Determining Hansen Solubility Parameters by StefanisPanayiotou Method for Fatty Acids Extraction by Petrochemical and Green Solvents

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Abstract –In recent 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, the use of ionic liquids.

Bio- or agro-solvents are an alternative that presents less risk and danger to the environmental impact than petroleum solvents. Terpenes, considered as solvents, are renewable, an interesting alternative to typical solvents. They are found in the essential oils and oleoresins of fruit and aromatic plants. α-pinene is a monoterpene likely to be an interesting alternative. It is 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.

In our study, we focused first on the determination and comparison ofSoxhletextracting 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 as petrochemical solvent.

No significant qualitative or quantitative difference could be highlighted between the different extracts. Thisallows 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 thenconsidered the determination ofα-pinene and n-hexane solvent power on fatty acids of used matrices. We applied the predictive method of Hansen solubility parameters, parameters determined by StefanisPanayiotouapproach.

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.

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TABLE1
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

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.

For each testusing n-hexane, mass of the sample is 30 g and volume of solvent is 300 mL. After 8 hours of extraction, the distillate in the flask was concentrated to dryness with a vacuum rotary evaporator; the flask is then cooled to room temperature in a desiccator and weighed to the nearest milligram.

The Soxhlet extraction using alpha-pinene was also performed according to the above standardized method. The recovery of oil was carried out using a Clevenger distillation of a mixture (oil+alpha-pinene), a method suggested by Virot et ***al***. for lipid extraction by d-limonene [5].

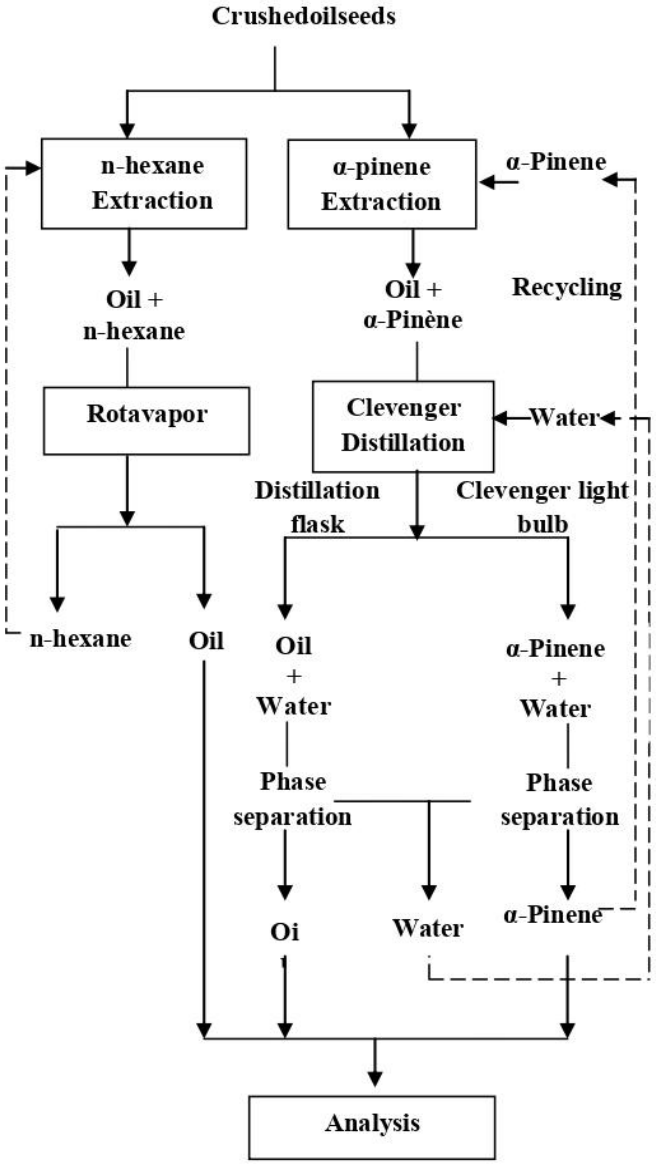

Fig. 1 Extraction procedure representation using α-pinene and n-hexane

Thus, once extraction with alpha-pinene wasachieved, 150 mL of distilled water was added to themixture (extracted oil+alpha-pinene) in the flask. Thenthe flask was connected to a Clevenger apparatus and acondenser. At the end of distillation, two binarymixtures consisting of two immiscible phases wereobtained: the first one (water/oil) in the distillation flask, and the second in the Clevenger glassware composed of water and alpha-pinene. The recovery of the different phases was performed by simple phase separation. The water and alpha-pinene were re-used, after checking that lipid was not detected in the Clevenger phases. Fig. 1 describes the various stages of the extraction by alpha-pinene.

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All extractions, both using n-hexane or alpha-pinene, were performed in triplicate, and the mean values were reported.

Qualitative and quantitative aspects have been considered in the results treatment [6].

V. CHROMATOGRAPHIC ANALYSES

In order to check if alpha-pinene undergoes degradation during the extraction of oils, the samples of alpha-pinene, pure and recovered after extraction, were analyzed by gas chromatography (GC) coupled with mass spectrometry (MS). GC–MS analyses were carried out in a Shimadzu QP2010 (Kyoto, Japan) gas chromatograph. The gas chromatograph was equipped with a CP-Wax (52 CB) capillary column 30 m x 0.32 mm x 0.5 µm (Varian, Walnut Creek, CA, USA). The velocity of the carrier gas (He) was at 47 cm/second.

Flow rate was held at 1.69 mL/minute and the column head pressure was 20 kPa. Samples were injected (2µL) with a split mode (ratio 1:15) and the injector temperature was set at 250°C. The oven temperature was increased from 60°C (1 minute) to 180°C at a rate of 20°C/minute, then increased from 180° to 230°C at a rate of 4°C/minute and held at 230°C for 15 minutes.

The mass spectra were recorded at three scans per second between 50 and 400 amu. The ionization mode was electron impact (EI) at 70 eV. Identification of common fatty acids was performed using the NIST'98 [US National Institute of Standards and Technology (NIST), Gaithersburg, MD, USA] mass spectral database.

FAMEs were analyzed by using an Agilent (Kyoto, Japan) gas chromatograph equipped with a flame ionization detector (FID). The detector temperature was 300°C. The other analytic conditions including the column type and column temperature, the injection temperature, split ratio, carrier gas and the linear velocity were the same as those in the GC–MS analysis. FAMEs were identified by retention time and comparison with purified FAME standards (Sigma Co. St Louis, MO, USA).

VI. HSPIP METHOD

The Hansen solubility parameter method is based on the δ solubility, which is divided into three main components: the first component δd relates to so-called "dispersion" forces of London (non-polar interactions), the second δp is related to the Keesom polarity forces (between permanent dipoles), finally the last δh represents the hydrogen bonding forces and more generally interactions involving electronic exchanges. Debye forces (between induced dipoles) are generally low in absolute value and neglected.

Hansen thus obtains a three-dimensional space (Fig.2) in which all liquid or solid substances can be located.

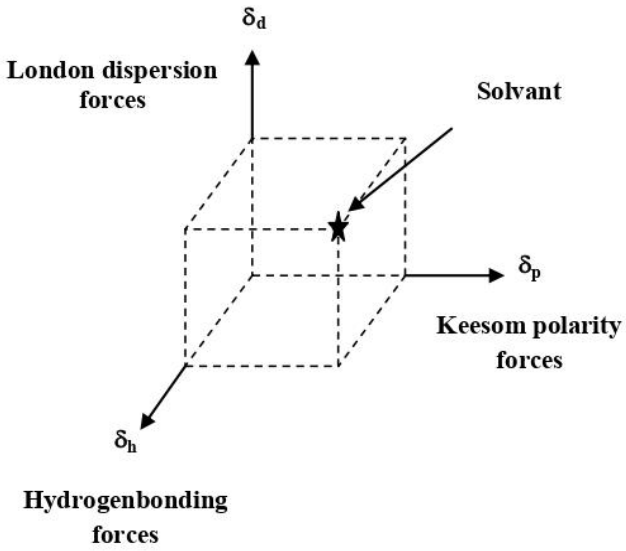

Fig.2 Three-dimensional representation of Hansen's solubility parameters

A point represents the combination of interactions that ensures the cohesion of the substance (Eq. 1).

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

For any solid substance to be soluble in a liquid, or for two liquids to be miscible, their situation in space must be close, that is, their solubility parameters should be close. Thus, compounds that have similar Hansen parameters have high affinity.

In this configuration, the previously described dissolution condition is extended to all three parameters. The factor to be minimized then becomes:

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

A: distance between compounds 1 and 2

The presence of the factor 4 in front of the dispersion parameters is motivated by the desire to make the system more symmetrical, the dispersion values being generally very low [7].

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In other words, for two substances to be miscible, it is necessary that their three solubility parameters are identical or very close.

The nonpolar interactions, which correspond to the δd component, concern all the molecules since they are attributable to the atoms that constitute them. Indeed, a nonpolar molecule also has electrons that can cause a momentary imbalance of the distribution of charges in the surrounding molecules, thus inducing a temporary dipole moment.

Even if they change constantly, these induced dipoles generate attractive forces all the more large as the molecular mass is high (high number of electrons). For saturated aliphatic hydrocarbons, for example, the London interactions are the only attractive interaction, which results in a vaporization energy equivalent to cohesion energy.

The second parameter of partial solubility δp is related to polar interactions, excluding hydrogen bonding. There are forces of electrostatic attraction between the polar molecules, the positive pole of the one attracting the negative pole of another. Interactions related to orientation forces between permanent dipoles are called Keesom forces [8].

The third parameter of partial solubility δh is related to interactions involving a hydrogen bond between a hydrogen atom with a positive partial charge and a strongly electronegative atom.

All these forces of attraction can be classified according to their intensity:

Hydrogen bonding forces > London Force>Keesom Force.

The method developed by the Greeks Stefanis and Panayiotou is recent [9]. These authors used modern statistical methods to process Hansen's data and developed three linear equations, from a two-step linear regression, to calculate each of the solubility parameters:

$$Y = \sum_i N_i C_i + W \sum_j M_j D_j \quad (3)$$

Ci corresponds to the first order contributions of a group i appearing N times in a molecule.

Dj corresponds to the possible second order contributions of a group j appearing M times in a molecule.

W is equal to 1 or 0, respectively if the test compound has or not second order contributions.

Y is a linear function that can correspond to δd, δp or δh.

These properties have many applications in the chemical, pharmaceutical and food industry, as well as in the protection of the environment [10]

The values calculated by the Stefanis-Panayiotou method are in agreement with Hansen's experimental values. The number of functional groups used to decompose the molecular structures is large, which makes the method recognized as one of the most accurate for the calculation of the three solubility parameters (HSPiP Software, 2010).

The computation of the relative energy difference (RED) allows to determine the miscibility force between a solvent and a solute (Eq. 4).

$$RED = A/R \quad (4)$$

R: radius of Hansensolubility sphere

HSPIP software offers different ways to calculate Hansen's solubility parameters. We can quote for instance Beerbower, Hoy, Van Krevelen [7-8, 11-12] and more recently, Stefanis and Panayiotou [9] and Yamamoto (HSPiP Software, 2010).

VII. RESULTS AND DISCUSSION

The extractions results of the different matrices are presented in Table 2 and Fig 3. 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. [13] and Virot et al. [5], 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.

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

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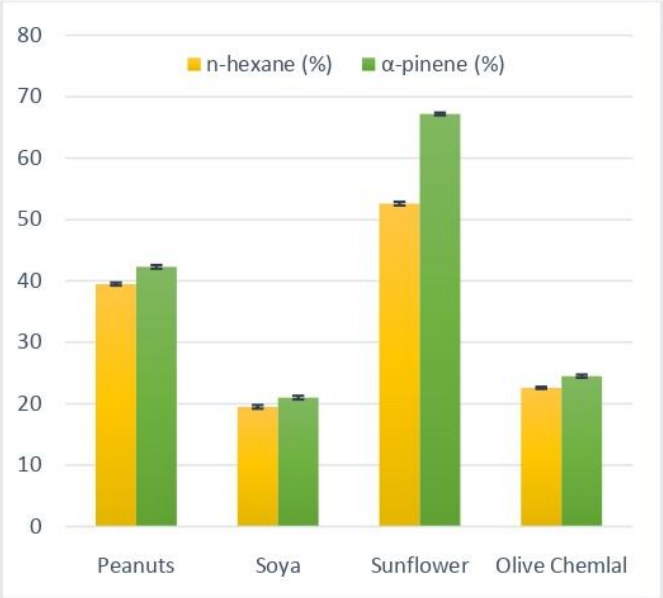

Fig. 3 Fatty acids' yields of different oils extracted by two used solvents.

Results show that recycling rate of alpha-pinene, which is close to 90%, is significantly higher than that of n-hexane, which reached 50%. In addition, the GC and GC/MS analysis of alpha-pinene recovered after extraction does not show any important degradation.

After extraction, fatty acids were converted in FAMEs and analyzed by GC–MS. The results also given in Fig. 3-5 indicate that fatty acids extracted by both solvents are equivalent in terms of compounds identified and relative proportions.

Peanuts (Fig. 4) and olives (Fig. 7) oils contain a majority of monounsaturated fatty acids (MUFAs) including oleic acid (C18:1), the main component,

Whereas soya (Fig. 5) and sunflower (Fig. 6) oils are richer in polyunsaturated fatty acids (PUFAs) with linoleic acid (C18:2) the principal compound.

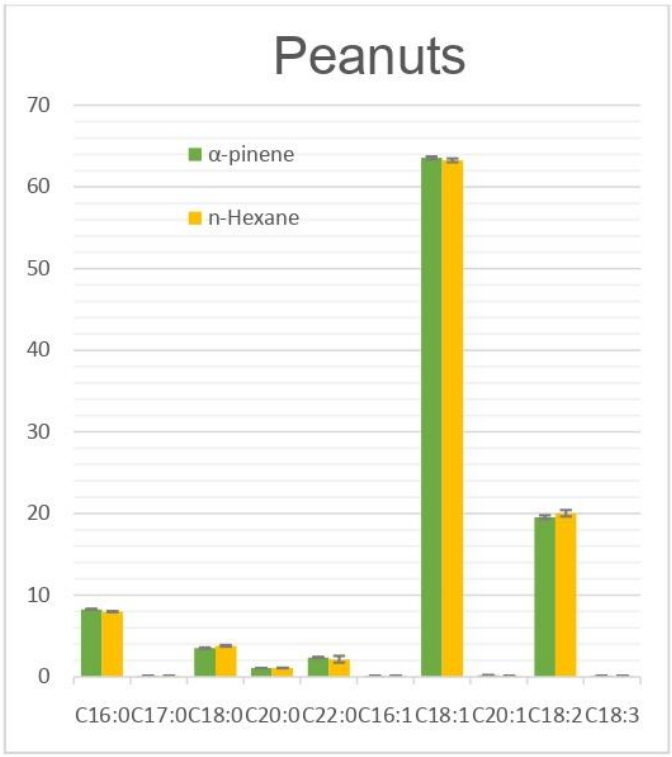

Fig. 4 Fatty acids' composition of Peanuts oils extracted by two solvents.

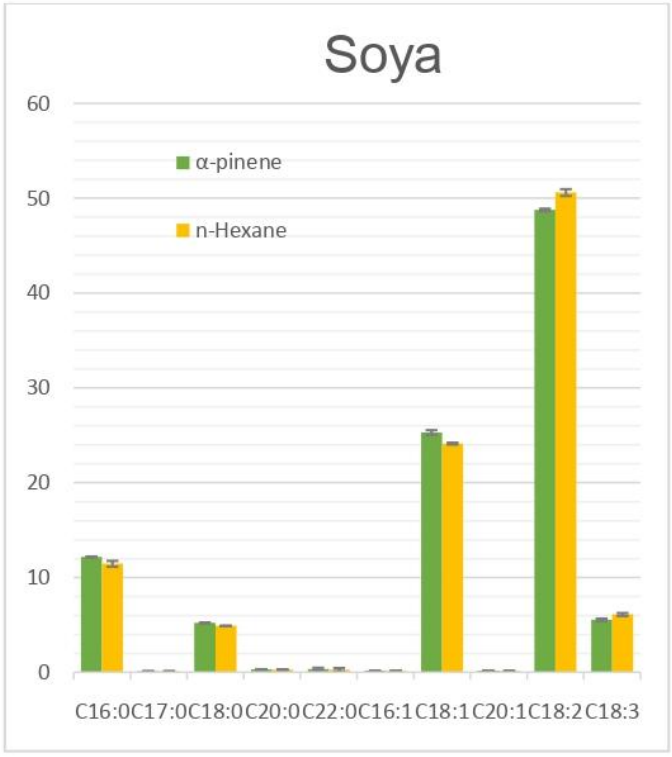

Fig. 5 Fatty acids' composition of Soya oils extracted by two solvents.

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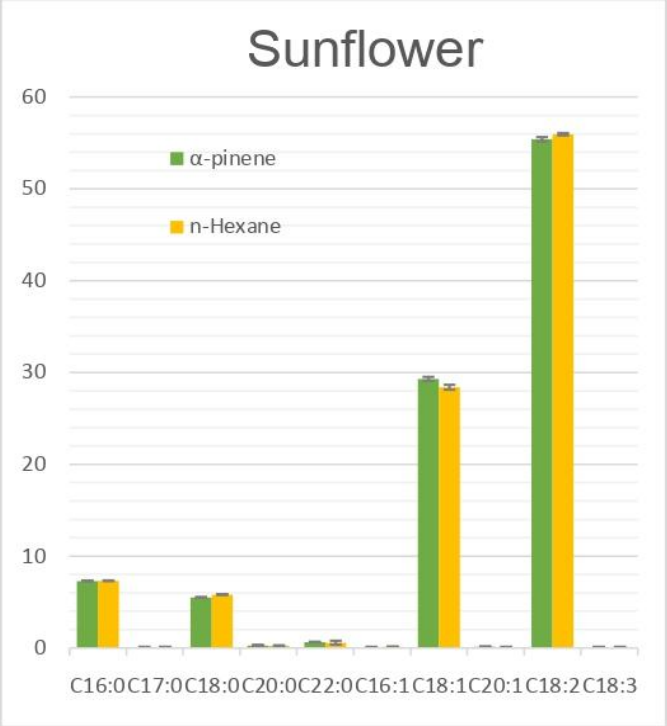

Fig. 6 Fatty acids' composition of Sunflower oils extracted by two solvents.

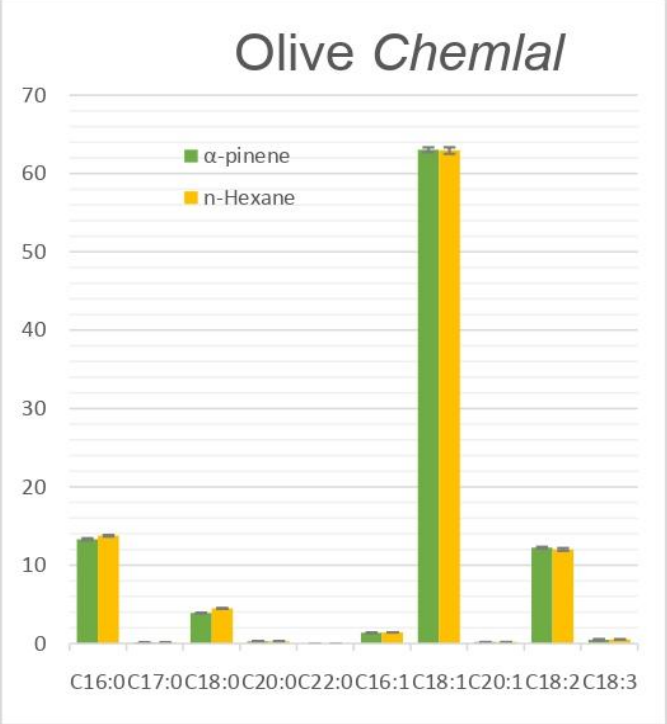

Fig. 7 Fatty acids' composition of Olive *Chemlal*oils extracted by two solvents.

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.

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

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. 8).

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 forceδh. The group is located near α -Pinène. We can also notice that the hexane is quite far from the group.

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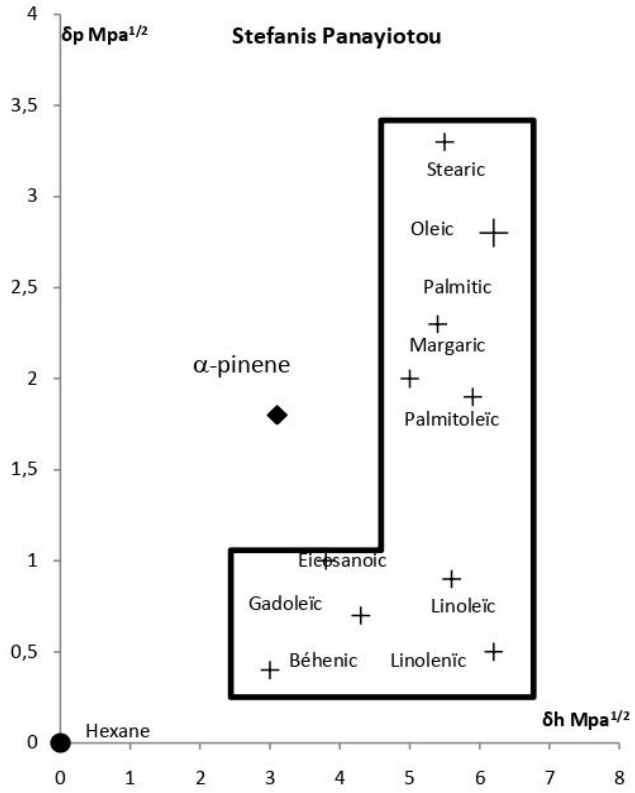

Fig.8 : Hansen solubility parameters representation in the two-dimensional space δpvsδh, using StefanisPanayiotou method

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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