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Solvent solutions: comparing extraction methods for edible oils and proteins in a changing regulatory landscape. Part 3: Impacts on the process☆

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Abstract – This article constitutes the third instalment in a comprehensive series dedicated to the comparative analysis of solvent solutions for oilseeds extraction. With some adaptations, all solvents considered except methanol would allow complete extraction of the meals. Nonpolar solvents such as hexane are penalized by their hydrophobicity in penetrating biological matrices, but their immiscibility with water makes their recycling simple and efficient. Their low energy requirement for evaporation and the use of live steam for final residue elimination are advantageous. Dichloromethane is similar to hexane in its low miscibility with water and high volatility, but its higher density could disrupt percolation by compacting the material bed. Ethyl acetate and 2-methyloxolane have limited miscibility with water, allowing for simple removal of process water, but residual water promotes higher solvent retention in the marc, making the desolventizer' s task more difficult and requiring higher solvent-to-solid ratios. Saturated methyl ethyl ketone contains even more water, potentially exacerbating these problems. Acetone, as well as ethanol and isopropanol, are completely miscible with water, thus prohibiting the separation of process water and requiring additional process steps such as pervaporation for alcohols and rectification for acetone. Substantial energy savings are possible with these solvents by separating oil from the miscella through cold precipitation, particularly in the case of ethanol, which has low miscibility with oil. An additional operation is the drying applied to the incoming material. Each solvent family therefore presents specific challenges and advantages, requiring tailored solutions to optimize extraction while maintaining efficiency, profitability, and product quality.

Keywords: Extraction / solvents / process / desolventization / distillation

Résumé – Cet article constitue le troisième volet d'une série consacrée à l'analyse comparative des solvants d'extraction des graines oléagineuses. Moyennant quelques adaptations, tous les solvants envisagés hors méthanol permettraient une extraction complète des tourteaux. Les solvants apolaires tels que l'hexane sont pénalisés par leur hydrophobicité pour pénétrer les matrices biologiques, mais leur immiscibilité avec l'eau rend leur recyclage simple et efficace. Leur faible besoin énergétique pour l'évaporation et l'utilisation de vapeur vive pour l'élimination finale des résidus sont avantageux. Le dichlorométhane est similaire à l'hexane par sa faible miscibilité avec l'eau et sa haute volatilité, mais sa densité plus élevée pourrait perturber la percolation en compactant le lit de matière. L'acétate d'éthyle et le 2-méthyloxolane ont une miscibilité limitée avec l'eau, permettant une élimination simple de l'eau de process, mais l'eau résiduelle favorise une rétention plus élevée de solvant dans le marc, alourdissant la tâche du désolvanteur et nécessitant des ratios solvant/solide plus élevés. Le méthyléthylcétone saturé contient encore plus d'eau, aggravant potentiellement ces problèmes. L'acétone, ainsi que l'éthanol et l'isopropanol, sont totalement miscibles avec l'eau, interdisant en cela la séparation de l'eau de process et nécessitant l'ajout d'étapes au procédé telles que la pervaporation dans le cas des alcools, et la rectification dans le cas de l'acétone. Des économies d'énergie substantielles sont possibles avec ces solvants en séparant l'huile du miscella par

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précipitation à froid, particulièrement dans le cas de l'éthanol peu miscible avec l'huile. Une opération supplémentaire est le séchage appliqué à la matière entrante. Chaque famille de solvants présente donc des défis et des avantages spécifiques, nécessitant des solutions adaptées pour optimiser l'extraction tout en maintenant l'efficacité, la rentabilité et la qualité du produit.

Mots-clés : Extraction / solvants / procédé / désolvantation / distillation

Highlights

- The miscibility of solvents with water is a crucial factor in determining their ease of implementation for oil extraction.
- Hexane, which exhibits the lowest miscibility, is the most advantageous solvent for trituration.
- When solvents and water are miscible, it becomes necessary to incorporate additional operations to manage water within the process.

1 Introduction

This article is part of a broader series dedicated to comparing potential solvents for use in vegetable oil extraction. The solvents under consideration include: technical hexane composed of a mixture of C6 alkane isomers dominated by n-hexane, Isohexane, cyclohexane, methanol (MeOH), ethanol (EtOH), isopropanol (IPA), acetone, methyl ethyl ketone (MEK), ethyl acetate (EA), dichloromethane or methylene chloride (DCM), and 2-methyloxolane, also known as 2-methyltetrahydrofuran (2-MeOx). Technical hexane, currently the solvent of choice for industrial oilseed processors, faces potential regulatory changes due to its toxicity and evolving societal expectations regarding food production processes. The shift to alternative solvents in oilseed processing can significantly alter various aspects of the extraction process. This part explores the potential modifications and challenges that arise from using different solvents. Unlike hexane isomers and dichloromethane (DCM), many alternative solvents exhibit higher water miscibility, which triggers a cascade of effects on lipid extraction efficiency, solvent recycling, water content management, and wastewater processing. These changes also impact oilseed preparation, solvent recovery from spent air, and safety procedures, as discussed in the Article 2 of this series. The interactions between solvents, biological matrices, and oils play a crucial role in extraction kinetics. Highly hydrophobic solvents have a lower ability to penetrate hydrophilic biological matrices, while highly hydrophilic solvents show poor miscibility with hydrophobic oils. The thermal properties of solvents influence the energy dynamics, necessitating retrofitting of heat exchangers. Methanol and ethanol, for instance, have been studied for their potential in simultaneous extraction and transesterification, which could improve extraction yields but pose economic feasibility challenges. This part will delve into the effects of solvent shifts on extraction yields, drawing from both laboratory and pilot plant studies. It will also discuss non-distillation techniques for oil-solvent separation to reduce energy costs. The use of live steam in the process, particularly for water-immiscible solvents, simplifies water removal, but other solvents require more attention to manage water presence and wastewater desolventization. The functioning of oil scrubbers in capturing solvent vapours will also be examined, along with the need to dry oleaginous materials to prevent water capture by hydrophilic solvents.

2 Impacts of the solvents on the efficiency of extraction

2.1 Simultaneous extraction and transesterification

We have seen in the Article 1 of this series at the paragraph dedicated to the solubility of oils in the solvent and about selectivity that there is a quite large variability among our range of solvents. If alcohols, especially methanol, can be considered as a poor solvent for oil extraction, it has nevertheless been studied in several works for specific use in reactive extraction. This is the one-step transesterification and extraction of fatty acid methyl esters (FAME). Given that a great part of the oils is produced for the biodiesel market, it has been envisaged to reduce the costs of the processing by carrying out the transesterification at the same time than the extraction operation. The pioneering study on this topic was published by Harrington and D'Arcy-Evans (1985) and proposed to conduct in situ transesterification of sunflower oil using methanol and H_2SO_4. Their idea was to improve the extraction yield by changing the solubility and viscosity of the triacylglycerol (TAG) by this transesterification. They claimed that their method was giving better yield, but it was made at lab scale and with a comparative hexane oil-yield that was disputable in regard to the industry performances. Before 2000, this first experiment was not followed by any other works according to this principle, but after 2005, with the interest for bio-based fuels, the number of publications about in situ transesterification has increased greatly, reaching more than five papers per year from 2010 to 2015. In a review, Makareviciene *et al.* (2020) found 63 research papers on this topic. They say that in the studies performed, the molar ratio of alcohol to oil ranged from 12 to 655 when using alcohol alone, and that at a low molar ratio methanol to oil (20:1, ~0.7:1 m/m) the transesterification reaction almost does not proceed. In addition, they note that the water content was playing a negative role in the transesterification rate due to the reversible character of the reaction promoted by the abundance of water. The document does not provide information about the purity of the FAME resulting from in situ transesterification, nor does it mention pilot plant studies. In France, a pilot project aimed at producing 20 kt of biodiesel per year has been experimented near La Rochelle. The Society Bioenergy was supposed to produce ethyl esters of rapeseed oil according to a process developed by the University of Poitier (Respire, 2010). However, the project did not demonstrate its economic

Table 1. Examples of lab-scale comparisons of extraction yields for alternatives solvents with hexane.

Solvent	Oilseed	Scale	Preparation	YDN	Impurities %	YDC	Source
2MeOx	Salmond	25 g Soxhlet (8h)	Lyophilisation			+2%	Cascant*et al.*, 2017
2MeOx	Black cumin	Soxhlet (8h)	Ground			+14%	Bourgou*et al.*, 2021
2MeOx	Basil	Soxhlet (6)	Ground			+13%	Bourgou*et al.*, 2021
2-MeOx	Rapeseed	Soxhlet (8h)	?			–0.7%	Sicaire *et al.*, 2015
EA	Spent coffee	10 g Soxhlet (6h)	Drying <10% w.c.	+8.9%	7%	+16.8%	Loyao Jr *et al.*, 2018
EA	Salmond	25 g Soxhlet (8h)	Lyophilisation			–3%	Cascant *et al.*, 2017
EtOH	Spent coffee	10 g Soxhlet (6h)	Drying <10% w.c.	–8.7%	37%	+45.7%	Loyao Jr *et al.*, 2018
EtOH	Rapeseed (Astrid)	15 g Soxhlet (6h)	Coarsely ground	–81%	50.0%	–62%	Li *et al.*, 2014
EtOH	Salmond	25 g Soxhlet (8h)	Lyophilisation			+6%	Cascant *et al.*, 2017
EtOH	Baru almonds	15 mL reactor	1.6 − 2.4 mm			–20%	Souza *et al.*, 2020
EtOH	Quercus suber fruits	Soxhlet (5h)	Coffee mill		76%	+320%	Ferreira-Dias *et al.*, 2003
EtOH 95%	Sunflower collets	10 g + 180 mL solv.	Ground	–2.5%	31%	+41%	Baümler *et al.*, 2016
EtOH 99%	Rapeseed	20 g 1:17 60°C 4h		–12%	11%	+6%	Sánchez *et al.*, 2018
EtOH 99%	Rapeseed	20 g 1:17 60°C 4h	Microwaves	–2%	10%	+7%	Sánchez *et al.*, 2018
EtOH 99%	Rapeseed	5.7 g Erlenmeyer	Flakes dried 3%			–59%	Perrier *et al.*, 2017
EtOH 99%	Rapeseed	5.7 g Erlenmeyer	Flakes dried 3%+US			–55%	Perrier *et al.*, 2017
EtOH+IPA	Baru almonds	15 mL reactor	1.6 − 2.4 mm			+18%	Souza *et al.*, 2020
IPA	Spent coffee	10 g Soxhlet (6h)	Drying <10% w.c.	–6.3%	27%	+28.2%	Loyao Jr *et al.*, 2018
IPA	Rapeseed (Astrid)	15 g Soxhlet (6h)	Coarsely ground	+25.5%	12.1%	+42.8%	Li *et al.*, 2014
IPA	Salmond	25 g Soxhlet (8h)	Lyophilisation			–9%	Cascant *et al.*, 2017
IPA	Baru almonds	15 mL reactor	1.6 − 2.4 mm			+8%	Souza *et al.*, 2020
IPA 99%	Rapeseed	5.7 g Erlenmeyer	Flakes dried 3%			–14%	Perrier *et al.*, 2017
IPA 99%	Rapeseed	5.7 g Erlenmeyer	Flakes dried 3%+US			–4%	Perrier *et al.*, 2017

US: ultrasounds.

feasibility and was abandoned in 2012 (La nouvelle République, 2012). Part of this was caused by the necessity to use dry ethanol and very dry rapeseed flakes, which increased the costs both for drying the incoming flakes and for drying the ethanol. In conclusion, in situ transesterification may function technically but its economic feasibility is still doubtful.

2.2 Extraction yields

Because of its low price, biological sourcing and acceptable toxicity, ethanol has been the object of a substantial number of studies and even industrial applications. It was first used as an extraction solvent in a semi-industrial application to extract soya oil in Northeast China in 1927 (Hron *et al.*, 1982). Since this solvent is more polar than the other solvents in this review (aside from methanol), it can extract much more substances than lipids. The oil resulting from ethanol extraction is darker and has more free fatty acids (FFA) (Magalhães *et al.*, 2023).

Table 1 gives literature examples of comparisons between extraction yields of various solvents versus hexane. The YDN (Yields differential in neutral oil) column gives the differential yield ratio according to equation (1), with Y_a = oil yield with alternative solvent, I_a = impurities in oil extracted with the alternative solvent, Y_h = the oil yield with hexane. YDC is the yield differential between the crude oil from alternative solvent and hexane according to equation (2).

$$\mathrm{YDN} = \frac{(Y_a - I_a - Y_h)}{Y_h} \quad (1)$$

$$\mathrm{YDC} = \frac{(Y_a - Y_h)}{Y_h} \quad (2)$$

Most of the studies were made using Soxhlets extractors, a laboratory device made for the determination of the lipid content in biological materials. The method requires a thorough comminution of the material which is subsequently subjected to repeated immersion cycles in the solvent. An essential precaution is to ensure that the compared solvents are recycled at equivalent flow rates, which is not straightforward as the flow depends on the heat transfer that brings the solvent to its boiling point, and the apparatus lacks a means to measure liquid flows.

Since the polar solvents are able to extract non-lipid substances, it is necessary to proceed to the determination of non-lipids in the extract for a better appreciation of the yields. The results given in Table 1 show that 2-MeOx provided better oil yields than hexane in three cases out of four. In general, these better yields were explained by a better recovery of polar lipids. In the case of EA, just two studies were found. The study using spent coffee grains resulted in higher oil recovery, but with 7% impurities. Most of the time EtOH was used dry. The yields ranged from −61% up to +320% on crude oil and the rate of impurities in crude oil ranged from 10% to 76%. In an experiment made in Erlenmeyer, the lower yields can be explained by the lower solubility of oil in ethanol, the relatively low ratio solvent to solid (4:1) and the temperature (50 °C). In most cases, Soxhlet experiments resulted in a much higher yield of crude oil, explained by a sizable proportion of

non-lipids in the extracts (the highest one on oak fruits was also explained by the low oil content in those fruits: 3%). The real lipid yields were generally lower. For IPA, crude oil yields ranged from −14% to +42%. IPA also extracted non-lipids and, in the experiment where their presence was measured, their concentration was quite high with 27% in coffee and 12% in rapeseed extracts.

What can be concluded from the lab-scale comparisons is that it is difficult to extrapolate them because they are far from representative of the industrial conditions and their predictive value is likely to be low. Soxhlet extractions are significantly more time-consuming than industrial extraction methods and operate with a continuous supply of fresh solvent. In contrast, countercurrent extraction exposes incoming flakes or prepress cakes to a miscella — a mixture of solvent, polar lipids, and neutral lipids — which can alter the diffusion dynamics. Shah and Venkatesan (1989) have shown that FFA were mostly kept in the lean miscella resulting from the cold precipitation of IPA-oil miscellas and that the presence of FFA in the IPA was allowing a higher retention of neutral lipids in this solvent. In consequence, it is likely that in countercurrent flow using such a lean-miscella, the lower oil/solvent miscibility could be partially compensated by the presence of these polar lipids. Indeed, the best way to appreciate the change induced by a solvent substitution is the realisation of a pilot plant extraction trial working with a solvent recycling made in conditions as close as possible than those which apply in the industry. Table 2 recapitulates available publications related to studies carried out in pilot plants. These studies are scarce because they need expensive installations and long duration experiments.

Among the nine studies shown in Table 2, only four were performed in real counterflow extractor, the others simulated counterflows or performed crossflow extractions. The solvents that have been evaluated are ethanol, isopropanol DCM and 2-MeOx. Except for the case of Citeau *et al.* (2018) who used a processing scheme which was not employing percolation for the solid-liquid separation but filtration as a mean to simulate centrifuge separation with high rate of solvent, the oil residues in the meal were generally satisfactory when proper conditions were applied. The case of the study by Quinsac *et al.* (2016) is somewhat surprising since 90.4% ethanol was not likely to be extracted with the same performance as hexane, even with two additional washes. In an unpublished study, the same protocol using 96% EtOH resulted in meal with 2.2% of oil versus 1.5% for hexane and 2.1% for IPA 87.8%. In the case of the Baker and Sullivan (1983) study, oil residues in the meal were lower for drier IPA. For Hron *et al.* (1992), a mechanical dewatering prior to desolventization was required to reduce the miscella retention in the marc and reach oil residues below 1%. For Zhang *et al.* (2002) a preparation by expander with a drainage cage greatly improved the IPA 95% extraction of cottonseed by reducing the initial oil content. In the studies with 2-MeOx, the results were highly efficient when the higher retention rate of miscella was compensated by a slightly higher solvent to solid ratio. The high oil residues found in the flakes extracted with hexane in the experience of Bartier *et al.* (2024) could be explained by the flakes thickness which is greater than what is typically found for soybean, *i.e.* 0.3 to 0.4 mm. The long duration of storage of the flakes before extraction may also have played a role. Lipids oxidation is likely to have diminished the hexane extraction yield since it is known by lipid analysts that oxidised lipids are not well extracted by pure hexane (Hara and Radin, 1978).

Even if no results are available for other solvents, it is likely that extraction performance is not the greatest limiting factor when technical solutions are found to overcome the issue resulting from the different properties of the solvents. The limiting factors arise from other aspects of the processing, like the constraints of solvent regeneration, the modification of energy requirement, the effect of solvent properties on product qualities and conversely, the impact of crude oil quality on the extractive performance of solvents.

3 Solvent regeneration

3.1 Oil solvent separation

In conventional extraction, the miscella is evaporated in two main steps as shown in Figure 1. The economizer using the heat of the desolventizer vapours heats the miscella to boiling point and evaporates a part of the solvent. Since the heat transfer depends on the temperature differential between each fluid, it is necessary to put the miscella under partial vacuum in order to reduce its boiling point to a sufficiently low level. This is why the condenser connected to the dome of the economizer is linked by a steam ejector to a second condenser functioning at atmospheric pressure. The miscella concentrate leaving the economizer is then "flashed", *i.e.* evaporated continuously in a second evaporator where the solvent concentration is reduced to below 10%. The stripping column uses direct steam to eliminate the solvent residues, and, in a last step, the oil is removed of its moisture in a dryer operating at low pressure. All the condensates are going to the decanter, where the wastewater is separated from the solvent and pass through a boiler in which the solvent residues are evaporated. The spent air is passed through the mineral oil absorber before exiting the system.

As already mentioned, the low oil miscibility in aqueous ethanol could be exploited as an advantage for reducing the energy consumption related to the solvent/oil separation. With hexane, this processing step is made by evaporation at a relatively weak expense because of the low latent heat of vaporisation (Δ_h), which is related to the weak intermolecular bonding in these solvents. Ethanol and IPA have 156 and 106% higher Δ_h than n-hexane, respectively, therefore using the same technology would require much more energy, especially as the lower miscibility of oil in alcohols induces that larger solvent-to-solid ratios must be used and thus larger quantities of miscella must be distilled. Beckel *et al.* (1948) have proposed another method in which the miscella is cooled at temperature below 25 °C to insolubilize the oil and separate it by decantation and redirecting the upper fraction called "lean miscella" towards the extractor. According to these authors, the theoretical energy required for solvent recycling would be only 70% of the hexane requirement, but this assessment does not include heat recovery done in modern extraction plants. This lean miscella contains a low concentration of triacylglycerol but also most of the FFA and the polar lipids (Citeau *et al.*, 2018). FFA are not considered as polar lipids because their carboxyl groups can interact with those of other FFA by exchanging hydrogen bonds that water cannot disrupt since

Table 2. Recapitulation of the studies made at pilot plant scale with alternative solvents.

Source	Oilseed	Scale	Preparation	Other conditions	Solvent	Oil residues in meal	Oil impurity	Remarks
Baker and Sullvian, 1983	Soybean	20 stages Kenedy counterflow	Flakes ~0.25 mm	2:1, 60°C, 70min	IPA+15%water	~3.5%	0.40%	
					IPA+12.3%water	~2.0%	0.40%	
					IPA+9.5%water	~1.0%	1.00%	
Hron et al., 1984	Cotton seed	500g batch percolator	Hulled, 2% w.c. Flakes ~0.26mm	1 wash with lean miscella 2.4:1, 77°C + 1 wash with fresh solvent	EtOH 95%	>2%	1.60%	10 min for 1rst contact then recycled by cold precipitation and then recycled to extraction 8 times totalling 90 min. Last wash by 300 mL of 95% EtOH
				same than above + mechanical dewatering		>1%	1.60%	
Johnson et al., 1986	Cotton seed	Continuous Crown, 40 kg/h 0.15 m bed	Flakes ~0.28 mm, double rolling	run 56 h, 1.6:1	DCM	0.24	0.2% gossypol	
					Hexane	1.58	0.14% gossypol	
Zhang et al., 2002	Cotton seed	300 g batch percolator / simulation of counter-current by recirculation of miscellas	Hulled 12% w.c. flaked ~0.3 mm, heated 80°C → Flakes 34.3% oil, 5.4% w.c.	~2.2:1 75°C	IPA 95%	~5%		7 extraction steps
			Hulled 12% w.c. flaked ~0.3 mm, heated 80°C + expander with drainage cage → collets 22.2% oil 4.6% w.c.	~2.2:1 75°C		~1%		2.4, 2.0, 1.7 and 1.3% oil residues in meals for respectively 88, 93, 97 IPA and Hexane
Sicaire et al., 2015	Rapeseed	6 L batch percolator	Pre-press cake	5 steps 1.5:1 55°C	2MeOx (dry)	0.80%		
					Hexane	1.80%		
Quinsac et al., 2016	Rapeseed	6 L batch percolator	Press-cake	5 steps 5L:2kg,50°C	Hexane	1.5%		
				7 steps 5L:2kg 64°C	EtOH 90.4%	1.6%		
				7 steps L:2kg, 67°C	IPA 85.2 %	1.3%		
Citeau et al., 2018	Rapeseed	Nutsche filter (immersion + stirring) 100 g	Wet milling in solvent (high shear)	15:1, 50°C 4 washes 10 min per wash	hexane	3.20%		Non-distillation system
					EtOH 95.6%	3.60%	~10%	
					EtOH 92.0%	6.70%	~13%	
					IPA 87.8%	5.30%	~13.5%	
					IPA 84.2%	6.40%	~15%	
Rapinel et al, 2020	Rapeseed cake	340 kg/h (Crown type IV extractor*)	pre-press	1.3:1	2MeOx 4.5% water	0.30%		
Bartier et al. (2024)	Soybean flakes	4 kg/h (Crown type IV extractor*)	0.7 mm flakes aged of 17 months	Solvent not recycled	MeOx +4.1%water	0.46%		Solvent holding of the marc 42.4% for Me0x vs. 28.5% for hexane
					MeOx +2.7%water	0.52%		
					MeOx +1.0%water	0.48%		
					MeOx		PV 12.5	
					Hexane	1.94%	PV 2.6	

* Crown IV extractors are immersion extractors.

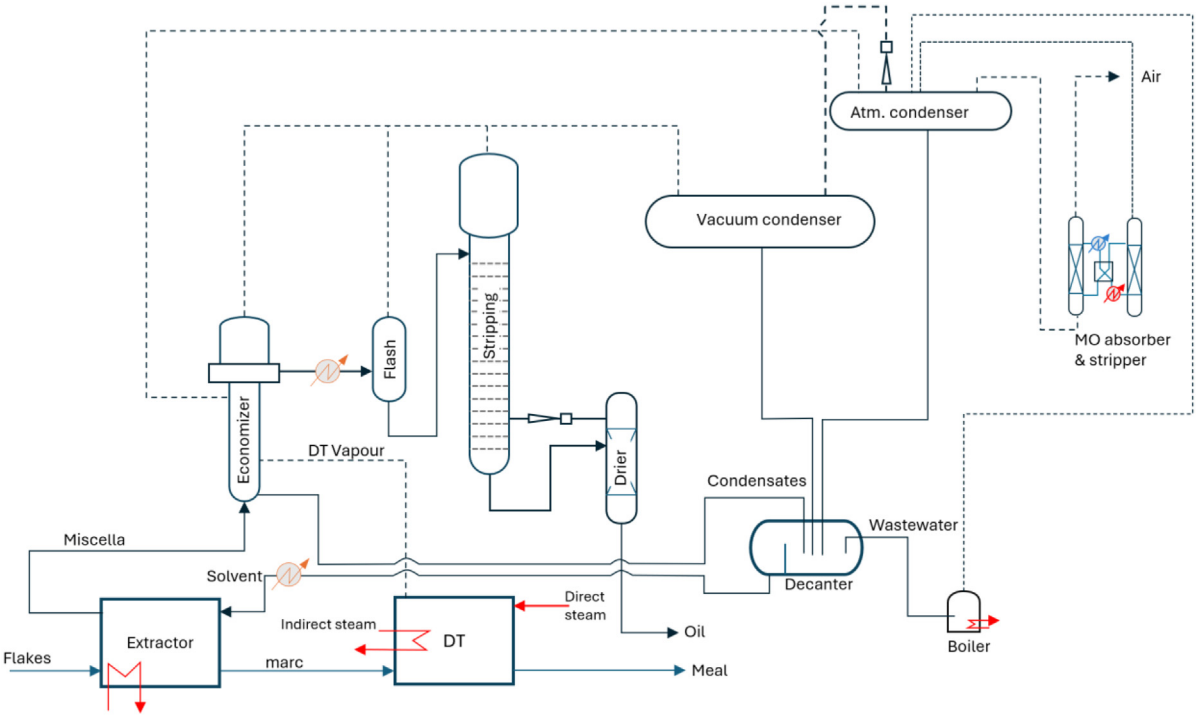

Fig. 1. Flowsheet of a conventional solvent recovery system adapted from Le Clef and Kemper (2015).

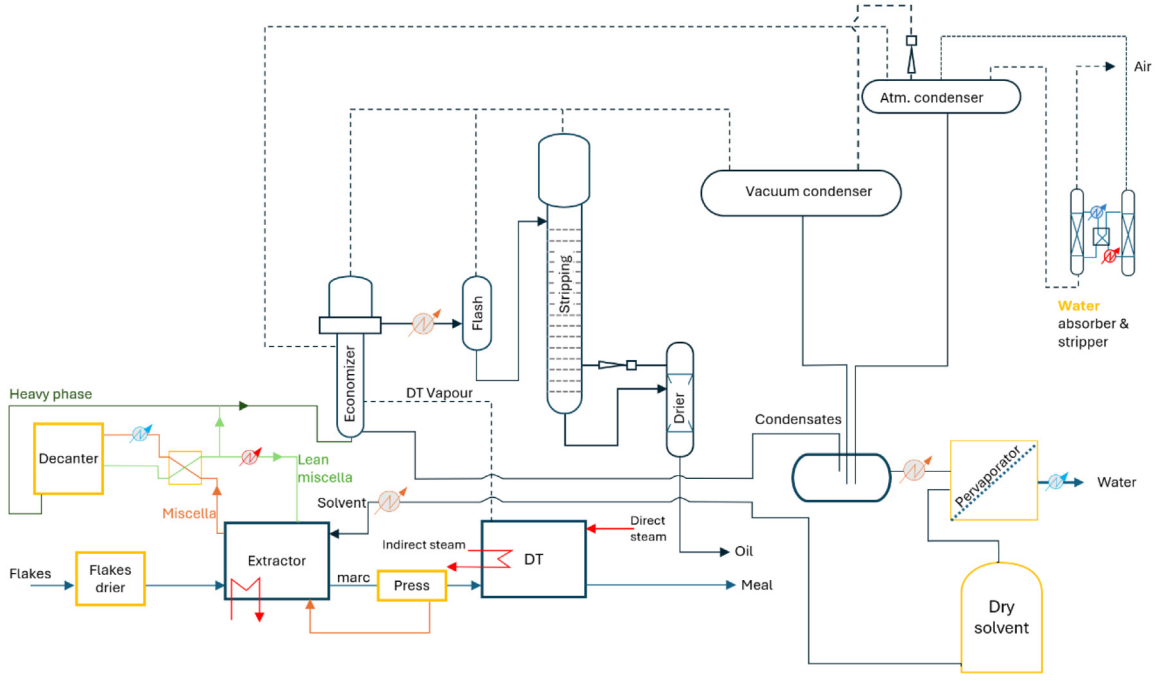

Fig. 2. Flowsheet of non-distillation scheme for the solvent recovery according to Lusas *et al.* (1997).

water is immiscible in the miscella. This is not the case for EtOH or IPA, as a consequence, the FFA are driven into the solvent phase in the presence of these solvents. Shah and Venkatesan (1989) have suggested using this property to neutralise the oils. As already discussed, phospholipids were following a similar path with higher concentration in lean miscella. In an extraction scheme with constant recycling without exit route for these polar compounds, an equilibrium is reached in which the high concentration in polar lipids both limits their extraction and increases their concentration in the heavy phase after coalescence. Carré *et al.* (2018) proposed using the enthalpy (Δh) of vapours generated during meal

desolventisation to evaporate a portion of the lean miscella. This lean miscella contains polar lipids, sugars, and phenolic compounds. By implementing this approach, an exit route for these substances could be established, potentially resulting in improved oil quality and increased protein concentration in the meal. Additionally, this method could facilitate the partial removal of undesirable substances such as bitter molecules, dark colour pigments, glucosinolates, and gossypol in cottonseeds.

Lusas *et al.* (1997) have suggested another technical pathway, shown in the Figure 2, in which the solvent combines partial non-distillation with regular distillation followed by pervaporation to eliminate the excess water in the system.

Harris and Hayward (1950) evaluated a comparable oil recovery method at pilot scale using acetone containing 5% water. To the best of our knowledge, this paper is the only reported investigation using acetone in this way. With non-alcoholic hexane substitute, distillation is the most likely route for the miscella separation. Dijkstra (2012), in a letter to the editor of the JAOCS, questioned the relevance of an article proposing the use of membrane separation for the preconcentration of oils, on the basis that this preconcentration is already done in the industry by using the heat contained in the vapour stream of the desolventizer. He also criticised the authors for underestimating the problems of fouling by the impurities in miscellas, particularly in the presence of water. With regard to the reliability requirement in force for crushers, it is therefore likely that the current technology would be retained with some adaptations to cope with the changes in energy requirements. These changes would concern the size of heat exchangers and boilers and possibly the pipes connecting them. The largest capital cost could result from the necessity to change the size of the desolventizer and the economizer, where the heat from the desolventizer is transferred to the miscella for recovering the energy of the meal desolventization. Table 2 in the Article 4 of this series (energy) gives an assessment of the shift in desolventizer heat requirements. In brief, this method estimates the solvent's effect on marc retention capacity using Hansen's solubility parameter δh. The parameter is utilized to evaluate both the quantity of solvent requiring evaporation and, through its latent heat of vaporization, the heat necessary for desolventization. Furthermore, the method incorporates the latent heat of water vapor in the desolventizer vapor stream, calculated based on the water content of the water-solvent azeotrope plus the additional water required to exceed the azeotropic (molar) water concentration by 5%. The marc retention estimator was developed to address the absence of comparable experimental data across all solvents under consideration. For example, it predicts the retention of 304 kg of 2-MeOx in the marc of soybean flakes versus 248 kg with hexane. Moreover, the azeotrope water/2-meOx containing 10.6% of water (mass), the vapours exiting the DT must contain 11.65% of water versus 6.0% with hexane.

The ratios of heat to be transferred from the desolventizer vapours to the miscella for a solvent compared to n-hexane is calculated by equation (3):

$$Q = \frac{\Delta_{h(x)}}{\Delta_{h(a)}} \tag{3}$$

With $\Delta_{h(x)}$ = latent heat of vaporisation of the vapours from desolventizer for the solvent x, and a for the alkane n-hexane. According to the simulation given in the part 4, Table 2, line E, the Q ratios are:

- iso-Hexane 97%
- Cyc.Hexane 125%
- MeOH 732%
- EtOH 300%
- IPA 309%
- Acetone 137%
- MEK 205%
- EA 170%
- DCM 99%
- 2-MeOx 156%

3.2 Solvent recycling and management of the water in the solvent

According to the way the solvents are recycled, their water content could require special attention. As already noted for EtOH, which is totally miscible in water, it is necessary to keep the solvent dry in order to preserve its capacity to dissolve oils. This is also true for IPA, but to a lesser extent since it remains more efficient at higher water content than ethanol and this property limits the need to dry the incoming flakes or press cake to a very low water content. With ketone, for the same reason, there is also a necessity for keeping the solvent as dry as possible, and more so with acetone than with MEK. In hexane recycling and other non-miscible solvents, the water / organic phase separation is made in static decanters. This technique is not possible for miscible solvents, which means that the excess water must be managed differently. Available techniques include drying the incoming solid material, rectifying the solvent in distillation columns, using pervaporation, and replacing the steam ejectors used to generate vacuum in the miscella/oil separation by other technologies like dry vacuum pumps.

Direct steam is employed for facilitating the removal of the solvent in the last stages of separation. When the solvent concentration in the oil becomes low, its partial pressure in the vapour phases decreases so that high vacuum or high temperature would be required to eliminate the residues to an acceptable level. High vacuum is costly and elevated temperature could damage the crude oil; therefore, it is preferable to desaturate the vapour phase by addition of water vapour in the system. It is the equivalent of introducing dry air into a humid atmosphere to evaporate the excess water. The advantage of water vapours is that it condenses and leaves the system as a liquid that is easy to separate from the solvent if the solvent is immiscible with water. It does not overload the vacuum system because its condensation can occur before the suction device, which maintains the low pressure in the system. This method proves highly effective, delivering excellent technical results while maintaining cost-efficiency. It is also used for the same reason during meal desolventization, and the vapours exciting the desolventizer have a water content that is slightly higher than the concentration of water-hexane

azeotrope (5%). As desolventizers are working at atmospheric pressure, this excess water is required to facilitate the vaporisation of the solvent. We will see in part 4 about energy that this feature has a strong impact on the energy consumption in the desolventizer if the solvent is an azeotrope with a high-water content.

In result, for solvents that have weak water solubility (EA, DCM and 2-MeOx), the consequences would be limited to the solvent bringing some water into the extractor, which has a more or less effect on the solvent hold-up in the marc. According to Stephenson (1992), the water solubility in MEK is limited to 11.3% at a temperature of 29.7 °C. We do not dispose of the ternary miscibility for oil-water-MEK systems, but Pons and Eaves (1967) have shown that with oil-water-acetone at 30 °C, oil miscibility decreased dramatically between 10-15% of the water. In consequence, given the higher affinity of MEK for hydrophobic substances, it could be assumed that a water content of 11.3% is unlikely to limit oil extraction and no further dewatering is required if this high water remains in the miscella and does not migrate to the meal. This condition is far from being warranted, considering that in water-saturated MEK, the interaction of the water with the MEK is likely weaker than with the biological matrix, and that a significant proportion of this water is likely to migrate towards the meal. We will see later in the article about 2-MeOx that such migration could strongly modify the solvent retention in the marc.

With the solvents that have a higher water solubility, *i.e.* MeOH, EtOH, IPA, and acetone, a rectification step is required for restoring the solvent capacity to extract the lipids by reducing its water content. The separation of two miscible liquids by distillation is possible if there is a difference between the concentrations of the water in the liquid and vapour phases. At azeotrope concentration, both phases have the same concentration, therefore, it is not possible to separate the substances. Figure 2 in the Article 4 (energy) of this series shows the vapour/liquid equilibriums (VLE) for EtOH, IPA, acetone and MEK. Acetone is the only solvent of interest without azeotrope, therefore, its separation from water could be done at any level by rectification.

Lusas *et al.* (1994), assert that pervaporation is the most effective method for removing water from isopropanol (IPA), enabling the extraction system to operate with a lower water content in the solvent, specifically at 5%. Pervaporation consists of using nanoporous membranes to evaporate the water and retain the isopropyl alcohol, which has a bigger molecule size. In this case, only the latent heat of water vaporisation is required. Conversely, this technique demands expensive hardware and requires vacuum and low-temperature coolant to condensate the water under vacuum. In their final report on replacing hexane with isopropanol for cottonseed extraction, Lusas *et al.* (1997) compared the energy costs of various solutions. They found that the most energy-efficient method for processing 1 tonne of collets involved a series of steps. This optimal process included drying the collets from 13% to 5.5% moisture content, employing mechanical pre-desolventization of the marc, separating miscella/oil through chilling and precipitation for reusing the lean miscella in the extractor, and implementing a pervaporation step on the DT and oil stripper condensates to eliminate excess water (Fig. 2). This combination of techniques resulted in the lowest energy consumption per tonne of processed collets. The overall excess of energy input was limited to 16% by comparison with hexane. Unfortunately, this study was not encompassing the CAPEX in the comparison. With the additional processing steps and the limited life duration of the membranes it is likely that a fair share of the energy costs are converted into capital costs.

3.3 Static separation of dichloromethane and issues related to its density

A specificity of DCM is its greater density than water. In result, the phase separator should be revamped to modify the directions of the heavy and light phases. This aspect would be benign beside the issue related to workload and energy requirements imposed on the pumps moving the solvent through each operation in the oil mill. The pumps are designed according to the capacity and the pressure required. The pressure results from the density, the gravity, and the elevation to be overcome (engineering toolbox, 2003). Therefore, there is a direct relationship between the power and the liquid density which in the case of DCM and hexane is a factor 1.9 likely to be too large to be compatible with the tolerances accepted by most of the installed pumps. 2-MeOx with its density of 0.855 would require 1.22 times more power at constant mass flow which is much more likely to be acceptable.

4 Treatment of spent air and water

4.1 Processing of wastewater

As specified earlier, the system collects several streams of additional water resulting from the use of direct steam in solvent stripping, and from the driving steam of the ejectors used to depressurise the distillation vessels. According to Cheng *et al.* (2018), a hexane extraction facility produces 55 kg of wastewater for each ton of processed soybean. This paper does not provide any details about the origin of this water, and it comes from sources other than just the extraction plant, especially the boiler that generates blowdown/purges and requires salt water for the regeneration of softener resins. For the necessity of this comparison, only the desolventization is considered as a source of variation and a direct steam allocation to the oil stripping is set at 5% of the oil flow, *i.e.* 8.5 kg/t of flakes. In addition, 1.5 kg/t is allocated to the driving steam of the ejectors. These figures are given arbitrarily in the absence of data in the literature and knowing that in reality, they may vary from one plant to another.

In the case of ethanol and isopropanol, the addition of γ line in Table 2 of part 4, and these 10 kg of other water inputs give respectively 54 kg/t agter 115 kg give respectively 54 kg/t and 115 kg/t of additional water . As this water is miscible with the solvent, removing it from the system necessitates a combination of rectification and pervaporation techniques. This problem could be easier to solve with acetone, because it does not have an azeotrope with water and rectification remains possible at any water concentration, but the energy cost could still be high.

With MEK, an excess of water can be recovered by two phase decantation, but this MEK-saturated water will contain about 25% solvent requiring a multistep stripping. EA, which

has a solubility in water of 83 g/L and 2-MeOx a miscibility of 140 g/L, would also require a multistep stripping.

A simulation made with ChemSep version 8 (Kooijman and Taylor, 2022), has been done to compare the flows and energy demand for water saturated in EA (83 g/L) or in MEK (250 g/L). The thermodynamic parameters were DECHEMA for *K*-values, NTRL for activity coefficients, Antoine for vapour pressure. A ten trays column with a reflux ratio of 0.2 and a boiler specification for a solvent concentration below 1×10^{-4} (molar) was simulated. For a flow of 100 kg/s of water, the power required by the reboiler was 35 and 54 MW for respectively EA and MEK. The condensates represented 8.95% of the water stream and contained 7.8% of water in the case of ethyl acetate. The condensates represent 30.4% of the wastewater stream and contain 17.7% of water with MEK. The condensates from both solvents would be biphasic, the heavy phase could be refluxed, and the organic phase could be returned to the extractor. In the case of MEK, this reflux would increase the energy requirement.

4.2 Spent air purification

To mitigate the risk of vapor leaks, the extractor and desolventizer are connected to a suction device that generates a negative pressure differential of 20–30 Pa between the internal environment of these sealed processing systems and the ambient atmosphere. This aspiration drives a small airflow saturated with solvent vapours, which requires passage on an absorption column to prevent the release of this solvent in the environment. Absorption columns function like reverse distillation, in which a miscible liquid absorbs the substance in the vapour phase to an equilibrium depending on the temperature, the reciprocal concentrations of the solvent in the vapour and liquid phases, and the affinity of the solvent to the absorbent liquid. In the case of hexane, this liquid is a mineral oil (MO) in which hexane is soluble and that is not oxidable by the airflow. To maximise the removal of solvents from the spent air, the column should be designed to expose a large surface area of mineral oil to the airflow. Additionally, the solvent content in the mineral oil must be continuously removed to maintain the lowest possible solvent concentration in the final air output. At the exception of DCM, the compared solvents have a sufficient miscibility in cold water to be absorbed by water instead of mineral oil. Water has the advantage of being cheaper, has a lower environmental footprint and reduces the risk of cross contamination (a small amount of MO can be carried to the solvent condenser during the stripping of MO, see Fig. 1). Even if this risk is controlled by oil-mills, who can use MO without toxic components like aromatic hydrocarbons, a MO-free system would be safer.

If water is used as an absorption medium, the stripping will give vapours with a relatively high-water content. According to VLE from literature data, the solvent concentration in vapours from liquid water with 5% solvent would be 39% for EtOH (Costa *et al.*, 2020), 26.2% for IPA (Khalfaoui *et al.*, 1997), 63% for acetone (Brunjes and Bogart, 1943), 75% for MEK (Othmer *et al.*, 1952) and 56% for EA (Mohammed et al., 2011). No data were found for 2-MeOx. These figures indicate that this stream would bring more water into the system, but this is a small input. Assuming that the volume of spent air is roughly twice the volume of incoming flakes, at a bulk density of 0.33, this means that about 6 m^3 of spent air saturated with solvent should be processed for each ton of flakes. Using the partial pressure from Table 1 of the the Article 1 of this series. (physical properties) and the VLE made on the hypothesis of a 5% solvent concentration in the absorption water, the amount of additional water returned to the extractor would be 0.4, 0.5, 1.3, 0.5 and 1.0 kg/t of flakes. In the case of 2-MeOX, it would be between 0.6 and 1.2 with a VLE in the range 0.6–0.8.

5 Impacts of the solvents on the oilseeds preparation

The main impact that a water-miscible solvent could have on the requirements of the oil-containing material is the control of its water content. This was shown long ago in the case of ethanol because vegetable oils have a low miscibility with ethanol. Rao *et al.* (1955), Rao and Arnold (1956) published saturation curves of oil-ethanol-water mixtures as a function of the water content in the solvent and temperature. Typically, these curves showed that the presence of water was strongly reducing the vegetable oil miscibility in ethanol while temperature was increasing it. Absolute ethanol and 98.0% EtOH were showing total miscibility at temperatures close to the boiling point. At azeotropic concentration (95.4%) it was not possible to solubilise more than ~18% of vegetable oils at 78 °C, and ~8% at 91.5 °C (pressurised extractor). Since to avoid losses by solvent vaporisation, it is generally not possible to work above 5–10 °C below the boiling point, the practical saturation limits encountered for real extraction are around 10% and 5% for 95.4% and 91.5% EtOH, respectively. These values are much lower than the concentrations reached in counterflow extraction using hexane. Consequently, a substantially larger volume of solvent must be employed to attain the same yield. Additionally, it is crucial to maintain the water content of the solvent as close as possible to the azeotropic concentration. This requirement implies that the oil-bearing material must not bring in water into the system since dry ethanol has a very strong affinity for water and is able to dehydrate the flakes or the press cake. Rao and Arnold (1958) carrying out pilot plant trials with cotton seeds found that the flakes must be dried to a water content of below 3% to avoid the limiting effect of water extracted from the flakes, but they used rectified solvent, *i.e.* with the possibility to restore the initial concentration of EtOH, which is an expensive step. When the solvent regeneration is done by a simple evaporation step or by cold precipitation, a lower water content in the oleaginous material is required.

Beckel *et al.* (1948) showed that it was possible to recover the oil by cooling the miscella down and letting the extracted oil to precipitate in order to reuse the lean miscella for new extraction. However, to keep the system functioning, a moisture content of the flakes of 2.5% was required. This low level of water is difficult to achieve by conventional drying, as the water to be removed is bound water. This drying should take place after the pre-press step because it would be difficult to operate the presses with a too low water content in the flakes (Carré, 2022). Conventional warm air dryers are not effective for this type of drying. The energy consumption significantly exceeds the latent heat of water vaporization. This

is due to factors such as bound water, internal diffusion resistances and the impossibility to saturate the drying air with water vapours leading to the necessity of heating much more air than when drying wetter material. For a rough estimation, doubling the latent heat of vaporization provides an acceptable approximation of the total energy costs. While this approach is not exact, it offers a practical rule of thumb for initial assessments of drying energy requirements. According to the data published by Carré (2012) about energy consumption during the crushing of rapeseed, a seed entering at 7.5% of water content would lose 32 kg/t of water during the conditioning prior to pre-press. This means that after the production of 320 kg of oil, around 6.6% water remains in the press cake. To reach a water content of 2.0%, about 31 kg of water have to be evaporated leading to an additional energy consumption of about 45 kWh per ton of crushed seed (+18.5%).

Isopropanol has been proposed in replacement of ethanol to overcome this problem since the IPA azeotrope has 12.3% of water content and a greater affinity for oils as shown in Table 2 and 3 the Article 1 of this series. Harris *et al.* (1947) studied the miscibility of cottonseed oil in aqueous lPA and EtOH as function of the temperature. With 91% IPA and 95% EtOH at 70 °C, miscellas were containing respectively 7.2% and 2.7% of oil concentration. They also observed that after mixing IPA and oil beyond the monophasic concentration, the free fatty acids were mostly retained in the solvent phase. The same team made continuous counterflow trials with multiple recycling of azeotropic IPA using cotton seed meat at 10% water content and partially recycling the solvent by cold precipitation of the oil. They stated that at this moisture level, the system was practically at equilibrium, as the meat neither absorbed nor released water into the solvent. They have also tested aqueous acetone (5% of water) in the same experiment. The water content in the meats was slightly above equilibrium and the solvent was absorbing a little water while the meal was slightly drier at the end of the extraction. Baker and Sullivan (1983) also investigated pilot plant studies using aqueous IPA at 15.0, 12.3 and 9.5% water content with soybean flakes at 10-11% of water content. In 12-hour runs, the water content in the lean miscellas leaving the oil precipitation step remained steady.

Apart from the previously studied alcohols, the impact of moisture content in the input material on solvent properties has not been extensively investigated for the other solvents under consideration, with the exception of 2-MeOx. Claux *et al.* (2021) showed that this solvent has a water miscibility limited to 4.5% and that its affinity for oils is not limited by this water content. Consequently, this solvent does not necessitate specific drying of the raw material prior to the extraction process. Bartier *et al.* (2024) showed that the water content of 2-MeOx was modified by contact with oleaginous material. In an experiment with soybean flakes, they observed that the miscella leaving the extractor was likely to have the same water content (1.6%), regardless of the water content (from 0% to saturation) of the MeOx used in countercurrent. In the 2-MeOx, soy flakes and water system, the equilibrium concentration of water in the liquid fraction depends on the affinity of the solids for water. The authors demonstrated this by measuring the water activity.

In conclusion, ethanol is the only solvent which could be severely affected in its potency as an oil extraction solvent in case of insufficient drying of incoming material.

Another possible modification in the preparation step potentially affected by the nature of the solvent is the degree of fluid erosion resistance of the oil-containing material. Hexane, being a low-density liquid, has minimal affinity for the hydrophilic substances in the defatted material. Consequently, the mass of miscella absorbed by the solid is relatively low, unlikely to cause significant consolidation of the solid bed in the extractor. In contrast, heavier solvents are more likely have a compaction effect of the material bed in the extractor reducing its porosity. This loss of porosity could adversely affect the bed's permeability, impacting the extraction process efficiency (Li *et al.*, 2014). Additional processing steps like pelletizing (Quinsac *et al.*, 2016) or expansion (Woerfel, 1995) could be required to avoid this kind of change.

6 Conclusion

In conclusion, the choice of solvent in oilseed processing plays a critical role in determining the efficiency, costs, and quality of the extraction process. Although solvents such as ethanol and isopropanol offer benefits like lower toxicity and the potential for biological sourcing, they present a significant challenge due to their higher water affinity and energy solvent recovery. These factors necessitate careful adjustments to the drying of oil-containing materials and the management of extraction conditions to maintain efficiency. The effects of solvent properties extend beyond the extraction phase, affecting the entire processing chain. For instance, the higher latent heat of vaporization of solvents like ethanol and isopropanol compared to conventional hexane requires significant retrofitting for extending the heat exchange capacity in devices like the economizer, the condensers and the desolventizer. In addition, the capacity of utilities (steam boiler, cooling tower) should be upgraded proportionally to the heat requirement of the alternative solvent. Alternative methods such as cooling the miscella to precipitate oil have been proposed to reduce these energy costs but require innovative operational adjustments. Furthermore, some solvent solutions could require a change in the oilseed preparation for reducing their water content or ensuring a better resistance to fluid erosion. The variations in solvent and process conditions highlight the need for pilot plant trials to accurately predict industrial-scale performance and address the specific challenges posed by different solvents.

Overall, while solvent shifts can potentially enhance certain aspects of oilseed processing, they also come with a multitude of consequences that must be meticulously managed. Achieving an optimal balance between efficiency, costs, and product quality requires a comprehensive under-

standing of these impacts and the implementation of tailored solutions to address the unique properties of each solvent.

Conflicts of interest

The authors have no conflicts of interest to disclose.

Author contribution statement

Patrick Carré: conceptualization, administration, original draft, review & editing. Maike Gärtner: validation, review & editing. Sarah Bothe: validation, review & editing. Thomas Piofczyk: conceptualization, validation, review & editing. Sara Hadjiali : validation, review & editing.

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