Alternative solvents to hexane for the extraction of rapeseed oil

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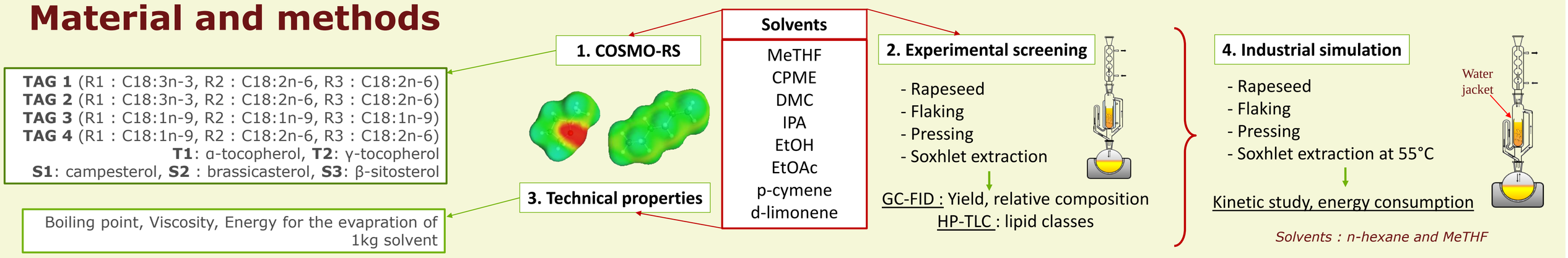
Introduction

Currently, the most commonly used solvent for extraction of vegetable oils is hexane thanks to its various advantages such as ease of removal or low boiling point, but it also provides ideal functionalities in terms of lipid solubility. Nevertheless it is produced from fossil resources and n-hexane which is one of the main constituents of technical hexane (mix of C6 isomers) is suspected to be reprotoxic which makes its use at industrial scale questionable. Indeed, with the emergence of new environmental issues, the oilseed sector aims at an anticipation of regulation that would imply a more sustainable oil extraction solvent. Finding new eco-friendly solvents has become a key issue for industry[1,2].

A COSMO-RS[3] simulation was conducted with some of the major triglycerides (TAGs) and micronutrients (tocopherols and sterols) occuring in rapeseed oil in order to evaluate their relative solubility regarding several bio-based solvents. These solvents were then tested for the extraction of rapeseed oil by means of Soxhlet extraction. The best candidate solvent was then selected for simulation of the industrial solvent extraction process.

[1] F. Fine, M. Abert Vian, A-S. Fabiano Tixier, P. Carré, X. Pages, F. Chemat. Les agro-solvants pour l'extraction des huiles végétales issues de graines oléagineuses. OCL 2013, 20(5) A502; [2] A.-G.Sicaire, M. Vian, F. Fine, F. Joffre, P. Carré, S. Tostain, F. Chemat. Alternative Bio-Based Solvents for Extraction of Fat and Oils: Solubility Prediction, Global Yield, Extraction Kinetics, Chemical Composition and Cost of Manufacturing. *Int. J. Mol. Sci.* **2015**, *16*, 8430-8453; [3] A. Klamt, G. J. P. Krooshof, et R. Taylor. COSMOSPACE: Alternative to conventional activity-coefficient models , AIChE J., vol. 48, n o 10, p. 2332–2349, 2002

Material and methods



1. COSMO-RS

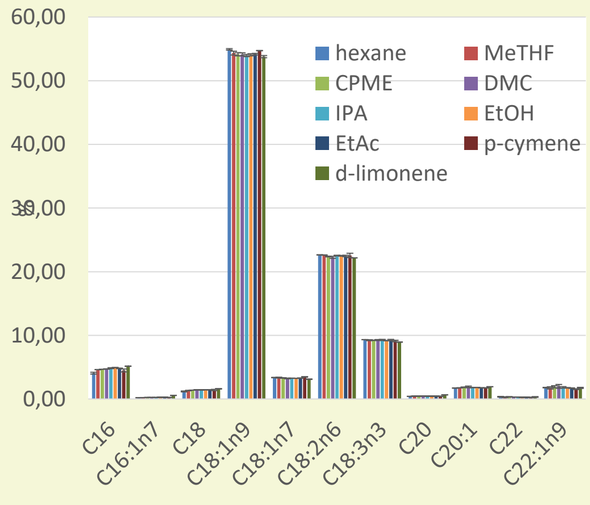
Relative solubility of major triglycerides, sterols and tocopherols present in rapeseed oil were assessed with COSMO-RS[3] in 2-methyltetrahydrofuran (MeTHF), cyclopentylmethylether (CPME), dimethylcarbonate (DMC), isopropanol (IPA), ethanol (EtOH), ethylacetate (EtOAc), p-cymene and d-limonene compared to n-hexane**; the logarithm of the best solubility is set to 0 and all other solvents are benchmarked against this reference solvent.**

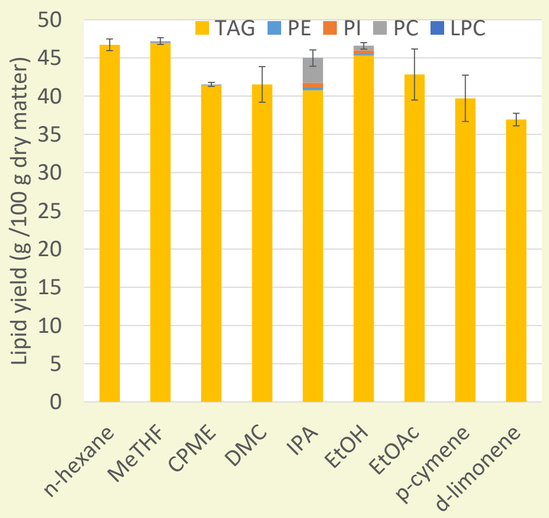
	TAG 1	TAG 2	TAG 3	TAG 4	T1	T2	S1	S2	S3
Hexane	0	-0.6390	0	0	-0.1356	-0.2974	-0.8087	-0.8017	-0.7582
MeTHF	0	0	0	0	0	0	0	0	0
CPME	0	0	0	0	0	0	0	0	0
DMC	-1.6227	-0.3153	-1.4633	-1.4228	-0.6462	-0.6102	-0.8877	-1.0366	-1.0650
IPA	-1.7726	-1.1684	-1.5248	-1.5552	-0.4937	-0.4291	-0.2366	-0.2687	-0.3015
EtOH	-2.7206	-1.8570	-2.4428	-2.4547	-0.9490	-0.8650	-0.5313	-0.5797	-0.6308
EtOAc	0	0	0	0	0	0	0	-0.0866	-0.0967
p-cym	0	0	0	0	-0.0928	-0.2018	-0.7401	-0.7829	-0.7714
d-lim	0	0	0	0	-0.0150	-0.1324	-0.6732	-0.6992	-0.6767

Reference | Better than reference | Worse than reference

2. Experimental screening

The analysis of extracts obtained after 8h Soxhlet extraction with the solvents show that there is **no significant difference in fatty acid composition** compared to the extract obtained with n-hexane. **More than 80 % of the constituents extracted with these solvents are TAG**. Other constituents found in oils extracted with MeTHF, CPME, IPA and EtOH are phospholipids and were present at variable amounts in extracts. Their presence which is not desirable in oil is due to the higher polarity of these solvents compared to n-hexane. **Quantitatively MeTHF appears to be the best among all other tested solvents.**





3. Technical properties of solvents

	Boiling point (°C)	Viscosity (20°C, cP)	E for 1 kg solvent evaporation (kWh)
Hexane	69	0.3	0.121
MeTHF	80	0.6	0.126
CPME	106	0.55	0.132
DMC	90	1.06	0.102
IPA	82	2.04	0.219
EtOH	78	1.1	0.265
EtOAc	77	0.42	0.127
p-cymene	177	0.79	0.154
d-limonene	176	0.92	0.157

Considering theoretical and technical approaches and regarding the experimental solvent screening, **MeTHF is the best alternative to *n*-hexane among all other tested solvents**; it has good solubilization abilities regarding desirable compounds in oil, the extracts are not significantly different from the extract obtained with n-hexane and its technical properties are not significantly different from *n*-hexane especially the energy required for solvent evaporation.

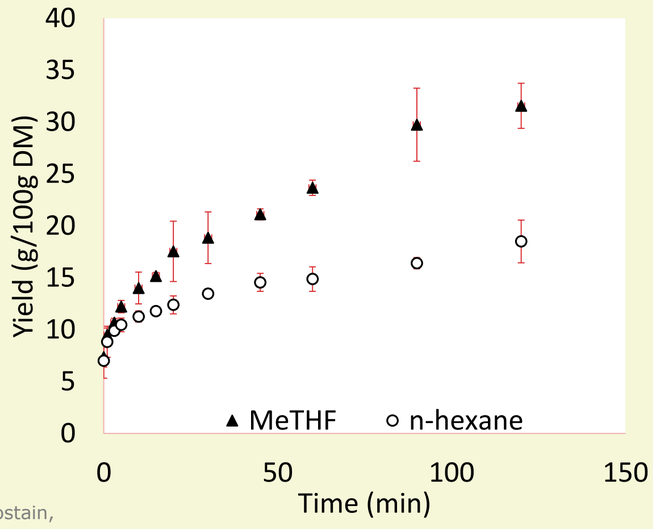
Selection of MeTHF

4. Industrial simulation : MeTHF *vs.* n-hexane[4]

The extraction of rapeseed oil from press cake was conducted with n-hexane and MeTHF.

Using MeTHF improves by 3.5 times the internal diffusion of oil, and allows at least a faster extraction than with hexane.

The entire process using MeTHF would require a global overconsumption of 85 MJ/t compared to the use of n-hexane[2,6], which represents an increase of 14% of the energy consumption.



[4] Sicaire, A.-G.; Vian, M.; Fine, F.; Joffre, F.; Carré, P.; Tostain, S.; Chemat, F.. *Int. J. Mol. Sci.* **2015**, *16*, 8430-8453.

Conclusion

The aim of the study was to investigate the use of alternative solvents to n-hexane, for the extraction of rapeseed oil. After a first selection using COSMO-RS predictions, MeTHF was experimentally compared to n-hexane.

MeTHF exhibited very promising performances, at both table-top scale and pilot scale, in terms of oil composition, extraction quality and extraction speed. There are good indications that the substitution might not induce a significant operating overcost.