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Solvent solutions: comparing extraction methods for edible oils and proteins in a changing regulatory landscape. Part 5: Impacts on the oil quality☆

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Abstract – This article constitutes the fifth part of a series dedicated to the comparative analysis of extraction solvents for oilseeds. This section evaluates the impact of various solvents on oil quality, focusing on enzymatic activity, oil acidity, peroxide value, fatty acid profiles, phospholipids, polyphenols, tocopherols, and sterols. For alcohols, such as ethanol, isopropanol, and methanol, results indicate an interesting suppression of enzymatic activity due to protein denaturation. Alcohols also lead to higher tocopherol content and lower acidity when solvent recycling employs a non-distillation process. Ketones, particularly acetone and methyl ethyl ketone, show potential for enzyme denaturation and exhibit low miscibility with phospholipids, which may impact the extraction process. Ethyl acetate is recognized for potentially enhancing enzymatic activity and extracting higher levels of antioxidants. Dichloromethane is effective in extracting more phospholipids compared to hexane. The use of 2-methyloxolane (2-MeOx) presents a potential issue of peroxide formation, leading to higher peroxide values in extracted oils. Additionally, 2-MeOx extracts higher amounts of phospholipids, polyphenols, and tocopherols, but results in lower sterol content for reasons not fully understood. Regarding fatty acid profiles, no study has shown a significant effect of solvent choice. These results highlight the complex interactions between solvents and oil components, illustrated by surprising findings such as the higher extraction of free fatty acids by alcohols. Despite a substantial number of studies, the presented results should be interpreted cautiously, as they were obtained under conditions not fully representative of industrial operations.

Keywords: Solvents / extraction / oil quality / phospholipids / tocopherols

Résumé – Solvants d'extraction : comparaison des méthodes d'obtention des huiles alimentaires dans un paysage réglementaire en évolution. Partie 5: Effets sur la qualité des huiles. Cet article constitue le cinquième volet d'une série consacrée à l'analyse comparative des solvants d'extraction des graines oléagineuses. Cette partie évalue l'impact des divers solvants sur la qualité de l'huile, en se concentrant sur l'activité enzymatique, l'acidité de l'huile, l'indice de peroxyde, les profils d'acides gras, les phospholipides, les polyphénols, les tocophérols et les stérols. Pour les alcools, tels que l'éthanol, l'isopropanol et le méthanol, les résultats indiquent une suppression intéressante de l'activité enzymatique due à la dénaturation des protéines. Les alcools entraînent également une teneur plus élevée en tocophérols et une acidité plus faible lorsque le recyclage du solvant utilise un schéma sans distillation. Les cétones, notamment l'acétone et la méthyléthylcétone, montrent un potentiel de dénaturation des enzymes et présentent une faible miscibilité avec les phospholipides, ce qui peut avoir un impact sur le processus d'extraction. L'acétate d'éthyle est reconnu pour potentiellement améliorer l'activité enzymatique et extraire des niveaux plus élevés d'antioxydants. Le dichlorométhane est efficace pour extraire plus de phospholipides par rapport à l'hexane. L'utilisation du 2-méthyloxolane (2-MeOx) présente un problème potentiel de formation de peroxydes, conduisant à des indices de peroxyde plus élevés dans les huiles extraites. De plus, le 2-MeOx extrait des quantités plus élevées de phospholipides, de polyphénols et de tocophérols, mais entraîne une teneur plus faible en stérols pour des raisons qui ne sont pas totalement

☆ Contribution to the Topical Issue: "Extraction solvents / Solvants d'extraction".

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comprises. En ce qui concerne les profils d'acides gras, aucune étude n'a montré d'effet significatif du choix du solvant. Ces résultats mettent en évidence les interactions complexes entre les solvants et les composants de l'huile, illustrées par des résultats surprenants comme l'extraction plus élevée d'acides gras libres par les alcools. Néanmoins, en dépit d'un nombre conséquent d'études analysées, il est impératif de souligner la fragilité des résultats présentés, lesquels ont été obtenus dans des conditions non représentatives des opérations industrielles.

Mots-clés : Solvants / extraction / qualité de l'huile / phospholipides / tocophérols

Highlights

- The nature of the solvents has little effect on the fatty acid profiles of oils but significantly influences the extraction of phospholipids.
- Phenolic compounds are poorly extracted by hexane.
- Tocopherols and phytosterols exhibit varying behaviors.
- Acidity is often lower with hexane, while the peroxide value appears to be reduced with ethanol and acetone.

1 Introduction

Oil quality is paramount in the oil mill industry, impacting both commercial value and consumer health benefits. Ensuring high oil quality involves preserving the oil from hydrolysis and oxidation. These two processes can significantly degrade the oil's properties: hydrolysis leads to the formation of free fatty acids, affecting taste and stability, while oxidation results in rancidity and loss of nutritional value. To mitigate these issues, the presence of natural antioxidants in the oil is crucial. Antioxidants such as tocopherols (a form of vitamin E) play a vital role in protecting the oil from oxidative damage. These compounds not only enhance the shelf life of the oil but also contribute to the health benefits associated with its consumption. Tocopherols, for instance, are known for their potent antioxidant properties, which help in scavenging free radicals, thereby preventing cellular damage in the human body (Saldeen and Saldeen, 2005). Moreover, micronutrients such as sterols are essential for maintaining the health of consumers. Sterols have been shown to lower cholesterol levels and support cardiovascular health, making them a valuable component of edible oils (Piironen *et al.*, 2000). Higher concentration of these micronutrients in the oil matrix enhances its nutritional profile and potentially confers health benefits to consumers. However, in the context of commodity oils, the quality criteria employed to ascertain market value typically do not encompass micronutrient content. Consequently, while increased extraction yields of these bioactive compounds may be advantageous from a public health perspective, they hold limited economic significance for oil mill operators.

This article, the fifth in a series dedicated to solvents usable in the vegetable oil extraction industry, focuses on the impact of different solvents on oil quality. The comparison between solvents, particularly ethanol *vs.* hexane, is based on extensive bibliographic research. This research involved analysing various studies to evaluate the efficiency and effects of these solvents on oil extraction, and covers data on free fatty acids, peroxide values, fatty acid profiles, phospholipids, unsaponifiable matter, total phenols, tocopherols, sterols, and waxes. Additionally, the article addresses the effect of the presence of water in the solvent and its possible consequences on product quality. The presence of water can influence enzyme activity during extraction, potentially leading to the formation of undesirable compounds such as free fatty acids and non-hydratable phospholipids. For instance, the very low water content of hexane limits enzyme activity in the extractor, whereas other solvents like ethanol can disrupt hydrogen bonding and hydrophobic interactions, thereby denaturing proteins and reducing enzyme activity. This comprehensive comparison aims to provide insights into the suitability of alternative solvents for preserving oil quality while ensuring the retention of beneficial micronutrients, potentially leading to improved extraction methods in the oil industry.

In this comparative study, we examine the effects of various solvents on oil quality, using hexane-extracted oil as a benchmark. Given the limited number of available studies, the diversity of plant matrices, and the heterogeneity of extraction methods employed, a rigorous statistical analysis is not feasible. However, we propose a qualitative assessment framework to identify meaningful trends and differences in oil quality parameters. Within this context, we employ the term "significant" to denote consistent and substantial deviations from hexane-extracted oil quality, rather than in its strict statistical sense. This approach allows us to highlight practically relevant differences that persist across multiple studies, despite variations in methodologies and matrices. In this comparison, we propose an interpretation of the available observations with full transparency, as the collected data are presented systematically.

2 Enzyme activity and water content

Hexane immersion of oleaginous material does not entirely inhibit enzyme activity. Simpson (1991) demonstrated that D-phospholipase activity can occur during extraction at 65 °C, leading to the formation of phosphatidic acid (PA) and non-hydratable phospholipids (PL). This activity remains relatively limited due to the minimal water content introduced by hexane into the extractor. However, alternative solvents in our comparison are likely to introduce higher water content.

In the case of ethanol, water-induced enzyme activity is less problematic. Ethanol disrupts the hydrogen bonding and hydrophobic interactions that stabilize the native three-dimensional structure of proteins, causing them to unfold or denature, thus losing their biologically active conformation (Acharya and Chaudhuri, 2021). Kamal *et al.* (2013) reported that methanol, isopropyl alcohol, and acetone can suppress

lipase activity when their concentrations in aqueous solutions exceed 40%. This suppression was attributed to interference at the reactive site between the enzyme and the substrate, rather than changes in protein conformation. Herskovits *et al.* (1970) demonstrated with chymotrypsinogen, myoglobin, and cytochrome c that long-chain alcohols (butanol, propanol) were more potent denaturants than short-chain alcohols (ethanol, methanol). Asakura *et al.* (1978) observed similar results with haemoglobin, where butanol and isopropyl alcohol denatured the protein at concentrations below 10%, compared to above 20% for ethanol and methanol. Similar effects have been reported for ketones, with methyl ethyl ketone (MEK) likely being a more potent denaturant than acetone. However, no available studies have demonstrated such behaviour under oil extraction conditions.

Khmelnitsky *et al.* (1991) proposed a method for assessing the denaturation capacity of various solvents based on their ability to interact with the water shell surrounding proteins. This method is consistent with previous findings, predicting higher potency for longer-chain solvents with more hydrophobic molecular surfaces. It also suggests that more hydrophobic solvents lack the capacity to reach the concentration threshold in the water phase necessary to disturb the proteins' water shell. Ethyl acetate (EA), dichloromethane (DCM), and 2-methyloxolane (2-MeOx) have water miscibility of 30 g/L, 1.3 g/L, and 44 g/L at 20 °C, respectively, which increase slightly at extraction temperatures. Consequently, when using water-saturated 2-MeOx, the water introduced into the extractor by the solvent may enhance certain enzyme activities during the extraction process. Ethyl acetate is suspected to have a similar effect, albeit to a lesser extent.

In a counterflow extractor, water accompanying the solvent tends to partition predominantly into the solid material rather than the miscella. As a result, most enzymatic activity does not affect the oil, as the additional water does not reach the section of the extractor where the oil is concentrated. If upstream water were influencing enzyme activity, this would be evident in the percentage of non-hydratable phosphorus present in the oil following the water degumming process. However, there is a lack of results in the available literature on this issue. The consequences of interest are likely to concern myrosinase activity in Brassicaceae, leading to the hydrolysis of glucosinolates. Given that isothiocyanates have positive Log $P_{o/w}$ values, this property could potentially be exploited to recover the deleterious breakdown products in the solvent phase and eliminate them during oil refining. Other activities, such as polyphenol oxidase, could lead to enzymatic browning of the meals, which is undesirable when using proteins as human food ingredients.

3 Ethanol *vs.* hexane

Table 1 presents a comparative analysis of oils extracted using ethanol and hexane, based on data compiled from the literature. The values reported for each parameter represent the difference between ethanol-extracted oils and hexane-extracted oils (ethanol minus hexane). Positive differences indicate higher extraction efficiency of the component by ethanol, while negative differences signify lower extraction compared to hexane. This comparative approach allows for a direct assessment of the relative extraction capabilities of these two solvents across various oil components.

Regarding free fatty acids (FFA), ethanol demonstrates inconsistent results: nine references report positive differences, while five show negative differences. Liauw *et al.* (2008) observed a significant negative difference in neem oil extraction, which they attributed to the presence of an active lipase in the seeds. This enzyme was capable of hydrolysing triacylglycerols during hexane extraction. However, when ethanol was employed, it denatured the enzyme, inhibiting its activity, as previously discussed. In contrast, Ayoola *et al.* (2014) reported a much weaker difference in their neem seed study, possibly due to the use of drier seeds during extraction. In cases where ethanol does not affect lipase activity, it appears to extract FFA more efficiently. This is particularly evident in rice bran oil, which typically exhibits high oleic acidity due to lipase action during rice grain polishing. Interestingly, this enhanced extraction is not explained by the Hansen solubility parameters, specifically considering the Ra distance between ethanol and free oleic acid calculated in Table 4 of Part 1 of this series of articles. Conversely, Batista *et al.* (1999) demonstrated that FFA can be extracted from vegetable oils using liquid-liquid extraction with short-chain alcohols, a result not predicted by the Hansen Solubility Parameters (HSP).

Regarding peroxide values, the results are heterogeneous, with three positive cases and six negative ones. The most significant positive difference was observed in canola oil extracted with ethanol by Sanchez *et al.* (2018). The authors attribute these differences to the additional processing steps required to obtain the final oil, as the presence of non-lipid compounds in ethanol extracts necessitated further operations compared to hexane extraction. They do not attribute the oil oxidation directly to the solvent but rather to its lack of specificity and the subsequent purification steps required to fractionate the extract. Bhatnagar and Gopala (2013) propose that the lower PV in their ethanol extract may be due to higher concentrations of antioxidants and Maillard reaction products co-extracted with the oils, potentially inhibiting hydroperoxide formation during extraction. Similarly, Sbihi *et al.* (2018) suggest that phenolic compounds, more readily extracted by ethanol, could protect the oil against oxidation. Based on these observations, it can be inferred that ethanol extraction is unlikely to have a direct impact on the peroxide value. However, any indirect effects, particularly those arising from the necessity of additional processing steps to remove non-lipid extracts, should be carefully managed to prevent oxidation. The presence of natural antioxidants in ethanolic extracts may inhibit oxidation in crude oils prior to refining and potentially mitigate the adverse impacts of the additional processing steps. In conclusion, while ethanol extraction itself may not directly influence PV, the associated extraction of non-lipid compounds and subsequent processing requirements can indirectly affect oil oxidation. Further research is warranted to optimize ethanol extraction processes and leverage the potential benefits of co-extracted antioxidants in maintaining oil quality.

Concerning the fatty acid profile, minor variations in oil composition have been observed in the majority of studies (eight out of eleven). These modifications in major fatty acids alter the profiles by up to 2–3%, which, while modest, represent statistically significant variations in composition.

Table 1. Literature data comparing oils from ethanol *vs.* hexane (results = ethanol − hexane).

Reference	Seeds	FFA%	PV (Meq O_2/kg)	Fatty acid profile (*vs.* hexane)	PL (%)	USM %	Total phenol (mg/kg)	Tocos (mg/kg)	Sterols (mg/kg)	Waxes (mg/kg)
Baülmer *et al.*	Sunflower press-cake				0.38			−13		−431
Bhatnagar and Gopala	Indian Niger	8.46	−4.5	↗ C18:2 (2%)		3	2002	161	4958	
Breil *et al.*	Yarrowia lipolitica			ns	↗PE, PC					
Loyao *et al.*	Spent coffee ground	−0.8		ns		−5		306		
Magalhães *et al.*	Peanut press cake	−0.65		↗ C16:0 (0.3%) ↘ C22:0 (0.2%)						
Sanchez *et al.*	Canola / simple dist.	0.33	3.87				56 *	377		
	Canola / multistep	0.45	7.74				ns	306		
Santos *et al.*	Favela seeds						15.9	−16	−62	
Sbihi *et al.*	Castor Zanzibariensis	0.14	−3.89	↗ Ric. (2.1%)		0.02		−77	48	
	Castor Impala,	0.31	−4.04	↗ Ric. (3.6%)	0.0	0.08		−177	122	
Chaabani *et al.*	Lentik, ground			↗ PUFA (2.1%)	0.15					
Liauw *et al.*	Neem seeds	−56	−2							
Ayoola *et al.*	Neem	−0.35								
Oladipo and Betiku	Moringa kernel,	2.43	0.95	↘ ΣMUFA (2.5%)						
Bandura *et al.*	Sunflower cake	−0.3	−0.2	↗ C8:2 (0.25%)	−0.04					
Tir *et al.*	Sesame			ns				35	384	
Capellini *et al.*	Rice bran (100%)	11.2			−0.37		100	207		
	Rice bran (95%)	12.6			0.27		1800	252		
Jedidi *et al.*	Tecoma seeds	1.9	−0.5	↗ C8:1 (3.6%)				239		
Number of positive differences		**9**	**3**		**4**	**3**	**5**	**8**	**4**	**0**
Number of negative differences		**5**	**6**		**2**	**1**	**0**	**4**	**1**	**1**

*: canolol; FA: free fatty acids; MUFA: monounsaturated fatty acids; ns: no significant difference; PC: phosphatidycholine; PE: phosphatidylethanolamine; phenol: phenolic compounds; PL: phospholipids; PUFA: polyunsaturated fatty acids; PV: peroxide value; Ric.: ricinoleic acid; Tocos: tocopherols + tocotrienols; USM: unsaponifiable matter.

Analysis of the fatty acid profiles from various results does not reveal consistent trends, such as a preference for more unsaturated fatty acids from one solvent to another. In the case of ricinoleic acid, a higher concentration is logically expected due to the presence of a hydroxyl group, similar to that found in alcohols, potentially enhancing oil-solvent interactions.

Regarding phospholipids, four studies report positive results and two negatives. As previously discussed, solvents with higher polarity tend to extract polar lipids more efficiently. However, the extraction process becomes more complex when the solvent is miscible with water, as this water can bind to phospholipids, rendering them insoluble in oil. Consequently, analytical results may vary depending on the sampling methodology employed.

The extraction of phenolic compounds demonstrates a more consistent trend, with superior extraction observed in all five studies. The differences are substantial, given that hexane is a poor solvent for these compounds. The enhanced extraction efficiency can be attributed to the shared hydroxyl groups between ethanol and polyphenols, which facilitates their interaction and subsequent extraction.

The presence of a hydroxyl group in tocopherols and sterols is counterbalanced by their large hydrophobic domains. According to the Hansen solubility parameters (HSP) presented in Table 4 of Part 1 of this series of articles (physical properties), hexane should theoretically provide superior extraction yields for these substances. However, empirical data reveal a discrepancy with this prediction. For tocopherols, eight cases demonstrated positive results and four negatives, contradicting the HSP-based prediction. Similarly, for sterols, the majority of results indicated higher concentrations in ethanol-extracted oil, with only one case showing a lower value. This apparent inconsistency can be elucidated by considering the localization of tocopherols and sterols within phospholipid membranes. Tocopherols exert their antioxidant activity within these membranes (Wang and Quinn, 2000), while sterols play a crucial role in maintaining membrane microfluidity and regulating important biological processes (Dufourc, 2008). Polar solvents such as ethanol can more effectively disrupt these membranes, thereby enhancing the accessibility of tocopherols and sterols for extraction. This phenomenon aligns with the observed higher unsaponifiable content in four cases. It is noteworthy that in the sole study analysing waxes in sunflower oil, this parameter appeared less extractable in ethanol. This observation suggests that the extraction behaviour of different lipid components may vary based on their specific chemical properties and structural characteristics. These findings underscore the complexity of solvent-based extraction processes and highlight the importance of considering not only the solubility parameters but also the structural organization of lipid components within cellular membranes when predicting and interpreting extraction efficiencies.

Ethanol demonstrates a significant impact on oil quality due to its enhanced affinity for minor lipids. This advantageous effect, however, may be offset by the concurrent extraction of additional impurities, potentially necessitating a purification step. Such purification processes, especially those involving water-based washings, could potentially negate some of the initial benefits. It is crucial to note that the majority of literature findings stem from laboratory-scale extractions, which may not accurately represent industrial-scale countercurrent extraction processes involving oil-solvent separation methods without distillation. When considering this broader perspective, it is reasonable to anticipate that the solvent's effect on minor compounds may be less pronounced, as some of these compounds are likely to be retained in the lean miscella and subsequently returned to the meal.

4 Isopropanol *vs.* hexane

Table 2 presents fifteen studies encompassing nineteen potential comparisons. Regarding oleic acidity, ten cases demonstrated that isopropanol (IPA) yielded oils with lower acidity, while five exhibited higher acidity. Similar to ethanol, the most substantial differences were observed in rice bran, which underwent significant hydrolysis prior to extraction. In this instance, IPA demonstrated superior extraction of free fatty acids (FFAs). In the studies conducted by Backer and Sullivan (1983) and Harris and Hayward (1950), the IPA oils were recovered using a non-distillation method, which explains four negative results. Notably, the water concentration in IPA did not significantly affect the FFA levels. Loyao *et al.* (2018) suggested the possibility of hydrolysis occurring during hexane extraction, while Seth *et al.* (2010) and Jisieike and Betiku, (2020) did not provide explanations for their observations. Shah and Venkatesan (1989) investigated the liquid-liquid extraction of FFAs using IPA and found that FFAs preferentially partitioned into the isopropanol phase. While Hansen solubility parameters offer a valuable framework for predicting solubility, they do not fully account for the intricacies of liquid-liquid extraction systems. Specifically, they do not consider the unique interactions and phase behaviours that play a crucial role in the selective extraction of FFAs using short-chain alcohols.

The peroxide values also give a mixed results with three positives and two negatives. The authors of the studies did not elaborate on the causes of these differences.

Regarding the fatty acid profile, the majority of studies (seven out of eight) reported either non-significant differences (four studies) or relatively minor variations. However, Chaabani *et al.* (2019) observed a notable deviation, with isopropanol (IPA)-extracted oil exhibiting higher linoleic acid content and lower oleic acid content compared to hexane-extracted oil. The authors did not provide a detailed explanation for this discrepancy, leaving the underlying mechanism open to further investigation.

Hansen Solubility Parameters predict a higher affinity of phospholipids for isopropanol compared to hexane. However, Baker and Sullivan's (1983) work reported lower phospholipid content in IPA-extracted oils, attributed to their oil recovery method, which retained polar lipids in the lean miscella. Breil *et al.* (2016) observed higher concentrations of phosphatidylcholine and phosphatidylethanolamine in IPA-extracted oil, aligning with theoretical expectations. Capellini *et al.* (2017) using a pressurised reactor, demonstrated significant variations in phospholipid content of rice bran oils extracted using ethanol or IPA, contingent upon solvent water content (6% in ethanol, 12% in IPA) and extraction temperature (60 °C or 80 °C). In ethanol extractions at 80 °C, water presence increased phospholipid concentration from 4.83% to 5.5%, while no significant difference was observed at 60 °C. Similarly, with IPA at 60 °C, phospholipid concentration increased from 3.52% to 4.16%, whereas at 80 °C, the concentrations were not statistically different. Due to these inconsistencies, the authors refrained from further elaboration on water's effect on phospholipid yields. The differences reported by Proctor and Bowen (1996), as well as those found by Chaabani *et al.* (2019), were relatively minor.

Regarding phenolic compounds, the results are comparable to those observed with ethanol, with all available studies demonstrating enhanced extraction using isopropanol. For tocopherols and sterols, the findings are heterogeneous. Tocopherols exhibited positive shifts in five out of eight cases, while sterols showed positive shifts in two out of four cases. As with ethanol, these differences appear to be less related to the reciprocal Hansen Solubility Parameters (HSP) of the solutes and solvent, and more attributable to the capacity of polar solvents to dissolve the membranes in which these substances are located. Concerning the unsaponifiable content of oil, only two results were available. The study on spent coffee oil showed inconsistency with the higher tocopherol concentration observed. However, it is worth noting that spent coffee grounds possess unique characteristics that limit the extrapolation of these findings to other oilseeds. Saponins in camellia seeds were equally retrieved by both solvents. Johnson and Lusas (1983) observed that IPA-water at azeotropic concentration extracted gossypol from cotton seeds more rapidly than oil, but more slowly than aflatoxin. This finding is particularly significant as it allows for the removal of gossypol from the meal, potentially enhancing the value of the proteins in the feed sector. According to Tanksley (1990), the presence of gossypol in hexane-extracted cottonseed meal is approximately 0.1%, which precludes its use in the diet of monogastric animals.

Overall, isopropyl alcohol exhibits effects on oil quality similar to those of ethanol, with a substantial portion of these effects linked to the oil recovery method—an aspect often overlooked in laboratory studies. Examination of the work by Baker and Sullivan and Harris and Hayward indicates that crude oil could potentially benefit from a significant reduction in free fatty acids (FFAs) and phospholipids when employing a non-distillation scheme. While the fatty acid profile is unlikely to undergo substantial modification, the retention of tocopherols and sterols in the lean miscella may occur if the partitioning follows patterns observed by Citeau *et al.* (2018) in their study of alcoholic deacidification of walnut oil through ethanol fractionation. In the final report on the potential replacement of hexane with IPA, conducted by Texas A&M University, Lusas (1997) did not provide data on tocopherols and sterols. This gap in the literature underscores the need for further research to elucidate the effects of this alternative extraction method on oil quality. Additional studies are required to observe and quantify

Table 2. Literature data comparing oils from isopropanol *vs.* hexane (result = IPA − hexane).

Reference	Seeds	FFA%	PV (Meq O_2/kg)	Fatty acid profile (*vs.* hexane)	PL (%)	USM%	Total phenol (mg/kg)	Tocos (mg/kg)	Sterols (mg/kg)
Baker and Sullivan	Soy (flakes) IPA 85	−0.78	0.0		−411 (ppm)				
	Soy (flakes) IPA 87.7	−0.61	0.2		−414 (ppm)				
	Soy (flakes) IPA 90.5	−0.66	0.2		−420 (ppm)				
Breil *et al.*	Yarrowia lipolitica			ns	↗PE, PC				
Cao *et al.*	Peony seeds (ground)			↘ PUFA (1.1%)			12.9	−24	−492
Harris and Hayward	Cotton seeds flakes	−0.9							
Li *et al.*	Rapeseed	0.3		ns				−18	448
Loyao *et al.*	Spent coffee ground	–		ns		−4.5		343	
Santos *et al.*	Favela seeds ground	−0.2		↘ C18:0 (0.6%)			35.2	−5	−3
Chaabani *et al.*	Lentik, ground			↗ PUFA (3.1%)	0.08				
Jisieike and Betiku	Rubber seeds ground	−0.69	−2.7	↘ C8:3 (0.6%)					
Seth *et al.*	Soy flakes reflux –	−1.15							
	Soy flakes, reflux +	−0.95							
Tir *et al.*	Sesame			ns				174	1312
Capellini *et al.*	Rice bran dry	8.9			−0.57		600	262.28	
	Rice bran 88	5.9			−0.43		1100	181.62	
Proctor and Bowen	Rice bran *vs.* Eth P	0.1			−10 (ppm)				
Uoonlue *et al.*	Camelia seeds	1.47	−1.32		0	ns #	297	69	
Nwabueze *et al.*	African Breadfruit	−0.06	0.63					−25.6*	
Number of positive differences		**5**	**3**		**2**	**0**	**5**	**5**	**2**
Number of negative differences		**10**	**2**		**6**	**1**	**0**	**3**	**2**

FFA: free fatty acids; PV: peroxide value; PL: phospholipids; phenol: phenolic compounds; Tocos: tocopherols + tocotrienols; ns: no significant difference; #: saponin; *: Vitamin E; USM: unsaponifiable matter.

the impact of this potential oil extraction method on various quality parameters.

5 Methanol *vs.* hexane

Table 3 presents the only available study reporting the effect of methanol on oil quality. The effects of methanol extraction compared to hexane extraction have been reported in only one study. The methanol-extracted oil exhibited significantly higher acidity than its hexane-extracted counterpart, aligning with the observed effects of other alcohols on free fatty acids. Similar to ethanol, the reduction in peroxide value was attributed to the extraction of antioxidants and Maillard reaction products, which are hypothesized to inhibit hydroperoxide formation. Regarding phenolic compounds, methanol is a widely recognized solvent for their extraction; thus, the higher concentration of these compounds in methanol-extracted oil is consistent with expectations. The observed concentrations of tocopherols and sterols are likely explained by the same indirect effect of membrane disruption characteristic of alcohols, as previously noted with other alcohol-based extractions.

6 Acetone *vs.* hexane

As shown in Table 4, the literature on acetone as an extraction solvent is less extensive than that on alcohols with only six studies available for analysis. Among these, Giuffré *et al.* (2017) utilized petroleum ether as a comparison solvent instead of hexane. Five studies examined oleic acidity, with four reporting higher acidity in acetone-extracted oils. Notably, the sole study demonstrating a negative difference employed 95% acetone in a non-distillation scheme on cotton seeds, where the majority of free fatty acids were retained in the lean miscella and subsequently returned to the extractor. Similar to alcohols, acetone demonstrates superior FFA extraction efficiency. However, this characteristic may be more readily attributed to the Hansen solubility parameters of FFAs and acetone, in contrast to alcohols where hydrogen bonding is likely to play a more significant role in the extraction process.

Peroxide values of acetone-extracted oils compared to those extracted with hexane (or petroleum ether) were lower in three observations and higher in one. Giuffré *et al.* attributed the difference in PV to the lower extraction temperature for acetone oils in the Soxhlet apparatus. As previously noted, Bhatnagar *et al.* associated the lower PV with enhanced extraction of antioxidant compounds.

Regarding fatty acid composition, five comparisons reported no significant differences, while one observed a slight reduction in the sum of polyunsaturated fatty acids. These findings suggest that acetone extraction likely has minimal impact on the fatty acid profile of the extracted oils.

In the context of phospholipid extraction, the absence of studies reporting phospholipid concentrations is both notable and expected, given the well-established low solubility of phospholipids in acetone—a solvent widely employed in

Table 3. Literature data comparing oils from methanol *vs.* extraction (results = MeOH − hexane).

Reference	Seeds	FFA%	PV (Meq O_2/kg)	Fatty acid profile (*vs.* hexane)	USM%	Total phenol (mg/kg)	Tocos (mg/kg)	Sterols (mg/kg)
Bhatnagar and Gopala	Ground seeds of Indian niger	6.12	−4.4	ns	2.64	2384	103	4790

FFA: free fatty acids; PV: peroxide value; PL: phospholipids; phenol: phenolic compounds; Tocos: tocopherols + tocotrienols; ns: no significant difference; USM: unsaponifiable matter.

Table 4. Literature data comparing oils form acetone and hexane (result = acetone − hexane).

Reference	Seeds	FFA%	PV (Meq O_2/kg)	Fatty acid profile (*vs.* hexane)	PL (%)	USM%	Total phenol (mg/kg)	Tocos (mg/kg)	Sterols (mg/kg)
Bhatnagar and Gopala	Indian Niger	1.83	−3.1	ns		1.26	230	23	4688
Cao *et al.*	Peony seeds			↘ PUFA (0.8%)			18.4	−15	−102
Harris and Hayward	Cotton seeds	−0.7							
Giuffrè *et al.*	Tomato seeds *	0.39	−3.3	ns			38		
	Tomato seeds *	1.07	−0.96	ns			118		
Gao *et al.*	Walnuts			ns			53	4	−281
Tir *et al.*	Sesame			ns			34	901	
Nwabueze and Okocha	African Breadfruit	0.07	0.58					−31#	
Number of positive differences		**4**	**1**			**1**	**5**	**3**	**2**
Number of negative differences		**1**	**3**			**0**	**0**	**2**	**2**

FFA: free fatty acids; PV: peroxide value; PL: phospholipids; phenol: phenolic compounds; Tocos: tocopherols + tocotrienols; ns: no significant difference; #: saponin; *: comparison with petroleum ether; USM: unsaponifiable matter.

industry for triacylglycerol removal from lecithin. The Hansen Solubility Parameter Ra distances presented in Table 4 of the first article of this series for phosphatidylcholine or phosphatidic acid in acetone are shorter than those in hexane, suggesting better miscibility. However, this theoretical prediction, analogous to the behaviour of free fatty acids in alcohols, is contradicted by empirical observations. The primary factor contributing to phospholipid insolubility in acetone lies in their molecular structure. Phospholipids comprise a hydrophilic phosphate head group and two hydrophobic fatty acid tails. While the nonpolar fatty acid tails could potentially dissolve in acetone, the highly polar phosphate group renders phospholipids overall quite polar and insoluble in nonpolar solvents such as acetone. The phosphate group forms strong hydrogen bonds with water molecules, enhancing phospholipid solubility in polar protic solvents like water, methanol, or chloroform/methanol mixtures. Acetone, being an aprotic solvent, cannot effectively disrupt these hydrogen bonds and solvate the phosphate group. Furthermore, phospholipids exhibit a tendency to self-assemble into bilayer structures in aqueous environments due to their amphiphilic nature. This organized structure further diminishes their solubility in nonpolar aprotic solvents like acetone. Methyl ethyl ketone, possessing similar aprotic properties, is also likely to be a poor solvent for phospholipids. However, the presence of water in these solvents alters this property, with water concentration modulating phospholipid solubility in ketones (Kinoshita *et al.*, 1997).

Acetone, similar to alcohols, demonstrates superior extraction of phenolic compounds compared to hexane, aligning with predictions based on their Hansen Solubility Parameter Ra distances. However, the results for tocopherols and sterols present a more nuanced picture. For tocopherols, three positive and two negative differences were observed, while sterols exhibited an equal distribution of two positive and two negative differences. The Hansen solubility criteria predicted lower miscibility for these compounds in acetone. Additionally, acetone's immiscibility with phospholipids was expected to impede the disruption of bonds between these molecules and cellular membranes. However, the observed results suggest that other factors may have counteracted these characteristics, which would otherwise have led to a predominance of negative outcomes. Once again, this discrepancy between theoretical predictions and empirical observations underscores the complexity of solvent-solute interactions in multicomponent systems and highlights the need for further investigation into the mechanisms governing the extraction of these bioactive compounds.

7 Ethyl acetate *vs.* hexane

Table 5 summarizes nine studies comparing oils extracted with hexane and ethyl acetate, along with one study using petroleum ether instead of hexane. All four studies examining

Table 5. Literature data comparing ethyl acetate and hexane (result = EA − hexane).

Reference	Seeds	FFA%	PV (Meq O_2/kg)	Fatty acid profile (*vs.* hexane)	PL (%)	USM%	Total phenol (mg/kg)	Tocos (mg/kg)	Sterols (mg/kg)
Breil *et al.*	Yarrowia lipolitica			ns	ns				
Cao *et al.*	Peony seeds			↘ PUFA (0.3%)			3.8	6	
Lohani *et al.*	Rapeseed					−0.12			
	Camelina					−0.14			
	Flax					−0.2			
	Mustard					−0.21			
Loyao *et al.*	Spent coffee ground	0.4		ns		−4		518	
Santos *et al.*	Favela seeds			ns			15.9	−16	−62
Chaabani *et al.*	Lentik, ground			↗ PUFA (0.5%)	0.005				
Giuffrè *et al.**	Tomato seeds	0.31	1.25	ns			500		
	Tomato seeds	5.91	0.51	ns			559		
Oladipo and Betiku	Moringa kernel	2.45	0.55	↘ ΣMUFA (0.5%)					
Gao *et al.*	Walnuts			↗ C18:3 (0.4%)			−5	−3	13
Number of positive differences		**4**	**3**		**1**	**0**	**4**	**2**	**1**
Number of negative differences		**0**	**0**		**0**	**5**	**1**	**2**	**1**

FFA: free fatty acids; PV: peroxide value; PL: phospholipids; phenol: phenolic compounds; Tocos: tocopherols + tocotrienols; ns: no significant difference; *: comparison with petroleum ether; USM: unsaponifiable matter.

free fatty acid content consistently reported higher levels in EA-extracted oils, aligning with predictions based on Hansen Solubility Parameter Ra distances. Similarly, the three available observations on peroxide values indicated higher levels in EA-extracted oils.

Regarding fatty acid profiles, nine comparisons were conducted. Five of these reported no significant differences, while the remaining four exhibited only minor variations without a discernible trend. These findings suggest that ethyl acetate extraction is unlikely to substantially alter the fatty acid profile of the extracted oils.

Limited data are available regarding phospholipid content in oils extracted with ethyl acetate compared to hexane. Breil *et al.* (2016) reported non-significant differences in oleaginous yeast extracts, while Chaabani *et al.* (2019) observed only minimal variations in Lentisk oil. The Hansen Solubility Parameter Ra distance criterion predicts favourable miscibility between EA and phospholipids. However, as previously noted, this criterion has not proven to be a reliable predictor of phospholipid behaviour in the solvents under consideration. Ethyl acetate, despite being classified as aprotic as ketones, demonstrates the capacity to dissolve phospholipids under certain conditions, such as in the presence of water or neutral lipids (Breil *et al.*, 2017).

Phenolic compounds were found in higher concentrations in four studies and lower in one, aligning with predictions based on Hansen Solubility Parameter criteria. Tocopherols and sterols exhibited balanced results, with an equal number of positive and negative differences compared to hexane extraction. For these substances, the HSP Ra distances with both solvents are relatively similar, which may explain the lack of a clear trend. Lohani *et al.* (2015) and Loyao *et al.* (2018) reported exclusively negative differences in unsaponifiable matter content. This observation is likely not attributable to tocopherols and sterols, as Loyao *et al.* noted a substantial positive difference for tocopherols specifically.

8 Halogenic solvents *vs.* hexane

Table 6 presents results for dichloromethane alongside those for chloroform and methanol-chloroform mixtures, due to the scarcity of direct comparisons with hexane.. Regarding free fatty acids, Giuffré *et al.* (2017) observed divergent results contingent upon their extraction method when using petroleum ether in lieu of hexane. The initial results were derived from hexane extraction, while the subsequent findings were obtained using a pressurized extractor. Consequently, under standard conditions, it is plausible that chloroform exhibits superior FFA extraction efficiency. Furthermore, the Hansen Solubility Parameters Ra distance criterion predicts enhanced miscibility between FFA and dichloromethane (DCM) compared to hexane.

Peroxide values are exclusively available for chloroform, albeit exhibiting divergent results in atmospheric extraction. Fatty acid profiles remain largely unaltered, as evidenced by four non-significant results. Johnson *et al.* (1986) observed contrasting effects on phospholipids contingent upon the presence of methanol in the solvent. Pure dichloromethane demonstrates lower Hansen Solubility Parameters Ra distances with phospholipids compared to hexane, while methanol exhibits the inverse relationship. This predictor also indicates superior compatibility between DCM and phenolic compounds relative to hexane, aligning with observed results. Conversely, hexane, tocopherols, and sterols display closer HSP Ra distances than DCM, a finding not corroborated by the limited available data.

9 2-Methyloxolane *vs.* hexane

Table 7 summarizes six studies comparing the effects of 2-methyloxolane and hexane on oil quality. Only one study addressed oil acidity, reporting positive results for both

Table 6. Literature data comparing oils form halogenic solvents (HS) and hexane (result = HS − hexane).

Reference	Solvent	Seeds	FFA%	PV (Meq O_2/kg)	Fatty acid profile (*vs.* hexane)	PL (%)	Total phenol (mg/kg)	Tocos (mg/kg)	Sterols (mg/kg)
Johnson *et al.*	DCM	Cottonseed				200	# 0.07%		
	DCM+MeOH	Cottonseed				−464			
Tir *et al.*	DCM	Sesame			ns			26	673
Giuffrè *et al.*	Chloroform	Tomato seeds *	0.28	−2.21	ns		52		
	Chloroform	Tomato seeds.*	−0.86	−6.58	ns		57		
Jedidi *et al.*	Chloroform	Tecoma seeds	0.8	1.5	↗ C8:1 (2.6%)			99.0	
Tir *et al.*	DCM+MeOH	Sesame			ns			56	734
Number of positive differences			**2**	**1**		**1**	**3**	**3**	**2**
Number of negative differences			**1**	**2**		**1**	**0**	**0**	**0**

FFA: free fatty acids; PV: peroxide value; PL: phospholipids; phenol: phenolic compounds; Tocos: tocopherols + tocotrienols; ns: no significant difference; *: comparison with petroleum ether.

anhydrous and water-saturated 2-MeOx. Three studies demonstrated a significant increase in peroxide value for 2-MeOx-extracted oils. The presence of water appears crucial in mitigating the significance of hydroperoxides. Although the direct comparison of results from a limited number of studies employing diverse extraction methods on various plant matrices may lack methodological rigor, an interesting trend emerges regarding 2-methyloxolane. It exhibits a substantially higher mean peroxide value of 13.3 MeqO_2/kg compared to ethanol, isopropyl alcohol, acetone, and ethyl acetate, which have mean values of −0.31, −0.50, −1.70, and 0.77 MeqO_2/kg, respectively. This discrepancy may be attributed to hydroperoxide formation in the solvent during storage, which could subsequently transfer to the oils during extraction. Experimental conditions may have exacerbated this effect, as laboratory protocols typically employ larger solvent quantities than industrial counter-current extraction processes. In industrial settings, the solvent is continuously regenerated at temperatures conducive to hydroperoxide decomposition and free radical elimination upon contact with antioxidants present in the oil-bearing material. However, this hypothesis necessitates validation through extended-duration trials under authentic industrial conditions.

Regarding fatty acid profiles, as observed with other solvents, a preponderance of non-significant results has been reported (five out of seven). When differences are detected, they remain minimal. The quantities of phospholipids extracted by 2-methyloxolane are consistently higher than those obtained with hexane in the three available studies, aligning with the Hansen Solubility Parameters predictor. Claux *et al.* (2021) demonstrated that soybean oil extracted using anhydrous 2-methyloxolane in a Soxhlet apparatus contained 123% more phospholipids than oil extracted with hexane under identical conditions. Water-saturated 2-MeOx yielded oil with a 178% increase in phospholipid content. Among the phospholipid classes, phosphatidylcholine exhibited the most substantial concentration increase, rising by 204% with anhydrous 2-MeOx and 286% with water-saturated 2-MeOx. This finding corroborates the results reported by Sicaire *et al.* (2015). Conversely, Breil *et al.* (2016) conducted a comparative analysis of various solvents for lipid extraction from dried biomass of the yeast *Yarrowia lipolytica*. Their investigation revealed an absence of phospholipids in hexane and 2-MeOx extracts, while phosphatidylcholine and phosphatidylethanolamine constituted 3.5% of the ethanol extract and 5.19% of the isopropyl alcohol extract. In the case of ethyl acetate and dichloromethane, no phosphatidylcholine was detected, and phosphatidylethanolamine comprised 1.25% of the EA extract and 0.93% of the DCM extract.

In the context of phenolic compounds, all eleven results demonstrate a positive trend, aligning with the Hansen Solubility Parameters (HSP) prediction. Tocopherols similarly exhibit this tendency, with four positive outcomes and one negative, despite the HSP Ra distance being lower for 2-methyloxolane (2-MeOx). More intriguingly, sterols present three negative results, which is contrary to expectations given their presumed higher miscibility in 2-MeOx based on HSP predictions.

10 Discussion and conclusion

The comparative analysis of various solvents for vegetable oil extraction reveals significant variations in their impact on oil quality, particularly regarding polar lipids. The fate of phospholipids is intricately linked to the oil recovery method when using ethanol or isopropanol. Cold precipitation techniques retain PLs in the lean miscella, which are subsequently returned to the extractor. Long-duration trials conducted at Texas A&M University's pilot plant demonstrated that the phosphorus concentration in crude oil obtained after precipitation at 25 °C was 481 ppm for isopropanol *vs.* 451 ppm for hexane with soybean oil, and 592 ppm *vs.* 651 ppm with cottonseed oil, respectively. Hexane and anhydrous ethyl acetate exhibit poor efficacy in phospholipid extraction. Conversely, ketones render PLs immiscible, potentially yielding phosphorus-free oils, although this has not been experimentally confirmed. Other solvents, such as dichloromethane and 2-methyloxolane, demonstrate enhanced PL extraction rates. These affinity characteristics for polar lipids are also likely to interact with preparation methods. For instance, it is known that the use of expanders on hexane-extracted soybean flakes can increase the phosphorus concentration in the oil by approximately

Table 7. Literature data comparing oils for 2-methyloxolane extraction and hexane (result = 2MeOx − hexane).

Reference	Seeds	FFA%	PV (Meq O_2/kg)	Fatty acid profile (*vs.* hexane)	PL (%)	USM%	Total phenol (mg/kg)	Tocos (mg/kg)	Sterols (mg/kg)
Bartier *et al.*	Soy flakes 99%		9.8	↗ ΣMUFA (0.2%)		0.2	3085		
Bourgou *et al.*	Black cummin seeds,			↘C18:0 (1.8%) ; ↘C20			2300	94	
	Black cummin seeds,			ns			900	25	
Breil *et al.*	Yarrowia lipolitica			ns	↗ PE				
Claux *et al.*	Soybean flakes 95.5%	1.85	10.94	ns	3.31 (%)			27	−161
	Soybean flakes (dry)	1.1	19.2	ns	1.9 (%)			26	−99
Rapinel *et al.*	Soybean flakes+ water						1113		
	Soybean flakes dry						284		
	Rapeseed + water						373		
	Rapeseed dry						115		
	Corn germs + water						55		
	Corn germs dry						293		
	Cotton seeds + water						342		
	Cotton seeds dry						143		
Sicaire *et al.*	Rapeseed, cake			ns				−62	−710
Number of positive differences		**2**	**3**		**3**	**1**	**11**	**4**	**0**
Number of negative differences		**0**	**0**		**0**	**0**	**0**	**1**	**3**

FFA: free fatty acids; PV: peroxide value; PL: phospholipids; phenol: phenolic compounds; Tocos: tocopherols + tocotrienols; ns: no significant difference; USM: unsaponifiable matter.

30% (Zhang *et al.*, 1994). In the case of a solvent that efficiently extracts polar lipids, such as 2-MeOx, the increase is likely to be less pronounced due to a higher extraction yield with regular flakes.

An increased recovery of PLs could be advantageous if lecithin is valorised after drying. However, it may prove disadvantageous if returned to the meal following a water degumming step, as some neutral oil is lost during this process. Galhardo and Dayton (2021) reported that 30–38% of non-PL lipids in the dry matter of water degumming gums are lost. This excess of PLs may partially explain the improved oil yields observed by several authors in solvent comparisons. It is noteworthy that this apparent yield enhancement could be significantly diminished after water degumming.

The interactions between membrane lipids and solvents can enhance the recovery of lipids preferentially located in membranes, such as sterols and tocopherols. For ethanol and isopropyl alcohol, this effect likely elucidates the discordance between experimental results and the poor theoretical miscibility with these substances. Acetone and ethyl acetate may be considered analogous to hexane for these compounds, albeit with potential divergences contingent upon the matrices and extraction methods employed. 2-Methyloxolane appears to exhibit higher extraction efficiency for tocopherols but lower efficiency for sterols compared to hexane. This observation is somewhat counterintuitive when considering the Hansen Solubility Parameter Ra distance between these solvents and the compounds of interest. For hexane, the Ra distances are 5.61 and 5.73 for γ-tocopherol and campesterol, respectively. In contrast, 2-MeOx shows Ra distances of 3.11 and 3.44 for the same compounds (Table 4, Article 1 of this series). While there is a slight difference between the Ra values for tocopherol and sterol with 2-MeOx, this disparity is minimal compared to the substantial gap observed with hexane. The discrepancy between the expected and observed extraction efficiencies could be attributed to two potential factors. Firstly, the limited available data may not provide a statistically significant observation. Alternatively, it is plausible that under real-world conditions, HSP distances may not serve as a sufficiently reliable predictor of extraction efficiency. This phenomenon has been previously observed in the case of phospholipids and acetone, suggesting that the complexity of actual extraction systems may not be fully captured by HSP calculations alone.

Most studies report minimal changes in fatty acid profiles between different extraction solvents. When differences are observed, they are typically small (1–3% changes in major fatty acids). Ethanol and isopropanol occasionally show slight increases in polyunsaturated fatty acids compared to hexane. 2-MeOx has shown minor increases in monounsaturated fatty acids in some cases. Overall, solvent choice does not appear to substantially alter the fatty acid composition of extracted oils. The consistency in fatty acid profiles across different solvents is advantageous, as it ensures that the dietary intake of these essential nutrients remains largely unaffected by the choice of extraction method.

Polar solvents like ethanol, isopropanol, and acetone consistently extract higher amounts of phenolic compounds compared to hexane. 2-MeOx also shows superior extraction of phenolics. Ethyl acetate generally extracts more phenolics than hexane but less than alcohols. Chlorinated solvents like dichloromethane also extract more phenolics than hexane. The increased extraction of phenolic compounds can enhance the protection of the oils against the oxidation during extraction and crude oil storage, but after refining only a slight fraction of these substances will remain the final oil.

The peroxide value (PV) serves as a critical indicator of oil oxidation and quality. Various extraction solvents exhibit

differential impacts on the PV of oils. Alcohols such as ethanol and isopropanol typically yield lower PVs compared to hexane, presumably due to enhanced extraction of antioxidant compounds. Acetone similarly tends to produce oils with lower PVs than hexane. Chlorinated solvents like dichloromethane demonstrate inconsistent results. Generally, polar solvents appear to better preserve oil quality in terms of PV. However, 2-methyloxolane has been observed to significantly elevate PVs, potentially due to the transfer of hydroperoxides formed in the solvent during extraction. Experimental methodologies may have exaggerated this trend. For instance, Soxhlet extraction at high temperatures could degrade antioxidants added to stabilize 2-MeOx, promoting solvent oxidation and subsequently altering the PV of the extracted oil. Additionally, the evaporation process under reduced pressure at 40 °C might lead to triglyceride hydrolysis and oil oxidation. Further research is warranted to more accurately assess this potential adverse effect of 2-MeOx on oil quality, particularly under conditions more representative of industrial extraction processes. Long-duration trials under authentic industrial conditions could provide more definitive insights into the impact of 2-MeOx on oil oxidation and quality.

The first part of this article has highlighted the significant impact that different solvents can have on enzyme activity during oil extraction. The presence of water in the solvent can enhance enzyme activity, leading to the formation of undesirable compounds such as free fatty acids and non-hydratable phospholipids. Hexane, due to its low water content, inhibits phospholipase activity to some extent but does not completely suppress it. In contrast, solvents such as ethyl acetate or 2-methyloxolane may potentially enhance phospholipase activity when used at their water saturation levels, as they introduce additional water into the extraction system. Alcohols can denature proteins and reduce enzyme activity due to their ability to disrupt hydrogen bonding and hydrophobic interactions. These aspects must be taken in consideration in the retrofitting of existing extraction plants to avoid negative impacts on the oil quality.

The Hansen solubility parameter approach has shown its utility and relevance, but also its limits in these solvents comparisons. Notable discrepancies between HSP predictions and experimental extraction results show that other parameters are also coming into play. For example, HSP calculations often predict better solubility and extraction at lower temperatures, while experimental studies frequently show improved extraction yields at higher temperatures (Sanchez-Camargo *et al.*, 2019). This mismatch likely stems from HSP theory not accounting for temperature-dependent factors like increased vapour pressure of solutes at elevated temperatures, which can enhance extraction. Additionally, HSP predictions are based solely on molecular interactions, while actual extraction processes involve complex mass transfer phenomena within solid matrices that are not captured by the HSP model. Some studies have found good agreement between HSP-predicted optimal solvents and experimental results, particularly for simple liquid-liquid extractions (Milliman, 2012). However, for more complex solid-liquid extractions from plant materials, additional factors like matrix effects, diffusion limitations, and solvent penetration into cellular structures play important roles that are not reflected in HSP calculations (Novaes *et al.*, 2023). HSP remains a valuable tool for initial solvent screening and optimization, researchers should be aware of its limitations. These predictions need to be validated with experimental data, especially for complex natural product extractions.

In summation, it is imperative to recognize the inherent limitations of the conclusions drawn from this comprehensive literature review. The preponderance of data originates from laboratory-scale investigations, and, at most, pilot-scale experiments conducted under conditions that only tangentially reflect the operational parameters of industrial extractions. Our analysis has elucidated that the methodology employed for oil recovery, whether through distillation or precipitation *via* temperature modulation, can exert substantial influence on the partitioning of polar lipids, the preservation of antioxidant moieties, and the complexation of oxidizing metal species. It is only within the context of authentic industrial conditions that we can fully elucidate and quantify the impact of various solvents on oil quality. In the absence of robust and empirically validated references, numerous uncertainties persist regarding this subject, necessitating further investigation and rigorous experimentation under scaled-up, industry-relevant conditions. This underscores the critical need for future research to bridge the gap between laboratory findings and industrial applications, thereby enhancing our understanding of the complex interplay between extraction methodologies and resultant oil properties.

Conflicts of interest

The authors have no conflicts of interest to disclose.

Author contribution statement

Patrick Carré: conceptualization, administration, original draft, review & editing. **Sarah Bothe**: administration, validation, review & editing. **Chandra dev Borah**: validation, review & editing. **Thomas Piofczyk**: conceptualization, administration, validation, review & editing. **Sara Hadjiali**: validation, review & editing.

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