A STUDY OF DIFFERENT FORMULATIONS OF WALL SUPPORT SYSTEMS FOR MICROENCAPSULATION OF ANTIOXIDANT ESSENTIAL OILS

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Abstract

Essential oils from native plants cultivated in Mendoza, Argentina are reported as having antioxidant properties on lipids. Examples of these plants are rosemary (*Rosmarinus officinalis*), "jarilla mendocina" (*Larrea sp.*), "tomillo mendocino" (*Acantholippia seriphioides*), origanum (*Origanum vulgare*), tarragon (*Artemisia sp.*), lavandins (*Lavandula sp.)* and eucalyptus (*Eucalyptus sp.*). The objective was to solve the problem of volatility and stability that these essential oils exhibit during handling and storage. The essentials oils were extracted by vapor stripping and then emulsified with different formulations of water suspensions of wall support systems (Arabic gum; Maltodextrin, Food Grade; and Cellulose microcrystalline, Food Grade) using both, a hand-held propeller-blender and a high pressure double-effect homogenizer working at inlet and exit pressures of 20.26 and 10.13 MPa, respectively. The microencapsulation of the essential oils was achieved by drying the emulsions in a spray-dryer Niro-Atomizer Minor, operated at a rotor speed of 24,000 r.p.m., and inlet and outlet drying temperatures of 180°-200°C and 90°-95°C, respectively. The wall support-essential oil emulsions studied were: (I) 60% water, 30% arabic gum and 10% essential oil; (II) 60% water, 20% arabic gum, 10% maltodextrin and 10% essential oil; (III) 60% water, 10% arabic gum, 20% maltodextrin and 10% essential oil; (IV) 60% water, 30% maltodextrin and 10% essential oil; and (V) 60% water, 10% arabic gum, 20% Cellulose microcrystalline and 10% essential oil. Essential oil retention values (entrapment) in the powders ranged from a high of 87.5% with formulation (I), to a low of 34.7% with formulation (V). The final moisture content of the powders was between 3.60% and 4.00% and they exhibited good flowability and low degree of hygroscopicity.

1. Introduction

International regulations regarding the use of additives in foodstuffs have become more rigorous than in the past, consequently there is a worldwide tendency towards the use of non-artificial food additives extracted with non-organic solvents.

Food additives are in constant review by the "Codex Alimentarius", COPTAN and ISO 9000 codes, European Union, Argentine Food Code (Codigo Alimentario Argentino, 1995) and Annex Mercosur Norms (Normas Mercosur, 1993), FAO (FAO, 1975-76) and the FDA who defines whether or not a substance is GRAS (Generally Recognized as Safe).

The Argentine Society for Research of Aromatic Products (SAIPA) has published in its journal "Prensa Aromatica" (Aromatic Press) different articles related to the extraction of essential oils and oleoresins with non-organic solvents, as well as their use in foods, cosmetic and pharmaceutical products, i.e. as antioxidants (Prensa Aromatica, 1996, N°4,7,8; Tymoschuck *et al.*, 1996).

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Presently, IRAM in collaboration with SAIPA and the industry are developing Quality Control standards, regarding extraction and packaging of different essential oils and oleoresins from wild and domesticated native plants, with nutritional and therapeutic properties.

Due to their volatility and ease of oxidation in the presence of oxygen, essential oils can be lost or degraded during handling and storage, defeating the purpose for which they were obtained. Microencapsulation constitutes a viable technology, which allows the preservation and utilization of many food ingredients (i.e., essential oils), as seasoning or antioxidant agents, in different food processes. This technology has been used for many years in the pharmaceutical industry and is now being used extensively in the food industry.

Spray drying is by far the most commonly used microencapsulation technique in the food industry (Dziezak, 1988). The process involves the preparation of a water dispersion containing the coating material or wall support system (generally a food-grade hydrocolloid) and the active ingredient to be encapsulated. The dispersion is then homogenized and atomized in small droplets inside the spray dryer, where it is dried into a fine powder.

Many researchers have studied different encapsulating agents and infeed concentrations to achieve the maximum retention of essential oils during spray drying-microencapsulation (Leahy *et al.*, 1983; Reineccius and Bangs, 1985; Reineccius and Risch, 1986; Kim Ha and Reineccius, 1988; Sheu and Rosenberg, 1995; Lin *et al.*, 1995). Mixtures of guar gum and maltodextrin, in different proportions, have been reported to show good retention power. However, there are many new commercial products in the market (such as Miracap, Encapsol 855, Capsule, N-Lock, etc.), that exhibit equal or better entrapment capacity.

Studies started in 1992 in the School of Agronomy (FCA) of the National University of Cuyo (UNCuyo) permitted the advancement, in the Mendoza region, in matters related to the extraction of essential oils from different native plants grown in Mendoza, Argentina. To further progress along these lines, the objectives of this study were: (a) to obtain and characterize essential oils of different species, such as: rosemary (*Rosmarinus officinalis*), "jarilla mendocina" (*Larrea sp.*), "tomillo mendocino" (*Acantholippia seriphioides*), origanum (*Origanum vulgare*), tarragon (*Artemisia sp.*), lavandin (*Lavandula sp.*) and eucalyptus (*Eucalyptus sp.*), by distillation with saturated water vapor (vapor stripping), and (b) to study different formulations of wall support systems for microencapsulation of the essential oils previously obtained by spray drying, in order to solve the problem of volatility and stability that these oils exhibit during handling and storage.

2. Material and methods

The following species were studied: (a) wild native plants growing in the Mendoza region, "jarilla mendocina" (*Larrea sp.*) and "tomillo mendocino" (*Acantholippia seriphioides*); and (b) plants grown and collected in experimental plots of the FCA, rosemary (*Rosmarinus officinalis*), origanum (*Origanum vulgare*), tarragon (*Artemisia sp.*), lavandin (*Lavandula sp.*) and eucalyptus (*Eucalyptus sp.*).

Essential oils were extracted by distillation with saturated water vapor (vapor stripping) at both, laboratory and pilot scale from leaves, branches and flowers.

The laboratory setup is made of glass consisting of a column, 1.00-m long and 0.10-m in diameter, attached to a 2-liter balloon at one end and connected, through a U-tube, to a coiled water condenser at the other end. Distilled water was placed in the balloon and heated with an electric mantle to boiling point. The raising water vapor passed through the material packed in the column extracting the essential oils. The mixture oil-vapor was then condensed in the water-refrigerated coil and the condensate separated by density difference in an overflow glass tube placed at the exit of the condenser.

The pilot-scale equipment is all stainless steel. The setup include a 0.50-m tall, 0.40-m diameter tank outfitted with a steam injection/distribution device at the bottom and a clamped lid at the top, sealed with a rubber gasket. The lid is welded to a 1.10-m long, 0.06-m diameter fractionation column, randomly packed with small basket-type cylinders made of stainless steel mesh. The column is connected to a coiled water condenser, which discharges the condensate in a separation vessel. The material was weighted and placed inside the tank, uniformly distributed into several layers separated by perforated plates. After clamping the lid, saturated steam was injected through the bottom at a constant pressure of 24.5 kPa.

Net time of vapor-extraction was 60 minutes in both equipment. The amount of oil extracted in each experiment was recorded to determine yield. The collected essential oils were immediately sealed in glass containers under nitrogen atmosphere and stored at 0°C for further determinations of density and refraction index, and for microencapsulation. Density was measured with a 5-ml picnometer and the index of refraction with a Hilger & Watts Ltd. refractometer. Both measurements were performed at 20°C. Several distillation runs were necessary to collect enough sample to carry out the microencapsulation experiments.

The following encapsulating agent were used: Arabic gum (E-414); Maltodextrin, and Cellulose microcrystalline (Avisel RC591 AD.CAP.; FMC Corp., 1993). They were tested individually and in mixtures of two in different proportions.

The polymers were slowly added to measured amounts of distilled water at room temperature under constant agitation. After achieving an homogeneous suspension, the essential oils were added to obtain the testing emulsions. Two emulsifying methods were experimented: (1) with a hand-held propeller-blender and (2) with a high pressure double-effect homogenizer (Gaulin) working at inlet and exit pressures of 20.26 and 10.13 MPa, respectively. Table 1 shows the emulsions studied, expressed by weight (w/w). A constant ratio of encapsulating agent to essential oil of 3:1 was used in all the emulsions.

The emulsions were dried in a spray-dryer Niro-Atomizer Minor, operated at a rotor speed of 24,000 r.p.m., and inlet and outlet drying temperatures of 180°-200°C and 90°-95°C, respectively. The collected powders were immediately sealed in glass containers and later tested for oil retention and moisture content. Oil retention (entrapment) was assessed by measuring the amount of essential oil extracted from 50 gr samples of powder by vapor stripping, using the laboratory distillation equipment. Moisture content was determined by placing duplicate samples in oven at 105°C for 6 hours. The values of moisture content were further verified through mass balances.

3. Results

3.1. Distillation of essential oils

The physical properties, yield, appearance and aroma of the essential oils extracted from the different species can be described as:

Rosemary: 0.45 to 0.65% (v/w) extraction yield, obtaining a colorless to light yellow oily liquid with particular soft anise-camphory aroma. Density from 895 to 920 kg/m^3 and index of refraction between 1.465 and 1.470.

Jarilla Mendocina: 0.09 to 0.15% (v/w) extraction yield, obtaining an oily liquid, light yellow with typical wild grassy smell. Density between 874 and 925 kg/m^3, and index of refraction from 1.587 to 1.625.

Tomillo Mendocino: 0.75 to 0.90% (v/w) extraction yield, giving a yellow-green oily-viscous liquid with density between 854 and 912 kg/m^3, and refraction index from 1.472 to 1.481.

Origanum: 1.60 to 2.30% (v/w) extraction yield, obtaining a light yellow oily liquid with distinct pungent smell. Density from 938 to 963 kg/m^3 and index of refraction between 1.502 and 1.508.

Tarragon: 0.40 to 0.70% (v/w) extraction yield, giving a yellow-green oily liquid with slight soft anise aroma. Density from 933 to 945 kg/m^3 and index of refraction from 1.516 to 1.517.

Lavandin: extraction yield between 3.00 and 6.00% (v/w), obtaining a colorless to intensely yellow oily liquid with strong distinctive smell. Density from 890 to 905 kg/m^3 and index of refraction between 1.465 and 1.469.

Eucalyptus: 0.03 to 3.00% (v/w) extraction yield, giving a colorless oily liquid with characteristic pungent smell. Density from 876 to 906 kg/m^3 and index of refraction between 1.446 and 1.459.

The range of values of yield, density and index of refraction of essential oils, obtained for the different experiments are summarized in Table 2.

3.2. Microencapsulation of essential oils

For each formulation of encapsulating agent/essential oil, the emulsifying method employed did not give differences with regards to oil retention in the powders.

The spray drying experiments were carried out at a constant emulsion feed rate of 0.267 kg/min. The amount of emulsion dried each time was 400 g. Average values of essential oil retention (entrapment) and final moisture content of the powders were respectively, 87.5%, 79.8%, 70.1%, 62.3% and 34.7%, and 3.60%, 3.80%, 3.90%, 4.00 and 4.15% for formulations I, II, III, IV and V. These values are summarized in Table 3.

4. Discussion and Conclusions

The results obtained for the different plants studied are well within the range listed in the literature. The species showing the highest yield in oil extraction were Origanum, Eucalyptus and Lavandin. The broad range of oil extraction yield shown for eucalyptus was obtained from 35 different species, out of which only three gave values below 0.10%.

Oil extraction by water vapor stripping is an appropriate technology, which requires relatively inexpensive equipment, uses a non-toxic natural solvent and provides high quality essential oils with high demand in the international market.

The apparently equal degree of emulsion obtained with either mixing method employed must be interpreted in light of the sample size processed. The hand-held propeller-blender was rather over-designed for the small size of the samples used, allowing a high degree of mixing. When dealing with industrial scale samples, a high pressure double-effect homogenizer might be more efficient in providing more homogeneous emulsions.

The wide range of oil retention values determined in the powders (from 87.5% with formulation I, to 34.7% with formulation V) showed Arabic gum as the best encapsulating agent. Although, mixtures of arabic gum and maltodextrin do not show such high entrapment capacity, they are very good nevertheless, particularly when considering that the price of maltodextrin is about one-tenth the price of arabic gum. The low final moisture content of the powders (between 3.60% and 4.00%) and low degree of hygroscopicity ensures a satisfactory conservation during storage. They also exhibited good flowability.

5. References

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Table 1 - Composition of emulsions tested in microencapsulation experiments, in % w/w

COMPOSITION	EMULSION TESTED				
(% w/w)	I	II	III	IV	V
Water	60	60	60	60	60
Arabic gum	30	20	10	-	10
Maltodextrin	-	10	20	30	-
Cellulose microcrystalline	-	-	-	-	20
Essential oil	10	10	10	10	10

Table 2 - Values of yield, density and index of refraction of essential oils of different species

SPECIES	YIELD (% v/w)	DENSITY (kg/m^3 at 20°C)	REFRACTION INDEX (at 20°C)
Rosemary (*Rosmarinus officinalis*)	0.45 - 0.65	895 - 920	1.465 - 1.470
Jarilla Mendocina (*Larrea sp.*)	0.09 - 0.15	874 - 925	1.587 - 1.625
Tomillo Mendocino (*Acantholippia seriphioides*)	0.75 - 0.90	854 - 912	1.472 - 1.481
Origanum (*Origanum vulgare*)	1.60 - 2.30	938 - 963	1.502 - 1.508
Tarragon (*Artemisia sp.*)	0.40 - 0.70	933 - 945	1.516 - 1.517
Lavandins (*Lavandula sp.*)	3.00 - 6.00	890 - 905	1.465 - 1.469
Eucalyptus (*Eucalyptus sp.*)	0.03 - 3.00	876 - 905	1.446 - 1.459

Table 3 - Average values of essential oil retention and final moisture content of powders

DETERMINATION	MICROENCAPSULATION EXPERIMENT				
(%w/w)	I	II	III	IV	V
Oil retention	87.50	79.80	70.10	62.30	34.70
Moisture content	3.60	3.80	3.90	4.00	4.15