonds. Its value can range from 90 to 150 for vegetable oils, and greater than 150 for fish oils. It is determined by the AOCS method number Cd 1d-92 [91].

vii. Determination of the fatty acid profile: It is carried out to know the composition of the fatty acids that make up the triacylglycerides of the oil; in this way, it is possible to know the amount of saturated, monounsaturated, and polyunsaturated present. It is carried out by gas chromatography of the previously methylated sample to convert the triacylglycerides into fatty acid methyl esters. For marine oils, the AOCS Ce 1b-89 methodology is used [92].

3.2 Composition of marine oils

Particularly for fish oils, the constitution and proportion of its lipid components depend on the extraction process, the species, and the geographical and environmental conditions; hence, the emphasis on carrying out an adequate characterization that allows obtaining information about the composition of fatty acids and their physicochemical properties, which can give an idea of the quality of the oil and its nutritional value, important considerations for a subsequent design of oil processing according to the desired product.

For this type of oil, triacylglycerides occupy the largest proportion (~90%); the moisture content and the percentage of free fatty acids vary according to the extraction treatment and storage conditions, these being around 0.5–1% and 2–5%, respectively [81]. The amount of phospholipids can vary from 1 to 1.5%, and in terms of the content of the unsaponifiable fraction (sterols, tocopherols, pigments, alcohols, and hydrocarbons), it is normally less than 2%, although it can constitute up to 8% of the oil under certain seasonal and feeding conditions [93].

The fatty acid profile allows a chromatogram to be obtained from which the type and content of fatty acids belonging to saturated, monounsaturated fatty acids or PUFAs is determined. The profile of fish oils is known to be complex, varying by marine species. There are fatty acids that occur in trace amounts and some are generally common to all species. For example, high contents of PUFAs have been found in tuna oil (35% w/w) [94], in cod liver (18% w/w), and anchovies (16.5% w/w) [95].

Fatty acid		Anchovy	Tuna	Krill	Salmon		Cod liver
					Wild	Farm	
Myristic	C14:0	2.7–11.5	ND-5.0	5.0–13.0	2.0–5.0	1.5–5.5	2.0–6.0
Pentadecanoic	C15:0	ND-1.5	ND-2.0	NA	ND-1.0	ND-0.5	ND-0.5
Palmitic	C16:0	13.0–22.0	14.0–24.0	17.0–24.6	10.0–16.0	6.5–12.0	7.0–14.0
Palmitoleic	C16:1	4.0–12.6	ND-12.5	2.5–9.0	4.0–6.0	2.0–5.0	4.5–11.5
Margaric	C17:0	ND-2.0	ND-3.0	NA	ND-1.0	ND-0.5	NA
Stearic	C18:0	1.0–7.0	ND-7.5	NA	2.0–5.0	2.0–5.0	1.0–4.0
Vaccenic	C18:1 ω7	1.7–3.7	ND– 7.0	4.7–8.1	1.5–2.5	NA	2.0–7.0
Oleic	C18:1 ω9	3.6–17.0	10.0–25.0	6.0–14.5	8.0–16.0	30.0–47.0	12.0–21.0
Linoleic	C18:2 ω6	ND-3.5	ND-3.0	ND-3.0	1.5–2.5	8.0–15.0	0.5–3.0
α-Linolenic	C18:3 ω3	ND-7.0	ND-2.0	0.1–4.7	ND-2.0	3.0–6.0	ND-2.0
γ-Linolenic	C18:3 ω6	ND-5.0	ND-4.0	NA	ND-2.0	ND-0.5	NA
Stearidonic	C18:4	ND-5.0	ND-2.0	1.0–8.1	1.0–4.0	0.5–1.5	0.5–4.5
Arachidic	C20:0	ND-1.8	ND-2.5	NA	ND-0.5	0.1–0.5	NA
Eicosenoic ω-9	C20:1 ω9	ND-4.0	ND-2.5	NA	2.0–10.0	1.5–7.0	5.0–17.0
Eicosenoic ω-11	C20:1 ω11	ND-4.0	ND-3.0	NA	NA	NA	1.0–5.5
Arachidonic	C20:4 ω3	ND-2.5	ND-3.0	NA	0.5–2.5	ND-1.2	ND-1.5
Eicosatetraenoic	C20:4 ω3	ND-2.0	ND-1.0	NA	1.0–3.0	0.5–1.0	ND-2.0
Eicosapentaenoic	C20:5 ω3	5.0–26.0	2.5–9.0	14.3–28.0	6.5–11.5	2.0–6.0	7.0–16.0
Heneicosapentaenoic	C21:5 ω3	ND-4.0	ND-1.0	NA	ND-4.0	NA	ND-1.5
Erucic	C22:1 ω9	ND-2.3	ND-2.0	ND-1.5	ND-1.5	3.0–7.0	ND-1.5
Ketoleic	C22:1 ω11	ND-5.6	ND-1.0	NA	1.0–1.5	NA	5.0–12.0
Docosapentaenoic	C22:5 ω3	ND-4.0	ND-3.0	ND-0.7	1.5–3.0	1.0–2.5	0.5–3.0
Docosahexaenoic	C22:6 ω3	4.0–26.5	21.0–42.5	7.1–15.7	6.0–14.0	3.0–10.0	6.0–18.0

Table 6.
Ranges of fatty acid profiles of some fish oils determined by gas-liquid chromatography (expressed as percentages of total fatty acids). ND = not detected, defined as <0.05%. NA = not available; ω3 = omega-3 series, ω6 = omega-6 series, ω7 = omega-7 series, ω9 = omega-9 series [95].

While the monounsaturated fatty acids, oleic acid (C18:1) is the most abundant, and as for the saturated ones, large amounts of myristic acid (C14:0) and palmitic acid (C16:0) can be found in almost all the species analyzed [94].

It is important to mention that the positional distribution of the different types of fatty acids in the glycerol molecule of triacylglycerides, especially, the ω-3 PUFAs, has a strong influence on digestion and absorption in the human body, as well as on its oxidative stability [96]. In marine oils, DHA is generally found in the sn-2 position, while EPA can be found in any position of the glycerol molecule [97]. **Table 6** below presents a comparison of the fatty acid profile of oils from different fish species reported by the CODEX Alimentarius Commission of the World Health Organization.

Regarding specific tuna oils, various authors in different locations have reported relatively similar fatty acid profiles. The percentages of PUFAs vary from 28 to 44%, with DHA being the most abundant, followed by EPA and, to a much lesser extent, DPA [94, 95, 98]. Oleic acid represents the highest percentage of monounsaturated, and of the saturated, myristic acid stands out.

3.3 Lipid deterioration

Fats and oils can undergo different deterioration processes that, in addition to reducing the nutritional value of the food, produce volatile compounds that impart unpleasant odors and flavors. The degree of deterioration depends on the type of fat or oil, the handling given to it [99], and the storage conditions, being the most affected oils of marine origin, followed by vegetable oils and finally animal fats, due to the fact that the first they contain a greater amount of PUFAs prone to the deterioration [1]. Some examples are:

i. *Lipolysis* - This type of deterioration is due to chemical and/or enzymatic hydrolysis of acylglycerides, breaking the ester bonds of lipids, produced by enzymatic action (lipases) or by heating in the presence of water, and results in the release of fatty acids (now FFA) in the oil.

ii. *Oxidation processes* - The oxidation of lipids is one of the main causes of the deterioration of the organoleptic quality of foods, producing abnormal odors and flavors, generally called "rancid." It is carried out mainly in unsaturated fatty acids, although it is also carried out with other substances of biological interest such as tocopherols and carotenoids [26]. Depending on the factor that acts as a source of energy to start oxidation, it can be classified as photo-oxidation (due to light), thermo-oxidation (when exposed to temperatures greater than 60°C), or auto-oxidation (occurs when organic compounds react with molecular oxygen) [100].

Fats have a certain resistance to oxidation processes depending on the initial natural content of antioxidant and/or prooxidant substances. Oxidation is slow until this resistance is overcome, at which point it accelerates rapidly. To delay these processes, it is possible to add natural or synthetic antioxidants to the oil, which help reduce oxidation through different mechanisms: inactivation of pro-oxidant metals through chelation, elimination of free radicals by phenolic compounds (tocopherols, BHT, and BHA), or removal of simple O2 species by compounds, such as astaxanthin [101].

3.4 Quality requirements

The quality of oil can be defined based on parameters established by various international organizations or regulations, as well as by the use that will be given to the oil. In the case of edible oils destined for concentrated supplements of ω-3, it is suggested to take into account the parameters described below in **Table 7**, in order to ensure a safe product for the consumer, as well as to establish restrictions and conditions that may be included in the time of process design.

4. Models of thermodynamic and physicochemical properties of lipids

As has already been described, vegetable and animal oils are mixtures of lipids, mainly fatty acids in the form of triacylglycerides, phospholipids, and unsaponifiable matter, among others. Therefore, the composition and proportion of these compounds vary significantly according to the source of origin, having a direct impact on the

Characteristic	Disadvantage or potential problem	Specification
Color	Dark oils may contain contaminants normally removed during refining. The color may be indicative of overheating.	No specification
Acidity index	High values of acidity can indicate a low-quality oil or deteriorated during storage. The acidity value is defined as twice the content of free fatty acids.	2 mg KOH/g of refined oil or < 1% FFA max.
Peroxide index (PI)	It is the first measure of oxidation in an oil.	5 meq/g O2 max.
p-anisidine index (AI)	Measures oxidation products; it reflects the oxidation that has taken place during the lifetime of the oil.	20meq/g O_2 max.
TOTOX index	Relationship between the two previous indices reflects the total oxidation of the oil.	26 meq/g O_2 max.
Humidity	Considered an impurity, high levels of humidity during storage can deteriorate the oil.	0.20% max.
Phospholipids	They act as prooxidants and form deposits at the bottom of storage tanks.	<50 ppm phosphorus.
Soaps	They are formed in the presence of moisture and during neutralization, they can reduce the stability of the oil.	0.005% max.
Total cholesterol	Part of the unsaponifiable fraction. It is not usually removed.	No specification
Iron	Considered a pro-oxidant, it is removed during degumming and refining.	1.5 mg/kg in refined oil max.
Copper	Considered a prooxidant, it is removed during degumming and refining.	0.1 mg/kg in refined oil max.
Arsenic	Heavy metal is present in seawater. It is removed during refining.	0.1 mg/kg max.
Lead	Heavy metal is removed during refining.	0.1 mg/kg max.
Mercury	Heavy metal is removed during refining.	0.1 mg/kg max.

Table 7.
Guide to quality parameters and potential areas of problems or disadvantages. Adapted from [81, 95, 102].

Physical characteristics of marine oils	
Specific heat, cal/g	0.50–0.55
Heat of fusion, cal/g	~54
Combustion heat, cal/g	~9500
Melting point, °C	10–15
Flash point, °C as triglycerides as fatty acids	~360 ~220
Boiling point, °C	>250
Specific gravity at 15°C 30°C 45 °C	0.92 0.91 0.90
Viscosity, cp, at 20 °C 50 °C 90 °C	60–90 20–30 ~10

Table 8.
Main characteristics of marine oils in general [93].

physicochemical properties and the appropriate design of the processing applied to the oil to obtain products suitable for use and consumption by humans [81].

Lipids are not commonly tabulated in property databases, and their polyfunctional structure requires a careful model analysis [103]. Properties, such as melting and boiling temperature, density, viscosity, and liquid-vapor equilibrium data, have been experimentally reported for different sources of oils and fats, the most studied being those of vegetable origin. However, the wide range of lipid species and the enormous number of different configurations that fatty acids can have in the triacylglyceride molecule make it difficult to fully characterize all properties of a given species. It is possible to take some general characteristics (**Table 8**) for a preliminary process design.

As not, all the properties of the lipids of interest have been determined in the literature and due to the difficulty, cost and time consumption involved in carrying out complete experimental studies, it is possible to resort to property prediction methods using mathematical models. In particular, group contribution (GC) methods have been widely used to complement the information available for process design [104].

4.1 Group contribution methods

The use of GC methods is based on the structural information of the molecule to predict specific properties; each substance is considered to be formed by the union of suitably defined structural groups, and each one of them is assigned a certain value as a contribution to said property, assuming that it is the same in every compound where it is present. The property of the pure compound is a function of the frequency in which these groups appear and their contributions. In principle, they are additive methods, where the contributions of each group toward property are added to obtain the approximate final value of the property [104–106].

Various prediction methods with GC for physical and thermodynamic properties with a focus on pure lipid compounds have been developed by various authors, among which those reported in **Table 9** stand out.

GC Method	Properties to estimate	Characteristics	Reference
Lydersen	Critical properties: T_c, P_c y V_c	Prototype and predecessor of other more sophisticated models.	[107]
Ambrose	Critical properties: T_c, P_c y V_c	Improvement in the prediction accuracy of critical properties with respect to Lydersen.	[108]
Klincewicz & Reid	Critical properties: T_c, P_c y V_c	Precision is comparable to the ambrose method.	[109]
Chein-Hsiun Tu	Critical temperature T_c	Refined method to obtain the critical temperature of organic compounds.	[110]
Joback & Reid	T_c, P_c, V_c, T_b, T_m, $\Delta H°_f$, $\Delta G°_f$, $C°_p$, ΔH_v, ΔH_m, ρ_L	Develop models for the prediction of 11 properties of pure compounds.	[111]
Constantinou & Gani (CG)	T_c, P_c, V_c, T_b, T_m, $\Delta H°_f$, $\Delta G°_f$, ΔH_v	More sophisticated model based on a multilevel approach.	[112]
Marrero & Gani (MG)	T_c, P_c, V_c, T_b, T_m, $\Delta H°_f$, $\Delta G°_f$, ΔH_v, ΔH_m	Multilevel approach based on groups of the first, second and third order. It is one of the most widely used today.	[113]
Kolská (2005)	ΔH_v, ΔS_v	Method used for organic compounds in general.	[114]
Kolská (2008)	Heat capacity $C°_p$	Method used for organic compounds in general based on groups of first, second, and third order.	[115]
Ceriani (2009)	$C°_p$ y ΔH_v	Focus on lipid compounds: fatty acids, esters and fatty alcohols, and TAGs.	[116]
Ceriani (2011)	Liquid viscosity μ_L	Focus on fatty compounds and esters for biodiesel.	[117]
Ceriani (2013)	P^{vp} y ΔH_v	Focus on lipid compounds: fatty acids, esters, fatty alcohols, and TAGs.	[118]
Díaz-Tovar (2011)	Liquid density ρ_L	Review of different GC methods, special emphasis on density and temperature-dependent properties.	[28]
Zeberg & Stenby	T_m y ΔH_m	Method used only for saturated triglycerides.	[119]
Moorthy	T_m y ΔH_m	Method used for saturated and unsaturated TAGs. It is quite accurate, although it requires complex calculations.	[120]
UNIFAC original	Vapor-liquid equilibrium (VLE)	Original, revised, and extended UNIFAC method for EVL prediction.	[121]
LLE-UNIFAC	Liquid-liquid equilibrium (LLE)	UNIFAC method for prediction of ELL.	[122]
Dortmund-UNIFAC	Vapor-liquid equilibrium (VLE)	Modified Dortmund-UNIFAC method for a more accurate prediction of EVL.	[123]

Nomenclature: T_c: critical temperature, P_c: critical pressure, V_c: critical volume, T_b: boiling temperature, T_m: melting temperature, $\Delta H°_f$: standard enthalpy of formation (298 K), $\Delta G°_f$: standard Gibbs free energy (298 K), $C°_p$: heat capacity, ΔH_v: enthalpy of vaporization, ΔS_v: entropy of vaporization, ΔH_m: enthalpy of fusion, ρ_L: liquid density μ_L: liquid viscosity, P^{vp}: vapor pressure.

Table 9.
Examples of group contribution methods used in lipids and organic compounds in general.

The range of application and the reliability of these methods depend on several factors [124]:

i. The definition of the groups is used to represent the molecular structure of the pure components.

ii. The property prediction model.

iii. The quantity and quality (in terms of information) of the experimental data set used in the regression to estimate the model parameters.

Another challenge with GC methods is that the selected property model may not have all the necessary parameters, such as groups and/or their contributions, for a specific property, so it is necessary, for the construction of the database of properties, to evaluate these factors when selecting the prediction methods to use. It is important to take into account that, as the number of carbon atoms and unsaturation in the molecule increases, the properties reported in the literature are scarce, so, although it is essential to have predictive models for these cases, the accuracy in the estimation of the properties can decrease, due to the sensitivity that these properties have with the exact conformation of the molecule [104].

5. Conclusions

The revaluation of waste and by-products, mainly in the food and oleochemical industries, is a fundamental part of the necessary transition toward a more sustainable and circular economic model. The future development of the industry must not neglect social issues and must focus on providing quality and accessible products to the communities that cooperatively represent the workforce and progress of humanity. In conclusion, the revaluation of food waste (fish oil) in a circular economy approach is an opportunity to close the link between food, water, and energy, as well as to incorporate the sustainable perspective to human progress.

Note

Figures and Tables are original from their authorship.

Author details

Alicia Román-Martínez
Universidad Autónoma de
San Luis Potosí, Facultad de Ciencias Químicas, San Luis Potosí, México

*Address all correspondence to: alicia.romanm@uaslp.mx

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