Bio-Refinery of Oilseeds: Oil Extraction, Secondary Metabolites Separation towards Protein Meal Valorisation-A Review

Mohamad Nehmeh, Ivonne Rodriguez-Donis, Alexandre Cavaco-Soares, Philippe Evon, Vincent Gerbaud, Sophie Thiebaud-Roux

processes

MDPI

Review

Bio-Refinery of Oilseeds: Oil Extraction, Secondary Metabolites Separation towards Protein Meal Valorisation—A Review

Mohamad Nehmeh [1,2], Ivonne Rodriguez-Donis [1,*], Alexandre Cavaco-Soares [3], Philippe Evon [1], Vincent Gerbaud [2] and Sophie Thiebaud-Roux [1,*]

1 Laboratoire de Chimie Agro-Industrielle (LCA), Université de Toulouse, INRAE, Toulouse INP, CEDEX 4, 31030 Toulouse, France; mohamad.nehmeh@ensiacet.fr (M.N.); philippe.evon@toulouse-inp.fr (P.E.)
2 Laboratoire de Génie Chimique (LGC), Université de Toulouse, CNRS, Toulouse INP, CEDEX 4, 31030 Toulouse, France; vincent.gerbaud@toulouse-inp.fr
3 ITERG, ZA Pessac, 11 Rue Gaspard Monge CS 20428, 33600 Pessac, France; a.cavacosoares@iterg.com
* Correspondence: ivonne.rodriguezdonis@ensiacet.fr (I.R.-D.); sophie.thiebaudroux@ensiacet.fr (S.T.-R.)

Abstract: Edible oil extraction is a large and well-developed sector based on solvent assisted extraction using volatile organic compounds such as hexane. The extraction of oil from oilseeds generates large volumes of oilseed by-products rich in proteins, fibres, minerals and secondary metabolites that can be valued. This work reviews the current status and the bio-macro-composition of oilseeds, namely soybean, rapeseed, sunflower and flaxseed, and the refining process, comprising the extraction of oil, the valorisation and separation of valuable secondary metabolites such as phenolic compounds, and the removal of anti-nutritional factors such as glucosinolates, while retaining the protein in the oilseed meal. It also provides an overview of alternative solvents and some of the unconventional processes used as a replacement to the conventional extraction of edible oil, as well as the solvents used for the extraction of secondary metabolites and anti-nutritional factors. These biologically active compounds, including oils, are primordial raw materials for several industries such as food, pharmaceutical or cosmetics.

Keywords: oilseed; oil extraction; alternative solvents; protein meal; secondary metabolites; anti-nutritional factors

Citation: Nehmeh, M.; Rodriguez-Donis, I.; Cavaco-Soares, A.; Evon, P.; Gerbaud, V.; Thiebaud-Roux, S. Bio-Refinery of Oilseeds: Oil Extraction, Secondary Metabolites Separation towards Protein Meal Valorisation—A Review. *Processes* **2022**, *10*, 841. https://doi.org/10.3390/pr10050841

Academic Editors: Irena Zizovic

Received: 21 March 2022
Accepted: 21 April 2022
Published: 24 April 2022

1. Introduction

Agriculture feedstocks undergo a series of various mechanical, thermal, chemical and/or biochemical transformations (simple or complex, small or large scale), known as food processing. Food processing aims at converting the inedible raw material to foodstuff, ensuring the safety of the product, and enhancing its preservation and shelf life [1–3]. Any by-product resulting from processing or any discarded material resulting from the food chain in general, is considered as a waste. By-products can contain high amounts of bioactive compounds (e.g., protein, vitamins, antioxidants . . .) that present diverse health effects and can be valorised in different domains (food, cosmetics, pharmaceutical . . .) [4]. Overall, main products and by-products are the output of a so-called bio-refinery.

The extraction of oil from lipid-bearing materials, such as oilseeds, generates large volumes of by-product rich in proteins, fibres and minerals, known as oilseed cake or meal [5]. There exists certain ambiguity in the use of the terms "cake" and "meal". The former is a by-product of the mechanical pressing step, while the latter refers to the by-product obtained by a solvent assisted extraction step whether or not it was preceded by a pressing step [4,6–8].

Mechanical pressing is the traditional method used for oil extraction, but is limited in term of yield. Solvent extraction is another method widely employed to recover the leftover oil in the oil-bearing materials, frequently using hexane as a solvent. This latter does not meet the requirement of green chemistry, as it is a highly flammable and volatile

organic compound (VOC) derived from petroleum, in addition to being classified as a CMR 2 (carcinogenic, mutagenic and reprotoxic) chemical. Solvent assisted lipid extraction requires huge amounts of solvents, resulting in significant energy consumption and losses during the solvent's recovery distillation [9]. Typically, approximately 4 tons of hexane and 4 tons of soybean or rapeseed are needed for the extraction of 1 ton of soybean or rapeseed oil [10]. The fixed capital investment per kilogram of feedstocks for an "on farm" plant, an industrial mechanical pressing plant and a hexane extraction plant, ranges between USD 0.01–0.74, 0.06–0.89 and 0.04–1.88, respectively. Furthermore, the unit production cost of a kilogram of oil, produced "on-farm", ranges between USD 0.27 and 2.3, and meanwhile this cost increases to USD 0.85–4.06 for industrial scale mechanical pressing, and to USD 0.56–5.74 for hexane extraction, depending on the production volume [11]. In resume, hexane is not an eco-friendly solvent, hence the interest in finding renewable, greener and sustainable alternatives.

Oilseeds are of great importance, accounting for 20% of the world grain production [12]. Compared to oil production from agricultural feedstocks, oil palm, soybean, rapeseed, sunflower, peanut and cotton are the most abundant oils, produced and traded around the world (Figure 1). These 7 oils account for over 90% of the total oil production worldwide, whilst there are over 25 kinds of oil in commerce [13]. Among oilseed oils, soybean, rapeseed and sunflower oils are the most produced, both worldwide and in France (cf. Table 1).

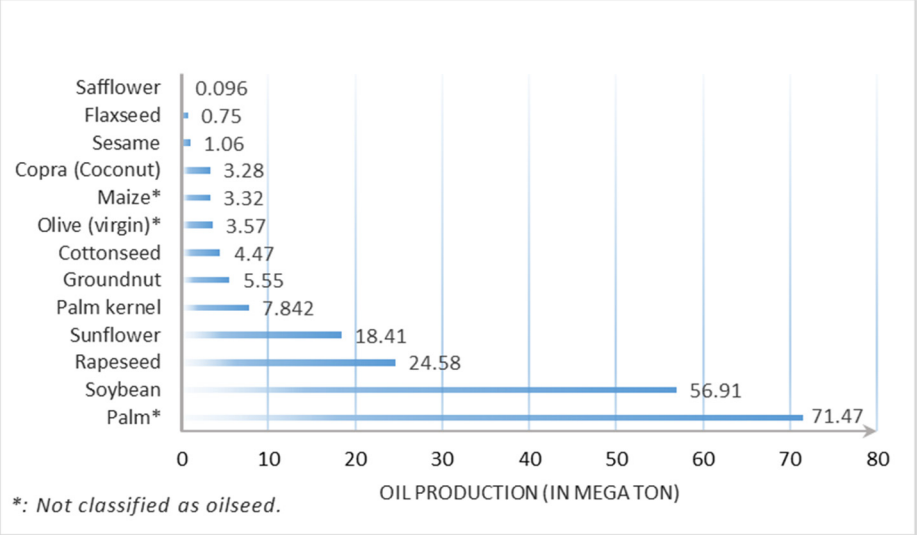

Figure 1. Worldwide oil production in 2018 (in Mega ton). Data adapted from FAOSTAT [14].

Table 1. Main oil production in France, and the percentage increase in flaxseed and sesame seed oil production, between 2010 and 2018. Data adapted from FAOSTAT [14].

	Oil Production (in Kilo Ton)					Percentage Increase in Production (%)	
Year	**Rapeseed Oil**	**Sunflower Oil**	**Soybean Oil**	**Flaxseed Oil**	**Sesame Oil**	**Flaxseed Oil**	**Sesame Oil**
2010	1897.8	568.1	91.3	0.66	4.59	-	-
2011	1788.8	644.6	117.2	0.66	4.70	0	2.33
2012	1987.7	590.8	116.6	0.66	4.74	0	0.77
2013	1912.9	578.8	98.0	0.66	4.95	0	4.41
2014	2044.0	568.0	105.0	4.30	4.60	551.52	−6.90
2015	2054.9	566.3	128.3	4.10	4.89	−4.65	6.23
2016	1916.4	496.7	145.1	5.50	4.79	34.15	−2.11
2017	1861.0	529.8	152.6	7.60	5.44	38.18	13.64
2018	1782.7	615.0	149.6	10.00	5.73	31.58	5.24

Flaxseed oil production in the world and in Europe is also gaining momentum and is included herein. For example, Table 1 presents the main oils produced in France between 2010 and 2018. Among these, flaxseed oil ranks fourth, with a production almost double that of sesame oil in 2018. Furthermore, the percentage increase in production of flaxseed oil since 2014 is preponderantly higher than that of sesame oil. On top of that, flaxseed oil is the only one among the rest that is rich in C18:3 α-linolenic acid (ALA), according to the data given in the standard for named vegetable oils by the Food and Agriculture Organization of the United Nations and the World Health Organization [15]. Groundnut and sesame oils are rich in C18:1 monounsaturated oleic acid and C18:2 polyunsaturated linoleic acid, while safflower and cottonseed oil are rich in C18:2 only. These fatty acid composition and lipid profiles are similar to those of soybean, rapeseed and sunflower oils (cf. Table 7). Palm kernel and coconut oil, on the other hand, are rich in saturated C12:0 lauric acid. The positive health effects of flaxseed oil and ALA are discussed later herein (cf. Section 2.1.4).

Figure 2 presents the main producers of rapeseed, soybean, sunflower and flaxseed oils, respectively. The largest producer of soybean oil is China (29%), followed by the USA (19%) and Brazil (16%). Canada (17%), China (15%) and Germany (13%) are the main producers of rapeseed. Sunflower oil production is dominated by Ukraine and the Russian Federation, accounting for over 50% of the world's production. Regarding flaxseed, China is the main producer (30%), followed by Belgium (16%). The distribution of the production areas is sometimes limited to a particular region or continent, generally due to the soil structure, the climate conditions and the industrial interest in these renewable resources, as well as historical and cultural factors. This distribution, added to a growing consumption of and demand for vegetable oils and oilseed meals, creates a global complex and growing market for oilseeds [16]. The increasing demand and growing market are reflected by an increase in production over the years, which is presented in Tables 2 and 3.

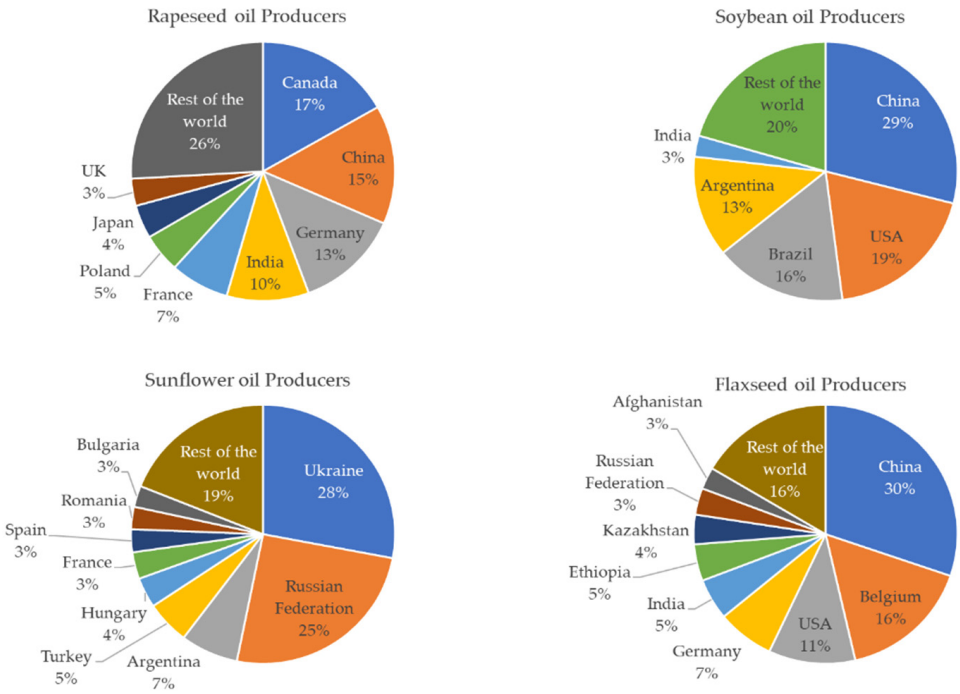

Figure 2. Major oil-producing countries in 2018. Data adapted from FAOSTAT [14].

Table 2. Change of the global oilseed production (in Mega ton) between 2010 and 2021. Data adapted from [a]—FAOSTAT [14] and [b]—USDA [17].

Production (Mt)	Rapeseed	Soybean	Sunflower	Flaxseed
2010 [a]	59.8	265.1	31.5	1.8
2011 [a]	62.8	261.6	40.1	2.2
2012 [a]	62.6	241.3	36.6	2.0
2013 [a]	73.1	277.7	45.3	2.3
2014 [a]	74.5	306.3	42.6	2.7
2015 [a]	70.3	323.3	44.3	3.1
2016 [a]	68.2	335.9	47.5	2.9
2017 [a]	76.6	359.5	48.6	2.9
2018 [a]	75.2	344.6	51.9	3.0
2019 [a]	70.5	333.7	56.1	3.1
2018/2019 [b]	72.9	361.3	50.7	-
2019/2020 [b]	69.2	339.9	53.9	-
2020/2021 [b]	72.7	366.2	49.1	-
2021/2022 [b]	67.5	384.0	56.0	-

Table 3. Change of the global oil production (in Mega ton) between 2010 and 2021. Data adapted from [a]—FAOSTAT [14] and [b]—USDA [17].

Production of Oil (Mt)	Rapeseed	Soybean	Sunflower	Flaxseed
2010 [a]	22.83	40.71	12.59	0.55
2011 [a]	23.09	42.33	13.29	0.55
2012 [a]	24.03	42.19	15.05	0.61
2013 [a]	24.34	42.85	13.69	0.59
2014 [a]	26.26	45.95	16.13	0.63
2015 [a]	26.14	49.99	15.33	0.69
2016 [a]	24.43	51.81	16.10	0.76
2017 [a]	24.20	56.43	18.30	0.77
2018 [a]	24.58	56.91	18.41	0.75
2018/2019 [b]	27.83	56.01	19.62	-
2019/2020 [b]	28.08	58.54	21.20	-
2020/2021 [b]	29.19	59.32	19.16	-
2021/2022 [b]	27.42	61.74	21.80	-

The aim of this review is to comparatively evaluate the bio-refining process of the selected oilseeds, that is, soybean, rapeseed, sunflower and flaxseed. Their composition is described, focusing on the macro-chemical profiles as well as the key nutrients. The conventional process for the extraction of oil and that of secondary metabolites from oilseeds is then detailed. In addition, the main alternative solvents and processes used in the extraction of lipids from the oilseeds, and of secondary metabolites of interest from the oilseed meal, are assessed based on a critical comparison with the actual conventional process.

2. Composition of Oilseeds

As discussed in the introduction, oilseeds are cultivated all around the world for diverse reasons, e.g., cultural, historical or economic, among others. Different varieties of each oilseed are thus created due this worldwide distribution of agriculture in particular conditions. The diverse varieties combined with genetic breeding leads to a wide variety of oilseed biochemical composition, characteristics, yield, and other properties such as pathogen resistance.

2.1. Oilseeds

2.1.1. Soybean

Glycine max (L.) *Merr.*, better known as soybean, is an ancient crop, domesticated in northeast China in the 1125–256 BCE era (the Zhou Dynasty). It is thought that soybean crops reached the European countries around the years 1730–1820 CE (The Netherlands (1737), France (1740), England (1790), Croatia (1804) and Serbia (1817)), and the United States and North America around 1765 [18–20]. Yield and pathogen resistance, among other quality traits (composition, adaptability), are some of the primordial qualities improved by breeding of soybean [19]. Soybean is mostly well-known for its high-quality protein, but it also contains attractive phytochemicals that are beneficial to human and even animal health, namely isoflavones and lignans, among others [21]. Isoflavones present in soybean, specifically genistein and daidzein, are used as a prevention of breast and prostate cancer, at daily doses [22]. It is thought that occurrences of some cancer and cardiac conditions are reduced in populations with high soy intake [23,24].

In addition to its food application (salad oil and dressing, mayonnaise, margarine [18]), soybean oil or its FAME (fatty acid methyl ester) methyl soyate (a bio-based solvent) are exploited in industry, mainly for the production of inks, coatings, paint, composites, lubricants and soap [25]. In general, soybean oil contains relatively low amounts of saturated and monounsaturated fatty acids (cf. Table 7), namely palmitic and oleic acids. Both compounds are known to have opposite health benefits, as the former increases LDL-cholesterol while the latter decreases it [25,26]. On the other hand, the oil contains high amounts of beneficial polyunsaturated fatty acids, viz., linoleic and linolenic acids [25], known to lower the risk and mortality of coronary heart diseases as well as cancer risk [27]. Soybean meal makes up to 79% [20] of the seed's total mass. It is generally used as livestock high-protein feed, or as protein isolates and concentrates as a food [18]. Nevertheless, soybean contains anti-nutritional factors, namely enzyme inhibitors, that limit the beneficial effects and use of soybean meal.

2.1.2. Rapeseed

Brassica napus, commonly known as rapeseed or canola, is one of the world's most abundant oil crops. It is a prehistoric crop thought to be first cultivated around 2000 BCE [28]. The traditional varieties of these oilseeds produce an oil rich in erucic acid (up to 60%, known as HEAR (high erucic acid rapeseed) oil) [29]. Among others, the Australia New Zealand Food Authority ANZFA classifies this long-chain fatty acid as a natural toxin [30]. A high consumption of erucic acid can have undesirable health effects, and injurious effects on the heart's muscle [31]. This high erucic acid crop was thus cultivated in small quantities, mainly for the use of its oil in industrial applications [28].

Rapeseed has been modified genetically into breeds producing LEAR (low erucic acid rapeseed) oil (5% erucic acid or less), first produced in Canada in 1968. These new crops, denoted "single-zero" or "single-low" rapeseed, underwent further modification giving "double-zero" or "double-low" rapeseed (rapeseed 00) with a relatively low content of erucic acid and glucosinolates (GSL) [28,32]. In animal feed, the breakdown of glucosinolates reduces the nutritional levels of rapeseed and can be toxic for animals. In 1979, the Western Canadian Oilseed Crushers Association registered the double-zero rapeseed (<2% erucic acid, <3 mg/g (30 µmol/kg [28]) of glucosinolates) under the name canola (CANadian Oil, Low Acid) [33,34]. Further plant breeding efforts resulted in "triple-zero" or "triple-low" rapeseed, with low erucic acid, low glucosinolates and reduced dietary fibre content (9–10%) [35,36].

Currently, rapeseed oil is considered as one of the most important and healthiest oils [8,37]. Rapeseed oil displays interesting and attracting advantages. It is rich in monounsaturated (oleic acid) and polyunsaturated (linoleic and α-linolenic acid (ALA)) fatty acids, but also contains low amounts of saturated fatty acids [28,37]. It also lacks cholesterol and contains fat-soluble vitamins, phenolic compounds, sterols and tocopherols [8]. These bioactive compounds can help prevent cancer, diabetes, neurovegetative diseases and heart diseases [38]. Furthermore, the consumption of rapeseed reduces the serum cholesterol

levels as well as total cholesterol concentrations [28]. Rapeseed cake/meal makes up to 60% by weight of the grain after oil extraction [39], with a significant protein content, which have been used in dairy substitutes, bakery products and salad dressings [8]. However, the presence of some anti-nutriments (glucosinolates, phenolic acids [6]) and some enzymes (myrosinase [40]) in the cake/meal limit its use and require proper treatments.

2.1.3. Sunflower

Sunflower, or *Helianthus annuus*, is an ancient oilseed crop, indigenous to North America [41], specifically the southwestern United States [20], thought to be first cultivated by the American Indians in 4625 BCE [42]. In the sixteenth century, sunflower was exported to Spain and Europe during a Spanish expedition, and then introduced to Russia [20,41–43]. In addition to oilseed sunflower (black seed with a thin hull), two other important varieties of this plant exist (black with white strips or colourful, larger seeds with thicker hull), namely confectionary sunflower and ornamental sunflower [41,42].

Currently, oil-sunflower is one of the major oil-producing crops grown throughout the world. Sunflower can be used as food (unprocessed seed as snacks, processed as a premium quality edible oil or ingredient in butter and bread), for livestock feed, or in industry (paint, cosmetics, biodiesel, lubricants) [8,41,42]. The consumption of sunflower seeds is attributed to an antigen, anti-pyretic, anti-asthmatic, anti-hypoglycaemic, anti-tumour, anti-inflammatory and antioxidant activity, as well as diuretic, vermifuge, cathartic and anti-microbial activity [44]. The positive health effects of sunflower are attributed to its composition. In fact, sunflower oil is a low-cholesterol edible oil, rich in monounsaturated (oleic acid) and polyunsaturated (linoleic acid) fatty acids (ca. 90%), lecithin, tocopherols, phenolic compounds, peptides, vitamins and minerals [8,43,44]. However, the fatty acid composition varies depending on the sunflower species, environmental conditions and processing methods [41,43].

Sunflower cake/meal is another nutritional constituent of the seeds. It represents 36 [41] to 55% [20] of the seed's total mass, and is used as a composite ingredient in bakery products (pasta, bread, flapjacks, pretzels, ramen, protein bars, etc. [45]). This oilseed by-product is characterized by an attractive nutritional value for food and livestock feed. Nevertheless, it contains anti-nutritional factors (saponins, enzyme inhibitors), hence the need for adequate treatment of the cake/meal before consumption [41], as was mentioned for previous oilseeds.

2.1.4. Flaxseed

Linum usitatissimum, also known as flaxseed in North America or linseed in Europe, is an ancient oilseed crop [46,47] cultivated around the world, with a higher crop yield in the Araucanía Region, Chile [48]. The yield and the biochemical composition of the seed are hugely affected by the environmental conditions and the cultivars. The two major grown cultivars are oil flax (producing more seeds) and fibre flax (containing more protein in its seeds, generally taller and with less branches). The latter is cultivated for the fibre from its stem, while both cultivars' seed can be used for oil production [49–51].

The seed was considered as a non-edible field crop [52]. Flaxseed oil has been industrially used for centuries, for paint, plastics, soap, coatings, inks, varnishes, linoleum and herbicide adjuvants [46,52–55]. Nevertheless, the oil can be processed into edible products. The demand of the oil is increasing due to its high omega-3 (α-linolenic acid) content (up to 70% of total fatty acids [56]), making flaxseed one of the most auspicious oilseed as a functional food [57]. This essential fatty acid is thought to reduce LDL (low density lipoprotein), responsible for heart diseases. Tocopherol and tocotrienol (vitamin E derivatives) and sterols are also present in the lipid fraction [54]. Flaxseed is an important source of bioactive molecules, having diverse positive health effects (protection against diabetes [54], cardiovascular diseases, osteoporosis [51], anti-inflammatory activity and laxative activity [58]) as well as phenolic compounds (blocking agents for cancers induced by aromatic carcinogens [55]), explaining the increased interest in the crop [47].

Higher oil demand and production increases the by-product generation, i.e., the flaxseed cake and meal (ca. 55% of the seed on dry basis), which have high nutritional potential [54]. Proteins constitute an interesting proportion of flaxseed, and its pattern and composition are similar to that of soybean [46]. Furthermore, linseed's carbohydrate content is low, and it is gluten free [48]. The defatted cake/meal contains large amounts of protein, dietary fibre or mucilage, phenolic compounds and lignans [55]. Despite the possible benefits, flaxseed cake and meal are not suitable for food applications, and their use is limited in livestock feed [52] due to the presence of cyanogenic compounds (cyanogenic glycosides potentially degradable to noxious HCN). Therefore, there is a need for the detoxification of flaxseed meals to convert it into edible foodstuffs.

The health benefits and medicinal values of flaxseed are attributed to its omega-3 and phenolic compound content [55], yet according to Shim et al., 2014 [46], almost none of the earlier studies on flaxseed oil consumption have confirmed that its produced health benefits result from ALA rather than other bioactive molecules present in the oil. Furthermore, the health benefits of flaxseed cannot be attributed to a single bioactive compound present in the seed.

2.2. Key Nutriments

The biochemical composition of each of the oilseeds can vary widely, as can be observed in Table 4 (biochemical composition of the seeds) and Table 7 (lipid profiles of the seeds' corresponding oils). It is highly influenced by environmental conditions (temperatures, climate) as well as by the seeds' cultivated varieties [22,33,37,43,51]. Tables 5 and 6 present the biochemical composition of the seeds' cakes and meals respectively.

Table 4. The biochemical composition of oilseeds.

Composition (%)	Rapeseed	Soybean	Sunflower	Flaxseed
Moisture	7.6–10.1	5.6–11.5	7.2–8.2	4–8
Dry matter	89.9–92.4	88.5–94.4	91.8–92.8	92
Crude lipids	28.5–54.9	15.5–24.7	44.5–54.46	30–47
Crude proteins	18.43–18.6	32–43.6	14.8–20.78	20.7
Ash	4	4.5–6.4	3.02–3.2	3–4
Crude fibre	8.5	5.6–31.9	8.6–15.9	9.1
Total sugars	5.4	7.5	2.5	2.7
Starch	3.5	5.3	1.2	5.5
NDF [1]	16.0–18.5	10–14.9	22.03–28.8	23.8
ADF [2]	10.43–13	7–11.1	15.3–19	12.9
Lignin	5.9	0.9	6	5.3
Ref.	[59–61]	[61,62]	[43,59,61]	[48,54,61]

[1] NDF: Neutral Detergent Fibre (hemicellulose, cellulose, and lignin). [2] ADF: Acid Detergent Fibre (cellulose and lignin).

Table 5. The biochemical composition of oilseeds' cakes.

Composition (%)	Rapeseed	Soybean	Sunflower	Flaxseed
Moisture	8	6.8–15.2	7.6–9	8.8
Dry matter	90–92	84.8–93.2	91–92.4	91.2
Crude lipids	11.8–13.1	8.9	14.6–30.2	9.8
Crude proteins	31–34.9	43.8–47.5	23.9–34.1	32.3
Ash	5.1–6.2	6.1–6.4	5.2–7.5	5.7
Crude fibre	9.7–11.6	5.1–6	8.6–25.4	8.8
Total sugars	9.2	8.7	5.8	3.9
Starch	6	4.7	3.6	6.6
NDF	16.8–26.9	12.7	41	21.6
ADF	14.7–18	7.4	29.1	13.6
Lignin	6.5–8.3	0.7	9.8	5.7
Ref.	[63–65]	[63,64]	[43,63,64]	[63]

Table 6. The biochemical composition of oilseeds' meals.

Composition (%)	Rapeseed	Soybean	Sunflower	Flaxseed
Moisture	8.7–11	10.4–12	5.6–11.1	12.1
Dry matter	89–91.3	88–89.6	88.9–94.4	87.9
Crude lipids	2.2–3.2	1.5–2.2	1.5–2.75	3.4
Crude proteins	33.9–37	41.5–48.5	23.7–32.0	32
Ash	6.3–7	6.4–6.7	5.3–6.5	5.7
Crude fibre	11.5–12.7	3.9–6.8	26.2–41.0	10
Total sugars	9.4–9.5	9.5	5.3	4.5
Starch	5.6–6.8	5.5	3.3	8.2
NDF	25.1–28.1	8.8–26.4	26.8–41.7	21.8
ADF	16.4–18.5	5–9.5	22.4–29.9	13.7
Lignin	7.4–8.6	0.4	7.7–26.8	5.9
Ref.	[5,59,63]	[59,63,66]	[5,59,63,65]	[63]

2.2.1. Lipids

Lipids are a key component of living cells, along with proteins, carbohydrates and nucleic acids [67]. Their structure is complex due to diverse transformations they undergo during their biosynthesis [68]. The term "lipid" denotes a heterogenous group of biological substances, sparingly soluble in aqueous solvents (hydrophobic), but in many cases soluble in organic solvents such as hydrocarbons (e.g., hexane, benzene), ethers (e.g., diethyl ether) or alcohols (e.g., methanol). Lipids can either originate from the partial or the complete carbocation-based isoprene condensation (sterol and prenol lipids), and/or carbanion-based thioesters' condensations (fatty acyls, saccharolipids, polyketides, glycerolipids, glycerophospholipids and sphingolipids) [69,70]. This includes oils (liquid at ambient temperature), fats (generally greasy solids), and fatlike matters, and comprises a myriad of lipids with diverse structural and functional properties covering a broad range of substances, such as fatty acids, neutral fats, phospholipids, carotenes, sterols, terpenes and others [67–69,71,72]. Lipids can be classified as polar lipids and neutral lipids. The latter include glycerides, triacylglycerols (TAGs), fatty acids, sterols, etc., while the former include phospholipids and glycolipids [72,73]. The definition as well as the classification based on polarity is commonly used, but is not exhaustive, as some lipid substances can be rather hydrophilic (more polar), e.g., very short-chain (C1–C4) fatty acids [72].

Sunflower seed and rapeseed have the highest crude lipid content, ranging between 44.5% and 54.4% for sunflower, followed by rapeseed with a content of 28.5 to 54.9%, as per Table 4. Flaxseed's lipid content varies between 30–47%, while soybean contains the least amount of lipid among the four oilseeds with only 15 to 25%. As shown in Table 7, the lipid composition varies widely, depending on the oilseed breed, yet the four oilseeds and their diverse breeds show a high content of C18 unsaturated acids (oleic, linoleic and linolenic acids) and thus the liquid aspect of these oils at room temperature. While the commonly used and widely available low erucic acid rapeseed variety (canola) generally shows a high oleic acid content (up to 76%) and a lower linoleic acid content (up to 30%), sunflower and soybean lipid content can differ widely, with either a dominance of oleic acid (up to 84% for soybean and 90% for sunflower) or a dominance of linoleic acid (up to 59% for soybean and 74% for sunflower). Similarly, flaxseed can either contain a large amount of linoleic acid (up to 73%) or a large amount of linolenic acid (up to 70%) with lower amounts of oleic and linoleic (up to 36 and 30%, respectively).

Table 7. Fatty acid profile (in %) of oilseeds' oil. Data adapted from [15,20,61,74].

	Fatty Acids	RAPESEED Oil	Soybean Oil	Sunflower Oil	Flaxseed Oil
C6:0	Caproic acid	ND	ND	ND	ND
C8:0	Caprylic acid	ND	ND	ND	ND
C10:0	Capric acid	ND	ND	ND	ND
C12:0	Lauric acid	ND	ND–0.1	ND–0.1	ND–0.3
C14:0	Myristic acid	ND–0.2	NA	ND–0.2	ND–0.2
C16:0	Palmitic acid	2.5–7.0	6–13.5	2.6–7.6	4.0–11.3
C16:1	Palmitoleic acid	ND–0.6	ND–0.3	ND–0.3	ND–0.5
C17:0	Margaric acid	ND–0.3	ND–0.1	ND–0.2	ND–0.1
C17:1	Heptadecenoic acid	ND–0.3	ND–0.1	ND–0.1	ND–0.1
C18:0	Stearic acid	0.8–3.0	2.0–5.4	2.1–6.5	2.0–8.0
C18:1	Oleic acid	51–76	17–30 [a] 84 [b]	14.0–39.4 [c] 43.1–75 [d] 75–90.7 [e]	9.8–36.0
C18:2	Linoleic acid	13–30	48.0–59.0 [a] 2 [b]	48.3–74 [c] 8.7–45.3 [d] 2.1–17 [e]	8.3–30.0 [f] 73 [g]
C18:3	Linolenic acid	5.0–14.0	4–11.0	ND–1	43.8–70.0 [f] 2–3 [g]
C20:0	Arachidic acid	0.2–1.2	0.1–0.6	0.1–0.5	ND–1.0
C20:1	Gadoleic acid	0.1–4.3	ND–0.5	ND–0.5	ND–1.2
C20:2	Eicosadienoic acid	ND–0.1	ND–0.1	ND	ND
C20:4	Arachidonic acid	0.1	NA	NA	NA
C22:0	Behenic acid	ND–0.6	ND–0.7	0.3–1.6	ND–0.5
C22:1	Erucic acid	ND–2.0	ND–0.3	ND–0.3	ND–1.2
C22:2	Docosadienoic acid	ND–0.1	ND	ND–0.3	ND
C22:6	Docosahexaenoic acid	0.1	NA	NA	NA
C24:0	Lignoceric acid	ND–0.3	ND–0.5	ND–0.5	NA
C24:1	Nervonic acid	ND–0.4	ND	ND	NA

ND: non-detectable, defined as <0.05%. NA: not available. Values with similar superscript (a to g) are associated.

However, knowledge of gross fatty acid composition is not sufficient to assess completely nutritional and physicochemical behaviour of lipids. Fatty acids are mainly present in oils in the form of TAG, with lower amounts of monoacylglycerols (MAG), diacylglycerols (DAG) and free fatty acids (FFA). In addition to the effect of the double bond location and the chain length of fatty acids, the composition of the TAG can alter the nutritional value of the oil [75]. The properties of oil depend on specific stereo-distribution of the fatty acids [75,76], which depend heavily on the enzymatic reactivity and operating conditions. For example, the precise distribution of fatty acids on the triacylglycerol backbone of triglycerides impacts their body assimilation. Additionally, vegetable oil phase behaviour (liquid or solid, melting range) also depends on TAG mixture composition and fatty acid distribution on each TAG. These properties can be modified through the restructuring of TAG by the rearrangement of the individual fatty acids, either by chemical catalytic interesterification (random distribution) or enzymatic interesterification (regioselective) [76,77].

2.2.2. Proteins

Proteins are a very large family of bio-macromolecules. These molecules, with an extremely complex structure, occur naturally in all living organisms, with diverse biological functions (enzymes, antibodies, hormones, etc.) and high nutritional value. Proteins are made of a combination of 1 or several of the 20 amino acids identified, bonded with peptides [23,78]. Among the amino acids, 12 can be synthetized by the human body and are thus considered as non-essential. Humans need to consume the remaining eight essential amino acids, as they are not capable of producing them. The growth and repair of human muscle necessitates the presence of all amino acids [23].

Theoretically, numerous three-dimensional configurations may exist for these polypeptides containing up to hundreds of covalent bonds, yet a precise folded conformation with the lowest possible molecule's free energy, making up a thermodynamic equilibrium state, is always achieved under specific conditions (pH, ionic strength conditions, temperature) [79]. This folding is embodied in terms of four levels. The primary structure refers to the sequence of amino acids in a polypeptide chain, the secondary to the conformations and folding of short sequences in the chain, the ternary to the overall spatial arrangement of the secondary folded structural units into larger functional polypeptide and the quaternary to the assembly of polypeptide units and their three-dimensional arrangement [79,80].

In food products, some properties of the protein are primordial for a desirable sensory feature, namely emulsifying, gelling, foaming, texturizing, curdling, flavour and fat-binding properties. Depending on the vulnerability of inter-molecular interactions, protein denaturation can occur during food processing (caused by temperature, shear, ionic strength, pH, etc.), altering intensely the proteins' functional properties [79].

Low lipid content in the oilseeds means higher protein content, which is the case with soybean. While the protein content of rapeseed, flaxseed and sunflower seeds is fairly similar, reaching up to 20% (cf. Table 4), soybean has a higher protein content, varying between 32 and 43%. The protein content in the seeds' cakes is further improved, reaching up to 32, 34, 35 and 48% for flaxseed, sunflower, rapeseed and soybean, respectively. Minor improvement in the protein content of the meal resulting from solvent extraction is observed. These relatively high protein contents in the cakes and meals are hampered by a more or less interesting amino acid profile. As can be seen in Table 8, it is usually due to a deficiency in sulphur-containing amino acids, such as methionine and lysine, considered to be indispensable amino acids. Sunflower protein is well balanced, but its lysine content is low, while the lysine content of soybean and rapeseed protein is sufficient, but they contain less methionine than sunflower [20,62,66]. Flaxseed's lysine content, similar to sunflower, is low, but also contains lower amounts of methionine.

Table 8. Amino acid composition (in %) of the oilseeds' protein.

	Amino Acid	Rapeseed	Soybean	Sunflower	Flaxseed
Ala	Alanine	3.9–4.5	3.6–4.6	4.1	4.3–5.4
Arg	Arginine	5.6–6.8	6.2–7.8	8.5–9.1	9.2–11.8
Asp	Aspartic acid	6.2–7.2	7.1–11.9	8.7–10.2	9.3–12.5
Cys	Cystine	1.7–2.8	1.1–2.1	1.8–2.2	1.1–3.8
Glu	Glutamic acid	16.6–20.2	9.1–19.7	21.0–21.9	19.6–26.3
Gly	Glycine	4.3–5.5	3.7–4.5	5.1–5.6	4.8–7.0
His	Histidine	2.6–2.8	2.3–3.0	2.4–2.8	1.4–2.9
Ile	Isoleucine	3.7–4.2	4.5–5.3	3.9–4.5	4–6
Leu	Leucine	6.3–7.4	7.1–7.8	6.1–6.9	3.5–6.8
Lys	Lysine	5.8	5.8–6.4	3.5–3.9	1.8–4.1
Met	Methionine	1.8–2.2	1.1–2.7	1.9–2.6	1.4–2.2
Phe	Phenylalanine	3.5–4.2	3.9–5.5	4.6–5.1	4.6–5.9
Pro	Proline	6.0–7.5	3.6–5.5	5.0–5.1	3.1–5.2
Ser	Serine	3.7–4.4	4.9–6.4	3.9–4.2	4.5–5.8
Thr	Threonine	3.8–4.6	3.7–4.0	3.2–3.8	3.6–4.9
Trp	Tryptophan	1.2–1.3	1.3–7.6	1.1–1.4	1.8
Tyr	Tyrosine	2.6–3.1	3.2–4.1	1.4–2.9	1.5–2.9
Val	Valine	4.8–5.5	4.6–5.2	4.8–5.8	4.6–5.6
Ref.		[40,81,82]	[20,46,64,81–84]	[20,40,64,82]	[46,47,54,85]

2.2.3. Anti-Nutriments

Oilseeds contain various anti-nutriments in diverse quantities, depending on the cultivars as well as the environmental conditions. The anti-nutritional effect of these compounds is interrelated to their concentration [86]. Some compounds are present in all four oilseeds, such as phytic acid, and some others are more specific to a certain

seed. Flaxseed, for example, contains cyanogenic glycosides and linatine [54], while glucosinolates are present in rapeseed [86]. Table 9 presents the content of these secondary metabolites in oilseeds as well as in the corresponding cakes and meals.

Table 9. Secondary metabolites content (in %) of oilseeds and oilseeds' cake and meal.

Secondary Metabolites	(%)	Rapeseed	Rapeseed Cake	Rapeseed Meal
Total Phenolics			1.77–1.97 [c] [87]	0.64–1.84 [88] 0.531–1.666 [c] [5,39,87]
Phenolic acids (and derivatives)	Total		1.31–1.5 [87]	0.916–1.455 [87]
	Sinapic acid		0.029–0.044 [87]	0.032–0.041 [87]
	cis-Sinapic acid		0.035 [d] [89]	0.037–0.047 [90]
	trans-Sinapic acid		0.03 [d] [89]	0.444–0.871 [90]
	Sinapoyl glucose		0.237–0.401 [87]	0.135–0.199 [87]
	Sinapine	1–1.5 [91]	0.990–1.131 [87] 0.42 [d] [89]	0.547–1.8 [39,87,90,92]
Tannins	Total			0.2–3 [88,92]
Flavonoids	Isoquercetin			0.049–0.0596 [90]
Other Anti-Nutriments	GSL	10–20 [a] [91]		
	Phytic acid	1–7 [88,91]		3–6 [92]
	(%)	**Soybean**		**Soybean Meal**
Total Phenolics				
Phenolic acids (and derivatives)	Total	1–25 [b] [20]		0.0736 [h] [93]
	p-Hydroxybenzoic acid			0.0139 [h] [93]
	trans-Ferulic acid			0.0157 [h] [93]
	trans-p-Coumaric acid			0.0094 [h] [93]
	trans-Caffeic acid			0.006 [h] [93]
	Syringic acid			0.0289 [h] [93]
Flavonoids	Total	0.25 [e] [94]		0.28 [e] [94]
	Isoflavones	0.12–0.42 [20]		
Other Anti-Nutriments	Phytic acid	1.0–2.2 [20,95]		
	Saponins	0.09–6.16 [20,95]		
	(%)	**Sunflower**		**Sunflower Meal**
Total Phenolics		1–4 [62]		3.5 [5]
Phenolic acids (and derivatives)	Total			1.0037 [h] [93]
	p-Hydroxybenzoic acid			0.0074 [h] [93]
	Chlorogenic acid	0.5–2.8 [g] [62]		2.7 [20]
	Ferulic acid			
	trans-Ferulic acid			0.0072 [h] [93]
	trans-p-Coumaric acid			0.0056 [h] [93]
	Vanillic acid			0.0008 [h] [93]
	Caffeic acid	0.05–0.29 [g] [62]		0.2 [20]
	trans-Caffeic acid			0.9791 [h] [93]
	Quinic acid	0.12–0.25 [g] [62]		0.38 [20]
Other Anti-Nutriments	Phytic acid	1.6–1.7 [20]		
	(%)	**Flaxseed**		**Flaxseed Meal**
Total Phenolics		0.235–0.389 [f] [51]		

Table 9. *Cont.*

Secondary Metabolites	(%)	Rapeseed	Rapeseed Cake	Rapeseed Meal
Phenolic acids (and derivatives)	Total	0.8–2.767 [48,54,55]		8.44 [54], 0.0811 [h] [93]
	p-Hydroxybenzoic acid	1.719 [54]		6.454 [54], 0.0026 [h] [93]
	Chlorogenic acid	0.72 [54]		1.435 [54]
	Ferulic acid	0.161 [54], 0.0015–0.0047 [51]		0.313 [54]
	trans-Ferulic acid			0.0376 [h] [93]
	Coumaric acid	0.087 [54], 0.00077–0.0011 [51]		0.13 [54]
	trans-p-Coumaric acid			0.0061 [h] [93]
	Gallic acid	0.029 [54]		0.017 [54]
	Vanillin	0.022 [54]		0.042 [54]
	Vanillic acid			Traces [93]
	Sinapic acid	0.018 [54]		0.027 [54]
	trans-Sinapic acid			0.0291 [h] [93]
	Protocatechuic acid	0.007 [54]		0.007 [54]
	Caffeic acid	0.0011–0.004 [51,54]		0.015 [54]
	trans-Caffeic acid			0.0053 [h] [93]
Flavonoids	Total	0.035–0.07 [48]		
Lignans	Total	1.33 [53]		
	SDG [1]	0.0062–0.0145 [51]		
	SECO [2]	0.0077–0.0244 [51]		
Other Anti-Nutriments	Phytic acid	0.80–1.50 [54]		

[a] µmol/kg. [b] ppm. [c] g of sinapic acid equiv./100 g. [d] g/100 g dry basis as trans-sinapic acid equiv. [e] g genistein equiv. (GE)/100 g of DM. [f] g of gallic acid equiv./100 g of sample. [g] % DM (dry matter). [h] oilseed flour, [1] SDG: secoisolarisiresinol diglucoside. [2] SECO: secoisolariciresinol.

Phenolic Compounds

Phenolic compounds (PC) are secondary metabolites extensively spread throughout the plant kingdom. Simple phenolics or polyphenols display a positive impact on health due to their anti-microbial, anti-mutagenic, anti-inflammatory, anti-carcinogenic, anti-cardiovascular disease, atherogenic, and antioxidant effects. Many PC are a part of the human diet, as they are present in fruits, legumes, oilseeds and beverages [39,54,93,94,96]. In general, phenolic compounds are very valuable antioxidants. However, high amounts of PC as well as some of their derivatives can affect the taste and the colour of the meal, turning it bitter and darker in colour, thus reducing its palatability and limiting its use as food or feed [88]. PC can also decrease the digestibility of the protein by bonding with them, reducing their solubility [62]. The major PC found in oilseeds are phenolic acids, with smaller amounts of flavonoids, tannins and lignans.

Rapeseed is rich in phenolic acids, mainly sinapic acid (SA) (or sinapinic acid) in its free or esterified form, sinapine (SP) (or sinapoylcholine), making up ca. 80–90% [92,93] of the total phenolic compounds present in rapeseed. The seeds contain 1–1.5% of sinapine and this content increases up to 1.8% in rapeseed meal (cf., Table 9). SP does not have a real anti-nutritional factor aside from turning the rapeseed meal to a brown colour with a bitter taste. This compound may also produce a fishy or off-flavour taste in brown eggs laid by susceptible hens [92]. Tannins present in rapeseed (up to 3%) also reduce the palatability of rapeseed products by contributing to the darker colour and bitter taste [88]. They also tend to bind with proteins, preventing their hydrolysis and thus digestion [93]. Other phenolic acids, such as p-hydroxybenzoic, caffeic, cinnamic, and p-coumaric acids, are also present in rapeseed [39,93].

Sunflower's main phenolic compound is chlorogenic acid (up to 2.8% DM (dry matter), cf. Table 9), an ester of caffeic acid with a quinic acid moiety, as well as lower amounts of free caffeic acid. The presence of phenolic compounds in sunflower contributes to a grey coloration of the meal. Furthermore, chlorogenic acid may undergo oxidation, involving the

transformation of a lysine group [20] and hence reducing the amount of this indispensable amino acid already present in insufficient quantities in sunflower [62].

While rapeseed and sunflower are rich in phenolic acids, soybean is rich in isoflavones (ca. 0.5%), a subfamily of flavonoids. Isoflavones (substituted derivatives of isoflavone) are similar to oestrogenic hormones, capable of activating oestrogen receptors [95]. These compounds present beneficial effects on humans (menopausal women specifically), such as preventing colon, prostate and breast cancers, but also a disruptive anti-oestrogenic property on humans and animals [94]. Isoflavones appear to have a negative effect on fertility and reproduction [95], which was demonstrated in a meta-analysis published in 2009 by L. Hooper [97]. Tocopherols (having a vitamin E activity) are the main active antioxidants in soybean, with lower amounts of phenolic acids (p-Hydroxybenzoic, ferulic, p-coumaric, caffeic acids [93]).

Several PC are present in flaxseed, including phenolic acids (up to 2.7%), lignans (up to 1.3%) and lower amounts of flavonoids (cf. Table 9). Among the phenolic acids present in flaxseed, p-hydroxybenzoic, coumaric, sinapic and chlorogenic acid are the main ones [54,93]. Lignans lead to benefits for health, as they reduce cardiovascular risks, prevent diabetes [55] and possess an antioxidant activity (e.g., secoisolariciresinol diglucoside).

The presence of phenolic compounds in the cake or meal is controversial. Despite the positive health effect of these molecules and their antioxidation potential, they might interact with proteins and form unwanted complexes, altering the nutritional and functional properties of both proteins and phenolics. The structural properties (secondary and tertiary) of proteins can be affected, thus reducing the solubility of proteins and the digestibility of some amino acids. Similarly, the formation of these complexes might reduce the antioxidant activity of phenolics [98].

Glucosinolates

Glucosinolates (GSL), or thioglucosides ($C_6H_{11}O_6$-S-CR = N-OSO_3^-), mainly found in rapeseed, are formed by an oxime derivative (RR'C = NOH) with an anionic moiety (sulphate group), a glucose group linked via a sulphur atom and a variable side chain deriving from an amino acid. The breeding of rapeseed significantly reduced the concentrations of GSL to less than 30 µmol/kg. These anionic secondary metabolites are localized in all tissues of the Cruciferae (Brassicacaea *viz.* the mustards family) plants and play a defensive role in the plant as well as an important role in its development in case of nutriment deficiency. They are quite benign and only become biologically active after the damaging of specialized cells (myrosin cells) or some protein bodies containing myrosinase (thioglucosidase), an enzyme capable of hydrolysing the glucosinolates, producing molecules such as nitriles (RCN) and thiocyanates ($RSCN^-$) after several hydrolysis and rearrangement steps [40,62,86,99,100]. However, temperatures above 70 °C can deactivate this enzyme [62], but the hydrolysis of glucosinolates might still take place in the body through contact with the enzyme incoming from other food sources. GSL are capable of causing deleterious effects on livestock, such as disturbing the functioning of the thyroid, iodine deficiency and hypertrophy of the kidney and liver. They are lethal for pigs and can also increase mortality rates in poultry [40,86,101]. GSL are mainly present in rapeseed, with a content usually lower than 3 mg/kg [34] or 30 µmol/kg [28] for the bred varieties (canola, double- and triple-zero rapeseed).

Phytic Acid

Phosphorus is present in oilseeds majorly in the form of phytic acid (60–90% [54]), which hampers its digestibility. Furthermore, trace monovalent or divalent mineral cations (e.g., zinc, calcium, iron and potassium ions) can form complexes with phytic acid by chelation, limiting the availability and causing deficiencies of these elements [20,54,88,92]. The highest amount of phytic acid can be found in rapeseed (up to 7%), followed by sunflower seeds, soybean and flaxseed (ca. 1.6–1.7, 1–1.5 and 0.8–1.5%, respectively (cf. Table 9)).

Linatine

Linatine is a polar compound present in flaxseed. It is responsible for symptoms similar to those of vitamin B6 deficiency in flaxseed-fed chicks and poultry, i.e., poor growth, nervous disorders, anaemia and loss of appetite. Nevertheless, when eating up to 50 g of flaxseed daily, the vitamin B6 level was not affected in humans. Linatine content in flaxseed is estimated to about 100 ppm [46,54].

Cyanogenic Glycosides

Cyanogenic glycosides are nitrogenous compounds whose degradation and hydrolysis, by enzymatic or acidic ways, can produce hydrogen cyanide (HCN), a noxious compound capable of affecting the nervous and cardiovascular system, as well as hindering the breathing. Iodine deficiency can also be caused by the degradation of the cyanogenic glycosides into thiocyanates. Four types of cyanogenic glycosides are present in flaxseed, estimated to produce 19–100 mg of HCN equivalent/100 g of flaxseed, while the toxic dose of cyanide for adults is around 50–60 mg. A high protein diet (containing sulphur amino acids) can help detoxify cyanide in the case of a high consumption of flaxseed [46,54].

Other Anti-Nutritional Factors

Some oilseeds contain some enzyme inhibitors, such as protease and arginase inhibitors in sunflower [41], or trypsin, elastase and chymotrypsin inhibitors in soybean [102]. These enzymes can reduce the bio-availability of protein by decreasing their digestibility [66,102].

Soybean also contains allergens, viz., antigenic proteins capable of stimulating the immune system in animals (pigs, calves) or humans [66].

Saponins, a subclass of terpenoids, are another anti-nutritional factor present in soybean. In fact, these triterpene glycosides have a defensive anti-fungal activity. They have been reported to display an important role in the prevention of chronic degenerative diseases, a hypocholesterolemic effect, and anticarcinogenic activity [21,24], but they are associated with a bitter taste and are toxic for invertebrates and fishes [21].

3. Bio-Refinery of Oilseeds

The general process for the extraction of oil and secondary metabolites is presented in Figure 3. Commonly, mechanical extraction, so-called pressing, is the first oil extraction step after oilseed conditioning (cleaning, dehulling, heating, etc.). Pressing is regarded as a simple and safe process [3,103]. It can take place at low temperatures (cold press) or at high temperatures (hot press), which increases the oil recovery but may affect the oil colour and quality [11,33,56]. Pressing can be performed partially, leaving 15–20% residual oil in the cake [104,105], or totally, leaving about 5% [105]. Mechanical extraction yield can be influenced by the oilseed properties, such as moisture content [56]. When a 2% or less residual oil is required in the meal, solvent assisted oil extraction is used [106]. The required amount of residual oil in the meal depends on its final application; however, reaching the highest oil extraction yield is a substantial priority from an economical point of view.

Oilseeds are pressed, totally or partially, before solvent extraction, if they contain over 25% [10] or 30% oil [104], while direct solvent extraction is suitable for materials containing less than 20% lipids [33]. This process of solvent extraction can be applied directly on the oil seeds after a pre-treatment step consisting of damaging the seed structure (flaking, expanding, grinding, etc.), increasing the bulk density and enhancing the extraction speed.

In the industry, pressing is classically performed using continuous single-screw presses. Nevertheless, recent technological advances have highlighted the interest of twin-screw extrusion, which favours both the obtaining of a high-quality oil as well as a co-valorisation of the cake, including for applications in the field of renewable materials [107,108]. Sunflower [109,110], coriander [111] and jatropha [112] are some examples of oilseeds that were successfully processed for mechanical pressing of oil using the twin-screw extrusion technology.

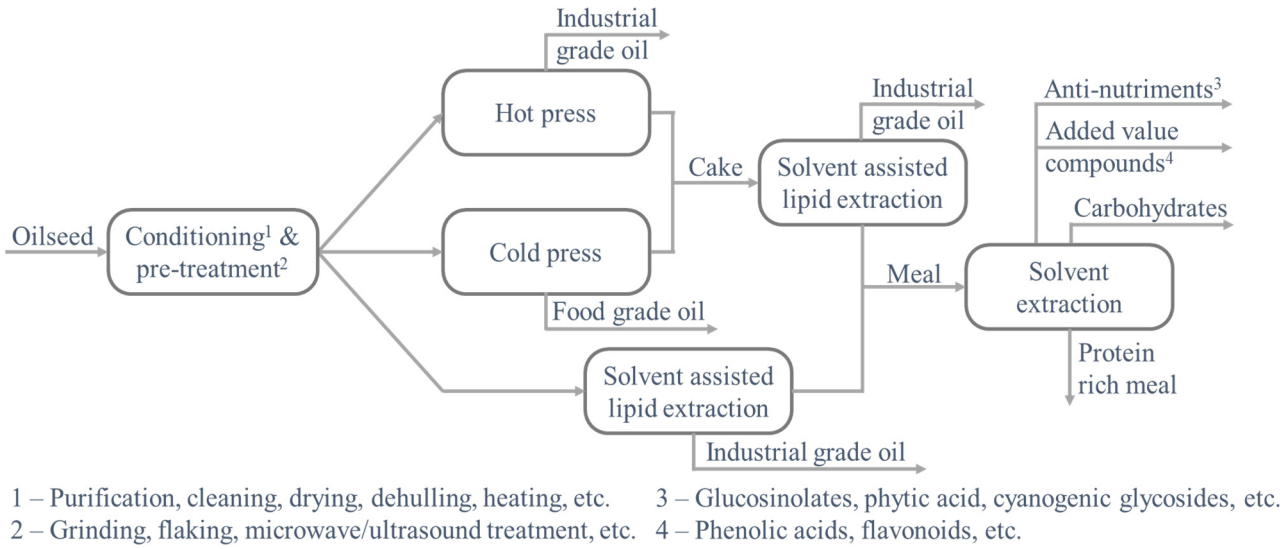

Figure 3. General process scheme of oil and metabolites' extraction from oilseeds.

It should also be noted here that the twin-screw extruder is a very good liquid/solid contactor [113]. It can therefore also be used for solvent extraction of residual oil after a first mechanical pressing stage, conducted or not in the same machine [107]. The twin-screw extruder is then used as a compact alternative to industrial extractors, which allow the solid to be moved on a belt against the current of the extracting solvent. For example, the residual sunflower oil can be extracted continuously in a twin-screw extruder by adding alcohols (e.g., 2-ethylhexanol and acidified 2-ethylhexanol) [114], fatty acid methyl esters [115] or even water [116,117].

Traditionally, the extraction of lipids is carried out by means of continuous extractors adapted to high processing capacities, and the solvents used are VOC, generally petroleum-based. These solvents are hazardous to the environment as well as to human health, and derivate from non-renewable resources. Solvent extraction is frequently conducted with hexane (a mixture of around 60% n-hexane and other hexane isomers) or with n-hexane. This step decreases the meal's residual oil content to less than 1% [104,118]. This gain in extraction yield is spoiled by a more complex process with a high operation cost (solvent transport and storage), an energy consuming solvent regeneration step, higher environmental impact (large volume of solvents, usually volatile), safety risks for operators (flammability, toxicity), and more importantly, lower oil quality compared to mechanically extracted oil [103]. Over 4 tons of rapeseeds or soybean seeds with a comparable amount of hexane are required for the extraction of only 1 ton of the corresponding oil. The solvent losses for an optimized recycling process can vary between 1 kg [10] and 3 L (ca. 2 kg) [105] per ton of rapeseed.

Hexane is a controversial non-polar solvent, despite its many advantages, viz., the selectivity for oil, a fairly low boiling point (ca. 66 °C), high stability, ease of separation and recycling [119]. It is, however, a non-renewable petroleum-based solvent, highly flammable, dangerous for human health (considered as a neurotoxin [10]) and for the environment (classified as an air pollutant according to the 1990 Clean Air Act [120], but also is a COV, hence contributing to greenhouse gas emissions and consequently to global warming). Yet, it is suitable for lipid extraction and available in high purity [56], and is still allowed for use in food applications and foodstuffs (conditioned to a residue lower to 1 mg/kg in oil as by the Directive 2009/32/EC [121]). Table 10 gathers the operating conditions and associated yields for the conventional and some unconventional processes used for the extraction of oil from oilseeds using hexane.

Table 10. Conventional hexane extraction of oil from various oilseeds.

Solvent	Sample Conditioning	Process Conditions	Assisted Extraction	Oilseed	Yield of Extraction (%)	Ref.
n-Hexane	Coarsely ground (moisture 8.69%)	8 h conventional Soxhlet extraction, L/S = 20 mL/g	Non	Rapeseed	58.2	[122]
n-Hexane [1]	Rapeseed cake	Pilot Soxhlet extraction, five washings of 30 min with L/S = 1.5 kg/kg, 55 °C	Non	Rapeseed	90.1	[123]
Hexane [2]	Rapeseed cake	Cellulose cartridge, 40 °C, L/S = 15	US pre-treatment 7.7 W/cm^2	Rapeseed	91.5	[124]
			Non		71.61	
Hexane 95%	Dried and flaked (moisture 3 wt.%)	Solvent extraction (stirred), L/S = 30, 50 °C, 2.5 h (including US)	Non	Rapeseed	≈70	[125]
			US treatment, 20 min, 12 kHz, 400 W		80	
n-Hexane	Ground (moisture 7.5–9%)	Soxhlet extraction 8 h	Non	Rapeseed	43.0 [b]	[126]
		Accelerated solvent extractor, 1500 psi, 120 °C, 90 min			36.4 [b]	
n-Hexane [1]	Coarsely ground (moisture 5.89%)	8 h conventional Soxhlet extraction, L/S = 10 mL/g	Non	Rapeseed	46.7 [a]	[119]
n-Hexane [3]	Ground	Stirred (4000 rpm) maceration (1 h), room temperature, L/S = 10 mL/g	Non	Rapeseed	43.2 [a]	[127]
n-Hexane [3]	Ground	Stirred (4000 rpm) maceration (1 h), 25 °C, L/S = 10 mL/g	Non	Rapeseed	38.4 [a]	[128]
		Soxhlet extraction 8 h, L/S = 8.5 mL/g			39.5 [a]	
Hexane	Ground	Conventional Soxhlet extraction of 8 h	Non	Soybean	18.8 [a]	[94]
n-Hexane [1]	Crushed seeds	Soxhlet extraction 8 h, L/S = 10 mL/g	Non	Soybean	19.5 [a]	[118]
				Sunflower	52.6 [a]	
n-Hexane [1]	Ground	Reflux extraction 2 h, 68 °C, L/S = 10 mL/g	Non	Sunflower	53.4 [b]	[129]
n-Hexane [1]	Ground (moisture ca. 6%)	Soxhlet extraction 6 h, 70 °C, L/S = 5 mL/g	Non	Flaxseed	27.5 [b]	[130]
n-Hexane	Ground (moisture 7.5–9%)	Soxhlet extraction 8 h	Non	Flaxseed	35.6 [b]	[126]
		Accelerated solvent extractor, 1500 psi, 120 °C, 90 min			28.4 [b]	

[1] Analytical grade. [2] Technical grade. [3] HPLC grade. [a] Oil yield (g/100 g DM (seed)). [b] Oil yield (g/100 g initial material).

Following the extraction, a first separation step, through centrifugation or filtration, is sometimes required to separate the solid phase, called the marc (i.e., meal/solvent mixture) from the liquid phase, known as the miscella (i.e., oil/solvent mixture) [10]. Fine particles have to be separated from the miscella to limit their interference on the heat transfer during the distillation. A prepressing followed by solvent extraction results in lower amounts of particles compared to a direct solvent extraction [73]. The miscella then passes in a stripper with the injection of water vapor or noble gas to separate the oil and recover the solvent [56]. In order to prevent the deterioration of the crude oil, brief contact with the steam (at ca. 120 °C) is required [11]. Other processes such as multistage flash distillation under partial vacuum are sometimes used. During this separation step, the solvent is evaporated by heating all the resulting miscella to the boiling point of the solvent, hence making this step an energy intensive part of the oil extraction process [10]. The recovered solvent is recycled and reused in the extraction process [11].

Steam may be introduced to the marc containing hexane in order to remove it through the formation of an heteroazeotrope with water. To finish the desolventization process, the meal is passed through a toaster to remove any hexane residue but also to deactivate certain enzymes [11,56]. In contrast, the toasting process (ca. 100–110 °C) might cause the degradation of thermolabile constituents (proteins, for example), which decreases the nutritional value of the resulting meal [103].

Crude oil then undergoes several treatment steps, such as degumming, alkali refining, bleaching, deodorization, winterization, hydrogenation, etc. [105], depending on the posterior application of the oil (industry, food or others). On the other hand, the oilseed meal also undergoes some processes, mainly for the extraction of valuable compounds, the removal of anti-nutritional compounds, and sometimes the concentration of protein in terms of protein concentrates or isolates.

Extraction of secondary metabolites is also a solvent assisted extraction. The extraction procedure is commonly based on not very benign solvents, such as chloroform, hexane, benzene and methanol, yet other greener solvents can be used, such as ethanol, ethyl acetate and trivially, water [131,132]. Solvent selection depends on the solvent and the metabolite molecule properties, such as polar character, boiling temperature, solubility, heat of vaporization, etc. It is subject to compromise, as a high affinity for extraction between solvent and metabolites usually makes the solvent recovery more difficult. According to Alara et al. [131], the extraction of polyphenols in general is best conducted with polar solvents, due to the structure and solubility of polyphenols in these solvents. However, there exists no single universal acceptable solvent for this kind of extraction. The conventional methods for the extraction of bioactive compounds from plants in general are Soxhlet extraction, maceration and hydro-distillation (water, direct steam or water-steam distillation) [131–134]. This extraction step is then followed by a desolventization step of the meal, and a separation and purification step of the extracted bioactive compound.

4. Alternative Solvents/Processes for Lipid Extraction

A solvent is considered a green solvent (GS) when it is less harmful and has less environmental impact than the conventional solvent used in a given process [135]. A green extraction is based on the use of a GS as well as the reduction in the extraction's energy consumption, while conserving a high-quality product [136]. Conventional solvents such as hexane or chloroform, used for vegetable oil extraction, are rarely benign. They are often volatile organic compounds, harmful to health and to the environment, and are petroleum-based, a non-sustainable resource. In contrast, green solvents display interesting advantages, as they are not toxic or only slightly toxic, safe to use and handle, effective and frequently derived from renewable resources. They generally fulfil some of the 12 principles of green chemistry established by Anastas et al. [137,138]. A solvent does not have to meet all of the 12 principles to be considered green. Ethanol, for example, can be bio-synthesized from sugar-rich resources, and is considered a green extraction solvent despite it being highly flammable and potentially explosive [136]. Similarly, CPME (cyclopentyl methyl ether) is a safe and benign solvent but is produced from fossil sources [73,139].

The large range of lipid hydrophobicity hinders the use of a single solvent for the extraction of all lipids. Non-polar solvents (e.g., hexane) can extract more neutral, covalently bonded lipids (e.g., triacyclglycerols (TAG)), while polar solvents (e.g., ethanol) tend to extract more polar, hydrogen bonded lipids (e.g., phospholipids (PL)) [73].

Carré [86] notes that butane, ethyl acetate (EA), ethanol, CO_2 and acetone are compatible solvents with lipid extraction. These five solvents, in addition to propane, may be used without specified conditions (in conformity with good manufacturing practice) during the processing of food ingredients, food components, foodstuffs or raw materials, as of the Directive 2009/32/EC (it is forbidden to use acetone in the refining process of olive-pomace oil) [121]. The main alternative solvents and processes for the conventional hexane oil extraction are presented in Table 11.

Table 11. Alternative solvent for extraction of oil from various oilseeds.

Solvent	Sample Conditioning	Process Conditions	Assisted Extraction	Oilseed	Yield of Extraction (%)	Ref.
Alcohols						
Ethanol 95.6 wt.%	Crushed seeds in solvent, no mechanical pressing	Four stage cross-current extraction by immersion in preheated solvent (L/S: 15 g/g per stage; 10 min per stage, 42 rpm stirring, 50 °C)	Non	Rapeseed	92.7	[140]
Ethanol 92.0 wt.%					86.5	
Isopropanol 87.8 wt.%					89.3	
Isopropanol 84.2 wt.%					87.1	
Isopropanol 99%	Dried and flaked (moisture 3 wt%)	Solvent extraction (stirred) L/S = 30, 50 °C, 2.5 h (including US)	Non	Rapeseed	≈63	[125]
Isopropanol 99%			US treatment, 20 min, 12 kHz, 400 W		79	
Ethanol 96%					51	
Isopropanol [1]	Coarsely ground (moisture 8.69%)	8 h conventional Soxhlet extraction, L/S = 20 mL/g	Non	Rapeseed	83.1	[122]
Ethanol [1]					22.8	
Butanol [1]					78.3	
Ethanol [2]	Coarsely ground (moisture 5.89%)	8 h conventional Soxhlet extraction, L/S = 10 mL/g	Non	Rapeseed	46.6 [a]	[119]
Isopropanol [2]					45.0 [a]	
Ethanol 99.8 wt.%	Dehulled, flaked and expanded to form soybean collets, grounded	Batch extractions, 60 °C, L/S = 3 (mass), 175 rpm stirring	Non	Soybean	90.3–93.4	[141]
Ethanol 99.8 wt.%		Batch extractions, 90 °C, L/S = 3 (mass), 175 rpm stirring			89.0–92.5	
Ethanol 94.09 wt.%		Batch extractions, 60 °C, L/S = 3 (mass), 175 rpm stirring			28.2–31.3	
Ethanol 94.09 wt.%		Batch extractions, 90 °C, L/S = 3 (mass), 175 rpm stirring			92.5–96.0	
Ethanol 88.08 wt.%		Batch extractions, 60 °C, L/S = 3 (mass), 175 rpm stirring			2.9–6.6	
Furan Derivatives						
2-MeTHF	Ground	Conventional Soxhlet extraction of 8 h	Non	Soybean	23.5 [a]	[94]
2-MeTHF 95.5%					23.7 [a]	
MeTHF [1]	Finely ground	8 h Soxhlet extraction (standard ISO 659)	Non	Rapeseed	46.0 [a]	[123]
	Rapeseed cake	Pilot Soxhlet extraction, five washings of 30 min with L/S = 1.5 kg/kg, 55 °C			95.6	
2-MeTHF [2]	Coarsely ground (moisture 5.89%)	8 h conventional Soxhlet extraction, L/S = 10 mL/g	Non	Rapeseed	47.2 [a]	[119]
Terpenes						
p-Cymene [1]	Coarsely ground (moisture 8.69%)	8 h conventional Soxhlet extraction, L/S = 20 mL/g	Non	Rapeseed	88.9	[122]
d-Limonene [1]					80.8	
α-Pinene [1]					65.5	
p-Cymene [2]	Coarsely ground (moisture 5.89%)	Soxhlet extraction 8 h, L/S = 10 mL/g	Non	Rapeseed	39.7 [a]	[119]
d-Limonene [2]					37.0 [a]	
α-Pinene [1]	Crushed seeds	Soxhlet extraction 8 h, L/S = 10 mL/g	Non	Soybean	21.1 [a]	[118]
				Sunflower	67.2 [a]	
Pinane (cis/trans: 7:3)	Ground	Stirred (4000 rpm) maceration (1 h), room temperature, L/S = 10 mL/g	Non	Rapeseed	42.5 [a]	[127]
p-Menthane	Ground	Stirred (4000 rpm) maceration (1 h), 25 °C, L/S = 10 mL/g	Non	Rapeseed	37.1 [a]	[128]
		Soxhlet extraction 8 h, L/S = 8.5 mL/g			40.5 [a]	
Esters						

Table 11. *Cont.*

Solvent	Sample Conditioning	Process Conditions	Assisted Extraction	Oilseed	Yield of Extraction (%)	Ref.
Ethyl acetate [2]	Coarsely ground (moisture 5.89%)	8 h conventional Soxhlet extraction, L/S = 10 mL/g	Non	Rapeseed	42.8 [a]	[119]
Ethyl acetate	Ground (moisture 7.5–9%)	Accelerated solvent extractor, 1500 psi, 120 °C, 90 min	Non	Rapeseed	40.4 [b]	[126]
				Flaxseed	33.3 [b]	
Other Green Solvents						
CPME	Coarsely ground (moisture 5.89%)	8 h conventional Soxhlet extraction, L/S = 10 mL/g	Non	Rapeseed	41.5 [a]	[119]
DMC[2]					42.8 [a]	
Subcritical Alkanes						
n-Butane (95%)	Ground	Subcritical pilot plant unit (1.5 l liquified n-butane at 0.2 MPa and 20 °C), L/S = 20 mL/g, 2 h	SubFE, 0.2 MPa, 20 °C	Sunflower	36.6 [b]	[129]
			SubFE, 0.37 MPa, 40 °C		36.9 [b]	
n-Butane (99.5%)	Ground (moisture ca. 6%)	Subcritical fluid system, L/S = 20 mL/g, 57 min	SubFE, 0.5 MPa, 54 °C	Flaxseed	28.8 [b]	[130]
Propane (99.5%)	Milled (moisture 2.8%)	Laboratory scale extractor, 85 min, 0.8 cm^3/min solvent flow	SubFE, 8 MPa, 60 °C	Rapeseed	62.5 [c], 23.1 [a]	[142]
			SubFE, 12 MPa, 60 °C		64.4 [c], 23.8 [a]	
			SubFE, 10 MPa, 45 °C		55.9 [c], 20.7 [a]	
Propane (99.5%)	Milled (moisture 2.3%)	Laboratory scale extractor, 40 min, 0.8 cm^3/min solvent flow	SubFE, 8 MPa, 60 °C	Sunflower	92.7 [c]	[143]
			SubFE, 12 MPa, 60 °C		100 [c]	
			SubFE, 10 MPa, 45 °C		90.2 [c]	
n-Propane (99.5%)	Ground (moisture 6.50%)	Laboratory scale extractor, 30 g sample, 1 cm^3/min solvent flow, 60 min	SubFE, 10 MPa, 45 °C	Flaxseed	28.2 [a]	[144]
			SubFE, 8 MPa, 60 °C		28.6 [a]	
			SubFE, 12 MPa, 60 °C		28.8 [a]	
Supercritical CO_2						
CO_2 (99.5%)	Milled (moisture 2.8%)	Laboratory scale extractor, 480 min, 3 cm^3/min solvent flow	SFE, 25 MPa, 40 °C	Rapeseed	52.7 [c], 19.5 [a]	[142]
			SFE, 25 MPa, 60 °C		49.2 [c], 18.2 [a]	
			SFE, 22.5 MPa, 50 °C		48.1 [c], 17.8 [a]	
CO_2 (99.5%)	Milled (moisture 2.3%)	Laboratory scale extractor, 600 min, 3 cm^3/min solvent flow	SFE, 25 MPa, 40 °C	Sunflower	100 [c]	[143]
			SFE, 25 MPa, 60 °C		87.8 [c]	
			SFE, 22 MPa, 50 °C		75.6 [c]	
CO_2 (99.9%)	Ground	SFE system, 3 h, 40 g/min solvent flow, 100 g sample	SFE, 30 MPa, 50 °C	Flaxseed	35.3 [b]	[57]

[1] Analytical grade. [2] Technical grade. [a] Oil yield (g/100 g DM (seed)). [b] Oil yield (g/100 g initial material). [c] % relative to the quantity extracted with hexane after 20 h Soxhlet extraction.

4.1. Alcohols

Ethanol is a promising alternative to hexane. In addition to being safe for humans, it can be produced from bio-resources without any toxic waste generation [141]. Stress is also laid on the fact that the extraction of polar lipids is more effective using ethanol, due to its polar nature and mutual affinity [86]. Similarly, more polar lipids (MAG, DAG, FFA) might be extracted when using isopropanol, while more triacylglycerols are extracted when using hexane [122].

Increasing water content in the extraction solvent and increasing temperature negatively impact the nitrogen solubility index, hence decrease the protein solubility in the resulting meal [141]. In addition, a larger amount of ethanol is required for oil extraction compared to hexane (liquid to solid ratio L/S of up to 30 as per Table 11), due to ethanol's limited capacity (temperature dependent) for dissolving lipids. However, this can be exploited to insolubilize the lipids and recycle the solvent simply by cooling the miscella.

This can be regarded as an advantage since the heat of vaporization of ethanol is much higher than that of hexane (880 vs. 330 kJ/kg) [86].

Citeau et al. [140] studied the influence of water content in ethanol and isopropanol in the extraction of rapeseed oil from crushed seeds. Results show that a higher water content decreases the oil extraction yield (lower solubility) but increases the non-lipid extraction yield and impacts the protein functionality, decreasing the protein solubility, which reflects its denaturation. Similar results were obtained earlier in 2014 by Megumi Sawada et al. [141], who conducted a study on water content in ethanol in the extraction of oil from ground soybean collects, adding to that the positive impact of increasing temperature on the enhancement of oil transfer. Beckel et al.(1948) [145] and Rao and Arnold (1956–1958) [146–148] had formerly demonstrated this impact of temperature and water content.

Due to the absence of standardized samples, sample conditioning and processes, it is hard to compare different experimental work of authors. According to the work published by Li et al. in 2014 [122], the extraction of oil from coarsely ground rapeseed was more promising using isopropanol (83.1%) and butanol (78.3%) than ethanol (22.8%) (analytical grade solvents). In 2017, Perrier et al. [125] also obtained a higher extraction yield for 99% isopropanol compared to 96% ethanol, even with the use of ultrasound (cf. Section 4.7 Ultrasound). Meanwhile, in another study conducted by Sicaire et al. in 2015 [119], extraction of rapeseed with ethanol presented a similar yield to that obtained with isopropanol (solvents of technical grade). Amounts of 87.8 and 84.2% isopropanol extracted less rapeseed oil compared to 95.6% ethanol, but similar to 92% ethanol, according to the data given by Citeau et al. in 2019 [140]. These results may vary depending on the processing conditions (extraction process, temperature, liquid to solid ratio, agitation, etc.), sampling conditions (moisture content, drying efficiency, sample's surface area (crushed, flaked or ground seeds)) and the oilseeds' composition.

4.2. 2-MeTHF

2-methyltetrahydrofuran (2-MeTHF) or 2-methyloxolane ($C_5H_{10}O$) is a promising alternative for hexane in the oil extraction process. It is a sustainable bio-based solvent produced from renewable resources, namely lignocellulosic biomass (cellulose, hemicellulose and lignin) such as sugarcane bagasse and corn cobs [10,73,149–152]. The two pathways for the production of 2-MeTHF (levulinic acid or furfural pathway) are detailed in the review published in 2020 by Rapinel et al. [10]. 2-MeTHF is a colourless solvent with a strong ether odour, making its detection easier in the case of leaks. It has an attractive environmental footprint, as it can be degraded by air and sunlight abiotically [150] and is nontoxic (mutagenicity and genotoxicity [152]) and non-ozone depleting [151]. However, it is not FDA-approved for food contact yet. Furthermore, this solvent displays very interesting characteristics: wide range of solvation properties [149], ease of recycle [151] and partial water miscibility resulting in a better diffusion in moist samples [153]. 2-MeTHF has a higher boiling point compared to hexane (80 °C vs. 69), which allows extraction at a higher temperature [10].

In the work published in 2015 by Sicaire et al. [123], 2-MeTHF was compared to hexane for the oil extraction from finely ground rapeseed, using conventional Soxhlet extraction. The yield of extraction using 2-MeTHF was almost equal to that using hexane (45.96 and 46.34 g/100 g of DM, respectively). Meanwhile, 2-MeTHF performed better than hexane (extraction yield of 95.6 and 90.1%, respectively) in a pilot Soxhlet extraction of oil from rapeseed cake. Another advantage of using this alternative solvent, according to the same paper, is faster extraction kinetics, where only three washings are needed compared to five using hexane, to reach a yield of ca. 96%. A slightly better performance for 2-MeTHF on a laboratory scale was published by the same author [119] later that year, with a yield of 47.19 g/100 g and 46.7 for hexane. Recently, Claux et al. [94] investigated the use of 2-MeTHF as an alternative for the extraction of soybean oil from ground soybean seeds. To avoid a distillation step for the purification of the solvent after oil separation, aqueous

2-MeTHF (at saturation water content of 4.5%w at 55 °C) obtained after condensation and decantation of the water-2-MeTHF mixture (forming a 10.6%w water azeotrope at 71 °C), was also studied. Having a higher polarity than hexane, 2-MeTHF and aqueous 2-MeTHF gave higher oil yields (23.5 and 23.7, respectively, compared to 18.8 (g/100 g DM) for hexane), due to the extraction of more polar lipids (phospholipids). Furthermore, the two solvents extracted more phenolic compounds (isoflavones) than hexane (1684, 2044 and only 14 mg genistein equivalents (GE)/kg fat respectively), which might be the reason for the higher oxidative stability and antioxidant activity observed in the oils extracted with 2-MeTHF and aqueous 2-MeTHF. However, the protein dispersibility index (PDI) and KOH (potassium hydroxide) protein solubility were lower for the meals extracted with 2-MeTHF and aqueous 2-MeTHF. During the oil refining processes, the phospholipids and phenolic compounds in the 2-MeTHF and aqueous 2-MeTHF extracted oils can be removed and purified. The author observed swelling in the seeds during the extraction process using aqueous 2-MeTHF, hence more optimization is needed for the use of this solvent in its water saturated form. Both authors reported no significant differences in the lipid composition and fatty acid profile of the oils extracted with 2-MeTHF compared to that of hexane. More studies on the extraction of added-value secondary metabolites, anti-nutriments and proteins using 2-Me-THF are needed.

The price of 2-MeTHF remains the main drawback for its use in industry. While hexane's price is around 1 EUR/kg or less, the price of a kilogram of 2-MeTHF remains as high as EUR 7–9 [10,94]. The second economical drawback is the higher energy consumption for the separation of the solvent from the miscella and desolventization of the marc, caused by the higher enthalpy of vaporization and boiling point of 2-MeTHF. Additionally, a supplementary separation step is required, as 2-MeTHF forms an azeotrope with water [94]. However, 2-MeTHF presents a higher yield than the conventional hexane extraction, and, with further recycling optimization and loss reduction, the estimated global cost of the process is increased by only 0.47 EUR/ton in the case of rapeseed. Moreover, this oil is expected to have a better quality than the conventional hexane extracted oil [10].

4.3. Terpenes

Terpenes are an enormous and vast family of natural products (over 30,000) based on diene isoprene (C_5H_8) as a building block, and are structurally diverse (acyclic, mono- and poly-cyclic). They occur in all organisms (particularly in vascular plants, fruits, vegetables, some animals and flowers), are oxidizable and are degradable by micro-organisms such as fungus (aspergillus) or bacteria (pseudomonas). Terpenes include some essential oils, natural rubber, plant resins and carotenoids [154–157]. These compounds have several positive impacts on human health (anti-microbial, anti-fungal, anti-viral and anti-inflammatory activities [156]). They can be extracted or biosynthesized from natural and renewable resources.

The use of terpenes as an extraction solvent (such as p-cymene, d-limonene (present in the citrus fruits, by-product of the industry [157]) and α-pinene (present in mint, pine, ginger, etc. [118])) emerged in recent years and is gaining popularity as a class of green solvents [73]. D-limonene was first tested as a promising alternative solvent in the Soxhlet oil extraction from olives in 2008 by Virot et al. [158,159]. It is regarded as a biodegradable solvent with low environmental impact as well as low toxicity [149]. According to Bertouche et al., 2012 [118], α-pinene is another promising solvent, showing higher extraction yield than hexane (21.1 vs. 19.1 and 67.2 vs. 52.6 g/100 g DM from soybean and sunflower, respectively). In a study published in 2014 by Li et al. [122], the use of several terpenes (p-cymene, d-limonene and α-pinene) was investigated. The three solvents gave higher oil extraction yield than that of n-hexane (88.9, 80.8, 65.5%, respectively, compared to 58.2% for n-hexane, cf. Table 10). Two other studies from the same teams, conducted by Sicaire et al. [119,123], showed theoretically (based on HSP (Hansen Solubility Parameters) and COSMO-RS (Conductor-like Screening Model for Realistic Solvents) simulations) the potential of p-cymene and d-limonene for dissolving TAGs as well as sterols and to-

copherols, being equivalent or better than n-hexane. Experimental work from the first paper [119] validated the simulations, as oil yields of p-cymene and d-limonene were only slightly lower than that of hexane (39.71 and 36.94 compared to 46.71 g/100 g DM for n-hexane, cf. Table 10). Similar theoretical and experimental work for the extraction of rapeseed oil was conducted by Yara-Varón et al. in 2016 [127] on pinane (cis/trans: 7:3) (stable saturated derivative of α-pinene and β-pinene) and by Madji et al. in 2019 [128] on p-menthane (stable saturated derivative of d-limonene). Both solvents showed promising results, with a comparable oil yield to n-hexane (42.5 vs. 43.2 g/100 g DM for pinane and n-hexane, respectively [127], and 37.1 vs. 38.4 g/100 g DM for p-menthane and n-hexane, respectively [128]).

An important factor to take into consideration when using terpenes as extraction solvents is the separation of the solvent–oil mixture and the recycling of the solvent. The relatively high boiling points of terpenes compared to hexane (cf. Table 12) makes the usual separation of solvent by distillation hard and energy consuming. However, this separation can be conducted by heteroazeotropic separation, by adding water (50% (*v*/*v*) [119]). Most of the above-mentioned authors [118,119,122,158,159] used Clevenger distillation (hydrodistillation) to obtain two distinct heterogenous water–oil and water–terpene mixtures that are furthermore separated by a simple phase separation (liquid–liquid separation). Using this technique, a high recycling rate of terpene can be achieved (ca. 90% (98% purity) of α-pinene [118]).

Table 12. Boiling point of terpenes and hexane.

Solvent	Boiling Point (°C)	Reference
n-hexane	68.5–69	[118,122,123,126,127,160]
d-limonene	176–177	[73,122,128,160]
α-pinene	155–158	[73,118,122,160]
p-cymene	174–176	[73,122,160]
Pinane	157	[127]
p-menthane	170	[128]

D-limonene and α-pinene are indeed promising solvents for oil extraction, but the fact that they are unsaturated terpenes raises questions about their stability and degradation during the extraction and/or recycling. Pinane and p-menthane are saturated and are supposedly more stable. More work on these solvents and on terpenes in general is needed, as well as more investigation on their toxicity.

4.4. Other Organic Solvents

Ethyl acetate (EA), CPME and DMC (dimethyl carbonate) were also tested as hexane alternatives for the extraction of lipids from oil-bearing materials. Ethyl acetate (CH_3-COO–C_2H_5) is a transparent ester derived from acetic acid (CH_3-COOH) and ethanol (C_2H_5OH) and is characterized by a low toxicity level and a pleasant fragrance [161]. Ethyl acetate is less hazardous than hexane and is also 33% cheaper, with a similar boiling point and latent heat of vaporization, but EA is characterized by a higher viscosity and dielectric point compared to hexane [126]. Dimethyl carbonate is another green, biodegradable and benign solvent that can be a potential replacement for ethyl acetate. It is partially miscible with water (193 g/L), creating an azeotrope, and totally miscible with organic solvents such as alcohols [162]. DMC is a flammable colourless liquid with a methanol-like smell. This solvent can be produced from biomass, mainly though methanol carbonylation with oxygen. No special precautions are needed for handling DMC as it does not present any mutagenic or irritating effects, and is safe for metals as it does not cause corrosion [153,162]. CPME (C_5H_9-O-CH_3), on the other hand, is considered as a green solvent despite being petroleum-based [73,139], yet this multipurpose solvent can be produced from biomass, either through the methylation of cyclopentanol derived from furfural, or through the transformation of cyclopentene (with methanol addition) or cyclopentanone, both derived from adipic

acid [149,163]. CPME presents attractive characteristics such as high hydrophobicity (low water solubility of 1.1 g CPME/100 g [163], forming a positive azeotrope [164]), thus ease of drying, low enthalpy of vaporization, stability in strong acidic or basic atmosphere conditions, low toxicity, high flash point (compared to hexane) and narrow explosion range, but has a higher boiling temperature compared to hexane (106 °C) [149,152,163–165].

Lohani et al., 2015 [126], used an accelerated solvent extractor for the extraction of rapeseed and flaxseed oils from ground rapeseeds and ground flaxseeds, using ethyl acetate and hexane for comparison. In the extraction conditions (pressure of 1500 psi, temperature of 120 °C), ethyl acetate is in a subcritical state, having lower viscosity and smaller dielectric constant, thus decreasing its polarity. Using this process, the oil yield of EA was higher than that of hexane, reaching 40.38% for rapeseed and 33.33% for flaxseed, compared with 36.44 and 28.38% with hexane, respectively. However, these yields obtained in only 90 min were lower than those obtained with a conventional 8 h Soxhlet extraction with hexane (42.96% for rapeseed and 35.62% for flaxseed as per Table 10).

In another study also published in 2015 by Sicaire et al. [119], the use of EA, CPME and DMC as hexane alternatives was investigated for the extraction of rapeseed oil from coarsely ground rapeseeds using the conventional Soxhlet extraction. All three solvents had fairly similar oil yield (42.83%, 42.77% and 41.53% for EA, DMC and CPME, respectively), yet these yields were about 10% lower than that of hexane (46.71%).

4.5. Supercritical and Subcritical Fluids

Mechanical extraction and conventional solvent extraction present several downsides, viz., these methods are time consuming, and the degradation of some bioactive compounds during solvent separation as well as the solvent residues present real issues [144].

Supercritical fluid extraction (SFE) is a flexible and widely applied, environmentally friendly technique for the extraction of natural products. It allows fast and easy elimination of the solvent as well as high selectivity for lipids. The operation cost of SFE is low and the process is easy to scale up, but requires a high investment [73,166]. Supercritical fluids are characterized by a diffusivity similar to gases and a density similar to liquids [57,132]. CO_2 displays really attractive characteristics—cheap and widely available, benign, easy to separate from the miscella, possesses mild supercritical conditions (T_c = 31 °C, P_c = 7.38 MPa)—which ease process operation and solvent recovery, and most importantly it is non-flammable [73,143]. In contrast to CO_2, the high critical temperatures of n-butane (T_c = 152.8 °C, P_c = 3.6 MPa) and n-propane (T_c = 95.7 °C, P_c = 4.4 MPa) hamper their use in supercritical fluid extraction. Subcritical fluid extraction (SubFE) is another lipid extraction technique displaying attractive advantages compared to SFE, mainly due to the reduced operation temperature and pressure (hence less degradation of bioactive compounds and cake quality [167], as well as lower investment and operating cost) and the use of high diffusivity, density and low viscosity solvents, such as n-butane or n-propane [144,168]. Nonetheless, n-propane is less profitable due to higher operating pressure compared to n-butane, while n-butane is safer than n-propane. Moreover, no toxic solvent residue is present in the final product extracted with SubFE, similarly to those extracted with supercritical CO_2 [130], and separation of the miscella for the recovery of the subcritical solvents, if needed, can be performed by membrane filtration [167].

According to Nimet et al., 2011 [143], CO_2 SFE and propane SubFE of sunflower seed oil reached oil yields similar to that of a 20 h hexane Soxhlet extraction (41.0%). Nevertheless, the working pressure for CO_2 SFE (25 MPa, 40 °C) is almost double that of propane SubFE (12 MPa, 60 °C), and the extraction time is tremendously longer (600 min vs. 40 min). Furthermore, the protein content of the sunflower meal extracted with supercritical CO2 is comparable to that extracted with subcritical propane (ca. 46%). A similar comparative study on the extraction of rapeseed oil was published earlier by Pederssetti et al., 2010 [142], from the same team. The maximum oil yields of propane SubFE (23.8%) were higher than that of CO_2 SFE (19.5%), but both of these results were almost half of the yield obtained by the 20 h hexane Soxhlet extraction (37%). Wang et al.,

2020 [130], applied n-butane subcritical fluid extraction on flaxseed for the first time, and, at optimized conditions, reached an oil yield of 28.75 g/100 g of ground seeds compared to 27.53% with Soxhlet extraction using hexane. On the other hand, Zanqui et al., 2015 [144], reached a maximum flaxseed oil yield of 28.78 g/100 g DM with subcritical n-propane compared to only 24.58% using Soxhlet extraction with a petroleum ether/ethyl ether mixture. In another study by Rapinel et al. in 2017 [129], SubFE of sunflower oil with n-butane at low pressures (0.2 to 0.4 MPa) was less effective when compared to hexane extraction (36.9 vs. 53.4 g/100 g of ground seeds). In general, oils extracted by SubFE show higher quality (lower acid value meaning less oil oxidation and decomposition during the extraction [57,130]), higher content of phytosterols and carotenoids (antioxidants), better shelf-life (lower iodine value [130]) and better oxidation stability [130,143,144]. All above-mentioned authors observed no difference in the fatty acid profiles of the oil extracted by SFE or SubFE compared to conventional methods used. Meanwhile Pradhan et al., 2010 [57], reported higher unsaturated fatty acid content in the flaxseed oil extracted with supercritical CO_2 compared to that extracted with hexane.

At a given operating pressure for SubFE, increasing temperature positively affects the extraction yield [130,143,144] to a certain limit (e.g., 55 °C at 0.5 Mpa for n-butane [130]), where oil solubility decreased as the solvent's gasification rate increased due to the excessive temperature. In contrast, the increasing temperature had a negative effect on the extraction yield when using CO_2 SFE [142,143].

4.6. Ionic Liquids

Ionic liquids (IL) are charged salts generally composed of an organic cation with an inorganic or organic anion [169]. Due to their low-charge density, IL are characterized by a melting point lower than their salts and below 100 °C [170]. The discovery of the first ionic liquid, ethylammonium nitrate, occurred in 1914 by the Latvian chemist Paul Walden as a substitute for nitroglycerin in explosives [170]. However, it took almost 100 years for this extremely wide family of solvents to gain popularity (as of 2007) in the extraction sector [169]. IL's properties and behaviour can vary widely depending on the starting salts. In general, these solvents are characterized by a low vapor pressure, high solvation ability, improved selectivity, low flammability and high stability, due to their ionic trait [73,169,170]. Switchable solvents (SS) are a subfamily of IL, capable of switching from an ionic liquid under an atmosphere of CO_2 to a non-ionic liquid under an atmosphere of N_2. Each form of the solvent present unique physical and physicochemical properties (polarity, conductivity, solubility) [73].

In the work published in 2008 by Phan et al. [9], new methodologies for soy oil extraction from flaked seeds using a switchable-polarity solvent (SPS) and switchable-hydrophilicity solvent (SHS) were investigated. Lipids are miscible with the SPS in its low polarity form, thus inducing the extraction of oil, then decantation of the solvent from the oil is induced by the immiscibility of the oil in the solvent when switched to its high polarity form. Despite good separation, the amidine/alcohol mixture was discarded due to side reactions (transesterification) as well as the possible interference of the water from the soy with the switching process. Secondary amine SPS was also rejected for having slow separation kinetics as well as health hazards. Likewise, an SHS is capable of extracting lipids in its hydrophobic form, then becoming separated from the oil in its hydrophilic form with water and finally separated from water by switching again to its hydrophobic form. The amidine/excess water combination shows great extraction and separation properties, but it is not sufficiently hydrophilic, inducing difficult solvent regeneration [9].

4.7. Ultrasound

In general, sound waves are considered non-hazardous, safe and environmentally friendly. They are also perceived as a benign technology by the public, which makes its use and implementation in the foodstuff and food industry less controversial than other technologies such as microwaves (MW) or pulsed electric field (PEF). Physically speaking,

ultrasound (US) radiations are high-frequency pressure waves that transfer and dissipate energy into the system. Cavitation takes place when pressure waves are strong enough to create microbubbles in incompressible and inelastic mediums. Under the influence of ultrasounds, these bubbles expand and collapse, generating very localized high pressures and temperatures [171]. Reduced processing time as well as physical and chemical hazards, increased selectivity and yield, and enhanced quality and productivity are some of the advantages frequently offered by ultrasounds [172]. This clean technology is used in food processes, sequentially as a US pre-treatment prior to the extraction, or simultaneously to assist the extraction (UAE, ultrasound assister extraction). Ultrasounds have been successfully used for oil extraction, as they can increase the mass and heat transfer. The technology has several advantages compared to the conventional extraction, markedly cutting down the working time, processing cost, energy use and solvent quantities, with high accuracy and reproducibility [103,172,173]. Unlike microwave assisted extraction (MAE), the moisture content of the matrix or solvent used does not restrict the use of UAE [172]; nevertheless, some of the solvent's physical properties such as the viscosity, the vapor pressure or the surface tension can affect the cavitation formation and propagation, hence affecting the UAE's efficiency.

The use of US assisted hexane Soxhlet extraction reduced the duration of the process, for the same efficiency, by at least 50% and up to 87.5% according to Luque-Garcıa and Luque de Castro [174]. In contrast, Sicaire et al. [124] observed a 20% enhancement in the oil extraction yield from rapeseed cake compared to a conventional extraction on the one hand, and on the other hand, the application of ultrasounds on a multistage extraction process permitted reducing the number of stages to two instead of three, thus reducing the quantity of solvent used by one-third for the same extraction yield. Similarly, Perrier et al. [125] applied ultrasound in the first part of the extraction process (20 min out of 2.5 h of extraction), and obtained an extraction yield enhancement of about 10%, noting that the majority of the oil (ca. 65%) is extracted during the US treatment phase. All three above-mentioned authors ([124,125,174]) report no significant difference in the oil composition or the fatty acid profiles. However, Sicaire et al. [124] suggest that the extraction in the absence of oxygen decreased the peroxide value and thus limited the oil degradation during the extraction. In addition, UAE consumes only a fraction of the energy used in Soxhlet extraction (ca. 3% [173]) and emits only a fraction of the CO_2 emission (ca. 3% [173]). Hence, compared to conventional extraction, US can reduce the eco-footprint of the extraction (up to 30% [124]). According to Zdanowska et al. [175], the US pre-treatment prior to mechanical pressing increased the oil content of the seed (ca. 17%) and slightly reduced the protein content (ca. 3%). No significant yield increase in the mechanical oil extraction was noted; however, lower pressing temperature and higher energy efficiency (up to 25%) were observed.

5. Alternative Solvents/Processes for Secondary Metabolite Extraction

The extraction of plants' secondary metabolites is of a great interest. This extra process can take place either for the extraction and elimination of anti-nutriments, or for the valorisation of added-value molecules. Table 13 presents some of the solvents and processes used for the extraction of various secondary metabolites found in oilseeds.

Table 13. Solvent extraction of secondary metabolites from various oilseeds.

Solvent	Sample Conditioning	Process Conditions	Assisted Extraction	Oilseed	Molecule	Yield of Extraction (%)	Ref.
Alcohols							
Ethanol 95.6 wt.%	Crushed seeds in solvent, no mechanical pressing	Four stage cross-current extraction by immersion in preheated solvent (L/S: 15 g/g per stage; 10 min per stage, 42 rpm stirring, 50 °C)	Non	Rapeseed	GSL	44.1	[140]
Ethanol 92.0 wt.%						58.8	
Isopropanol 87.8 wt.%						58.8	
Isopropanol 84.2 wt.%						79.4	
Ethanol 45%	Pressed cake (moisture 7.9%)	L/S = 10 mL/g, 45 °C, 15 min	Non	Rapeseed	Total phenolic compounds	93.7	[89]
			US treatment, 15 min, 20 kHz, 750 W, 85 µm, 73 W·cm^{-2}			89.4	
		L/S = 10 mL/g, 65 °C, 15 min	Non			86.6	
			US treatment, 15 min, 20 kHz, 750 W, 85 µm, 73 W·cm^{-2}			91.5	
Ethanol 35%		L/S = 20 mL/g, 65 °C, 3 min	Non			96.3	
Methanol 60% *v*/*v*	Finely ground meal, dehulled, defatted by hexane Soxhlet extraction	3 extractions with: L/S = 10 mL/g, T_{room}, 30 min of gentle stirring, pH 6, 5000 g centrifugation for 10 min	Non	Rapeseed	Polyphenols	94.5	[176]
					GSL [1]	75.5	
					Sugars [2]	94.7	
Ethanol 60% *v*/*v*					Polyphenols	>99	
					GSL [1]	97.3	
					Sugars [2]	98.0	
Isopropanol 60% *v*/*v*					Polyphenols	95.9	
					GSL [1]	>99	
					Sugars [2]	97.1	
Methanol 50% *v*/*v*	Finely ground meal, dehulled, defatted by hexane Soxhlet extraction	3 extractions with: L/S = 10 mL/g, T_{room}, 30 min of gentle stirring, pH 6, 5000 g centrifugation for 10 min	Non	Sunflower	Polyphenols	94.4	[176]
					Sugars [3]	99.1	
Ethanol 50% *v*/*v*					Polyphenols	93.3	
					Sugars [3]	99.1	
Propanol 50% *v*/*v*					Polyphenols	97.8	
					Sugars [3]	99.6	
Isopropanol 50% *v*/*v*					Polyphenols	96.7	
					Sugars [3]	99.6	
Isobutanol 50% *v*/*v*					Polyphenols	87.8	
					Sugars [3]	99.1	
Methanol 70%	Ground, sieved and defatted seeds	3 extractions with: L/S = 9 mL/g, 1 min ultrasonication, 5000 g centrifugation for 10 min under refrigerated conditions	Non	Rapeseed	Sinapine	10.3 [a]	[87]
					Sinapic acid	1.2 [a]	
					SG [4]	0.1 [a]	
					TP [5]	12.0 [a]	
Ethanol 70%					Sinapine	8.0 [a]	
					Sinapic acid	0.9 [a]	
					SG [4]	0.1 [a]	
					TP [5]	8.8 [a]	
Isopropanol 70%					Sinapine	7.1 [a]	
					Sinapic acid	0.9 [a]	
					SG [4]	0.1 [a]	
					TP [5]	7.7 [a]	

Table 13. *Cont.*

Solvent	Sample Conditioning	Process Conditions	Assisted Extraction	Oilseed	Molecule	Yield of Extraction (%)	Ref.
DES							
ChCl: Gly[6] (1:1)	Defatted RSM	40 °C, 2 h, 1000 rpm (stirring), L/S = 10 mL/g	Non	Rapeseed	Polyphenols	67.5	[39]
ChCl: Gly (1:1)		60 °C, 2 h, 1000 rpm (stirring), L/S = 10 mL/g				85.0	
ChCl: Gly (1:1)		Scale up (250 g RSM), L/S = 10 mL/g, 60 °C, 200 rpm (stirring)				91.5	
ChCl:EG[7] (1:1)		40 °C, 2 h, 1000 rpm (stirring), L/S = 10 mL/g				72.9	
ChCl: EG (1:1)		60 °C, 2 h, 1000 rpm (stirring), L/S = 10 mL/g				85.9	

[1] Isothiocyanates (I.T.C.) + 5-Vinyloxazolidinethione (V.T.O.). [2] Et-OH soluble sugars. [3] Total soluble sugars. [4] Sinapoyl glucose. [5] Total phenolics. [6] Choline chloride-glycerol. [7] Choline chloride-ethylene glycol. [a] Content of phenolic compounds (mg/g).

5.1. Alcohols

The use of ethanol, isopropanol and alcohol-based solvents helps detoxify the oilseed meal (obtained after solvent assisted lipid extraction from the cake) and concentrate the protein: as polar solvents, alcohols are able to simultaneously solubilize some non-lipid components (such as glucosinolates and phenolic compounds) as well as oil, which can affect the miscibility and selectivity of oil [140]. The extraction capacity of alcohols depends on the size of the carbon chain as well as the alcohol purity.

In a paper published in 1983, Berot and Briffaud [176] studied the efficiency of methanol, ethanol and isopropanol (60% v/v alcohol content) for the extraction of secondary metabolites from rapeseed flour, and that of methanol, ethanol, propanol, isopropanol and isobutanol (50% v/v alcohol content) for the extraction of secondary metabolites from sunflower flour. In the case of rapeseed, 60% methanol was less efficient than 60% ethanol and 60% isopropanol for the extraction of GSL (75 vs. over 99%), while all three solvents extracted the majority of polyphenols and ethanol-soluble sugars (95 to 98%). However, none of these solvents extracted the phytic acid present in rapeseed flour. An increase of about 10–13% in protein concentration in the final meal was observed, depending on the capacity of the tested alcohols to extract the residual lipids left in the flour (4.85% DM). In the case of sunflower, methanol, ethanol, propanol, isopropanol and isobutanol (50% v/v) respectively removed 94.4, 93.3, 97.7, 96.6 and 87.7% of polyphenols and increased protein concentration (% of DM) from 59.2 to 69.5, 69.5, 67.5, 71 and 68.3. The amounts of soluble sugars in the final products were significantly low (ca. 0.1% of DM), with over 99% of the initial amount in the flour being removed with all solvents. Meanwhile, with increasing number of carbons in the alcohol, total lipid content in the final meal decreased.

According to Khattab et al., 2009 [87], 70% methanol is more efficient than 70% ethanol and 70% isopropanol for the extraction of phenolic compounds from rapeseed meal. The three solvents were tested for the extraction of total phenolic content (majorly sinapine, sinapic acid and sinapoyl glucose) from defatted canola fractions. In comparison with ethanol and isopropanol, methanol's extraction yield of total phenolic content (estimated as sinapic acid equivalent) was 36.5% and 54.6% higher and that of sinapine was 28.3% and 45.6% higher, respectively.

Citeau et al., 2019 [140], studied the influence of water content in ethanol and isopropanol in the extraction of rapeseed constituents. Results show that a higher water content increases the GSL extraction yield but decreases the yield of the simultaneous extracted oil. This extraction increased the protein concentration in the meal from 37.6 to about 42–43 g/100 g of DDM (defatted dry matter), but impacted the protein functionality, decreasing the protein solubility, which reflects its denaturation. In another work conducted in 2019 by Zardo et al. [89], the use of ultrasound in extraction longer than 3 min had no

significant difference on the extraction yield of phenolic compounds from rapeseed cake, while increasing ethanol purity had a negative impact on the yield. A similar tendency was observed in the work of Das Purkayastha et al., 2013 [88], for the extraction of phenolic compounds with methanol (70%, 80% and 90% purity); meanwhile the extraction with pure methanol gave higher yield than with aqueous methanol. Finally, increasing water content in methanol had a very negative effect on the extraction of total tannins, according to Das Purkayastha et al., 2013 [88].

5.2. Deep Eutectic Solvents

Eutectic is a term introduced by F. Guthrie in 1884, describing "bodies made up of two or more constituents, which constituents are in such proportion to one another as to give to the resultant compound body a minimum temperature of liquefaction" [177] (p. 462). The decrease in the melting point offers an enhanced solubility compared to the pure constituents [178].

The term deep eutectic solvents (DES) was first introduced by Abbott et al. in 2003, describing, at defined stochiometric proportions, mixtures comprising a (HBA) hydrogen bond acceptor (e.g., quaternary ammonia salt, menthol) and a (HBD) hydrogen bond donor (e.g., amines, amides, sugars, alcohols), forming a hydrogen bond complex and causing the freezing point of the system to be much lower than those of its individual components [39,106,178–181]. It was later revised to include systems comprising a Brønsted or a Lewis acid and base [73,181,182]. Not all eutectic mixtures are deep eutectic solvents, as the notion "deep" characterizes the mixture with a eutectic point temperature "far below" that of an ideal liquid mixture [178,181]. The DES is generally named as [HBA][HBD] or (HBA:HBD) (e.g., [ChCl][Gly] or (ChCl:Gly) for Choline chloride-Glycerol) [180].

DES emerged as a new class of potentially sustainable and green low-cost solvents. The rising interest of DES is also engendered by their extensive structural designability (due to the vast range of accessible HBDs and HBAs), their ease of preparation and their inertness [106,169,178,180]. DES are also reported to be green, environmentally friendly, non-toxic and highly biodegradable. Nevertheless, all these advantages of DES are highly dependent on the pure constituents of the mixture [106,169,178,181]. Common DES are a binary mixture of an HBA and an HBD, but ternary mixture DES do exist [183]. Some ionic compounds, such as Choline chloride [Ch+][Cl−], can be used as HBA, and DES do in fact share many characteristics with ionic liquids (IL) (nonflammability, high thermal stability, conductivity, negligible vapour pressures); however, the concept of DES is different than that of IL (pure liquid compound composed entirely of ionic species), hence DES should not be considered belonging to the IL [73,178,181]. DES based on natural pure constituents are sometimes called NADES (natural deep eutectic solvents), yet the classification and distinction between DES and NADES can be difficult, as some components (e.g., ethylene glycol, acetic acid) can be extracted from renewable resources or prepared from non-renewable ones [184].

Wongsirichot et al. [39] investigated the extraction of sinapic acid using deep eutectic solvents, precisely choline chloride-glycerol (ChCl:Gly) and choline chloride-ethylene glycol (ChCl:EG) from defatted rapeseed meal. The extraction yields were approximately 85% at 60 °C for ChCl:Gly (1:1 molar ratio) and ChCl:EG (1:1 molar ratio), compared to 67.5% and 72.9%, respectively, at 40 °C. When scaling up the process of the extraction (from 10 mL to 2.5 l), the mass transfer was improved due to the agitation, resulting in a higher extraction yield of 91.5% at 60 °C.

6. Conclusions

Currently, the use of hexane in foodstuff processing, especially bio-refinery of oilseeds, is allowed under certain limitations that are expected to strengthen due to hexane's toxicity, favouring the development of greener alternative solvents. The oilseed bio-refinery literature results' comparison is hampered by the absence of standardized samples, sample conditioning and processes. Indeed, oilseed composition varies considerably, depending on

cultivars and environmental conditions. Sample conditioning processes, such as dehulling, cooking, drying, crushing, grinding, flaking or milling, also create different shapes and sizes of samples, thus changing the surface area and interfering with the diffusion of solvent into the sample as well as out of it. Regarding the extraction, most results are compared to the conventional hexane Soxhlet extraction. This method is well-optimized, which creates an extra bias when judging the efficiency of alternative solvents of which processes are not fully optimized. In addition, the extraction yield values or the initial oil quantity in the sample are often missing in the literature. Among alternative solvents for hexane substitution, alcohols suitably perform oil extraction and are also capable of extracting secondary metabolites simultaneously, which might increase the oil stability. However, the water content of alcohols might affect the protein properties and functionalities in the oilseed meal. 2-MeTHF, CPME, DMC and EA have a comparable performance to hexane but only EA is FDA-approved for food contact. Terpenes provide a good extraction yield but a much higher boiling temperature, which makes the solvent regeneration step costly. Cost issues also arise regarding supercritical and subcritical fluid extraction. In perspective for exploring new alternatives, physicochemical properties of the best solvents should be gathered for further development of Computer Aided Molecular Design (CAMD) methodology based on reverse engineering in order to design potential solvent candidates for n-hexane substitution. Furthermore, regardless of the solvent chosen, optimization of the process to reach maximum extraction yield should be carried further than it is currently.

Author Contributions: Writing—original draft preparation, M.N.; project administration, funding acquisition and supervision, S.T.-R.; writing—review and editing, I.R.-D., V.G., P.E. and A.C.-S. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the 3BCAR Carnot Institute.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

2-MeTHF	2-MethylTetraHydroFuran
ALA	α-Linolenic Acid
ADF	Acid Detergent Fibre
CMR	Carcinogenic, Mutagenic and Reprotoxic
COSMO-RS	Conductor-like Screening Model for Realistic Solvents
CPME	Cyclopentyl Methyl Ether
DAG	Diacylglycerols (Diglycerides)
DDM	Defatted Dry Matter
DES	Deep Eutectic Solvents
DM	Dry Matter
DMC	Dimethyl Carbonate
EA	Ethyl Acetate
FAME	Fatty Acid Methyl Ester
FFA	Free Fatty Acid
GSL	Glucosinolates
GS	Green Solvents
HBA	Hydrogen Bond Acceptor
HBD	Hydrogen Bond Donor
HCN	Hydrogen Cyanide
HSP	Hansen Solubility Parameters
IL	Ionic Liquids
LDL	Low Density Lipoprotein
MAG	Monoacylglycerols (Mono-glycerides)

NADES	Natural Deep Eutectic Solvents
NDF	Neutral Detergent Fibre
P_c	Critical Pressure
PC	Phenolic Compounds
PL	Phospholipids
SA	Sinapic Acid
SFE	Supercritical Fluid Extraction
SG	Sinapoyl Glucose
SHS	Switchable-Hydrophilicity Solvents
SP	Sinapine
SPS	Switchable-Polarity Solvents
SS	Switchable Solvents
SubFE	Subcritical Fluid Extraction
TAG	Triacylglycerols (Triglycerides)
T_c	Critical Temperature
TP	Total Phenolics
UAE	Ultrasound Assisted Extraction
US	Ultrasound
VOC	Volatile Organic Compounds

References

1. Boye, J.I.; Arcand, Y. Current Trends in Green Technologies in Food Production and Processing. In *Sustainable Food and Beverage Industries*; Apple Academic Press: Cambridge, MA, USA, 2016; ISBN 978-0-429-18378-2.
2. Özilgen, S.; Özilgen, M. General Template for the FMEA Applications in Primary Food Processing. In *Measurement, Modeling and Automation in Advanced Food Processing*; Hitzmann, B., Ed.; Advances in Biochemical Engineering/Biotechnology; Springer International Publishing: Cham, Switzerland, 2017; pp. 29–69. ISBN 978-3-319-60111-3.
3. U.S. Congress, Office of Technology Assessment. Technologies Supporting Agricultural, Aquacultural, and Fisheries Development (Chapter 8). In *Integrated Renewable Resource Management for U.S. Insular Areas*; OTA-F-325; Government Printing Office: Washington, DC, USA, 1987; pp. 273–315.
4. Ancuța, P.; Sonia, A. Oil Press-Cakes and Meals Valorization through Circular Economy Approaches: A Review. *Appl. Sci.* **2020**, *10*, 7432. [CrossRef]
5. Lomascolo, A.; Uzan-Boukhris, E.; Sigoillot, J.-C.; Fine, F. Rapeseed and Sunflower Meal: A Review on Biotechnology Status and Challenges. *Appl. Microbiol. Biotechnol.* **2012**, *95*, 1105–1114. [CrossRef] [PubMed]
6. Baker, P.W.; Charlton, A. A Comparison in Protein Extraction from Four Major Crop Residues in Europe Using Chemical and Enzymatic Processes-a Review. *Innov. Food Sci. Emerg. Technol.* **2020**, *59*, 102239. [CrossRef]
7. Preece, K.E.; Hooshyar, N.; Zuidam, N.J. Whole Soybean Protein Extraction Processes: A Review. *Innov. Food Sci. Emerg. Technol.* **2017**, *43*, 163–172. [CrossRef]
8. Kotecka-Majchrzak, K.; Sumara, A.; Fornal, E.; Montowska, M. Oilseed Proteins–Properties and Application as a Food Ingredient. *Trends Food Sci. Technol.* **2020**, *106*, 160–170. [CrossRef]
9. Phan, L.; Brown, H.; White, J.; Hodgson, A.; Jessop, P.G. Soybean Oil Extraction and Separation Using Switchable or Expanded Solvents. *Green Chem.* **2009**, *11*, 53–59. [CrossRef]
10. Rapinel, V.; Claux, O.; Abert-Vian, M.; McAlinden, C.; Bartier, M.; Patouillard, N.; Jacques, L.; Chemat, F. 2-Methyloxolane (2-MeOx) as Sustainable Lipophilic Solvent to Substitute Hexane for Green Extraction of Natural Products. Properties, Applications, and Perspectives. *Molecules* **2020**, *25*, 3417. [CrossRef]
11. Cheng, M.-H.; Dien, B.S.; Singh, V. Economics of Plant Oil Recovery: A Review. *Biocatal. Agric. Biotechnol.* **2019**, *18*, 101056. [CrossRef]
12. Carré, P.; Pouzet, A. Rapeseed Market, Worldwide and in Europe. *OCL* **2014**, *21*, D102. [CrossRef]
13. Vinnichek, L.; Pogorelova, E.; Dergunov, A. Oilseed Market: Global Trends. *IOP Conf. Ser. Earth Environ. Sci.* **2019**, *274*, 012030. [CrossRef]
14. The Food and Agriculture Organization of the United Nations. FAOSTAT. Available online: https://www.fao.org/faostat/en/#data/QCL (accessed on 23 November 2021).
15. Codex Alimentarius Commission. Standard For Named Vegetable Oils Cxs 210-1999. In *Fats, Oils and Related Products*; Joint FAO/WHO Food Standards Programme Codex Committee: Rome, Italy, 1999.
16. Gosselet, N. The Global Market for Oilseeds: Prospects and Challenges for Morocco. *OCL* **2014**, *21*, D204. [CrossRef]
17. United States Department of Agriculture (USDA) Foreign Agricultural Service. USDA, PSD Online. Available online: https://apps.fas.usda.gov/psdonline (accessed on 23 November 2021).
18. Hymowitz, T. The History of the Soybean. In *Soybeans*; Johnson, L.A., White, P.J., Galloway, R., Eds.; AOCS Press: Urbana, IL, USA, 2008; pp. 1–31. ISBN 978-1-893997-64-6.

19. Orf, J.H. Breeding, Genetics, and Production of Soybeans. In *Soybeans*; Johnson, L.A., White, P.J., Galloway, R., Eds.; AOCS Press: Urbana, IL, USA, 2008; pp. 33–65. ISBN 978-1-893997-64-6.
20. Wolf, W.J.; Staff, U. by Soybeans and Other Oilseeds. In *Kirk-Othmer Encyclopedia of Chemical Technology*; American Cancer Society: Atlanta, GA, USA, 2007; ISBN 978-0-471-23896-6.
21. Salgado, J.; Donado-Pestana, C. Soy as a Functional Food. In *Soybean and Nutrition*; InTech: London, UK, 2011; ISBN 978-953-307-536-5.
22. Burssens, S.; Pertry, I.; Diasolua Ngudi, D.; Kuo, Y.-H.; Van Montagu, M.; Lambein, F. Soya, Human Nutrition and Health. In *Soybean and Nutrition*; InTech: London, UK, 2011; pp. 157–180. ISBN 978-953-307-536-5.
23. Hoffman, J.R.; Falvo, M.J. Protein–Which Is Best? *J. Sports Sci. Med.* **2004**, *3*, 118–130. [PubMed]
24. Kang, J.; Badger, T.M.; Ronis, M.J.J.; Wu, X. Non-Isoflavone Phytochemicals in Soy and Their Health Effects. *J. Agric. Food Chem.* **2010**, *58*, 8119–8133. [CrossRef] [PubMed]
25. Gerde, J.A.; White, P.J. Lipids. In *Soybeans*; Johnson, L.A., White, P.J., Galloway, R., Eds.; AOCS Press: Urbana, IL, USA, 2008; pp. 193–227. ISBN 978-1-893997-64-6.
26. Hitoshi, K.; Kozo, H.; Shingu, T.; Yoshio, K.; Ohtani, H.; Okura, Y.; Tanaka, K.; Yasunobu, Y.; Nomura, K.; Kajiyama, G. Opposite Effects on Cholesterol Metabolism and Their Mechanisms Induced by Dietary Oleic Acid and Palmitic Acid in Hamsters. *Biochim. Biophys. Acta-Lipids Lipid Metab.* **1995**, *1258*, 251–256. [CrossRef]
27. Messina, M.; Shearer, G.; Petersen, K. Soybean Oil Lowers Circulating Cholesterol Levels and Coronary Heart Disease Risk, and Has No Effect on Markers of Inflammation and Oxidation. *Nutrition* **2021**, *89*, 111343. [CrossRef]
28. Lin, L.; Allemekinders, H.; Dansby, A.; Campbell, L.; Durance-Tod, S.; Berger, A.; Jones, P.J.H. Evidence of Health Benefits of Canola Oil. *Nutr. Rev.* **2013**, *71*, 370–385. [CrossRef]
29. Shahidi, F. Rapeseed and Canola: Global Production and Distribution. In *Canola and Rapeseed: Production, Chemistry, Nutrition and Processing Technology*; Shahidi, F., Ed.; Springer US: Boston, MA, USA, 1990; pp. 3–13. ISBN 978-1-4615-3912-4.
30. Abbott, P.; Baines, J.; Fox, P.; Graf, L.; Kelly, L.; Stanley, G.; Tomaska, L. Review of the Regulations for Contaminants and Natural Toxicants. *Food Control* **2003**, *14*, 383–389. [CrossRef]
31. Vetter, W.; Darwisch, V.; Lehnert, K. Erucic Acid in Brassicaceae and Salmon—An Evaluation of the New Proposed Limits of Erucic Acid in Food. *NFS J.* **2020**, *19*, 9–15. [CrossRef]
32. Olsen, O.; Soerensen, H. Sinalbin and Other Glucosinolates in Seeds of Double Low Rape Species and Brassica Napus Cv Bronowski. *J. Agric. Food Chem.* **1980**, *28*, 43–48. [CrossRef]
33. Chew, S.C. Cold-Pressed Rapeseed (Brassica Napus) Oil: Chemistry and Functionality. *Food Res. Int.* **2020**, *131*, 108997. [CrossRef]
34. Oplinger, E.S.; Hardman, L.L.; Gritton, E.T.; Doll, J.D.; Kelling, K.A. *Canola (Rapeseed)*; University of Minnesota: Saint Paul, MN, USA, 1989. Available online: https://hort.purdue.edu/newcrop/afcm/canola.html (accessed on 16 November 2021).
35. Eriksson, I.; Westerlund, E.; Åman, P. Chemical Composition in Varieties of Rapeseed and Turnip Rapeseed, Including Several Samples of Hull and Dehulled Seed. *J. Sci. Food Agric.* **1994**, *66*, 233–240. [CrossRef]
36. Fenwick, G.R.; Curtis, R.F. Rapeseed Meal in Rations for Laying Hens: A Review of the Effect on Egg Quality. *J. Sci. Food Agric.* **1980**, *31*, 515–525. [CrossRef]
37. Xie, Y.; Wei, F.; Xu, S.; Wu, B.; Zheng, C.; Lv, X.; Wu, Z.; Chen, H.; Huang, F. Profiling and Quantification of Lipids in Cold-Pressed Rapeseed Oils Based on Direct Infusion Electrospray Ionization Tandem Mass Spectrometry. *Food Chem.* **2019**, *285*, 194–203. [CrossRef] [PubMed]
38. Yang, M.; Zheng, C.; Zhou, Q.; Huang, F.; Liu, C.; Wang, H. Minor Components and Oxidative Stability of Cold-Pressed Oil from Rapeseed Cultivars in China. *J. Food Compos. Anal.* **2013**, *29*, 1–9. [CrossRef]
39. Wongsirichot, P.; Gonzalez-Miquel, M.; Winterburn, J. Holistic Valorization of Rapeseed Meal Utilizing Green Solvents Extraction and Biopolymer Production with Pseudomonas Putida. *J. Clean. Prod.* **2019**, *230*, 420–429. [CrossRef]
40. Tranchino, L.; Costantino, R.; Sodini, G. Food Grade Oilseed Protein Processing: Sunflower and Rapeseed. *Plant Food Hum. Nutr.* **1983**, *32*, 305–334. [CrossRef]
41. Adeleke, B.S.; Babalola, O.O. Oilseed Crop Sunflower (Helianthus Annuus) as a Source of Food: Nutritional and Health Benefits. *Food Sci. Nutr.* **2020**, *8*, 4666–4684. [CrossRef]
42. Jocić, S.; Miladinović, D.; Kaya, Y. Breeding and Genetics of Sunflower. In *Sunflower*; Martínez-Force, E., Dunford, N.T., Salas, J.J., Eds.; AOCS Press: Urbana, IL, USA, 2015; pp. 1–25. ISBN 978-1-893997-94-3.
43. Muhammad Anjum, F.; Nadeem, M.; Issa Khan, M.; Hussain, S. Nutritional and Therapeutic Potential of Sunflower Seeds: A Review. *Br. Food J.* **2012**, *114*, 544–552. [CrossRef]
44. Mashwani, Z.-R.; Bashir, T.; Zahara, K.; Haider, S.; Tabassum, S.; Mudrikah, M. Chemistry, Pharmacology and Ethnomedicinal Uses of Helianthus Annuus (Sunflower): A Review. *Pure Appl. Biol.* **2015**, *4*, 226–235. [CrossRef]
45. de Oliveira Filho, J.G.; Egea, M.B. Sunflower Seed Byproduct and Its Fractions for Food Application: An Attempt to Improve the Sustainability of the Oil Process. *J. Food Sci.* **2021**, *86*, 1497–1510. [CrossRef]
46. Shim, Y.Y.; Gui, B.; Arnison, P.G.; Wang, Y.; Reaney, M.J.T. Flaxseed (*Linum usitatissimum* L.) Bioactive Compounds and Peptide Nomenclature: A Review. *Trends Food Sci. Technol.* **2014**, *38*, 5–20. [CrossRef]
47. Hall, C.; Tulbek, M.C.; Xu, Y. Flaxseed. *Adv. Food Nutr Res.* **2006**, *51*, 1–97. [CrossRef] [PubMed]
48. Dixit, S.; Kanakraj, S.; Rehman, A. Linseed Oil as a Potential Resource for Bio-Diesel: A Review. *Renew. Sustain. Energy Rev.* **2012**, *16*, 4415–4421. [CrossRef]

49. Farag, M.A.; Elimam, D.M.; Afifi, S.M. Outgoing and Potential Trends of the Omega-3 Rich Linseed Oil Quality Characteristics and Rancidity Management: A Comprehensive Review for Maximizing Its Food and Nutraceutical Applications. *Trends Food Sci. Technol.* **2021**, *114*, 292–309. [CrossRef]
50. Zhang, Z.-S.; Wang, L.-J.; Li, D.; Li, S.-J.; Özkan, N. Characteristics of Flaxseed Oil from Two Different Flax Plants. *Int. J. Food Prop.* **2011**, *14*, 1286–1296. [CrossRef]
51. Qiu, C.; Wang, H.; Guo, Y.; Long, S.; Wang, Y.; Abbasi, A.M.; Guo, X.; Jarvis, D.I. Comparison of Fatty Acid Composition, Phytochemical Profile and Antioxidant Activity in Four Flax (*Linum usitatissimum* L.) Varieties. *Oil Crop Sci.* **2020**, *5*, 136–141. [CrossRef]
52. Oomah, B.D.; Mazza, G. Flaxseed Proteins—A Review. *Food Chem.* **1993**, *48*, 109–114. [CrossRef]
53. Liu, J.; Shim, Y.Y.; Tse, T.J.; Wang, Y.; Reaney, M.J.T. Flaxseed Gum a Versatile Natural Hydrocolloid for Food and Non-Food Applications. *Trends Food Sci. Technol.* **2018**, *75*, 146–157. [CrossRef]
54. Bekhit, A.E.-D.A.; Shavandi, A.; Jodjaja, T.; Birch, J.; Teh, S.; Mohamed Ahmed, I.A.; Al-Juhaimi, F.Y.; Saeedi, P.; Bekhit, A.A. Flaxseed: Composition, Detoxification, Utilization, and Opportunities. *Biocatal. Agric. Biotechnol.* **2018**, *13*, 129–152. [CrossRef]
55. Herchi, W.; Arráez-Román, D.; Trabelsi, H.; Bouali, I.; Boukhchina, S.; Kallel, H.; Segura-Carretero, A.; Fernández-Gutierrez, A. Phenolic Compounds in Flaxseed: A Review of Their Properties and Analytical Methods. An Overview of the Last Decade. *J. Oleo Sci.* **2014**, *63*, 7–14. [CrossRef]
56. Shim, Y.Y.; Gui, B.; Wang, Y.; Reaney, M.J.T. Flaxseed (*Linum usitatissimum* L.) Oil Processing and Selected Products. *Trends Food Sci. Technol.* **2015**, *43*, 162–177. [CrossRef]
57. Pradhan, R.C.; Meda, V.; Rout, P.K.; Naik, S.; Dalai, A.K. Supercritical CO_2 Extraction of Fatty Oil from Flaxseed and Comparison with Screw Press Expression and Solvent Extraction Processes. *J. Food Eng.* **2010**, *98*, 393–397. [CrossRef]
58. Tang, Z.; Ying, R.-F.; Lv, B.-F.; Yang, L.-H.; Xu, Z.; Yan, L.-Q.; Bu, J.-Z.; Wei, Y.-S. Flaxseed Oil: Extraction, Health Benefits and Products. *Qual. Assur. Saf. Crops Foods* **2021**, *13*, 1–19. [CrossRef]
59. Bernard, J. Oilseed and Oilseed Meals. In *Reference Module in Food Science*; Elsevier: Amsterdam, The Netherlands, 2016; ISBN 978-0-08-100596-5.
60. Velasco, L.; Möllers, C.; Becker, H.C. Estimation of Seed Weight, Oil Content and Fatty Acid Composition in Intact Single Seeds of Rapeseed (*Brassica napus* L.) by near-Infrared Reflectance Spectroscopy. *Euphytica* **1999**, *106*, 79–85. [CrossRef]
61. INRAE CIRAD AFZ. Legumes and Oilseeds, Main Constituents. Available online: https://feedtables.com/content/table-as-fed (accessed on 24 September 2021).
62. Arrutia, F.; Binner, E.; Williams, P.; Waldron, K.W. Oilseeds beyond Oil: Press Cakes and Meals Supplying Global Protein Requirements. *Trends Food Sci. Technol.* **2020**, *100*, 88–102. [CrossRef]
63. INRAE CIRAD AFZ. Oil Byproducts, Main Constituents. Available online: https://feedtables.com/content/table-as-fed (accessed on 24 September 2021).
64. Ramachandran, S.; Singh, S.K.; Larroche, C.; Soccol, C.R.; Pandey, A. Oil Cakes and Their Biotechnological Applications—A Review. *Bioresour. Technol.* **2007**, *98*, 2000–2009. [CrossRef] [PubMed]
65. de Castro, A.M.; dos Castilho, L.R.; Freire, D.M.G. Characterization of Babassu, Canola, Castor Seed and Sunflower Residual Cakes for Use as Raw Materials for Fermentation Processes. *Ind. Crops Prod.* **2016**, *83*, 140–148. [CrossRef]
66. Banaszkiewicz, T. Nutritional Value of Soybean Meal. In *Soybean and Nutrition*; InTech: London, UK, 2011; ISBN 978-953-307-536-5.
67. *Oxford Dictionary of Biochemistry and Molecular Biology*; Smith, A.D., Datta, S.P., Smith, G.H., Campbell, P.N., Bentley, R., McKenzie, H.A., Eds. Oxford University Press: Oxford, UK; New York, NY, USA, 1997; ISBN 978-0-19-854768-6.
68. Fahy, E.; Cotter, D.; Sud, M.; Subramaniam, S. Lipid Classification, Structures and Tools. *Biochim. Biophys. Acta Mol. Cell Biol. Lipids* **2011**, *1811*, 637–647. [CrossRef]
69. Fahy, E.; Subramaniam, S.; Murphy, R.C.; Nishijima, M.; Raetz, C.R.H.; Shimizu, T.; Spener, F.; van Meer, G.; Wakelam, M.J.O.; Dennis, E.A. Update of the LIPID MAPS Comprehensive Classification System for Lipids. *J. Lipid Res.* **2009**, *50*, S9–S14. [CrossRef]
70. Perez, B.; Li, J.; Guo, Z. Chemistry and Properties of Lipids and Phospholipids. In *Food Lipids: Chemistry, Nutrition, and Biotechnology*, 4th ed.; CRC Press: Boca Raton, FL, USA, 2017; pp. 37–72. ISBN 978-1-4987-4485-0.
71. Gurr, M.I.; Harwood, J.L.; Frayn, K.N.; Murphy, D.J.; Michell, R.H. *Lipids: Biochemistry, Biotechnology and Health*; John Wiley & Sons: Hoboken, NJ, USA, 2016; ISBN 978-1-118-50113-9.
72. O'Keefe, S.; Sarnoski, P. Nomenclature and Classification of Lipids. In *Food Lipids: Chemistry, Nutrition, and Biotechnology*; CRC Press: Boca Raton, FL, USA, 2017; pp. 1–36. ISBN 978-1-4987-4485-0.
73. de Jesus, S.S.; Filho, R.M. Recent Advances in Lipid Extraction Using Green Solvents. *Renew. Sustain. Energy Rev.* **2020**, *133*, 110289. [CrossRef]
74. Mailer, R.J. Oilseeds: Overview. In *Encyclopedia of Food Grains*, 2nd ed.; Wrigley, C., Corke, H., Seetharaman, K., Faubion, J., Eds.; Academic Press: Oxford, UK, 2016; pp. 221–227. ISBN 978-0-12-394786-4.
75. Guan, M.; Chen, H.; Xiong, X.; Lu, X.; Li, X.; Huang, F.; Guan, C. A Study on Triacylglycerol Composition and the Structure of High-Oleic Rapeseed Oil. *Engineering* **2016**, *2*, 258–262. [CrossRef]
76. dos Santos, M.T.; Gerbaud, V.; Roux, G.A.C.L. Beyond Biofuels: Economic Opportunities, Recent Advances and Challenges in Property Modeling for Vegetable Oils. *Green Process. Synth.* **2014**, *3*, 401–410. [CrossRef]
77. Teles dos Santos, M.; Gerbaud, V.; Le Roux, G.A.C. Solid Fat Content of Vegetable Oils and Simulation of Interesterification Reaction: Predictions from Thermodynamic Approach. *J. Food Eng.* **2014**, *126*, 198–205. [CrossRef]

78. Koshland, D.E.; Haurowitz, F. Protein: Definition, Structure, & Classification. Available online: https://www.britannica.com/science/protein (accessed on 2 December 2021).
79. Damodaran, S. Protein: Denaturation. In *Handbook of Food Science, Technology, and Engineering-4 Volume Set*; CRC Press: Boca Raton, FL, USA, 2005.
80. Rodwell, V.W.; Kennelly, P.J. Proteins: Higher Orders of Structure. In *Harper's Illustrated Biochemistry*; McGraw-Hill: New York, NY, USA, 2003; pp. 30–39. ISBN 0-07-138901-6.
81. Shahidi, F. North American Production of Canola. In *Canola and Rapeseed: Production, Chemistry, Nutrition and Processing Technology*; Shahidi, F., Ed.; Springer US: Boston, MA, USA, 1990; pp. 15–23. ISBN 978-1-4615-3912-4.
82. Lammens, T.M.; Franssen, M.C.R.; Scott, E.L.; Sanders, J.P.M. Availability of Protein-Derived Amino Acids as Feedstock for the Production of Bio-Based Chemicals. *Biomass Bioenergy* **2012**, *44*, 168–181. [CrossRef]
83. Fetuga, B.L.; Babatunde, G.M.; Oyenuga, V.A. Protein Quality of Some Unusual Protein Foodstuffs. Studies on the African Locust-Bean Seed (Parkia Filicoidea Welw.). *Br. J. Nutr.* **1974**, *32*, 27–36. [CrossRef]
84. Arowora, K.; STEPHEN, E.; Imo, C.; Emmanuel, U. Quantification of Protein and Amino Acid Composition in Some Oilseeds. *Biochem. Mol. Biol.* **2017**, *2*, 8–11.
85. Bhatty, R.S.; Cherdkiatgumchai, P. Compositional Analysis of Laboratory-Prepared and Commercial Samples of Linseed Meal and of Hull Isolated from Flax. *J. Am. Oil Chem. Soc.* **1990**, *67*, 79–84. [CrossRef]
86. Carré, P. Reinventing the Oilseeds Processing to Extract Oil While Preserving the Protein. *OCL* **2021**, *28*, 13. [CrossRef]
87. Khattab, R.; Eskin, M.; Aliani, M.; Thiyam, U. Determination of Sinapic Acid Derivatives in Canola Extracts Using High-Performance Liquid Chromatography. *J. Am. Oil Chem. Soc.* **2010**, *87*, 147–155. [CrossRef]
88. Das Purkayastha, M.; Das, S.; Manhar, A.K.; Deka, D.; Mandal, M.; Mahanta, C.L. Removing Antinutrients from Rapeseed Press-Cake and Their Benevolent Role in Waste Cooking Oil-Derived Biodiesel: Conjoining the Valorization of Two Disparate Industrial Wastes. *J. Agric. Food Chem.* **2013**, *61*, 10746–10756. [CrossRef]
89. Zardo, I.; Rodrigues, N.P.; Sarkis, J.R.; Marczak, L.D. Extraction and Identification by Mass Spectrometry of Phenolic Compounds from Canola Seed Cake. *J. Sci. Food Agric.* **2020**, *100*, 578–586. [CrossRef] [PubMed]
90. Jiang, J.; Wang, Y.; Xie, T.; Rong, H.; Li, A.; Fang, Y.; Wang, Y. Metabolic Characteristics in Meal of Black Rapeseed and Yellow-Seeded Progeny of Brassica Napus–Sinapis Alba Hybrids. *Molecules* **2015**, *20*, 21204–21213. [CrossRef] [PubMed]
91. Wnukowski, P.; Smolders, G.J.F.; Veerman, C. Protein Isolation from Oil Seeds. Patent number WO2013013949A1, 31 January 2013.
92. Bell, J.M. Factors Affecting the Nutritional Value of Canola Meal: A Review. *Can. J. Anim. Sci.* **1993**, *73*, 689–697. [CrossRef]
93. Shahidi, F.; Ambigaipalan, P. Phenolics and Polyphenolics in Foods, Beverages and Spices: Antioxidant Activity and Health Effects—A Review. *J. Funct. Foods* **2015**, *18*, 820–897. [CrossRef]
94. Claux, O.; Rapinel, V.; Goupy, P.; Patouillard, N.; Vian, M.A.; Jacques, L.; Chemat, F. Dry and Aqueous 2-Methyloxolane as Green Solvents for Simultaneous Production of Soybean Oil and Defatted Meal. *ACS Sustain. Chem. Eng.* **2021**, *9*, 7211–7223. [CrossRef]
95. Cederroth, C.R.; Zimmermann, C.; Nef, S. Soy, Phytoestrogens and Their Impact on Reproductive Health. *Mol. Cell. Endocrinol.* **2012**, *355*, 192–200. [CrossRef]
96. Boudet, A.-M. Evolution and Current Status of Research in Phenolic Compounds. *Phytochemistry* **2007**, *68*, 2722–2735. [CrossRef]
97. Hooper, L.; Ryder, J.J.; Kurzer, M.S.; Lampe, J.W.; Messina, M.J.; Phipps, W.R.; Cassidy, A. Effects of Soy Protein and Isoflavones on Circulating Hormone Concentrations in Pre- and Post-Menopausal Women: A Systematic Review and Meta-Analysis. *Hum. Reprod. Update* **2009**, *15*, 423–440. [CrossRef]
98. Ozdal, T.; Capanoglu, E.; Altay, F. A Review on Protein–Phenolic Interactions and Associated Changes. *Food Res. Int.* **2013**, *51*, 954–970. [CrossRef]
99. Reau, R.; Bodet, J.-M.; Bordes, J.-P.; Dore, T.; Ennaifar, S.; Moussart, A.; Nicolardot, B.; Pellerin, S.; Plenchette, C.; Quinsac, A.; et al. Effets allélopathiques des Brassicacées via leurs actions sur les agents pathogènes telluriques et les mycorhizes: Analyse bibliographique. Partie 1. *OCL* **2005**, *12*, 261–271. [CrossRef]
100. Blažević, I.; Montaut, S.; Burčul, F.; Olsen, C.E.; Burow, M.; Rollin, P.; Agerbirk, N. Glucosinolate Structural Diversity, Identification, Chemical Synthesis and Metabolism in Plants. *Phytochemistry* **2020**, *169*, 112100. [CrossRef] [PubMed]
101. Tripathi, M.K.; Mishra, A.S. Glucosinolates in Animal Nutrition: A Review. *Anim. Feed Sci. Technol.* **2007**, *132*, 1–27. [CrossRef]
102. Stein, H.H.; Berger, L.L.; Drackley, J.K.; Fahey, G.C.; Hernot, D.C.; Parsons, C.M. Nutritional Properties and Feeding Values of Soybeans and Their Coproducts. In *Soybeans*; Johnson, L.A., White, P.J., Galloway, R., Eds.; AOCS Press: Urbana, IL, USA, 2008; pp. 613–660. ISBN 978-1-893997-64-6.
103. Koubaa, M.; Mhemdi, H.; Barba, F.J.; Roohinejad, S.; Greiner, R.; Vorobiev, E. Oilseed Treatment by Ultrasounds and Microwaves to Improve Oil Yield and Quality: An Overview. *Food Res. Int.* **2016**, *85*, 59–66. [CrossRef] [PubMed]
104. Johnson, L.A. Recovery, Refining, Converting, and Stabilizing Edible Fats and Oils. In *Food Lipids: Chemistry, Nutrition, and Biotechnology*; CRC Press, Taylor & Francis Group: Boca Raton, FL, USA, 2008; pp. 205–241. ISBN 978-1-4200-4664-9.
105. Matthäus, B. Oil Technology. In *Advances in Botanical Research*; Rapeseed Breeding; Academic Press: Cambridge, MA, USA, 2007; Volume 45.
106. Cunha, S.C.; Fernandes, J.O. Extraction Techniques with Deep Eutectic Solvents. *TrAC Trends Anal. Chem.* **2018**, *105*, 225–239. [CrossRef]

107. Uitterhaegen, E.; Evon, P. Twin-Screw Extrusion Technology for Vegetable Oil Extraction: A Review. *J. Food Eng.* **2017**, *212*, 190–200. [CrossRef]
108. Mouloungui, Z.; Valentin, R.; Candy, L.; Fabre, J.-F.; Lacroux, É.; Merah, O.; Cerny, M.; Giacinti, G.; de Caro, P.; Thiebaud-Roux, S. Huiles alimentaires et lipochimie. In *Chimie Verte et Industries Agroalimentaires: Vers une Bioéconomie Durable*; Editions Lavoisier: Paris Cedex, France, 2020; ISBN 978-2-7430-2513-7.
109. Lacaze-Dufaure, C.; Leyris, J.; Rigal, L.; Mouloungui, Z. A Twin-Screw Extruder for Oil Extraction: I. Direct Expression of Oleic Sunflower Seeds. *J. Am. Oil Chem. Soc.* **1999**, *76*, 1073–1079. [CrossRef]
110. Amalia Kartika, I.; Pontalier, P.Y.; Rigal, L. Extraction of Sunflower Oil by Twin Screw Extruder: Screw Configuration and Operating Condition Effects. *Bioresour. Technol.* **2006**, *97*, 2302–2310. [CrossRef]
111. Uitterhaegen, E.; Nguyen, Q.; Sampaio, K.; Stevens, C.; Merah, O.; Talou, T.; Rigal, L.; Evon, P. Extraction of Coriander Oil Using Twin-Screw Extrusion: Feasibility Study and Potential Press Cake Applications. *J. Am. Oil Chem. Soc.* **2015**, *92*, 1219–1233. [CrossRef]
112. Evon, P.; Kartika, I.A.; Cerny, M.; Rigal, L. Extraction of Oil from Jatropha Seeds Using a Twin-Screw Extruder: Feasibility Study. *Ind. Crops Prod.* **2013**, *47*, 33–42. [CrossRef]
113. Vandenbossche, V.; Candy, L.; Evon, P.; Rouilly, A.; Pontalier, P.-Y. Extrusion. In *Green Food Processing Techniques*; Chemat, F., Vorobiev, E., Eds.; Academic Press: Cambridge, MA, USA, 2019; pp. 289–314. ISBN 978-0-12-815353-6.
114. Dufaure, C.; Mouloungui, Z.; Rigal, L. A Twin-Screw Extruder for Oil Extraction: II. Alcohol Extraction of Oleic Sunflower Seeds. *J. Am. Oil Chem. Soc.* **1999**, *76*, 1081–1086. [CrossRef]
115. Kartika, I.A.; Pontalier, P.-Y.P.-Y.; Rigal, L. Twin-Screw Extruder for Oil Processing of Sunflower Seeds: Thermo-Mechanical Pressing and Solvent Extraction in a Single Step. *Ind. Crops Prod.* **2010**, *32*, 297–304. [CrossRef]
116. Evon, P.; Vandenbossche, V.; Pontalier, P.Y.; Rigal, L. Direct Extraction of Oil from Sunflower Seeds by Twin-Screw Extruder According to an Aqueous Extraction Process: Feasibility Study and Influence of Operating Conditions. *Ind. Crops Prod.* **2007**, *26*, 351–359. [CrossRef]
117. Evon, P.; Vandenbossche, V.; Pontalier, P.Y.; Rigal, L. Aqueous Extraction of Residual Oil from Sunflower Press Cake Using a Twin-Screw Extruder: Feasibility Study. *Ind. Crops Prod.* **2009**, *29*, 455–465. [CrossRef]
118. Bertouche, S.; Tomao, V.; Hellal, A.; Boutekedjiret, C.; Chemat, F. First Approach on Edible Oil Determination in Oilseeds Products Using Alpha-Pinene. *J. Essent. Oil Res.* **2013**, *25*, 439–443. [CrossRef]
119. Sicaire, A.-G.; Vian, M.; Fine, F.; Carré, P.; Tostain, S.; Chemat, F. Experimental Approach versus COSMO-RS Assisted Solvent Screening for Predicting the Solubility of Rapeseed Oil. *OCL* **2015**, *22*, D404. [CrossRef]
120. Office of Air and Radiation. The Clean Air Act Amendments of 1990. Available online: https://www3.epa.gov/airtoxics/smbus.pdf (accessed on 25 October 2021).
121. European Parliament, Council of 23 April 2009. Directive 2009/32/EC on the Approximation of the Laws of the Member States on Extraction Solvents Used in the Production of Foodstuffs and Food Ingredients. Available online: https://eur-lex.europa.eu/legal-content/EN/ALL/?uri=CELEX:32009L0032#ntr4-L_2009141EN.01000801-E0004 (accessed on 3 June 2021).
122. Li, Y.; Fine, F.; Fabiano-Tixier, A.-S.; Abert-Vian, M.; Carre, P.; Pages, X.; Chemat, F. Evaluation of Alternative Solvents for Improvement of Oil Extraction from Rapeseeds. *Comptes Rendus Chim.* **2014**, *17*, 242–251. [CrossRef]
123. Sicaire, A.-G.; Vian, M.; Fine, F.; Joffre, F.; Carré, P.; Tostain, S.; Chemat, F. Alternative Bio-Based Solvents for Extraction of Fat and Oils: Solubility Prediction, Global Yield, Extraction Kinetics, Chemical Composition and Cost of Manufacturing. *Int. J. Mol. Sci.* **2015**, *16*, 8430–8453. [CrossRef]
124. Sicaire, A.-G.; Vian, M.A.; Fine, F.; Carré, P.; Tostain, S.; Chemat, F. Ultrasound Induced Green Solvent Extraction of Oil from Oleaginous Seeds. *Ultrason. Sonochem.* **2016**, *31*, 319–329. [CrossRef]
125. Perrier, A.; Delsart, C.; Boussetta, N.; Grimi, N.; Citeau, M.; Vorobiev, E. Effect of Ultrasound and Green Solvents Addition on the Oil Extraction Efficiency from Rapeseed Flakes. *Ultrason. Sonochem.* **2017**, *39*, 58–65. [CrossRef]
126. Lohani, U.C.; Fallahi, P.; Muthukumarappan, K. Comparison of Ethyl Acetate with Hexane for Oil Extraction from Various Oilseeds. *J. Am. Oil Chem. Soc.* **2015**, *92*, 743–754. [CrossRef]
127. Yara-Varón, E.; Selka, A.; Fabiano-Tixier, A.S.; Balcells, M.; Canela-Garayoa, R.; Bily, A.; Touaibia, M.; Chemat, F. Solvent from Forestry Biomass. Pinane a Stable Terpene Derived from Pine Tree Byproducts to Substitute n -Hexane for the Extraction of Bioactive Compounds. *Green Chem.* **2016**, *18*, 6596–6608. [CrossRef]
128. Madji, S.; Hilali, S.; Fabiano-Tixier, A.-S.; Tenon, M.; Bily, A.; Laguerre, M.; Chemat, F. Para-Menthane as a Stable Terpene Derived from Orange By-Products as a Novel Solvent for Green Extraction and Solubilization of Natural Substances. *Molecules* **2019**, *24*, 2170. [CrossRef] [PubMed]
129. Rapinel, V.; Rombaut, N.; Rakotomanomana, N.; Vallageas, A.; Cravotto, G.; Chemat, F. An Original Approach for Lipophilic Natural Products Extraction: Use of Liquefied n-Butane as Alternative Solvent to n-Hexane. *LWT Food Sci. Technol.* **2017**, *85*, 524–533. [CrossRef]
130. Wang, S.; Zhang, Z.-S.; Zhang, T.-F.; Wang, X. Extraction and Characterization of Flaxseed Oil Obtained with Subcritical N-Butane. *J. Oleo Sci.* **2020**, *69*, 1011–1020. [CrossRef] [PubMed]
131. Alara, O.R.; Abdurahman, N.H.; Ukaegbu, C.I. Extraction of Phenolic Compounds: A Review. *Curr. Res. Food Sci.* **2021**, *4*, 200–214. [CrossRef]

132. Starmans, D.A.J.; Nijhuis, H.H. Extraction of Secondary Metabolites from Plant Material: A Review. *Trends Food Sci. Technol.* **1996**, *7*, 191–197. [CrossRef]
133. Azmir, J.; Zaidul, I.S.M.; Rahman, M.M.; Sharif, K.M.; Mohamed, A.; Sahena, F.; Jahurul, M.H.A.; Ghafoor, K.; Norulaini, N.A.N.; Omar, A.K.M. Techniques for Extraction of Bioactive Compounds from Plant Materials: A Review. *J. Food Eng.* **2013**, *117*, 426–436. [CrossRef]
134. Nandasiri, R.; Eskin, N.A.M.; Eck, P.; Thiyam-Höllander, U. Application of Green Technology on Extraction of Phenolic Compounds in Oilseeds (Canola). In *Cold Pressed Oils*; Ramadan, M.F., Ed.; Academic Press: Cambridge, MA, USA, 2020; pp. 81–96. ISBN 978-0-12-818188-1.
135. Häckl, K.; Kunz, W. Some Aspects of Green Solvents. *Comptes Rendus. Chim.* **2018**, *21*, 572–580. [CrossRef]
136. Chemat, F.; Vian, M.A.; Cravotto, G. Green Extraction of Natural Products: Concept and Principles. *Int. J. Mol. Sci.* **2012**, *13*, 8615–8627. [CrossRef]
137. Anastas, P.T.; Kirchhoff, M.M. Origins, Current Status, and Future Challenges of Green Chemistry. *Acc. Chem. Res.* **2002**, *35*, 686–694. [CrossRef]
138. Anastas, P.; Eghbali, N. Green Chemistry: Principles and Practice. *Chem. Soc. Rev.* **2010**, *39*, 301–312. [CrossRef] [PubMed]
139. Abreu, C.M.R.; Maximiano, P.; Guliashvili, T.; Nicolas, J.; Serra, A.C.; Coelho, J.F.J. Cyclopentyl Methyl Ether as a Green Solvent for Reversible-Addition Fragmentation Chain Transfer and Nitroxide-Mediated Polymerizations. *RSC Adv.* **2016**, *6*, 7495–7503. [CrossRef]
140. Citeau, M.; Regis, J.; Carré, P.; Fine, F. Value of Hydroalcoholic Treatment of Rapeseed for Oil Extraction and Protein Enrichment. *OCL* **2019**, *26*, 1. [CrossRef]
141. Sawada, M.M.; Venâncio, L.L.; Toda, T.A.; Rodrigues, C.E.C. Effects of Different Alcoholic Extraction Conditions on Soybean Oil Yield, Fatty Acid Composition and Protein Solubility of Defatted Meal. *Food Res. Int.* **2014**, *62*, 662–670. [CrossRef]
142. Pederssetti, M.M.; Palú, F.; da Silva, E.A.; Rohling, J.H.; Cardozo-Filho, L.; Dariva, C. Extraction of Canola Seed (Brassica Napus) Oil Using Compressed Propane and Supercritical Carbon Dioxide. *J. Food Eng.* **2011**, *102*, 189–196. [CrossRef]
143. Nimet, G.; da Silva, E.A.; Palú, F.; Dariva, C.; dos Freitas, L.S.; Neto, A.M.; Filho, L.C. Extraction of Sunflower (Heliantus Annuus L.) Oil with Supercritical CO2 and Subcritical Propane: Experimental and Modeling. *Chem. Eng. J.* **2011**, *168*, 262–268. [CrossRef]
144. Zanqui, A.B.; de Morais, D.R.; da Silva, C.M.; Santos, J.M.; Gomes, S.T.M.; Visentainer, J.V.; Eberlin, M.N.; Cardozo-Filho, L.; Matsushita, M. Subcritical Extraction of Flaxseed Oil with N-Propane: Composition and Purity. *Food Chem.* **2015**, *188*, 452–458. [CrossRef]
145. Beckel, A.C.; Belter, P.A.; Smith, A.K. Solvent Effects on the Products of Soybean Oil Extraction. *J. Am. Oil Chem. Soc.* **1948**, *25*, 7–9. [CrossRef]
146. Rao, R.K.; Arnold, L.K. Alcoholic Extraction of Vegetable Oils. III. Solubilities of Babassu, Coconut, Olive, Palm, Rapeseed, and Sunflower Seed Oils in Aqueous Ethanol. *J. Am. Oil Chem. Soc.* **1956**, *33*, 389–391. [CrossRef]
147. Kanth Rao, R.; Arnold, L.K. Alcoholic Extraction of Vegetable Oils. Part IV. Solubilities of Vegetable Oils in Aqueous 2-Propanol. *J. Am. Oil Chem. Soc.* **1957**, *34*, 401–404. [CrossRef]
148. Rao, R.K.; Arnold, L.K. Alcoholic Extraction of Vegetable Oils. V. Pilot Plant Extraction of Cottonseed by Aqueous Ethanol. *J. Am. Oil Chem. Soc.* **1958**, *35*, 277–281. [CrossRef]
149. Cañadas, R.; González-Miquel, M.; González, E.J.; Díaz, I.; Rodríguez, M. Evaluation of Bio-Based Solvents for Phenolic Acids Extraction from Aqueous Matrices. *J. Mol. Liq.* **2021**, *338*, 116930. [CrossRef]
150. Pace, V.; Hoyos, P.; Castoldi, L.; de Domínguez María, P.; Alcántara, A.R. 2-Methyltetrahydrofuran (2-MeTHF): A Biomass-Derived Solvent with Broad Application in Organic Chemistry. *ChemSusChem* **2012**, *5*, 1369–1379. [CrossRef] [PubMed]
151. Sicaire, A.-G.; Vian, M.A.; Filly, A.; Li, Y.; Bily, A.; Chemat, F. 2-Methyltetrahydrofuran: Main Properties, Production Processes, and Application in Extraction of Natural Products. In *Alternative Solvents for Natural Products Extraction*; Chemat, F., Vian, M.A., Eds.; Green Chemistry and Sustainable Technology; Springer: Berlin/Heidelberg, Germany, 2014; pp. 253–268. ISBN 978-3-662-43628-8.
152. Antonucci, V.; Coleman, J.; Ferry, J.B.; Johnson, N.; Mathe, M.; Scott, J.P.; Xu, J. Toxicological Assessment of 2-Methyltetrahydrofuran and Cyclopentyl Methyl Ether in Support of Their Use in Pharmaceutical Chemical Process Development. *Org. Process Res. Dev.* **2011**, *15*, 939–941. [CrossRef]
153. Tundo, P.; Selva, M. The Chemistry of Dimethyl Carbonate. *Acc. Chem. Res.* **2002**, *35*, 706–716. [CrossRef]
154. Eggersdorfer, M. Terpenes. In *Ullmann's Encyclopedia of Industrial Chemistry*; American Cancer Society: Atlanta, GA, USA, 2000; ISBN 978-3-527-30673-2.
155. Davis, E.M.; Croteau, R. Cyclization Enzymes in the Biosynthesis of Monoterpenes, Sesquiterpenes, and Diterpenes. In *Biosynthesis: Aromatic Polyketides, Isoprenoids, Alkaloids*; Leeper, F.J., Vederas, J.C., Eds.; Topics in Current Chemistry; Springer: Berlin/Heidelberg, German, 2000; pp. 53–95. ISBN 978-3-540-48146-1.
156. Paduch, R.; Kandefer-Szerszeń, M.; Trytek, M.; Fiedurek, J. Terpenes: Substances Useful in Human Healthcare. *Arch. Immunol. Ther. Exp.* **2007**, *55*, 315. [CrossRef]
157. Rodríguez-Llorente, D.; Cañada-Barcala, A.; Álvarez-Torrellas, S.; Águeda, V.I.; García, J.; Larriba, M. A Review of the Use of Eutectic Solvents, Terpenes and Terpenoids in Liquid–Liquid Extraction Processes. *Processes* **2020**, *8*, 1220. [CrossRef]
158. Virot, M.; Tomao, V.; Ginies, C.; Chemat, F. Total Lipid Extraction of Food Using D-Limonene as an Alternative to n-Hexane. *Chroma* **2008**, *68*, 311–313. [CrossRef]

159. Virot, M.; Tomao, V.; Ginies, C.; Visinoni, F.; Chemat, F. Green Procedure with a Green Solvent for Fats and Oils' Determination: Microwave-Integrated Soxhlet Using Limonene Followed by Microwave Clevenger Distillation. *J. Chromatogr. A* **2008**, *1196–1197*, 147–152. [CrossRef]
160. Dejoye Tanzi, C.; Abert Vian, M.; Ginies, C.; Elmaataoui, M.; Chemat, F. Terpenes as Green Solvents for Extraction of Oil from Microalgae. *Molecules* **2012**, *17*, 8196–8205. [CrossRef]
161. Adesina, A.Y.; Obot, I.B.; Sorour, A.; Mtongana, S.; Mamilla, S.B.; Almathami, A.A. Corrosion Challenges and Prevention in Ethyl Acetate (EA) Production and Related Processes—An Overview. *Eng. Fail. Anal.* **2021**, *127*, 105511. [CrossRef]
162. Pyo, S.-H.; Park, J.H.; Chang, T.-S.; Hatti-Kaul, R. Dimethyl Carbonate as a Green Chemical. *Curr. Opin. Green Sustain. Chem.* **2017**, *5*, 61–66. [CrossRef]
163. de Gonzalo, G.; Alcántara, A.R.; de Domínguez María, P. Cyclopentyl Methyl Ether (CPME): A Versatile Eco-Friendly Solvent for Applications in Biotechnology and Biorefineries. *ChemSusChem* **2019**, *12*, 2083–2097. [CrossRef]
164. Azzena, U.; Carraro, M.; Pisano, L.; Monticelli, S.; Bartolotta, R.; Pace, V. Cyclopentyl Methyl Ether: An Elective Ecofriendly Ethereal Solvent in Classical and Modern Organic Chemistry. *ChemSusChem* **2019**, *12*, 40–70. [CrossRef]
165. Watanabe, K.; Yamagiwa, N.; Torisawa, Y. Cyclopentyl Methyl Ether as a New and Alternative Process Solvent. *Org. Process Res. Dev.* **2007**, *11*, 251–258. [CrossRef]
166. Reverchon, E.; de Marco, I. Supercritical Fluid Extraction and Fractionation of Natural Matter. *J. Supercrit. Fluids* **2006**, *38*, 146–166. [CrossRef]
167. Tres, M.V.; Racoski, J.C.; Di Luccio, M.; Oliveira, J.V.; Treichel, H.; de Oliveira, D.; Mazutti, M.A. Separation of Soybean Oil/n-Hexane and Soybean Oil/n-Butane Mixtures Using Ceramic Membranes. *Food Res. Int.* **2014**, *63*, 33–41. [CrossRef]
168. Li, J.; Sun, D.; Qian, L.; Liu, Y. Subcritical Butane Extraction of Wheat Germ Oil and Its Deacidification by Molecular Distillation. *Molecules* **2016**, *21*, 1675. [CrossRef]
169. Benvenutti, L.; Zielinski, A.A.F.; Ferreira, S.R.S. Which Is the Best Food Emerging Solvent: IL, DES or NADES? *Trends Food Sci. Technol.* **2019**, *90*, 133–146. [CrossRef]
170. Passos, H.; Freire, M.G.; Coutinho, J.A.P. Ionic Liquid Solutions as Extractive Solvents for Value-Added Compounds from Biomass. *Green Chem.* **2014**, *16*, 4786–4815. [CrossRef]
171. Kentish, S.; Ashokkumar, M. The Physical and Chemical Effects of Ultrasound. In *Ultrasound Technologies for Food and Bioprocessing*; Springer: New York, NY, USA, 2010; pp. 1–12. ISBN 978-1-4419-7471-6.
172. Chemat, F.; Zill-e-Huma; Khan, M.K. Applications of Ultrasound in Food Technology: Processing, Preservation and Extraction. *Ultrason. Sonochem.* **2011**, *18*, 813–835. [CrossRef] [PubMed]
173. Chemat, F.; Rombaut, N.; Sicaire, A.-G.; Meullemiestre, A.; Fabiano-Tixier, A.-S.; Abert-Vian, M. Ultrasound Assisted Extraction of Food and Natural Products. Mechanisms, Techniques, Combinations, Protocols and Applications. A Review. *Ultrason. Sonochem.* **2017**, *34*, 540–560. [CrossRef] [PubMed]
174. Luque-García, J.L.; de Luque Castro, M.D. Ultrasound-Assisted Soxhlet Extraction: An Expeditive Approach for Solid Sample Treatment: Application to the Extraction of Total Fat from Oleaginous Seeds. *J. Chromatogr. A* **2004**, *1034*, 237–242. [CrossRef] [PubMed]
175. Zdanowska, P.; Dróżdż, B.; Janakowski, S.; Derewiaka, D. Impact of Preliminary Ultrasound Treatment of Rape Seeds on the Pressing Process and Selected Oil Characteristics. *Ind. Crops Prod.* **2019**, *138*, 111572. [CrossRef]
176. Berot, S.; Briffaud, J. Parameters for Obtaining Concentrates from Rapeseed and Sunflower Meal. *Plant Food Hum. Nutr.* **1983**, *33*, 237–242. [CrossRef]
177. Guthrie, F. LII. On Eutexia. *Lond. Edinb. Dublin Philos. Mag. J. Sci.* **1884**, *17*, 462–482. [CrossRef]
178. Martins, M.A.R.; Pinho, S.P.; Coutinho, J.A.P. Insights into the Nature of Eutectic and Deep Eutectic Mixtures. *J. Solut. Chem.* **2019**, *48*, 962–982. [CrossRef]
179. Abbott, A.P.; Capper, G.; Davies, D.L.; Rasheed, R.K.; Tambyrajah, V. Novel Solvent Properties of Choline Chloride/Urea Mixtures. *Chem. Commun.* **2003**, 70–71. [CrossRef]
180. Farooq, M.Q.; Abbasi, N.M.; Anderson, J.L. Deep Eutectic Solvents in Separations: Methods of Preparation, Polarity, and Applications in Extractions and Capillary Electrochromatography. *J. Chromatogr. A* **2020**, *1633*, 461613. [CrossRef]
181. Perna, F.M.; Vitale, P.; Capriati, V. Deep Eutectic Solvents and Their Applications as Green Solvents. *Curr. Opin. Green Sustain. Chem.* **2020**, *21*, 27–33. [CrossRef]
182. Smith, E.L.; Abbott, A.P.; Ryder, K.S. Deep Eutectic Solvents (DESs) and Their Applications. *Chem. Rev.* **2014**, *114*, 11060–11082. [CrossRef] [PubMed]
183. Sze, L.L.; Pandey, S.; Ravula, S.; Pandey, S.; Zhao, H.; Baker, G.A.; Baker, S.N. Ternary Deep Eutectic Solvents Tasked for Carbon Dioxide Capture. *ACS Sustain. Chem. Eng.* **2014**, *2*, 2117–2123. [CrossRef]
184. Gomez, A.; Biswas, A.; Tadini, C.; Furtado, R.; Alves, C.; Cheng, H. Use of Natural Deep Eutectic Solvents for Polymerization and Polymer Reactions. *J. Braz. Chem. Soc.* **2019**, *30*, 717–726. [CrossRef]