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An original approach for lipophilic natural products extraction: Use of liquefied *n*-butane as alternative solvent to *n*-hexane

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ABSTRACT

Recent trends in food extraction techniques have largely focused on finding solutions that minimize the use of toxic solvents or to find alternatives for *n*-hexane. As an original solution, a new process for extraction of natural product using liquefied gases has been developed at laboratory scale. The applicability of this new process was demonstrated using *n*-butane as alternative solvent to *n*-hexane. Extraction of lipophilic natural products such as carrot oleoresin, caraway aromas and sunflower oil was assessed using liquefied *n*-butane. COSMO-RS simulations allowed determination of the relative solubility of the lipophilic compounds in liquefied *n*-butane and *n*-hexane. This theoretical approach was validated with extraction experiments on carrots, caraway seeds and sunflower seeds. Compositions of the extracts were comparable but the extract yields were lower using *n*-butane. For example the extraction yields were, with *n*-butane and with *n*-hexane respectively, 36.9% and 53.4% for sunflower seeds oil, 10.9% and 15.0% for caraway seed essential oil, 25.7% and 55.8% for carrots oleoresin. However the extracts obtained by using *n*-butane are directly free of solvents and also food grade, as it is an authorized solvent for foodstuff production.

Keywords:
Innovative apparatus
Substitution solvent
Food ingredients
Liquefied gas

1. Introduction

Among the pool of organic solvents, *n*-hexane is certainly the most well-established industrial solvent for extraction of lipophilic natural products such as aromas, carotenoids, and vegetable oils (Chemat-Djenni, Ferhat, Tomao, & Chemat, 2010; Filly et al., 2014; Virot, Tomao, Ginies, & Chemat, 2008). The wide use of *n*-hexane is due to its physico-chemical parameters e.g. low boiling point, low polarity, and chemical stability (Johnson & Lusas, 1983). However, residual content in raw material, non-total recovery of hexane observed in industrial processes, growing environmental and health concerns are major constraints (Mikkelsen & Miljøstyrelsen, 2014). Indeed, *n*-hexane is categorized as reprotoxic category 2 and as aquatic chronic toxic category 2 substance (Sicaire, Vian, Fine, Carre et al., 2015) and is ranked on the list of substances prohibited in cosmetic products (Regulation (EC) No 1223/2009 of the European Parliament).

Scientific community and industrials are challenged to identify alternative solvents to *n*-hexane. This trend has stimulated researches on alternative solvents, most of which are produced from renewable resources such as woods, cereals, seeds, oils, fats (Chemat & Vian, 2014, pp. 205–219; Ishida & Chapman, 2009). As examples, studies have been performed regarding the extraction of rapeseed oils using MeTHF (Sicaire, Vian, Fine, Carre et al., 2015; Sicaire, Vian, Fine, Joffre et al., 2015), caraway seeds aromas using α-pinene (Filly, Fabiano-Tixier, Fernandez, & Chemat, 2015) and extraction of rice bran oil using limonene (Mamidipally & Liu, 2004). Such solvents have a good solvation power, are non-toxic and biodegradable (Chemat, 2011, p. 9). The main drawbacks of these solvents are their cost (MeTHF: 5€/kg (Sicaire, Vian, Fine, Carre et al., 2015; Sicaire, Vian, Fine, Joffre et al., 2015)), their relative high viscosity (*d*-limonene $= 9.0 \times 10^{-4}$ Pa s at 25 °C; α-pinene $= 1.3 \times 10^{-3}$ Pa s at 25 °C (Clará, Marigliano, & Sólimo, 2009)), their high boiling point (d-limonene = 175.5 °C at

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101.3 kPa (Chemat-Djenni et al., 2010); α-pinene = 158 °C at 101.3 kPa (Filly et al., 2015)) and the possible generation of off-flavors (Filly et al., 2015).

In the last decades, research for new solvents has revived the interest for the use of liquefied gases as extraction solvents. Many studies have been performed on natural product extraction using supercritical CO_2, but the high working pressure (7.5–45 MPa) has limited the industrial applications (Baysal, Ersus, & Starmans, 2000; Ben Rahal, Barba, Barth, & Chevalot, 2015; Coelho et al., 2012; Couto et al., 2010; Hubert & Vitzthum, 1978; Koubaa et al., 2015; Koubaa et al., 2016; Xu et al., 2011). More recently, some studies have been focused on extraction processes involving liquefied gases at lower pressure (200–1000 kPa), such as *n*-propane (da Silva et al., 2015; Sekhon, Maness, & Jones, 2015; Zanqui et al., 2015), *n*-butane (Novello et al., 2015; Yang, Teo, & Xu, 2004), dimethyl ether (Kanda & Li, 2011; Kanda & Makino, 2009; Oshita et al., 2015), tetrafluoropropene (Suberu, Yamin, Cornell, Sam, & Lapkin, 2016), tetrafluoroethane (Lapkin, Plucinski, & Cutler, 2006; Mustapa, Manan, Mohd Azizi, Nik Norulaini, & Omar, 2009), eventually with co-solvents (Jesus et al., 2013; Pessoa et al., 2015). All these studies describe a dynamic process with continuous solvent recirculation using pumps and/or compressors which are prone to cavitation issues (Brennen, 1995; Franc & Michel, 2005). Alternatively, a new process has been recently proposed (Fig. 1) which does not require the use of pumps and compressors. The unit designed has the specificity to rely on gravity for the liquefied gases circulation in the equipment. Consecutively, energy consumption is reduced compared to other liquefied gases processes using pumps and compressors. Extraction is enabled by liquefied gas contacting with a raw material inside an extractor during a set time. Then the mixture of liquefied solvent and extract is separated in an evaporator, allowing the liquefied gas to turn in a gaseous state. Therefore, no traces of the solvent remain in the extract.

In this paper, the applicability of this newly developed process has been investigated using *n*-butane for extraction of lipophilic compounds such as oleoresin, essential oil and vegetable oil. The choice of *n*-butane as alternative solvent to *n*-hexane was motivated by its close chemical structure, its gentle vapor pressure, its low price and its classification as authorized solvent for foodstuff production without limitation (Directive 2009/32/EC).

The potential of liquefied *n*-butane for extraction of lipophilic compounds will be compared to the conventional solvent *n*-hexane through two approaches: a theoretical approach with a predictive computational model, COSMO-RS (COnductor like Screening MOdel for Real Solvents), coupled with lab-scale trials. Three plant material traditionally extracted with *n*-hexane were chosen for the comparative study: carrots (*Daucus carota* L.) for the extraction of high-value products i.e. carotenoids, caraway seeds (*Carum carvi* L.) for the extraction of volatile aromatic compounds and sunflower seeds (*Helianthus annuus* L.) for the extraction of fats and oils. The extracts will be analyzed quantitatively (extraction yield) and qualitatively (GC, HPLC) in order to compare the efficiency of *n*-butane *versus* *n*-hexane for the extraction of lipophilic natural products.

2. Materials and methods

2.1. Chemicals

For extraction, *n*-hexane analytical grade (VWR International, Radnor, USA) and *n*-butane, 95% purity without mercaptan (Inventec Performance Chemical, St Priest, France) were used in this study.

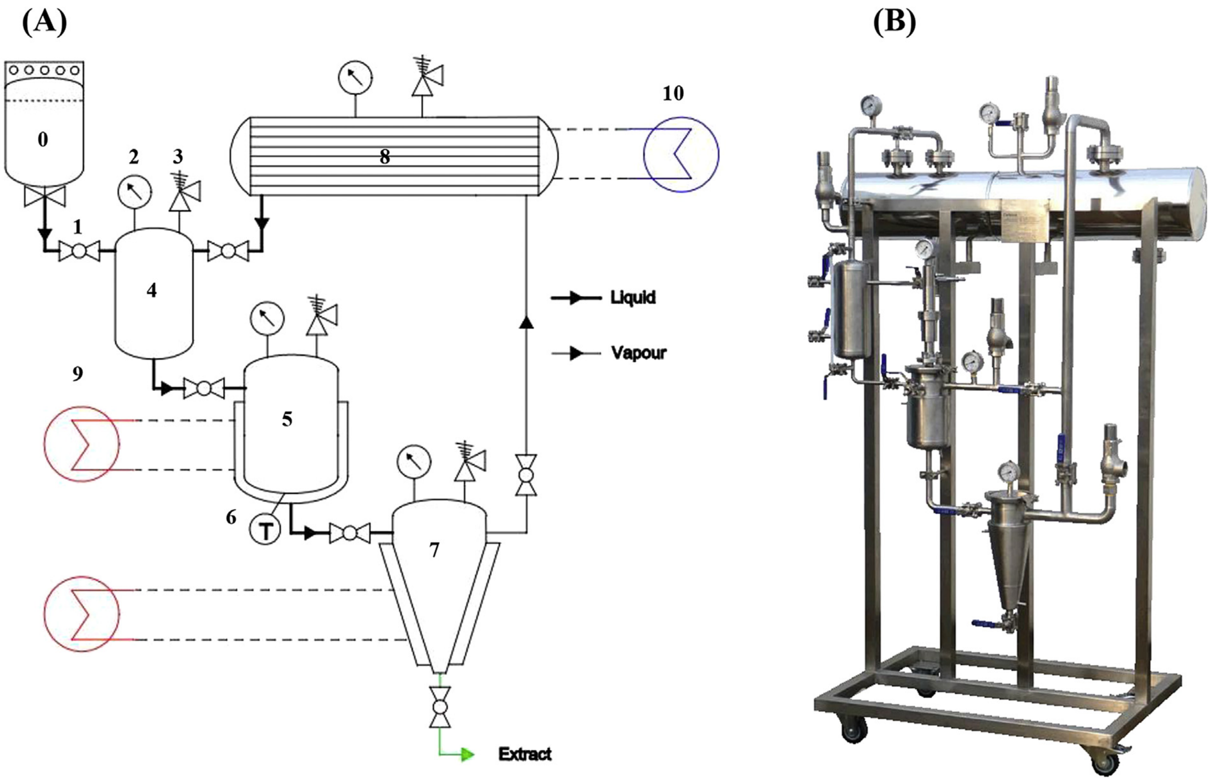

Fig. 1. (A) NECTACEL® Tailor-made extraction-unit for extractions using *n*-butane as solvent: **0**, *n*-butane bottle; **1**, valve; **2**, manometer; **3**, safety valve; **4**, solvent storage tank; **5**, double jacketed stainless extractor; **6**, thermometer; **7**, double jacketed stainless evaporator; **8,** stainless condenser; **9**, Heated bath circulator; **10**, Cooling bath circulator – (B) 1-L extraction unit manufactured by Celsius Sarl (Villette de Vienne, France).

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For analytical procedures, all reagents were HPLC grades. Acetonitrile, methanol, ammonium acetate, dichloromethane, chloroform, acetone, *tert*-butyl methyl ether (TBME) and trimethylsulfonium hydroxide (TMSH) were purchased from Sigma-Aldrich (St. Louis, USA).

β-carotene (>98% UV purity) was purchased from Extrasynthèse (Genay, France). Fatty Acids Methyl Esters mix (Supelco 37 FAME mix), pentadecanoic acid (C15:0, 99% purity), *d*-carvone (98% purity) and *d*-limonene (99% purity) were purchased from Sigma-Aldrich (St. Louis, USA).

2.2. Plant materials

Dried carrots and sunflower seeds were purchased in 2015 from Herbier du Diois (Châtillon-en-Diois, France). Caraway seed powder was purchased from L'île aux épices (Port-Vendres, France). The plant materials were prepared following the same procedures for both *n*-butane and *n*-hexane extractions. Dried carrot cubes and sunflower seeds were ground into a fine powder using a grinder (Kinematica AG Microtron MB 550, Luzern, Switzerland; grinding duration = 15 s) just before extraction. Caraway seed powder was used directly as is.

2.3. Liquefied gases apparatus and extraction procedure

Extractions were performed on a 1 L pilot plant presented in Fig. 1 (NECTACEL®, Celsius sarl, Villette de Vienne, France). The unit designed has the specificity to rely on gravity for the liquefied gases circulation in the equipment in an isobaric mode. After extraction, the liquefied gas is evaporated in an evaporator, where the liquefied gas turns into gas. Vapors are condensed in a condenser (cooling temperature = 0 °C) and stored in a storage tank which further supplies liquefied gases for extraction. This way about 95% of gas is recycled in 10 min.

Using liquefied gases as solvent for solid-liquid extractions requires an equipment resistant to the vapor pressure generated at room temperature (200–400 kPa). The unit comprises 4 stainless steel vessels (Fig. 1): a solvent storage tank (4), a double-jacketed stainless steel extractor of 1.5 L (5), a double-jacketed stainless steel evaporator (7) and a stainless steel condenser (8). Each vessel is equipped with a manometer (2) and a safety valve (3) and was manufactured in compliance with the PED Directive (Pressure Equipment Directive 97/23/CE) and ATEX Directive (EXplosive ATmosphere, Directive 2014/34/UE).

Liquefied *n*-butane extractions were performed using the following general procedure (Fig. 2). First, 75 g of ground material is introduced in a filtering sock (porosity 50 μm) placed inside the extractor (5) then the all device is placed under vacuum to remove oxygen. Next, the liquid *n*-butane is transferred from its bottle (0) to the storage tank (4). About 1.5 L of liquid *n*-butane is introduced into the extractor at room temperature under pressure (20 °C at 200 kPa). The solvent is then flowed by gravity to the extractor (5). The extractor is heated at the set temperature (20, 30 or 40 °C) *via* the double jacket during 2 h.

After 2 h of solid/liquid contacting, the solvent containing the extract is transferred to the evaporator (7) where the solvent is

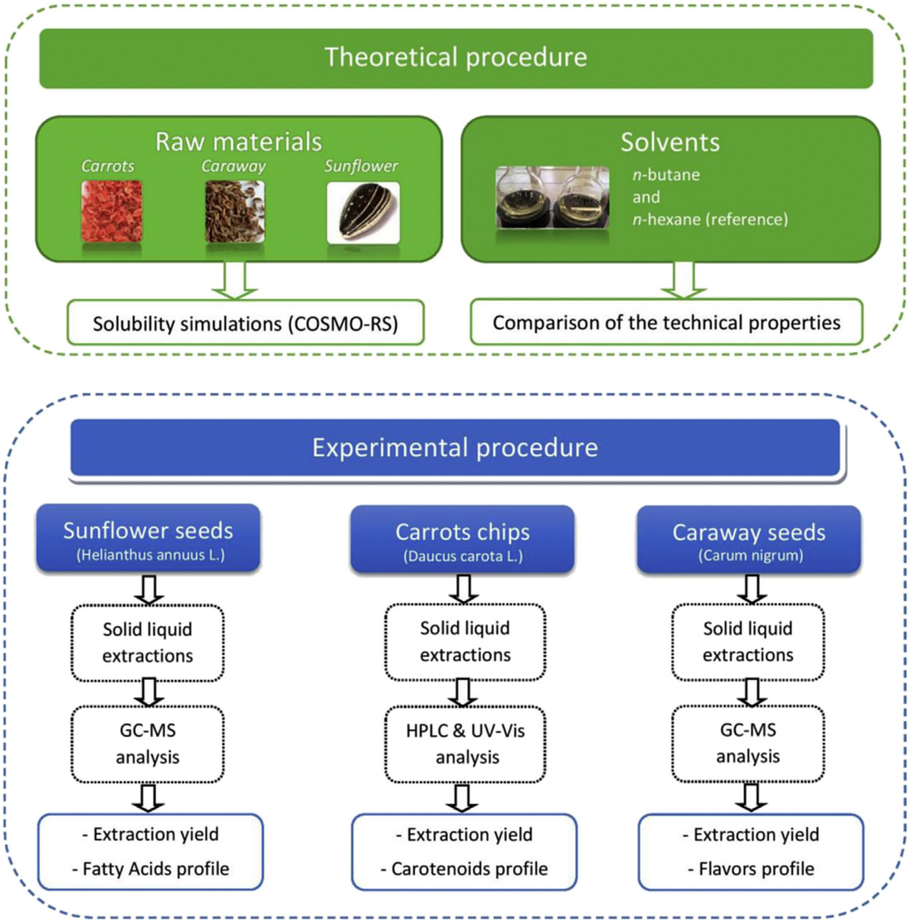

Fig. 2. Experimental procedure.

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evaporated. The vapors of solvent go up to the condenser (8) for recycling while the extract remains at the bottom of the evaporator. The remaining extract is collected in a flask, solubilized in 100 mL of *n*-hexane for analysis purpose and stored at 4 °C prior to analysis. Each extraction was made in triplicate.

2.4. *Reference: n-hexane extraction*

Reflux extraction using *n*-hexane was used as reference extraction procedure. 10 g of raw material are weighed and placed in a flask containing 100 mL of *n*-hexane. The mixture was heated at hexane boiling point (68 °C) during 2 h. After cooling at ambient temperature, the mixture was filtered (1.6 μm) to separate solid residues and then *n*-hexane was evaporated using a rotary vacuum evaporator (40 °C; 15 kPa). Extract was stored at 4 °C prior to analysis. Each extraction was made in triplicate.

2.5. *Extract analysis*

2.5.1. *Analysis of carotenoids by high performance liquid chromatography*

The protocol was adapted from (Yara-Varon et al., 2016). Identification of carotenoids in carrot oleoresin was performed by high performance liquid chromatography (Agilent 1100) equipped with a UV—Vis detector (Diode Array Detector) under the following conditions: Eluent, acetonitrile/methanol (with 0.6 g/100 g of ammonium acetate)/dichloromethane (ratio: 77/20/3, mL/mL/mL) in an isocratic mode; Injection volume, 10 μL; column, C18 column (150 × 3 mm - 3 μm - flow rate = 1.4 mL/min); temperature, 25 °C; detector, diode array detector set at 464 nm. Carrot oleoresin was diluted in chloroform prior to injection. Quantification was made using external calibration with a β-carotene standard (UV purity >98%). Results are expressed in grams per 100 g of oleoresin sample.

2.5.2. *Ultra Violet (UV) spectroscopy determination of total carotenoid content*

The protocol is adapted from (Yara-Varon et al., 2016). The carotenoid content in the extracts was measured spectrophotometrically (Biochrom Libra S22 UV/Vis Spectrophotometer, Cambridge, England) in a 1 cm optical path-length quartz cell at 450 nm for β-carotene in each extract against the *n*-hexane used as a blank. The following equation was used to calculate the carotenoid concentration, C (mg L^{-1}) (Strati & Oreopoulou, 2011):

$$C = \frac{A_{\lambda\max} \times 10^4}{A_{1cm}^{1\%}}$$

where $A_{\lambda max}$ is the absorbance of the extract at λ_{max} and $A_{1cm}^{1\%}$ is the absorption coefficient (absorbance at a given wavelength of a 1 g/100 g solution in a spectrophotometer cuvette with a 1 cm light path) of β-carotene in the respective solvent. The absorption coefficient was 2592 in *n*-hexane at 450 nm. Finally the yield of carotenoids in each extract was calculated and expressed as mg (β-carotene) 100 g^{-1} of dry matter.

2.5.3. *Gas chromatography analysis of aromatic compounds*

The detection of carvone and limonene in caraway essential oil was performed by gas chromatography (GC 7890, Agilent Technologies, Santa Clara, USA) equipped with a FID and quadrupole detector under the following conditions: vector gas, Helium (1.1 mL/min); injector temperature, 250 °C; injected volume, 1 μL; split, 1:100; column, VF-MAX type (30 m × 0.25 mm, film thickness x 0.25 μm, Agilent J&W Scientific, Folsom, USA); temperature gradient, 60 °C for 1 min, increased at 240 °C (rate: 3 °C/min) and held for 5 min. The detection is done by the FID at 250 °C. Carvi oleoresins are diluted in acetone prior to injection. For identified compounds, quantification is made with MS detector. Quadrupole is set at 150 °C with a source and transfer line at 230 °C. Helium flow rate is kept at 1.1 mL/min. Quantification of carvone and limonene is performed using external calibration with corresponding standards. Results are expressed in mass ratio carvone/limonene.

2.5.4. *Gas chromatography analysis of fatty acids*

Identification and quantification of fatty acids in sunflower oil was performed by gas chromatography (GC 3800 VARIAN Agilent Technologies, Santa Clara, USA) equipped with a FID detector under the following operating conditions: vector gas, Helium (207 kPa); injected volume, 1 μL; split, 1:50; column, DB32 type (60 m × 0.25 mm; film thickness x 0.25 μm, Agilent J&W Scientific, Folsom, USA); oven temperature, 120 °C; temperature program: 120 °C for 5 min, increased at 200 °C (rate: 5 °C/min) and held for 10 min, increased at 230 °C (rate: 2 °C/min) and held during 15 min.

Fatty Acid Methyl Esters were obtained according to the following procedure: triglycerides were diluted in TBME (100 mg of oil into 10 mL of TBME). To 200 μL of this mixture were added 100 μL of TMSH for transesterification and derivatization of fatty acids. Detection of eluted fatty acids methyl esters (FAMEs) is done by FID at 300 °C. Eluted FAMEs are identified by their retention time in comparison with a standard mix (Supelco 37 FAME mix, Sigma-Aldrich, USA). Quantification is performed by internal standard calibration (C15:0). Results are expressed in grams of a given fatty acid in 100 g of the sunflower oil sample.

2.6. *Statistical treatment*

The extraction yields were calculated according to the following equation:

$$Yield(\%) = \frac{massofextract\ (g)}{massofinitialplantmaterial\ (g)} \times 100$$

The repeatability of the results was expressed as standard deviation values (for caraway seeds and carrots) or pooled standard deviation values (for sunflower seeds). The pooled standard deviation (pooled SD) values were calculated as the square root of the sum of individual variances pondered by the individual degrees of freedom of each series of replicates (Box, Hunter, & Hunter, 1978).

2.7. *Computational method: COSMO-RS calculations*

The Conductor-like Screening Model for Real Solvents (COSMO-RS) is a calculation method developed by (Klamt, 2003). This approach combines quantum chemical with thermodynamical statistics for the determination and prediction of the chemical potential of a molecule in a liquid without any experimental data. Thus, COSMO-RS can be used as a decision-making tool for solvent screening (Filly et al., 2015; Sicaire, Vian, Fine, Carre et al., 2015; Sicaire, Vian, Fine, Joffre et al., 2015; Suberu et al., 2016).

COSMO-RS procedure comprised a first step at microscopic scale followed by a macroscopic step. Firstly the COSMO model is used to apply a virtual conductor environment for the molecule. In this environment the molecule induced a polarization charge density on its surface depicted on the σ-surface (see Fig. 3). During the quantum calculation self-consistency algorithm, the solute molecule is converged to its energetically optimal state in the conductor with respect to its electron density and geometry.

Based on the obtained polarization charge density the second

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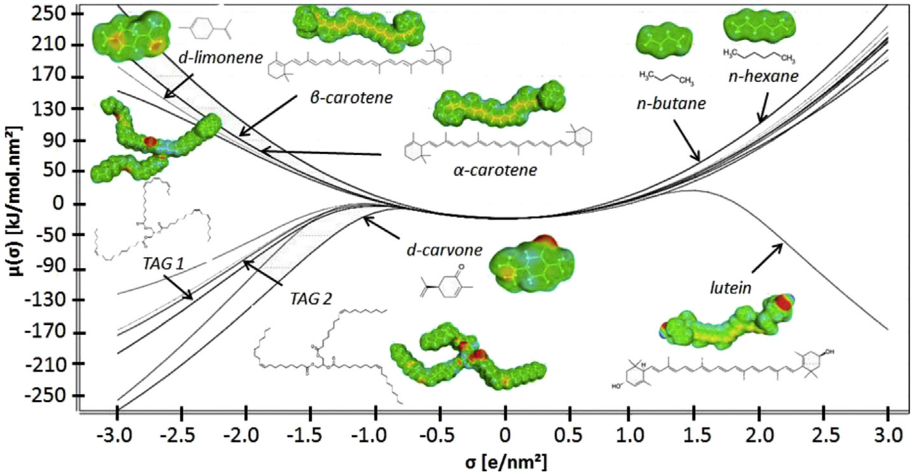

Fig. 3. σ-potentials of solutes and solvents calculated using COSMO-RS model.

step used a statistical thermodynamic calculation to quantify the solute interaction energy. The spatial distribution of the polarization charge σ of the molecule was then converted into a surface composition function (σ-profile). This σ-profile (see Fig. 4) provides information about the molecular polarity distribution. The thermodynamics of the molecular interactions was used to calculate the chemical potential of the surface segment (σ-potential) using COSMOthermX program (version C30 release 14.10). The σ-potential (see Fig. 3) can be interpreted as the affinity between a solvent S and the surface σ *via* electrostatic interactions and hydrogen bonds. The part of the negative charge of the molecule was located on the right side (acceptor hydrogen bonds) with positive σ values while the part of the positive charges was located on the left side (donor hydrogen bonds) with negative σ-values. Generally, the region σ ± 1 e/nm^2 was considered to be non-polar or weakly polar. The σ-profile and the σ-potential were used to interpret the affinity of the solvent for surface polarity, to understand the interaction between the compound and a list of solvents and finally, to estimate the thermodynamic properties of the system.

In addition, the software COSMOthermX allows calculation of the affinity between a solute and the solvent in terms of logarithm of the solubility in mole fractions (log10(x_solub)).

The logarithm of the best solubility (i.e. solute and solvent are miscible) is equal to 0 and all other solvents were given relative to the best solvent(s). Also, the logarithm was transformed into probability of solubility and was expressed in percentage. The calculations for solutes and solvents were performed at 25 °C.

2.8. *n-butane as alternative solvent to n-hexane: properties comparison*

In order to determine if *n*-butane can be an alternative to *n*-hexane, in a first part a comparison of technical properties was made. In a second part, the solubility of target lipophilic compounds in both *n*-butane and *n*-hexane was assessed by COSMO-RS simulation.

Table 1 reports physicochemical properties of *n*-butane and *n*-hexane. Data was obtained from ACD-labs and from Air Liquide gas encyclopedia. The energy of evaporation for 1 kg of solvent at 25 °C was calculated using the specific heat, the latent heat of

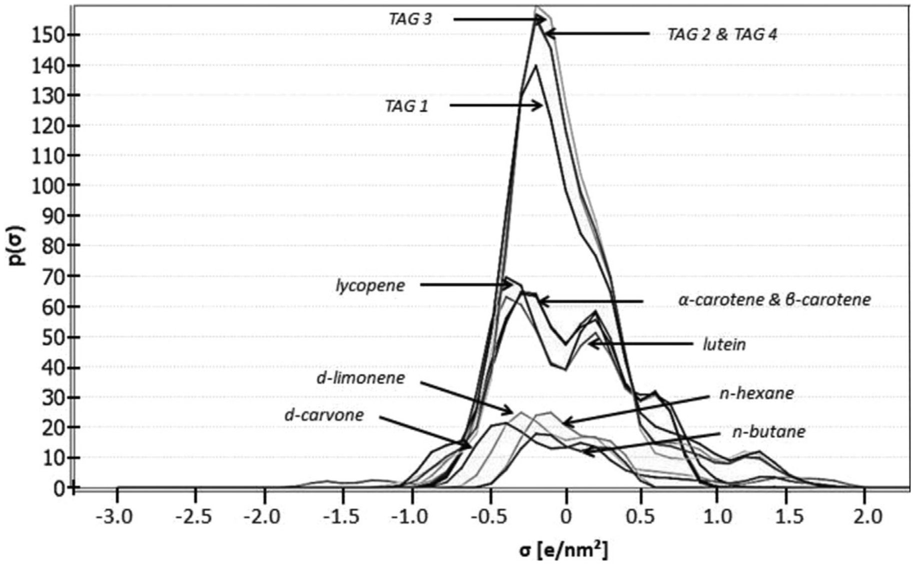

Fig. 4. σ-potentials of solutes and solvents calculated using COSMO-RS model.

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Table 1
Comparison of technical properties of *n*-hexane and *n*-butane (Source: ACD-Labs).

Properties	Unit	*n*-hexane	*n*-butane
Molecular weight	[g/mol]	86.2	58.1
Density (25 °C)	[kg/m^3]	0.65	0.57
Viscosity (25 °C)	[Pa.s]	3.2 10^{-4}	1.6 10^{-4}
Boiling Point (101.3 kPa)	[°C]	68.5	−0.5
Latent heat of vaporization	[kJ/kg]	334	386
Specific heat	[kJ/kg.°C]	2.23	2.4
Evaporation energy per kg of solvent (101.3 kPa)	[kW.h]	0.12	0.11
Equivalent CO_2 (1 kW h = 800 g of CO_2)	[g]	96	88
Solubility in water (25 °C)	[kg/m^3]	0.05	0.06
log10 P		3.9	2.9
Flash point	[°C]	−23	−60
Auto-ignition temperature	[°C]	225	287
Resource		Petroleum	Petroleum
Toxic		Yes	No
CMR[a] classification		2	/

[a] Carcinogenic, Mutagenic and or toxic to Reproduction.

vaporization and the boiling point.

Both *n*-butane and *n*-hexane have a similar lipophilic behavior, with close solubility in water (0.05 kg/m^3 and 0.06 kg/m^3 at 25 °C), log10 P value (2.9 and 3.9) and density (0.57 and 0.65 kg/m^3). The comparison of boiling points (bp) and flash points (fp) shows that *n*-butane is logically much more volatile than *n*-hexane (bp = −0.5 °C, fp = −60 °C and bp = 68.5 °C, fp = −23 °C respectively). *n*-butane also has a lower viscosity (1.6×10^{-4} Pa s vs. 3.2×10^{-4} Pa s). Comparison of evaporation energies shows that *n*-butane has a slightly better score than *n*-hexane, with 0.11 kWh and 0.12 kWh respectively (source: ACD labs). This small difference has a direct impact on the energy consumption regarding the equivalent CO_2 with respectively 88 g_{CO2} and 96 g_{CO2}. These calculations have been made according to the literature: to obtain 1 kWh from coal or fuel, 800 g of CO_2 will be emitted during combustion of fossil fuel (Farhat et al., 2011).

In conclusion, the two solvents have very close technical properties and due to safety and energetic considerations, *n*-butane could be an alternative to *n*-hexane as extraction solvent.

3. Results and discussion

3.1. Evaluation of target compound solubility in n-butane and in hexane

A COSMO-RS simulation was performed to determine the relative solubility in *n*-hexane and *n*-butane of several components from caraway seeds (carvone, limonene), from sunflower seeds (triacylglycerols (TAGs): TAG1 (R1: C18:3n-3, R2: C18:2n-6, R3: C18:2n-6); TAG2 (R1: C18:1n-9, R2: C18:1n-9, R3: C18:2n-6); TAG3 (R1: C18:1n-9, R2: C18:1n-9, R3: C18:1n-9); TAG4 (R1: C18:1n-9, R2: C18:2n-6, R3: C18:2n-6)) and from carrots (α-carotene, β-carotene, lutein, lycopene).

Table 2 reports the solubility results, expressed in probability of solubilization (%). As a reminder the simulations were performed at room temperature (25 °C) considering that both solutes and solvents were in a liquid state. According to the rule “like dissolve like”, *n*-butane and *n*-hexane, respectively a C4 and C6 *n*-alkane, should have nearly the same solubilization power towards each molecule. As expected, *n*-hexane and *n*-butane showed a high probability of solubilization (80–100%, i.e. log10(x_solub) > −0.1) for apolar solutes like carotenes, TAGs and limonene. Similarly, both solvents showed a low probability of solubility (0–30%, i.e. log10(x_solub) < −0.5) for more polar solutes such as carvone and lutein. It can be concluded that the COSMO-RS simulation suggests that *n*-butane is a good potential candidate for the substitution of *n*-hexane, with a very close polarity and an almost identical probability of solubilization.

3.2. Experimental study

Liquefied gas extraction using this new process is new to literature. In this section, the extraction performances of liquefied *n*-butane were compared to *n*-hexane for carotenoids from carrots,

Table 2
COSMO-RS: relative solubility (log10(x_solub)) and probability of solubility of solutes in *n*-hexane and *n*-butane at 25 °C. Dark grey: high probability of solubility (60–100%); grey: medium probability (20–60%); light grey: low probability (0–20%).

Matrix	**Solute**	***n*-hexane**		***n*-butane**	
		log10(x_solub)	Probability (%)	log10(x_solub)	Probability (%)
Sunflower seed	TAG 1	-0.64	23.0 %	-0.10	78.5 %
	TAG 2	0	100.0 %	0	100.0 %
	TAG 3	0	100.0 %	0	100.0 %
	TAG 4	0	100.0 %	0	100.0 %
Caraway seed	Carvone	-0.61	24.5 %	-0.57	26.9 %
	Limonene	-0.08	83.8 %	-0.03	93.1 %
Carrots	α-carotene	-0.03	93.7 %	0	100.0 %
	β-carotene	-0.04	91.3 %	0	100.0 %
	Luteine	-2.30	0.5 %	-1.96	1.1 %
	Lycopene	-0.27	53.8 %	0	100.0 %

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Table 3
Extraction yield and fatty acid composition of sunflower oil extracted with *n*-hexane and *n*-butane. Number of replicates = 3.

Fatty acids	*n*-butane			*n*-hexane
Pressure	200 kPa	280 kPa	370 kPa	*atm.*
Temperature	20 °C	30 °C	40 °C	Bp (68 °C)
unit : g/100 g				
C16	5.8	5.9	5.8	5.9
C16: 1 n-7	0.1	0.1	0.1	0.1
C18	2.6	2.6	2.7	2.6
C18: 1 n-9	29.9	29.7	30.4	29.4
C18: 2 n-6	55.8	56.3	55.1	56.7
C18: 3 n-3	0.4	0.4	0.4	0.4
C20	0.2	0.2	0.2	0.2
C22	1.8	1.6	1.8	1.6
Σ SFAs	10.4	10.3	10.5	10.3
Σ MUFAs	35.8	35.7	36.4	35.4
Σ PUFAs	56.2	56.7	55.4	57.1
Pooled SD	0.3	0.2	0.3	0.3
Extraction yield (%)	36.6 ± 0.6	36.7 ± 1.0	36.9 ± 0.4	53.4 ± 0.4

caraway essential oil and sunflower oil.

3.2.1. *Qualitative and quantitative comparison of extracts from sunflower seeds*

Extraction yields and fatty acid distribution in sunflower oils obtained with *n*-butane (at 20 °C, 30 °C and 40 °C) and *n*-hexane are compared in Table 3. The use of *n*-butane enabled to reach an average oil yield of 36.7% (Table 3). Increasing extraction temperature from 20 °C to 40 °C did not impact oil extraction, as observed by (Nimet et al., 2011). The lack of influence of temperature on the extraction yield tends to indicate that in this extraction, the limiting factor is not the internal transport but the mass transfer of oil into the bulk phase. This limitation could be overcome by adding a stirrer to homogenize the mixture and facilitate solvent contacting with the raw material. Extraction performed with *n*-hexane results in higher yields than with *n*-butane (53%, Table 3) probably due to the higher temperature for *n*-hexane extraction (20 °C–40 °C for *n*-butane and 68 °C for *n*-hexane).

Extracted sunflower oils from both solvents are composed of 55–57 g/100 g of poly-unsaturated fatty acids, 35–36 g/100 g of mono-unsaturated fatty acids and 10 g/100 g of saturated fatty acids. Fatty acids distributions are similar for both studied solvents. It is also interesting to notice that the temperature range (from 20 °C for *n*-butane to 68 °C for *n*-hexane) does not impact on fatty acid distribution, as observed by (Nimet et al., 2011). Sunflower oils can be extracted by *n*-butane with an equal fatty acid composition compared to *n*-hexane, even at low temperatures (20 °C).

3.2.2. *Qualitative and quantitative comparison of extracts from caraway seeds*

Comparison of caraway seeds extract in terms of yield and composition is reported in Table 4. Extraction yield using *n*-butane is dependent on temperature: an increase of 6.5%–10.9% could be noted by increasing extraction temperature from 20 °C to 40 °C. The highest extraction yield was reached for *n*-hexane (15% at 68 °C). Caraway seeds contain up to 6 g/100 g of essential oil and a higher amount of fatty acids (up to 8 g/100 g) (Bailer, Aichinger, Hackl, de Hueber, & Dachler, 2001; Laribi, Kouki, Bettaieb, Mougou, & Marzouk, 2013). Given the extraction yields obtained, the extract is most probably a mixture of essential oil and fatty acids.

In caraway, the main terpenes in essential oil are carvone and limonene (95 g/100 g of terpenic compounds) (Filly et al., 2015). It could be noted from our results that the proportion of carvone over limonene is quite high (over 70 g/100 g, Table 4). These results have also been obtained by other authors (Laribi et al., 2009; Sedláková, Kocourková, Lojková, & Kuban, 2003). Authors show that the carvone/limonene ratio varies according to drought (Laribi et al., 2009), to caraway variety (Sedláková et al., 2003), or according to the stage of development of caraway, where carvone seem to be accumulating over limonene at the later stages (Bouwmeester,

Table 4
Extraction yield and the relative abundance of carvone and limonene in each extract. Number of replicates = 3.

Solvent	T (°C)	P (kPa)	Time (h)	Extraction yield (%)	Ratio [carvone] / [limonene] * (g/100 g)	
					Carvone	Limonene
n-butane	20	200	2	6.5 ± 0.8	89.4 ± 4.8	10.6 ± 2.3
n-butane	30	380	2	8.4 ± 0.6	90.7 ± 2.3	9.3 ± 1.7
n-butane	40	470	2	10.9 ± 0.2	91.8 ± 3.2	8.2 ± 1.4
n-hexane	Bp	atm.	2	15.0 ± 0.7	70.5 ± 3.0	29.6 ± 2.4

*** Concentration ratio**

Table 5
Extraction yield and composition of carrot oleoresin obtained with *n*-hexane and *n*-butane. Number of replicates = 3.

solvent	T (°C)	P (kPa)	time (h)	carotenoid yield (mg 100 g^{-1} DM)	HPLC identified carotenoids (g/100 g)			
					α-carotene	β-carotene	lutein	lycopene
n-butane	20	200	2	14.8 ± 1.5	35.2 ± 0.1	64.8 ± 0.3	tr.	tr.
n-butane	30	380	2	23.1 ± 3.8	35.2 ± 0.1	64.8 ± 0.2	tr.	tr.
n-butane	40	470	2	25.7 ± 3.6	35.2 ± 0.2	64.8 ± 0.3	tr.	tr.
n-hexane	68	atm.	1	55.8 ± 7.6	36.0 ± 1.6	64.0 ± 1.2	tr.	tr.

tr., traces; DM, dry matter

Gershenzon, Konings, & Croteau, 1998).

As an oxygenated compound, the polarity of carvone is higher than limonene's which is a hydrocarbon. However, extracts using *n*-butane or *n*-hexane showed a higher proportion of carvone (70.5–91.8 g/100 g) than limonene (8.2–10.6 g/100 g). For *n*-butane, the proportion of carvone tends to increase with temperature (from 89.4 to 91.8 g/100 g with increasing temperatures from 20 °C to 40 °C). For *n*-hexane extract, a difference in range of proportions was noticed as a higher amount of limonene was detected (29.6 g/100 g against 8.2–10.6 g/100 g for *n*-butane extracts). Surprisingly, *n*-butane seemed to be more selective towards carvone than *n*-hexane.

3.2.3. Qualitative and quantitative comparison of extracts from dried carrots

Comparison of carotenoid yields obtained in liquefied *n*-butane show a positive impact of temperature with an increase from 14.8% to 25.7% at 20 °C and 40 °C respectively (Table 5). However a higher yield was obtained for the reference in *n*-hexane with 55.8%. This difference can probably be explained by the higher temperature of *n*-hexane extraction.

Extracts composition obtained with both *n*-butane and *n*-hexane were very similar with a proportion of α-carotene comprised between 35.2 and 36 g/100 g respectively and a proportion of β-carotene comprised between 64.8 and 64 g/100 g respectively. Those compositions are in accordance with previous results (Yara-Varon et al., 2016). Neither lycopene nor lutein were detected in quantifiable amount. This observation can be explained by the low fraction of lutein in carrots carotenoids (1–5 g/100 g) (Amosova, Ivakhnov, Skrebets, Ulyanovskiy, & Bogolitsyn, 2015) and by the low solubility of lycopene in apolar solvents, due to its relative high polarity. These results suggest an equal carotenoid composition in the raw material and that liquefied *n*-butane allowed extraction of a fraction of it.

Overall, these experimental data show that the developed process with the use *n*-butane is suitable for extraction of lipophilic compounds. Extraction could be achieved even at low temperatures (20 °C) for *n*-butane and with extraction yields increasing with temperatures (up to 40 °C). It could also be noticed that an equal extract composition was obtained with *n*-butane compared to *n*-hexane, except for caraway extracts, where a higher proportion of carvone upon limonene was obtained (80–90 g/100 g of carvone for *n*-butane extracts and 70 g/100 g of carvone for *n*-hexane extract). However, higher mass extraction yields were systematically obtained with *n*-hexane. This gap could be reduced by acting on different process parameters such as temperature and addition of a stirring device to enhance plant material-liquefied gas contacting. Kinetic limitation due to a slow mass transfer has been reported for compressed fluid processes such as supercritical CO_2 even if the continuous circulation of CO_2 throughout the matrix generates a stirring (Hasan & Farouk, 2013).

Experimental data and COSMO-RS simulation are well correlated for sunflower oil and carotenoids from carrots. It could be identified that only traces of lutein and lycopene were detected in carrot extracts (obtained with neither *n*-hexane nor *n*-butane), which could be justified by the low amount in our carrot sample. An inverse tendency in experimental data compared to simulation data was identified for carvone. A higher proportion of carvone over limonene was determined in all extracts.

4. Safety considerations

Liquefied gas extraction process is simple and can be readily understood in terms of the operating steps to be performed. However, the use of *n*-butane as liquefied gas can pose serious hazards in inexperienced hands (extremely flammable vapors). A high level of safety and attention to details when planning and performing experiments must be used by all the persons. They have to ensure that they seek proper information from knowledgeable sources and that they do not attempt to use this gas unless proper guidance is provided. Only approved equipment in dedicated laboratory or technological hall, with no ignition sources around and proper ventilation (such as ATEX in Europe or HAZLOC in North America), should be used. The same precautions must be taken for *n*-butane storage.

5. Conclusion

A new process developed for liquefied gases extraction was evaluated. In terms of application, the process was assessed using *n*-butane for lipophilic natural products extraction. Several technical properties of *n*-butane have been found interesting for extraction processes: chemically inert, easy to evaporate, non-toxic, cheap, commercially available and authorized without limitation for foodstuff production. A COSMO-RS theoretical study confirmed that *n*-butane has a similar solubilization potential to *n*-hexane. The performances of *n*-butane were compared to *n*-hexane for the solid-liquid extraction of three different classes of solutes: aromas, oils and carotenoids. These simulations were confirmed by lab-scale extractions on caraway seeds, sunflower seeds and carrots. The extraction yields obtained with *n*-butane were lower than *n*-hexane, most probably because of a slow mass transfer inside the solvent due to the lack of stirring. The promising results indicate that *n*-butane can be a non-toxic alternative to *n*-hexane extractions, paving the way to other liquefied gases for extraction.

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