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The use of Stefanis Panayiotou method for determining Hansen solubility parameters for fatty acids extraction by petrochemical and green solvents: α-pinene

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Abstract – In our study, we focused first on the determination and comparison of Soxhlet extracting fatty acid content of food matrices: peanut seeds, soybeans, sunflower seeds and olives (chemlal), using α-pinene as green solvent in substitution of n-hexane.

No significant qualitative or quantitative difference could be highlighted between the different extracts. This allows to conclude that the proposed solvent, α-pinene, is effective and valid for the recovery of oils and fats in oilseeds, and can then be a definite alternative to n-hexane. Even if its boiling temperature is higher than that of n-hexane (excess energy required for its heating), the fact that the recycling rate of α-pinene is almost total (90% against 50%) makes it more interesting, more reliable and safer for the environment.

We then considered the determination of α-pinene and n-hexane solvent power on fatty acids of used matrices. We applied the predictive method of Hansen solubility parameters, parameters determined by Stefanis Panayiotou approach.

Keywords- α-pinene, green solvent, fatty acid extraction, Hansen parameter.

I. Introduction

During the last years, research in the field of green solvents has focused on the search for agro-solvents to reduce the use of petroleum solvents, although they are very efficient and of a lower cost. Several innovations towards green solvents have been developed: solvent-free extraction technology, the use of water as an alternative solvent, and the use of ionic liquids. Bio- or agro-solvents are an alternative that presents less risk and danger on the environmental impact than petroleum solvents. Terpenes, considered as solvents, are renewable. They are then an interesting alternative to typical solvents. We found them in the essential oils and oleoresins of fruit and aromatic plants. The α-pinene is a monoterpene likely to be an interesting alternative. It represents the main constituent of turpentine oils of most conifers, and a component of wood oils, leaves and bark of a wide variety of other plants such as rosemary, parsley, basil, mint, lavender, sage and ginger.

II. VEGETABLE MATERIAL

Oilseeds (peanut seeds, soya and sunflower) used for fatty acid extraction were bought on the local market. The olives (chemlal) were harvested at Ighil Ali (Bejaia, Algeria).

III. SOLVANT

The solvents used for this study are α-pinene, a bio-solvent and n-hexane, a petrochemical solvent. Their properties are described in Table 1.

IV. EXPERIMENTAL PROTOCOL

The Soxhlet extraction of the oils using n-hexane and α-pinene was carried out according to the standard procedure (ISO 659-1998) [4] and illustrated in Fig. 1. Qualitative and quantitative aspects have been considered in the results treatment [5].

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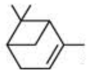
TABLE 1
PHYSICAL AND CHEMICAL PROPERTIES OF N-HEXANE AND α-PINENE [1-3]

Properties	n-Hexane	α-Pinene
Chemical structure		
Molecular weight (g/mol)	86,17	136,26
Specific gravity (25°C)	0,65	0,874
Viscosity (cP, 25°C)	0,32	1,293
Boiling point (°C)	68,74	156-158
Refractive Index	1,3723	1,4636
Solubility in water (wt%, 25°C)	0,00123	Insoluble
Dielectric constant (20°C)	1,89	2,76
Flash point (°C)	23	32
Surface tension, dyne/cm (25°C)	18,4	25,3 ± 3,0
Odour	Petroleum	Turpentine resin
Environmental impact	Top	Low
Renewable	No	Yes
Toxic	Yes	No

V. EXPERIMENTAL PROTOCOL

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VI. HSPIP METHOD

The Hansen solubility parameter method is based on the δ solubility, which is divided into three main components: δd (London dispersion forces), δp (Keesom polarity forces) and δh (hydrogen bonding forces). The method is based on the following equations:

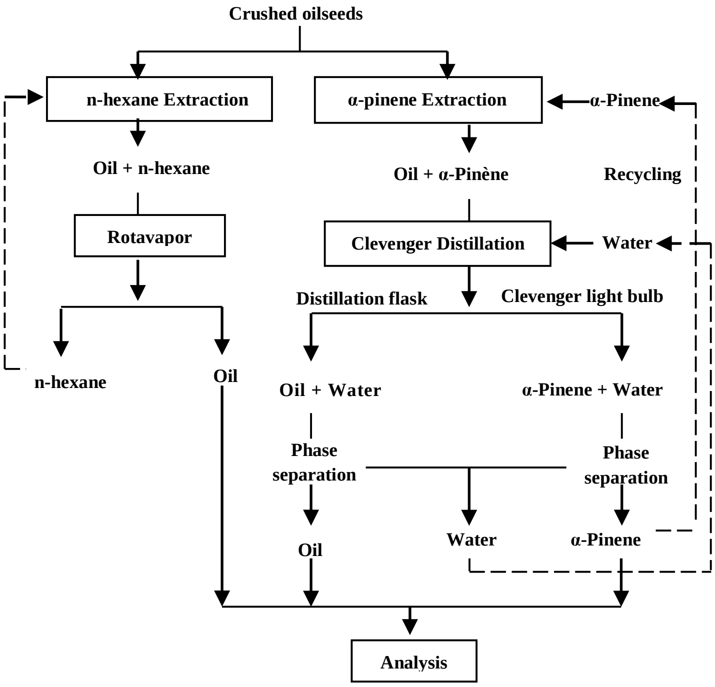
$$\boldsymbol{\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2} \quad (1)$$

$$\boldsymbol{A^2 = 4(\delta_{d1} - \delta_{d2})^2 + \left(\delta_{p1} - \delta_{p2}\right)^2 + (\delta_{h1} - \delta_{h2})^2} \quad (2)$$

A: distance between compounds 1 and 2

The computation of the relative energy difference (RED) allows to determine the miscibility force between a solvent and a solute.

Fig. 1 Extraction procedure representation using α-pinene and n-hexane



$$\boldsymbol{RED = A/R} \quad (3)$$

R: radius of Hansen solubility sphere

HSPIP software offers different ways to calculate Hansen's solubility parameters. We can quote for instance Beerbower, Hoy, Van Krevelen [6-8] and more recently, Stefanis and Panayiotou [9] and Yamamoto (HSPiP, 2010).

VII. RESULTS AND DISCUSSION

The extractions results of the different matrices are presented in Table 2. The oil yields of the α-pinene extractions are slightly higher than those obtained with n-hexane. This difference, also emphasized by Liu et al. [10] and Virot et al. [11], is certainly due to the slightly more polar nature of α-pinene relative to n-hexane which would cause a greater solubilization power for triglycerides. In addition, the diffusion is improved thanks to the higher boiling temperature of α-pinene, which decreases the oil viscosity.
In order to calculate the Hansen solubility parameters (HSP), the decomposition of the studied molecule into functional groups predominates. The knowledge of the chemical structure of the compounds studied is very important.

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The solubility parameters calculated by the HSPiP software are presented in Table 3.

TABLE 2 OIL CONTENT OF THE DIFFERENT MATRICES OBTAINED BY SOXHLET EXTRACTION WITH N-HEXANE, α -PINENE

Solvant / Food matrix	n-hexane (%)	α-pinène (%)
Peanuts	39,5 ± 0,23	42,3 ± 0,29
Soya	19,5 ± 0,29	21,1 ± 0,20
Sunflower	52,6 ± 0,20	67,2 ± 0,21
Olive *Chemlal*	22,6 ± 0,16	24,5 ± 0,24

TABLE 3 HANSEN SOLUBILITY PARAMETERS DETERMINED BY THE STEFANIS PANAYIOTOU METHOD,
(HSPIP, 2010)

Solvents (RED = 0)	HANSEN solubility parameters				
Compound name	δd	δp	δh	RED pinene	RED Hexane
a-pinene	16,9	1,9	2	0	0.8
Hexane	15,2	3,1	4,7	0.8	0
Palmitic C16:0	15,8	2,3	5,4	**0,2**	0,4
Margaric C17:0O	15,9	2	5	**0,39**	0,45
Stearic C18:0	15,9	1,7	4,6	**0,42**	0,5
Eicosanoid C20:0	15,9	1	3,8	**0,61**	0,67
behenic C22:0	15,9	0,4	3	**0,67**	0,87
Palmitoleic C16:1	16,3	1,9	5,9	**0,28**	0,69
Oleic C18:1	16,3	1,3	5,1	**0,64**	0,72
Gadoleic C20:1	16,3	0,7	4,3	**0,71**	0,82
Linoleic C18:2	16,7	0,9	5,6	**0,94**	0,96
Linolenic C18:3	17,2	0,5	6,2	**0,12**	0,25

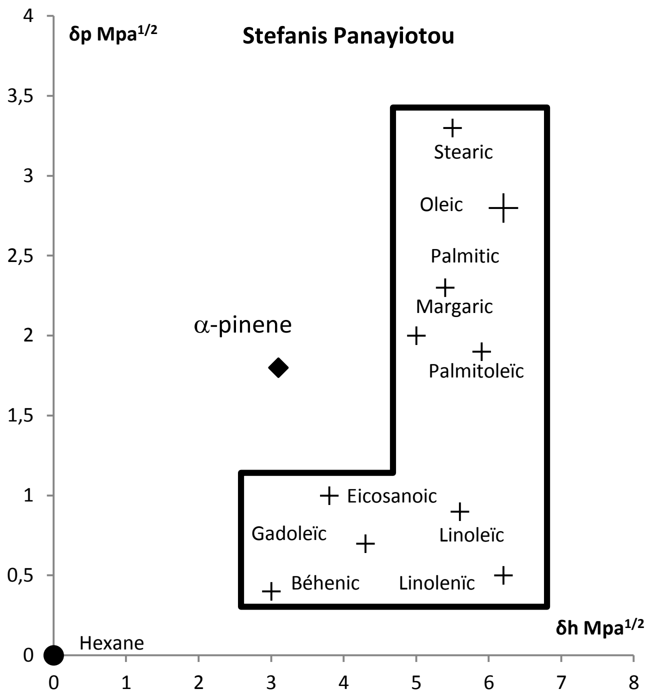
RED = 0 perfect solvent. 0 <RED <1 good solvent. RED> 1 bad solvent

The results in Table 3 show that for all fatty acids, RED_{Pinene} is lower than RED_{Hexane}, which is itself less than 1. This means that α-Pinene and n-Hexane are good solvents for fatty acids extraction and that α-Pinene is better than n-Hexane.

In order to more easily compare the values obtained by the algorithm, the diagram representing δp as a function of δh was analyzed (see Fig. 2).

We notice that the fatty acids grouped together and representing an inverted "L", cover an area between 0.4 and 3.1 $Mpa^{1/2}$ for the attraction force δp, and between 2 and 6 , 2 $Mpa^{1/2}$ for the hydrogen bonding force δh. The group is located near α -Pinène. We can also notice that the hexane is quite far from the group.

Fig.2 : Hansen solubility parameters representation in the two-dimensional space δp vs δh, using Stefanis Panayiotou method



VIII. CONCLUSION

The study carried out for the determination of oils and fats in oilseeds shows that the results obtained with the two solvents are comparable, allowing to conclude that α-pinene is effective and valid and can substitute n-hexane. The fact that the recycling rate of α-pinene is almost total (90% against 50% for hexane), makes it a more reliable and safer alternative for the environment, despite its higher boiling point than that of n-hexane (surplus energy required).

The computation of Hansen parameters is a good approach for determining the solubility of a compound relative to a solvent. The results obtained show that α-pinene is an adequate solvent for fatty acids extraction, confirming hence the experimental results.

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