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Solvent solutions: Comparing extraction methods for edible oils and proteins in a changing regulatory landscape. Part 4: Impacts on energy consumption☆

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Abstract – This study compares various solvents for edible oil extraction, focusing on their energy consumption impacts. The research examines traditional hexane and alternative solvents, using both theoretical calculations and experimental data. The article presents a thermodynamic analysis of solvent-water separation using ChemSep software for rectification simulations. Results show significant differences in energy requirements, with acetone being potentially the most efficient and alcohols (ethanol and isopropanol) requiring substantially more energy at desolventization step. Solvent hold-up in the marc is a crucial factor affecting desolventization energy consumption. Experimental data from a pilot plant study on rapeseed cake extraction is presented, showing higher retention rates for ethanol and isopropanol compared to hexane. For other solvents, retention rates are estimated using the Hansen solubility parameter δh. Energy requirements for meal desolventization are calculated, considering factors such as solvent properties, marc composition, and steam usage. Alternative solvents generally show higher energy consumption compared to hexane. With a hypothetical non-distillation scheme the heat required is +76% for ethanol, +32% for isopropanol, −21% for acetone. It is +42% for the acetone solvent in traditional miscella evaporation. Methyl ethyl ketone (MEK) would require +66%, ethyl acetate 33% and 2-methyloxolane +35% more heat. Dichloromethane and isohexane require a little less energy because of their low boiling point while cyclohexane requires 5% more. The study also discusses the implications of solvent choice on desolventizer-toaster-dryer-cooler (DTDC) design and operation, highlighting potential challenges with high-moisture in the meal resulting from intensive use of direct steam.

Keywords: Solvents / energy / extraction / desolventisation / drying

Résumé – Comparaison des méthodes d'extraction pour les huiles alimentaires et les protéines dans un contexte réglementaire en évolution. Partie 4 : Impacts sur la consommation d'énergie. Cette étude compare l'impacts sur la consommation d'énergie du procédé d'extraction des huiles de plusieurs solvants. Ce travail examine l'hexane traditionnel et des solvants alternatifs, en utilisant à la fois des calculs théoriques et des données expérimentales. L'article présente une analyse thermodynamique de la séparation solvant-eau à l'aide du logiciel ChemSep pour les simulations de rectification. Les résultats montrent des différences significatives dans les besoins énergétiques, l'acétone étant potentiellement le plus efficace tandis qu'éthanol et isopropanol nécessitent nettement plus d'énergie, notamment lors de l'étape de désolvantation. La rétention de solvant dans le marc est un facteur crucial affectant la consommation d'énergie de désolvantation. Des données expérimentales d'une étude pilote sur l'extraction de tourteau de colza sont présentées, montrant des taux de rétention plus élevés pour l'éthanol et l'isopropanol par rapport à l'hexane. Pour les autres solvants, les taux de rétention sont estimés à l'aide du paramètre de solubilité de Hansen δh. Les besoins énergétiques pour la désolvantation du tourteau sont calculés, en tenant compte de facteurs tels que les propriétés du solvant, la composition du marc et l'utilisation de vapeur. Les solvants alternatifs montrent généralement une consommation d'énergie plus élevée que l'hexane. Avec un procédé

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

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sans distillation, la chaleur requise serait de +76% pour l'éthanol, +32% pour l'isopropanol, −21% pour l'acétone. Elle est de +42% pour l'acétone si le miscella est distillé classiquement. Le méthyléthylcétone nécessiterait +66%, l'acétate d'éthyle +33% et le 2-méthyloxolane +35% de chaleur supplémentaire. Le dichlorométhane et l'isohexane nécessitent un peu moins d'énergie en raison de leur faible point d'ébullition, tandis que le cyclohexane en requiers 5% de plus. L'étude discute également des implications du choix du solvant sur la conception et le fonctionnement du désolvanteur-toasteur-sécheur-refroidisseur (DTDC), soulignant les défis potentiels liés à l'humidité élevée du tourteau résultant de l'utilisation intensive de vapeur directe.

Mots clés : Solvants / énergie / extraction / désolvantation / séchage

Highlights

- In terms of thermal energy saving, hexane is surpassed only by dichloromethane and acetone using an untested non-distillation scheme.
- Isopropanol; ethyl acetate; and 2-methyloxolane require approximately 30-35% more heat than hexane.
- Ethanol and methyl ethyl ketone lag significantly behind.

Abbreviations

A:	Enthalpy of vaporisation of the water in the DT' vapours (MJ for 1000kg of flakes)
B:	Enthalpy of vaporisation of the solvent in the DT' vapours (MJ for 1000kg of flakes)
Cp_{meal}:	specific heat of the meal ~2MJ/kg/°C
Cp_o:	specific heat of the oil (MJ/kg).
Cp_s:	specific heat of the solvents 'S' (see Table 1 in 1rst part of this series of articles) (MJ/kg).
Cp_w:	specific heat of the water (MJ/kg).
D:	total heat consumption by the DT (MJ for 1000 kg of flakes)
E:	Enthalpy in the DT' vapours (MJ for 1000 kg of flakes)
F:	Enthalpy for the vaporisation of the solvent contained in the miscella (MJ for 1000 kg of flakes)
G:	Difference between the heat required to evaporate the solvent from the miscella and the heat contained in the DT' vapours (MJ for 1000 kg of flakes).
L_s:	fraction of water added to the vapours for a water concentration 5% above azeotropic concentration.
M_{DDM}:	Mass of defatted dry material in 1 unit of flakes.
M_f:	flakes mass (1000 kg).
M_{meal}:	$(M_f - M_o)$ (830 kg).
$Mmol_{water/s}$:	molar mass of water or solvent s.
M_o:	extractable oil mass in the flakes (170ks);
M_w:	Mass of water in the flakes (100 kg).
q:	Mass of water that must be dried in the marc (kg for 1000 kh of flakes).
Rd:	coefficient of drying efficiency (0.9).
T_{az}:	solvent azeotrope temperature (°C).
T_{DT}:	temperature of meal in DT (°C).
T_{dist}:	final temperature of the oil in distillation (100 °C).
T_{ext}:	temperature in the extractor = T_{az} x 0.9 (°C).
T_{init}:	initial temperature (25 °C).
u:	water content of the miscella (kg for 1000 kg of flakes).
W:	Enthalpy for drying the meal (MJ for 1000 kg of flakes).
X:	Sensible heat for bringing the fresh solvent and oil-bearing material to the extractor temperature (MJ for 1000 kg of flakes).
X':	sensible heat for heating the extractor in the case of ethanol, IPA and acetone in non-distillation schemes (MJ for 1000 kg of flakes).
α:	solvent retained in the marc after extraction (kg for 1000 kg of flakes)
β:	Amount of solvent in the miscella after extraction (kg/1000 kg of flakes)
γ:	amount of water in the DT' vapours at azeotropic concentration in kg for 1000 kg of flakes
Δh_w:	latent heat of vaporisation of water (2.2 MJ/kg)
Δh_{ws}:	latent heat of vaporisation of the solvent s (see Table 1a MJ/kg).
δ_h:	Hansen solubility parameter for hydrogen bonding.
ϵ:	Mass of direct steam condensed (kg for 1000 kg of flakes)
π:	water content of the meal at the outlet of the desolventisation (kg for 100 kg of wet meal)
π_f:	final water content of the meal (12%).
σ_{sw}:	water solubility in the solvent s (kg/kg).
ϕ_s:	oil concentration in the final miscella (g/g).
ω_s:	water concentration in the azeotrope of the solvent s

1 Introduction

The global vegetable oil industry is facing increasing pressure to adopt more sustainable and environmentally friendly practices. One area of focus is the extraction process, where traditional hexane-based methods are being scrutinised due to environmental and health concerns. This has led to a growing interest in alternative solvents for oil extraction, each with its own set of advantages and challenges. This article is the fourth

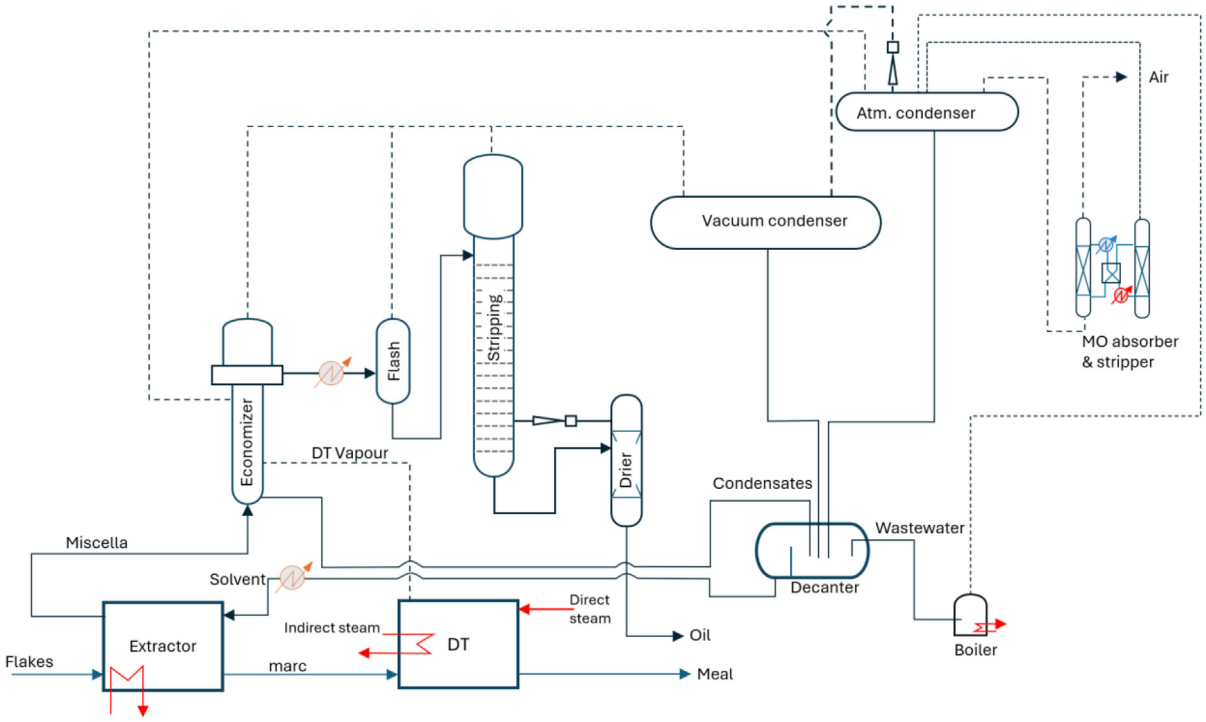

Fig. 1. Flowsheet diagram of a conventional solvent extraction adapted from Le Clef & Kemper (2015).

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). These solvents have the advantage of being listed in Annex 1 of Directive 2009/32/EC, although for some, adjustments would be required. Solvents such as ethanol or isopropanol exhibit beneficial characteristics in terms of health safety and acceptability but have limited oil-dissolving power. Another, DCM, offers the advantage of being non-flammable but have a less desirable toxicity profile. Solvents such as acetone, MEK, or ethyl acetate, have intermediate properties, being more effective than alcohols and less toxic than hexane, without, however, matching its ease of use. 2-MeOx is the subject of significant industrial development and presents an advantageous technological and toxicological profile, albeit with some drawbacks to consider.

In this part, a comprehensive analysis of the energy requirements for different stages of the extraction process is provided, with a particular focus on solvent recovery and meal desolventization. The study employs both theoretical models and experimental data to compare the energy demands of traditional hexane with alternative solvents. It examines factors such as solvent-water separation, solvent retention in the meal, and the heat required for desolventization. Detailed calculations and simulations are presented to illustrate the potential energy impacts of switching to alternative solvents. This analysis is crucial for the oilseed processing industry as it navigates the complex landscape of regulatory changes, sustainability goals, and operational efficiency. This document provides a thorough examination of the energy implications of different solvents. In doing so, it offers valuable insights for decision-makers contemplating the transition to new extraction technologies. The findings presented here contribute to the broader discussion on the future of edible oil extraction, balancing the need for more sustainable practices with the practical considerations of energy consumption and process efficiency.

1.1 Short presentation of the process

Although the effects of different solvents on the process are presented in the third article of this series, we will recapitulate here, for readers who may only read this particular article, the various unit operations of the oilseeds crushing process as well as their interconnections that enable the recycling of a portion of the consumed heat. We will also address the additional operations that a change in solvent may necessitate. Readers who have already familiarized themselves with Part 3 may proceed directly to the subsequent chapter.

Figure 1 represents the flowsheet diagram of a conventional solvent extraction plant. The extractor receives recycled solvent and prepared oleaginous material. It produces liquid miscella and marc, the latter being the residue of the solid matrix from which oil has been extracted, containing a variable amount of solvent. This marc is transferred to the desolventizer (Fig. 4) where the entire mass is heated to a temperature slightly above the boiling point of water to facilitate solvent evaporation using both indirect and direct steam. For indirect steam, the heat exchange occurs *via* a metal tray within which steam condenses without coming into contact with the meal. For direct steam, vapor is injected into contact with the meal in the lower part of the

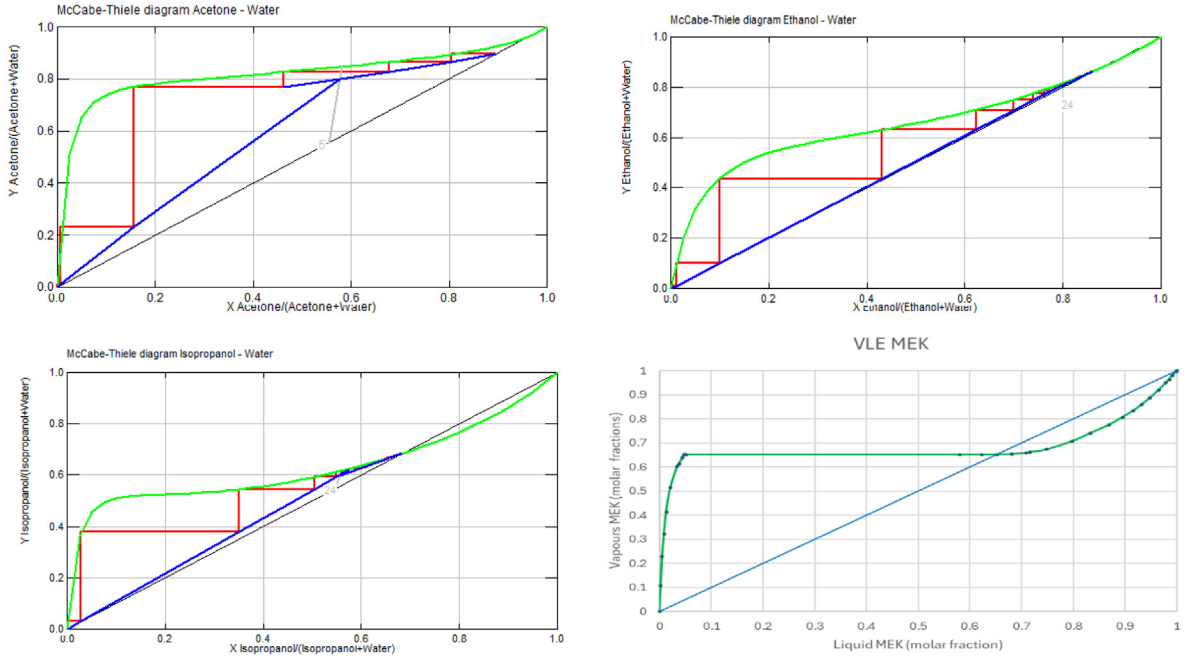

Fig. 2. McCabe-Thiele diagrams for model distillation of acetone, ethanol, and isopropanol generated using ChemSep software. The simulations assume an initial water concentration of 20 mass% in each mixture. X axis represents the molar concentration of the solvent in the liquid phase, Y, the molar concentration of the solvent in the vapours phase. The vapour/liquid equilibrium diagram of MEK corresponds to experimental data obtained by Cho *et al.* (1983).

equipment and ascends counter-currently towards the marc inlet zones. A portion of this steam condenses within the solid, transferring its latent heat of vaporization, thereby increasing the moisture content of the material. The vapours exiting the desolventizer contain a proportion of water that depends on the solvent's ability to form an azeotrope. The aim is to slightly exceed this azeotropic concentration to ensure proper solvent desorption. The vapours from the desolventizer pass through equipment called an "economizer," where their latent heat is used to preheat the miscella and initiate its evaporation for oil recovery. The concentrated miscella is subsequently heated to evaporate most of residual solvent. The oil is then stripped of remaining solvent traces by passing through a stripping column where direct steam is used to complete solvent recovery. As direct steam contact may cause oil to absorb moisture, the oil undergoes a vacuum drying stage before being cooled and stored. Solvent condensates are transferred to a decanter that separates water and solvent condensates. The aqueous effluent passes through a reboiler to eliminate trace amounts of solvent that water may contain, while the used air is passed through a mineral oil absorption system. This system captures non-condensed solvent vapours and, after reheating the mineral oil, redirects these vapours to a condenser.

1.2 Specific preparation

For solvents whose performance could be decreased by absorption of the water contained in the flakes or prepress-cake, **preliminary drying** of the incoming material may be required. In the case of seeds such as rapeseed and sunflower, which undergo pre-pressing before solvent extraction, drying can occur during the conditioning phase preceding mechanical extraction. Flakes typically undergo a cooking process during which drying can be pushed to 2-3% water content without compromising pressing quality, as presses generally function better with drier matrices. Should more extensive drying be necessary, additional drying of the cake would be conducted using hot air dryers. Soybean flakes would likely prove more challenging to dry due to the initial water content of the beans (10-12%). After drying, they would probably lose their mechanical integrity, potentially causing solvent percolation issues. The use of an expander prior to drying would be essential to ensure optimal extraction is maintained.

1.3 Non-distillation scheme

With ethanol, isopropanol and acetone, **non-distillation scheme** has been proposed to avoid the recovery of the oil by evaporation of the solvent. This procedure uses the low solubility of the oils in these solvents at low temperatures for separating the oil from the solvent. After extraction, the miscella is cooled to the lowest possible temperature, the oil precipitate and being heavier than the solvent it can be separated by decantation. The solvent phase called "lean miscella" contains a residual amount of oil but can be redirected to the extractor after reheating. A fraction of the lean miscella can be reprocessed by evaporation using the latent

heat of vaporisation of the desolventizer for the recovery of the lipids trapped in this fraction.

Another aspect to consider is the **elimination of process water** from the recovered solvent, which can prove more complex for solvents in which water can dissolve to significant levels. Rectification is a feasible step in the absence of an azeotrope between water and the solvent, or when such an azeotrope does not present a problematic concentration. In the case of alcohols, pervaporation offers a more efficient solution.

2 Energy required to remove water in the solvent (Ethanol, isopropanol, acetone, methyl ethyl ketone)

In order to perform a thermodynamic comparison between these solvents, the simulation of the distillation of 100 kg/s of a mixture with 80:20 (m/m) solvent to water composition was made. For this purpose, ChemSep version 8 (Koojman et Taylor, 2022) was used, a simulation software designed to predict the operation of distillation columns. The thermodynamic parameters for acetone, EtOH and IPA were DECHEMA for K-values, NTRL for activity coefficients, Antoine for vapour pressure. Figure 2 shows the McCabe-Thiele diagrams given by ChemSep.

- Acetone: with an 8 trays column fed by the 5th with a reflux ratio of 0.5 and an acetone concentration target in the bottom of 0.01% (mass fraction) gives 82.7 kg/s of condensates containing 99.998% of the acetone in the feed. These condensates contain 3.3% of water (mass). The boiler requires 81.7 MW of energy, *i.e.*, 227 kWh/t.
- Ethanol: A simulation was conducted for a distillation column comprising 30 theoretical trays. Due to the smaller concentration gradient in the Vapor-Liquid Equilibrium (VLE) near the azeotropic point, the column dimensions for ethanol separation necessitated an increase compared to those required for acetone. The feed was introduced at tray 24, with the reflux ratio set at 7. A target ethanol residue concentration of 0.1% in the bottom flow was specified. The simulation yielded a condensate flow rate of 85.1 kg/s with a water content of 6.0%. The reboiler duty was calculated to be 643.2 MW. These parameters translate to an energy consumption of 1787 kWh per tonne of feed processed.
- IPA: the UNIFAC model was employed for K-value calculations, replacing NRTL to enhance azeotropic concentration prediction accuracy. A 30-tray distillation column was simulated with feed introduced at tray 24. The reflux ratio was set at 2, and a target IPA residue concentration of 0.1% in the bottom fraction was specified. The simulation yielded a condensate flow rate of 91.1 kg/s with a water content of 12.2%. The reboiler duty was calculated to be 257.0 MW, corresponding to an energy consumption of 731 kWh per tonne of feed processed.
- MEK: Figure 2 shows the vapours/liquid equilibrium according to Cho *et al.* (1983). Methyl ethyl ketone forms an azeotrope that starts at a concentration of 17 g/100 g in the liquid phase (5.1% molar) and can only be exited at a concentration of 90 g/100 g (70.8% molar). The water content in the vapor phase is 11 g/100 g (34.8% molar). Consequently, removing water from this solvent *via* rectification poses significant challenges

Reducing the water concentration to an acceptable level in acetone can be achieved with relatively low energy input. The rectification process is significantly more energy-intensive in the case of ethanol due to the small concentration difference between the vapor and liquid phases in the azeotropic region. This phenomenon is somewhat less pronounced for isopropanol; however, when compared to acetone, this operation remains energy-demanding for this solvent. Pervaporation should be preferred as a method for water elimination because its heat requirement is limited to the latent heat of water vaporisation. The saving in energy cost is partially counterbalanced by higher capital costs for the membranes and their utilities, so the dehydration of the solvent is still a disadvantage for water miscible solvents.

3 Effect of the solvents on meal desolventization

3.1 Energy consumption and solvent hold-up in the marc

The factors that influence the energy consumption at the desolventization operation are:

- The miscella retention rate in the marc,
- The water content of the marc (hydrophilic substance in the solid are retaining some of the water brought to extractor by the fresh solvent),
- The specific heat of the solvent,
- The latent heat of vaporisation of the solvent.

According to Zhang *et al.* (2002), the IPA 95% holdup in cottonseed marc was 55% with flakes and 33% with collets. Lusas *et al.* (1997) in their pilot-plant trials observed IPA holdup in collets of ~43% with cotton seeds and ~38% with soybean collets. For comparison with hexane, Watkins *et al.* (1989) observed 39.5% and a range of 18 to 27% with collets in cottonseed. With 95% ethanol Hron et Koltun (1984) obtained a marc from flakes with 60% of volatile material. Baker and Sullivan (1983) added a press to mechanically reduce the solvent holding of the marc they obtained after extracting soy flakes with IPA. To the best of our knowledge, this operation is not feasible at industrial scale because of the safety concerns that such a process raises. Indeed, the temperature can reach the self-ignition temperature of the solvent quite readily in case of a problem in presses. Alternative methods, such as centrifugal dewatering—sometimes employed in facilities producing protein concentrates through hydroalcoholic extraction of white soybean flakes—could be explored. However, this approach has not been documented in the literature.

As there are few pilot scale studies available providing reliable data on the performances of alternative solvents, information about the solvent holdup in the marc are even scarcer. To fill this gap of information on the holding capacity of rapeseed or sunflower prepress-cakes we are disclosing an unpublished study made at the CREOL pilot plant in 2009 in which the solvent retention rate was measured on a rapeseed

Table 1. Evaluation of the energy consumption required for the desolventization of 100 kg of rapeseed meal.

	Solvent in 100 kg of marc (kg)	Solvent for 100 kg of meal (kg)	Enthalpy of vaporisation of the solvent (kJ/100 kg)	Enthalpy of the steam in vapours (kJ/100 kg)	Sensible heat (kJ/100 kg)	Total heat (kJ/100 kg)	Total energy variation *vs.* hexane	Mass water condensed kg/100 kg	Water content of the meal
n-Hexane	22.1	28.3	9 421	4 004	9 389	22 815	0%	4.62	15.9%
iso-Hexane	22.1	28.3	9 138	4 004	9 573	22 716	0%	4.59	15.9%
cyclo-Hexane	22.2	28.6	10 298	6 659	7 805	24 763	9%	4.44	15.7%
Methanol	43.2	76.0	150 323	4 835	9 631	164 788	622%	39.26	36.8%
Ethanol	40.4	67.9	57 859	10 307	7 252	75 418	231%	15.98	24.1%
Propan-2ol	37.6	60.3	40 131	21 218	6 826	68 176	199%	11.53	21.1%
Acetone	28.7	40.2	20 920	5 200	10 390	36 510	60%	7.69	18.3%
MEK	26.9	36.8	16 292	14 556	6 887	37 735	65%	5.69	16.7%
Ethyl acetate	28.9	40.6	17 464	9 400	8 008	34 873	53%	6.25	17.2%
DCM	28.8	40.4	13 297	2 336	13 322	28 955	27%	6.53	17.4%
2-MeOx (1)	26.1	35.4	12 875	10 257	7 672	30 804	35%	5.04	16.2%
2-MeOx (2)	42.0	72.4	26 359	31 813	8 145	66 317	191%	8.47	18.9%

(1) Solvent hold-up according to our assessment. (2) solvent hold-up according to Bartier *et al.* (2024).

prepress cake extracted by hexane, EtOH 96% or IPA 87.8%. The press cake was dried in the case of EtOH to 2% w.c., 7% in the case of IPA, and used as it in the case of hexane (10.1% w.c.). The extractions were made in a 6 L percolator on 2 kg of cake disposed in a ~350 mm bed depth. Extractions were made with 5 successive washes of 5 L of solvent heated at 50 °C for hexane and 7 washes at ~70 °C for EtOH and IPA. The solvent was recirculated at a flow rate sufficient to soak the upper layer of the bed during 10 min. After the extraction cycle, the marcs were holding 22.1%, 40.7% and 37.3% of solvent for respectively hexane, EtOH and IPA and 10.2, 2.2 and 19.1% of water (in the same order).

The differences in hold-up capacity cannot be explained by only the density of the liquids. The water content of the solvent and its affinity for the hydrophilic biomass is likely to play a role. In order to give an idea of the potential holding capacity of the different solvent, we propose to use the δ_h coefficient of the HSP (hydrogen bonding capacity) since we observe a good alignment of EtOH and IPA values in the experimental data when plotting hold-up capacity and δ_h (Fig. 3).

It is not pretended that this relationship would reflect with accuracy the real holding capacity of the other solvents. In absence of real values, this approach fills a gap and makes it possible to give an order of magnitude of the differences in energy requirement to remove the solvent from the meals.

In their experiment utilizing a miniature Crown IV extractor with aged soybean flakes, Bartier *et al.* (2024) reported volatile material content in the marc of 28.5% for hexane and values ranging from 40.5% to 50.6% for 2-MeOx, varying as a function of the initial solvent's water content. The lowest liquid retentions were observed with solvent containing 1% water, while the highest were recorded with solvent approaching water saturation (4.1%). The extraction was performed on flakes containing 20.3% oil on a dry matter basis and 4.1% water on a wet basis. Following the operation, the resulting marc contained 48% volatile matter, of which 42% was solvent. The resulting miscella exhibited a water content of only 1.6%, indicating the absorption of some of its water content by the meal. The value observed for hexane aligns closely with the one used in this comparison. However, the reported value for 2-MeOx is substantially higher than our assessment (26.1%), indicating a significant discrepancy in the measurements. While an experimental estimation is generally preferable to a purely theoretical one, the data presented by Bartier *et al.* raises some concerns regarding its reliability. The reported material balance for lipids shows inconsistencies that warrant further examination. Specifically, given an initial oil content of 21% on a dry basis and oil residues in the meal below 2%, one would expect the concentration in the miscella to be substantially higher than the reported values of 14.6 and 13.4 g/100 g for 2-methyloxolane and hexane, respectively. This discrepancy suggests that further validation of the experimental methodology and results may be necessary to ensure the accuracy of the conclusions drawn. Given the age of the flakes (17 months), it is possible that a portion of the oxidised lipids were not extracted, significantly increasing the marc's retention capacity. For the following comparisons, the assessment based on rapeseed press-cake and not for soybean flakes has been used. Bartier's results will be also presented as a basis for comparison (Bartier *et al.*, 2024).

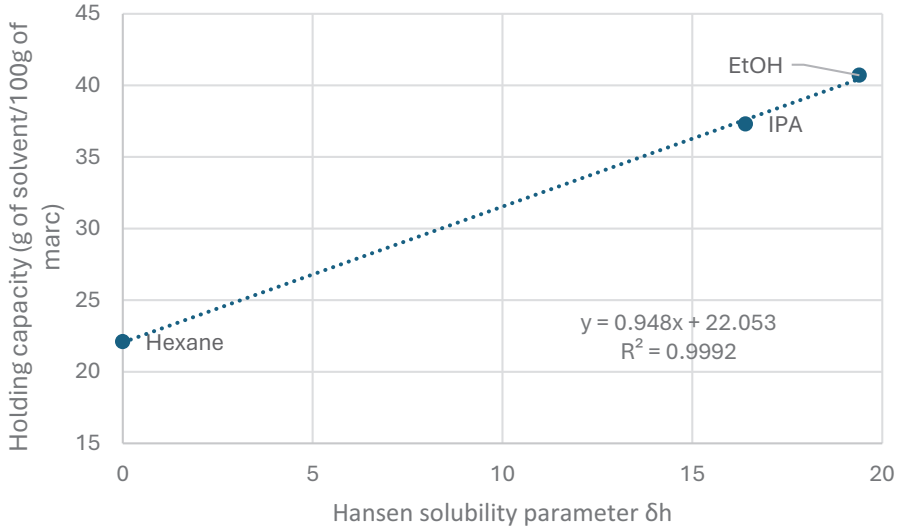

Fig. 3. Experimental solvent hold-up in the marc as function of the Hansen solubility parameter δ_h.

Table 1 gives a rough assessment of the energy that would be consumed by the desolventization of the meal. The sensible heat is the amount of heat required to bring the temperature of the meal from the extractor temperature (90% of the boiling point or azeotrope temperature of the solvent) to 100 °C and the solvent retained in the marc from extractor temperature to its boiling temperature. The enthalpy of the steam in the vapours is the latent heat of vaporisation of the water present in the vapours (azeotropic concentration + 5% [molar]). Total heat summarises the enthalpy of vaporisation of the solvent, the enthalpy of the steam in the vapours and the sensible heat.

Methanol which has already been ruled out for its poor miscibility with oil is definitely disqualified for its huge energy requirement. Ethanol and isopropanol are also showing major increases in energy need for this step which is likely to impact their attractiveness as extraction solvent for oilseeds. The case of 2-MeOx underscores the critical importance of accurately assessing solvent hold-up, as the discrepancy between our theoretical predictions and Bartier *et al.*'s experimental observations is substantial. It also shows the importance of the energy cost of the water steam in the vapours. This part of the energy will be recovered later, therefore, its global impact on energy consumption is likely to be cushioned.

DCM looks less demanding with a 27% increase. This increase is somewhat surprising considering the low heat of vaporisation of this solvent. The low temperature in the extractor (34 °C) partly explains that figure because much more heat is required to bring the meal to 100 °C than for the other solvents. In addition, the HSP δ_h of DCM also predicts a high solvent retention in the marc. Ethyl acetate 53% increase is mainly explained by the solvent heat of vaporisation 29% above the one of hexane and the largest solvent hold-up in the marc. The water azeotrope which contains 8.5% of water explains the rest of the increase. Acetone would demand 60% more steam for the desolventization which is less than MEK (65%) mainly because MEK' azeotrope with 14% of water drives much more steam in the vapours than acetone which does not form azeotrope.

The final water content of the meals was calculated on the basis of the same initial water content in the marc (12%) which is purely hypothetical, and the addition of the condensed direct steam which represents 54% of the total heat input. This figure just illustrates the differences in energy requirement since adjustments in water content are likely to be managed in order to limit the water input in the case of solvent with water miscibility.

Obviously, these figures should not be taken literally, as they are not based on experimental data, with the exception of ethanol, IPA, and 2-MeOx but they do take account of the latent heat of vaporisation effect, which is an established fact, the azeotropic concentrations of water in the vapours and of the undeniable change in solvent retention in the marc, also attested for 2-MeOx by Claux *et al.* (2021) who reported "a higher solution uptake by the vegetable matrix" with the water saturated solvent.

3.2 Desolventizer operation

Figure 4 presents the general disposition of a desolventizer-toaster-dryer-cooler. The wet marc is introduced by the top and pass to several trays where it is heated by indirect steam to evaporate a significant proportion of the solvent. Subsequently, it descends onto a series of trays where it comes into contact with direct steam in a countercurrent flow. The steam traverses the trays through specifically designed orifices. In the lower section of the equipment, it undergoes drying by hot air injection, followed by cooling with cold air. Direct steam is the steam injected in the desolventizer to evaporate the solvent and displace the partial pressure of solvent vapours for readily reaching the required residues level. The substantial difference in the latent heat of vaporization between hexane and water allows for the efficient use of indirect steam. This difference enables indirect steam to supply a significant portion of the heat required for the operation. According to Demarco et Gibon (2020), hexane marc of soybean contains 26 to 30% of hexane in mass, a majority of the heat required to evaporate the solvent comes from direct steam. The residence

Table 2. Assessment of the heat required for the desolventization of the meal and distillation of the miscella of 1000 kg of soybean flakes based on the assumption that hexane marc would contain ~30% of solvent.

	n-Hexane	iso-Hexane	Cyc.Hexane	MeOH	EtOH*	IPA*	Acetone*	Acetone	MEK	EA	DCM	2-MeOx
Input flakes (kg) M_f	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000
Oil in flakes (kg) M_o	170	170	170	170	170	170	170	170	170	170	170	170
Water in Flakes (kg) M_w	100	100	100	100	100	100	100	100	100	100	100	100
Water in Flakes after drying (kg) M'_w	100	100	100	100	10	60	70	70	100	100	100	100
Flakes drying (MJ) Q_d					396	110	83	83				
Defatted flakes (kg)	830	830	830	830	740	790	800	800	830	830	830	830
Solvent in the marc (kg) α	248	248	249	423	357	359	292	292	288	304	304	282
Solvent in the miscella (kg) β	680	680	680	3 230	2 259	1 530	680	680	680	680	680	680
DT water in vapours @ azeotrope+5% (kg) γ	16	16	26	12	23	57	5	5	52	32	8	37
DT Enthalpy of water in vapours (MJ) A	35	35	58	27	50	126	10	10	114	70	18	82
DT Enthalpy of solvent vaporisation (MJ) B	83	80	90	837	304	239	152	152	128	131	100	103
DT-sensible heat (MJ) C	78	80	65	77	51	51	83	83	57	66	110	64
Total DT heat (MJ) A+B+C = D	196	195	213	940	405	417	245	245	298	267	228	248
Mass/water condensed direct steam (kg) ε	34	33	32	191	74	61	49	49	39	41	44	35
Water content of the meal π	15.5%	15.4%	15.3%	28.5%	10.3%	14.2%	14.0%	14.0%	16.0%	16.2%	16.5%	15.6%
Enthalpy in DT vapours (MJ) A+B = E	118	115	148	864	354	365	162	162	242	201	117	184
Water content in the miscella (kg) u	0.2	0.0	0.2	0.0	106	213	28	28	93	21	1	31
Enthalpy for miscella distillation (MJ) F	**262**	**244**	**280**	**6 453**	**2 225**	**1 562**	**447**	**447**	**544**	**376**	**253**	**353**
Residual miscella distillation (MJ) F-E = G	156	141	147	5 675	1 906	1 233	301	301	327	195	147	187
Water to remove from the meal (kg) q	34	34	33	191	–	21	19	19	39	42	44	66
Enthalpy for meal drying (MJ)W	83	83	80	468	0	52	48	48	95	102	109	162
Reaching extraction temperature (MJ) X / X'	119	117	141	372	174	153	63	109	199	171	29	152
Final heat consumption (MJ) D+G+W	555	535	581	7 455	975	731	437	785	919	736	513	750
Final heat consumption (kWh/t of flakes)	154	149	161	2 071	271	203	121	218	255	204	142	208
Variation vs hexane	0%	-3%	5%	1244%	76%	32%	-21%	42%	66%	33%	-8%	35%

*) calculations done according to a non-distillation scheme. X' (Eq. (19)) was used for EtOH, IPA and acetone instead of X (Eq. (18)).

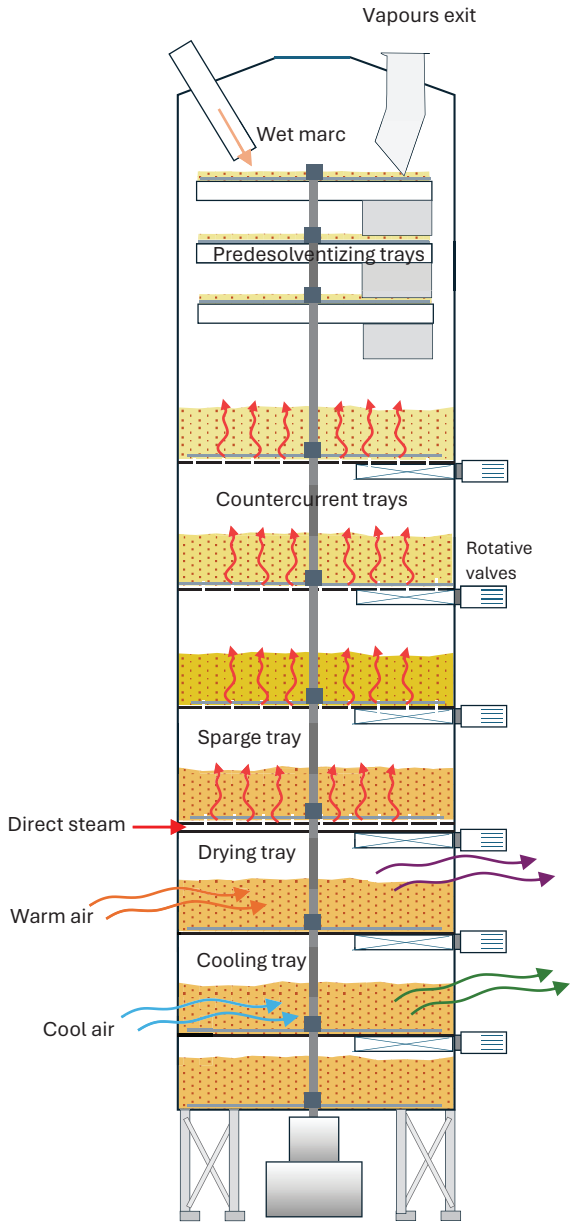

Fig. 4. Desolventizer-toaster-dryer-cooler configuration according to Kemper (2024).

time in the part of the desolventizer where the temperature is above 100 °C ranges between 20 and 30 min. The typical temperature during this exposure to direct steam is 107 °C. The moisture content in the flakes rises from 12 to 19% at the highest and decreases to 17.5% in the last tray because of the overheated character of the steam. According to the data in Figure 11 of this publication, indirect steam reduces the marc solvent content from 30% to 23%, while direct steam does the rest in the lower part of the desolventizer. This means that indirect heating removes 46% of the hexane and direct steam 54%. Demarco and Gibon state that 70% of total steam consumed in soybean crushing plants are used by the desolventizer. In a book dedicated to sunflower processing, Le Clef and Kemper (2015) provide the following information: the initial temperature of the marc is 59°C, with a solvent content of 25-30%. The vapor temperature ranges from 70−75°C, while the temperature during desolventization phases is 67°C. The majority of heat is supplied by direct steam. The exit temperature of the meal reaches 109°C, and the final hexane content in the meal is between 100-500 ppm.

The repartition between direct and indirect steam is determined by the device design. The effectiveness of heat exchange from indirect steam is constrained by the surface area of the pre-desolventizing trays. Concurrently, the application of direct steam to the meal is limited by moisture content considerations. The meal's moisture must be kept below a critical threshold to prevent it from becoming sticky. Exceeding this threshold could lead to clogging of the rotary valves that facilitate the meal's movement between trays. Because the DTDC is the costliest piece of equipment in the plant, its capacity determines the capacity of the rest of the facility. A solvent substitution would have a more or less strong impact on the DTDC capacity and consequently on the whole oil-mill. According to the figures of Table 1, any solvent switch would have an important impact on the DTDC capacity which can be estimated as proportional to the variation in heat requirement, given that this device can be described as a heat exchanger. The boiling temperature of the solvent-water azeotrope or the solvent if this one does not have an azeotrope with water will also play a role because the heat transfer is proportional to the temperature differential between the source and the sink. For this aspect, cyclohexane, ethanol, IPA, MEK and EA, would have a negative effect on the heat transfer capacity, and DCM a positive one.

The column "mass of water condensed" in Table 1 has been calculated on the hypothesis that 54% of heat required would be supplied by the condensation of direct steam in the meal and the "water content in the meal" results from addition of this condensed steam to 12% of water already present in the meal (wet basis). Based on our empirical observations, moisture contents up to approximately 20% remain within acceptable limits regarding the risk of forming adhesive agglomerates and causing obstruction issues. However, beyond this approximate threshold, the moisture level may be considered excessive for safe extractor operation. In consequence, desolventization of alcoholic marc in absence of preliminary drying of the flakes could require a change in the repartition of the heat transfer with a larger share transferred from indirect steam. The design of the desolventizer would have to be revised by increasing the number of pre-desolventization trays.

For solvents exhibiting both water miscibility and low polarity, particularly methyl ethyl ketone, 2-methyloxolane, and ethyl acetate, a water-saturated solvent entering the extractor is likely to transfer a significant proportion of that water to the marc (Bartier et al., 2024). That is also possible with IPA at azeotropic concentration, but the experimental data were not showing a transfer of water when the rapeseed press-cake was dried to a 7% water content. In the case of EtOH 96% and rapeseed cake at ~2% of water, a slight transfer from the dried rapeseed to the miscella was observed (+0.8%).

4 Miscella distillation, heat recovery and overall heat consumption

As already mentioned in the introduction, a large part of the energy required for distilling the miscella is supplied by the

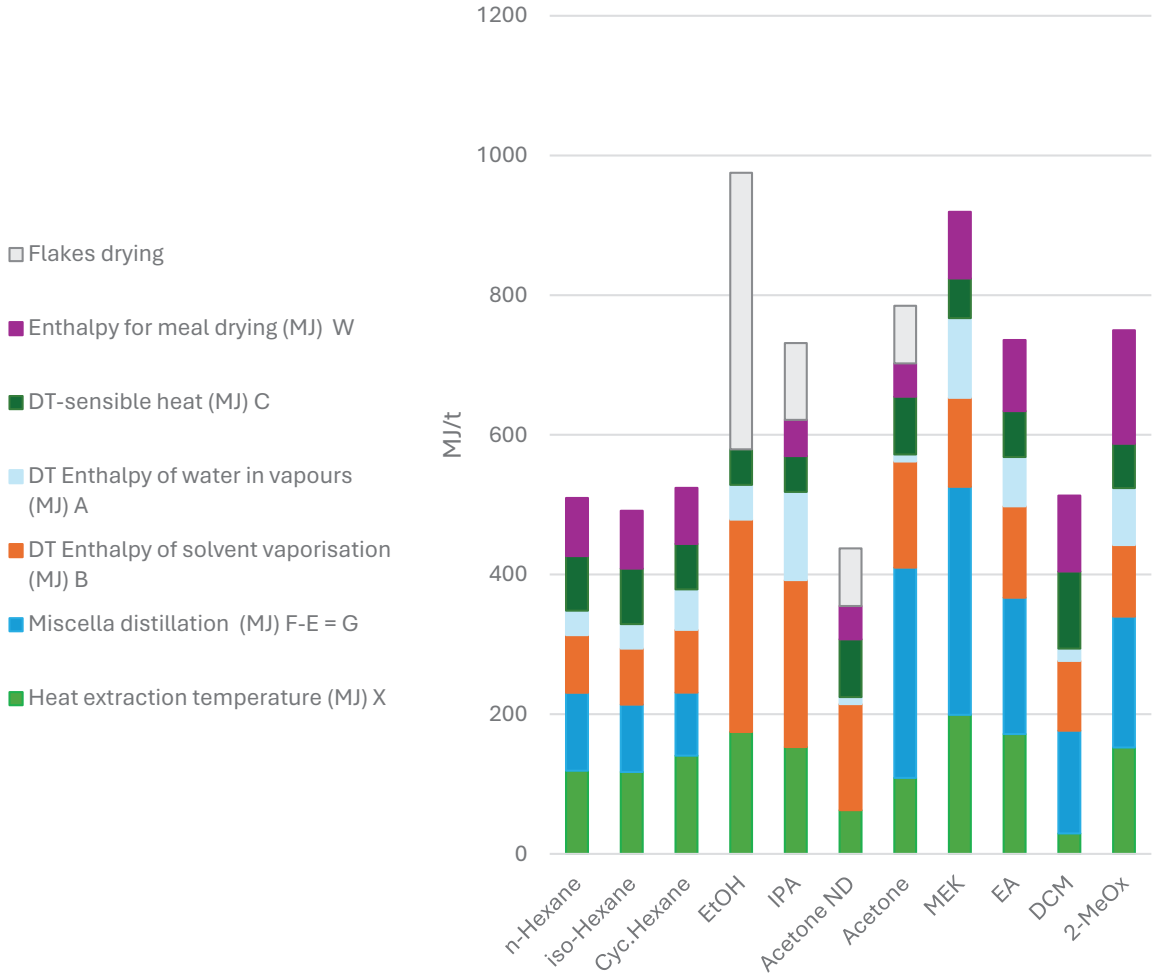

Fig. 5. Comparison for each solvent of the heat requirement origin according to calculation methods in annex.

heat contained in the DT vapours in a device called "economizer". In Table 2 we present the combination of the thermal energy consumed in the desolventizer-toaster-drier-cooler (DTDC) and for the miscella distillation after the recovery of the heat contained in the DT vapours. It is based on a new assumption about the solvent hold-up in the marc made to match the 30% in soybean flakes mentioned by Demarco et Gibon. For this transposition, we assumed that the differences between rapeseed press-cake and soybean flakes hexane hold-up are related to differences between drainage duration, marc depth in the extractor, and the size of macropores around the solid material. In other words, we assumed that there would be no additional solvent intra-particular uptake by the matrices and that only extra-particular volume would be concerned. On the second hand, we did not consider the differences in solvent density because heavier solvents are likely to be less retained in the larger pores and by lack of better information, we assumed that the mass retention was constant.

The simulation assumed an economizer efficiency of 90%, a miscella composition of 20% oil by mass, and a feed of 1000 kg soybean flakes containing 17% extractable oil and 10% water. The detail of the calculations is given in annex at the end of this article.

The heat required to evaporate the solvent from miscella (F) does not consider the additional stripping of the solvent residues, but considering the incertitude surrounding these calculations, we assume that it can be neglected since no significant differences are expected between the solvents. The differences at the level of heat requirement for the miscella distillation (F) of non-alcohols solvents are only related to their differences in latent heat of vaporisation since we hypothesise the same oil concentration at the outlet of the extractor.

Methanol is immediately disqualified as a viable option, with its energy consumption ratio equivalent to 1244% of hexane's, precluding any possibility of optimization. The reasons for this are unequivocal: firstly, the oil's low solubility in methanol necessitates the use of large solvent volumes; secondly, methanol's latent heat of vaporization is 5.9 times higher than that of hexane. These factors combined render methanol energetically unfavourable for this application.

In the case of other alcohols, we considered that the miscellas were less concentrated because of limited solubility of oils in these solvents. Concentrations ϕ_s were set at 5, 7 and 10% for respectively MeOH, EtOH and IPA and the masses of solvent in miscella (β, Eq. (2)) calculated accordingly. The saturation value considered for MeOH was not based on experimental results but set to 5% for the need of the comparison (even if it could be considered as over-optimistic). For EtOH, IPA and acetone, a modified processing was simulated in which the flakes are dried prior to the extraction at

1, 6 and 7% (wb.) of residual water. The amount of heat for this drying is assessed on the line Q_d of Table 2. The latent heat of vaporisation was corrected by factors 2 for EtOH and 1.25 for IPA and acetone to take account of the reduction of drying efficiency for low water content. The solvent dehydration was not included in the calculation. The effect of a mechanical pre-desolventization like in Lusas *et al.* (1997) could decrease the desolventizer duty, but the feasibility of this technique being disputable, this option was not retained. Another source of optimisation lies in using the heat of the miscella for warming the solvent going back to extractor. In this simulation, we assumed that 80% of the heat available in the miscella could be recycled for warming the new solvent (combination of lean miscella and condensates coming from the desolventizer, the heavy phase distillation and some lean miscella evaporation).

With this optimization where the miscella is not evaporated in totality, the variation in heat requirement for EtOH and IPA *versus* hexane strongly decreases from 439 and 305% to 76 and 32%. These savings are important but not sufficient to overcome the effects of the higher latent heat of vaporisation of these solvent and their bigger retention in the marc.

Figure 5 shows graphically the repartition of the heat consumption for each solvent except for the methanol which would have overshadowed the other solvents. For EtOH, the largest causes of heat consumption are related to desolventization and the intensive drying of the flakes prior to the extraction. The efficiency of that drying could be improved but EtOH would remain the most energy consuming method of extraction (MeOH aside). Intensive pre-extraction drying eliminates the need for meal drying after desolventization, streamlining the process. IPA, as stated in the literature, requires less energy than EtOH but remains far above the benchmark with 32% of additional heat requirement. High solvent retention in the marc is the main cause of this. Moreover, this solvent is rich in water which must be vaporised, and more direct steam is condensed in the meal and must be dried.

With acetone it is also difficult to foresee the cycle of the water in the system. In theory, non-distillation recovery of the oil could be possible with acetone but there is no available data about the composition of the phases resulting of miscella cooling, and the feasibility of using the lean miscella for new extractions. The study of gives little details on the acetone recycling except a ternary miscibility diagram for the system acetone-water-oil which shows that 5% of water strongly limits the oil miscibility while Pons and Eaves (1967) found a higher threshold above 10%. Nevertheless, calculations in Table 2 were using the same method as with alcohols, considering a non-distillation scheme to reduce the energy consumption. For clarity, Figure 5 shows for acetone both methods of calculation. Most of the differences between these methods are related to the reduction of consumption for the distillation. Overall non-distillation heat consumption is 21% below hexane which makes acetone attractive on the basis of these assumptions. Conversely, with distillation, this solvent would remain below the EtOH in regard to the energy issue and in the same order of magnitude as IPA. Miscella distillation and a higher sensible heat for reaching extractor temperature are the cause of this difference. However, these assessments are based on assumptions whose reliability is much less established than our knowledge of EtOH and IPA.

Methyl ethyl ketone requires 66% more energy than hexane ranking second after EtOH in Figure 5. The heat requirement increase is evenly distributed between all the sinks because of higher solvent hold-up in the marc, higher latent heat of vaporisation and an azeotrope with higher water content. The vapor-liquid equilibrium curve in Figure 2 reveals a crucial characteristic of the system. Over a broad range of water concentrations in the liquid phase, the vapor phase maintains a remarkably constant composition, with approximately 35% molar concentration of water (equivalent to 14% by mass). This plateau in vapor composition persists across a significant portion of the curve, indicating a robust equilibrium state. Notably, once the liquid mixture surpasses the azeotropic concentration, the vapor phase begins to exhibit a higher water content than the liquid phase. This behaviour suggests that attempts to reduce water content in the miscella below this threshold would be particularly challenging, as the system naturally resists further dehydration.

With ethyl acetate, an oil mill would consume about 33% more heat than hexane. The higher heat requirement comes mainly from the higher latent heat of vaporisation (+29%) and larger amount of direct steam required to displace the water concentration in the DT vapours beyond the solvent azeotrope. It is important to note that, according to our initial hypothesis, we estimated the water concentration in these vapours to exceed the azeotropic concentration by 5 percentage points. The azeotropic concentrations for hexane and ethyl acetate are 5% and 8.5%, respectively. The third most significant discrepancy lies in the meal drying process, which requires 22% more energy. This increase is attributed to the marc's higher solvent retention, resulting in greater direct steam condensation.

DCM, with the combination of a low boiling point (40 °C) and a latent heat of vaporisation close to the one of hexane has the potential to reduce the heat consumption by 8%. The marc would retain more DCM than hexane, but this increase is compensated by the lower heat required to reach extractor temperature and the distillation temperature.

2-methyloxolane would require about 35% more heat than hexane. Every compartment is slightly larger than its hexane equivalent with a latent heat of vaporisation 9% higher, a higher retention in the marc (21%), and a higher presence of water in the solvent. The heat consumption of this solvent is comparable to that of ethyl acetate and isopropanol, positioning these three as the most promising eco-friendly alternatives from an energy efficiency perspective. This assessment excludes acetone in non-distillation scenarios, given the uncertainties surrounding the assumptions made in that particular evaluation.

Iso-hexane with its low boiling point is likely to give a slight reduction of the energy consumption (-3%) while cyclohexane with its higher boiling point (80 vs 69 °C) and a latent heat of vaporisation 8% higher could lead to a 5% increase in heat requirement.

5 Conclusion

The comparison of energy consumption across different solvents in oilseed extraction is a complex and multifaceted issue. This study has revealed significant variations in energy

requirements for solvent recovery and meal desolventization among various solvents, with some alternatives to hexane showing substantially higher energy demands. However, it is crucial to recognize that these initial energy assessments do not represent the final word on solvent viability. Several key points must be considered:

a) Potential for optimization: Many alternative solvents, particularly alcohols like ethanol and isopropanol, have the potential for significant energy reduction through additional processing steps.
b) Trade-offs between energy and capital costs: Implementing energy-saving measures often requires increased capital investment. For instance:
   a. Solvent dehydration through pervaporation could substantially reduce the energy needed for alcohol-water separation.
   b. Implementing mechanical dewatering of the marc prior to desolventization could significantly reduce the energy demands. This approach would be particularly beneficial in scenarios where direct steam condensation is the primary heat source, as it would minimize the subsequent drying requirements.
   c. Technological advancements: Ongoing research and development may lead to more efficient extraction and recovery processes for alternative solvents, potentially narrowing the energy gap with hexane.
   d. Optimizing the oilseed preparation process to lower the oil content of the input material could yield multiple benefits. This modification would potentially: decrease the volume of solvent required for extraction and reduce solvent retention in the marc. The reduction in solvent retention would be a direct consequence of the lower initial oil content. With less oil to extract, the process would create smaller micro-cavities in the spent cake. These reduced cavities would have a diminished capacity to retain the liquid phase, thereby decreasing overall solvent retention.
c) Holistic assessment: Energy consumption is just one factor in solvent selection. Other considerations include solvent cost, environmental impact, worker safety, and product quality.
d) Regulatory landscape: Future regulations may prioritise environmental and safety concerns over energy efficiency, potentially favouring some alternative solvents despite higher energy use.
e) System-wide impacts: Changes in solvent choice can affect the entire processing system, from extraction efficiency to meal quality, which must be factored into overall assessments.
f) A special attention should be given to the effect of solvent switching to the capacity of the main device in the extraction plants which is the desolventizer. An increase in heat consumption is deemed to proportionally reduce the capacity of this device and by consequence to the whole facility. This would strongly impact the crushing cost of the oilseeds.

In conclusion, while this study provides valuable insights into the relative energy demands of various solvents, it also underscores the need for a more comprehensive evaluation. Future research should focus on optimising processes for alternative solvents, exploring innovative energy-saving technologies, and conducting thorough life-cycle assessments. As the industry moves towards more sustainable practices, the balance between energy efficiency, environmental impact, and economic viability will be crucial in determining the most suitable extraction solvents for the future.

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Annex

Calculations

$$\alpha = \left(M_f - M_o\right).\frac{(22.053 + 0.948.\delta_h)}{100} \quad (1)$$

$$\beta = \frac{(M_o - M_o.\phi_s)}{\phi_s} \quad (2)$$

$$L_s = \frac{Mmol_{water}}{Mmol_s}.\omega_s.0.05 \quad (3)$$

$$\gamma = \frac{(\omega_s + L_s).\alpha}{(1 - \omega_s - L_s)} \quad (4)$$

$$A = \gamma.\Delta h_w \quad (5)$$

$$B = \alpha.\Delta h_s \quad (6)$$

$$C = M_{meal}.(T_{DT} - T_{ext}).Cp_{meal} + \alpha.(T_{az} - T_{ext}).Cp_s \quad (7)$$

$$D = A + B + C \quad (8)$$

$$= 0.54.(B + C)/\Delta h_w \quad (9)$$

$$\pi = \frac{(M_w +)}{(M_{meal} +)} \quad (10)$$

$$E = A + B \quad (11)$$

$$u = \frac{\beta.\sigma_{sw}}{(1 - \sigma_{sw})} \quad (12)$$

$$F = \beta.\Delta h_s + \beta.(T_{dis} - T_{ext}).Cp_s + u.\Delta h_w + u.(T_{dis} - T_{ext}).Cp_w + M_o.(T_{dis} - T_{ext}).Cp_o \quad (13)$$

$$G = F - E \quad (14)$$

$$M_{DDM} = M_F - M_o - M_w \quad (15)$$

$$q = M_{DDM}.\frac{\pi}{(1 - \pi) - M_{DDM}.\frac{\pi_f}{(1 - \pi_f)}} \quad (16)$$

$$W = q.\Delta h_w/Rd \quad (17)$$

$$X = (T_{ext} - T_i).\left[M_f.Cp_f + (\alpha + \beta).Cp_s + (\alpha + \beta).\frac{\sigma_{sw}}{1 - \sigma_{sw}}.Cp_w\right] \quad (18)$$

$$X' = X - 0.8.(T_{ext} - T_i).\left(\beta.Cp_s + M_o.Cp_o + \beta.\frac{\sigma_{sw}}{1 - \sigma_{sw}}.Cp_w\right) \quad (19)$$