WALL MATERIAL SELECTION FOR MICROENCAPSULATING *GLICINE MAX* AND *PUNICA GRANATUM* OILS BY SPRAY DRYING

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Abstract: Pomegranate seed oil, even though highly sensitive to oxidation, has been extensively studied due to its anti-inflammatory potential. Microencapsulation by spray drying can protect the oil and increase its shelf life. Modified starch, maltodextrin and gum arabic are evaluated by a mixture design to get the better wall material composition. The better response for drying process yield (41%) and oxidative stability (42%) were achieved using modified starch and gum arabic at the same proportion as wall material.

Keywords: oxidative stability, seed oil microencapsulation, agro-industrial by-product.

Introduction

The industry of fruit juices plays a growing part in global market. The generated residues can become an environmental problem if not properly disposed. Such residues may contain several bioactive compounds that can help to prevent diseases and maintain health. The seeds in pomegranate residue generated from juice extraction contain a special oil rich in poly unsaturated fatty acids and phenolic compounds with high anti-oxidant capacity[4].

Pomegranate seed oil contains more than 70% of punicic acid, an unsaturated fatty acid with 18 carbons and 3 conjugated double bonds (C18:3), isomer of linolenic acid, of the ω-3 family. Reported data[1,2] have shown that punicic acid presents anti-tumour and anti-inflammatory properties. Brazil has the second largest soybean production in the world, and pressed soybean oil is stable and contains vitamins E, K, lecithin and a high content of linoleic acid, an essential fatty acid of the ω-6 family. A blend of these oils may provide the recommended nutritional specifications to the ω-6/ω-3 ratio in human nutrition[5] while making it a more affordable product, capable of reach wider markets.

However, the large number of unsaturated chains make pomegranate oil highly reactive and thus, highly sensitive to oxidative rancidity. In order to be commercialized, it must be stable and secure. Spray drying is one of the most industrially used processes for microencapsulating process and makes it possible toprotect a sensitive material by creating a physical barrier (shell) between the material (core) and oxidizing agents such as oxygen and light[6]. Figure 1 shows a scheme of spray drying process.

Spray drying the oil in the suitable conditions with the appropriate wall material (or encapsulating material) can create stable oil microcapsules that both protect the oil against rancidity and increase its shelf life. A good wall material protects the core and increases the yield since it increases the glass transition temperature of the product, reducing its stickiness, wall deposition at the drying chamber and the agglomeration tendency of the powder[7].

The inlet temperature, the inlet air flow rate, the feed flow rate and the encapsulating material are parameters that control the characteristics of the product. For microencapsulation by spray drying a first step of formulating with carriers that do not interact with the molecule to be

encapsulated, for protection from heat and facilitate its flow into the tower to prevent adherence of product to the equipment walls is required. The encapsulating agents most commonly used are modified or hydrolyzed starch and gum arabic.

Fig. 1. Spray drying processing

The aim of this study was to select the wall materials for encapsulating a mixture of soybean oil and pomegranate seed oil in order to prevent oxidative rancidity and increase the shelf life of final product.

Material and method

Material: Fresh pomegranates (*Punica granatum* L.) fruits were supplied by Boa Fruta farm, located in Petrolina, Brazilian semiarid region.

Pomegranate oil: the seeds with 10% moisture content were triturated in a knife mill and crushed in continuous hydraulic press to yield a crude oil[10]. After decanting for separation of the impurities, pomegranate oil obtained was used in the formulation.

Soybean oil: organic soybean oil obtained by cold pressing (Organic®) was purchased in store specialized in high quality products in local trade, ®).

Formulation: Pressed pomegranate seed oil was diluted in organic cold pressed soybean oil at 20%. Modified Starch (MS, Capsul®, Ingredion™), Maltodextrin DE5 (MD, Globe® 1805) and Arabic Gum (GA, Vetec) were used as encapsulating materials in a simplex centroid three level mixture design, as can be seen in Table 1. The proportion selected for oil:wall material was 1:4, and the total ratio of water (62.5%) and oil (7.5%) in the emulsion were fixed for all tests.

Table 1. Parameters of mixed experimental design

Test	Encapsulating material		
	Maltodextrin (%)	Gum Arabic (%)	Modified Starch (%)
1	30.0	--	--
2	--	30.0	--
3	--	--	30.0
4	15.0	15.0	--
5	15.0	--	15.0
6	--	15.0	15.0
7	10.0	10.0	10.0
8	10.0	10.0	10.0
9	10.0	10.0	10.0

Fixed proportion of water (62.5%) and oil (7.5%).

Spray drying: Figure 2 shows the simplified scheme of the spray drying process. for each test the oil, Encapsulating material and water were mixed to form an emulsion with the ultra turrax, which was led to Buchi B-290 spray dryer at inlet temperature 150 ºC, co-current spray gas flow rate 414 $L*h^{-1}$ and feed flow rate 0.36 $L*h^{-1}$. The powder product was packed in sealed metallic packaging and stored at -18 ºC until the moment of analyses. The yield (Y) was calculated as the ratio of the mass of product (dry basis) and mass of solids in the feed.

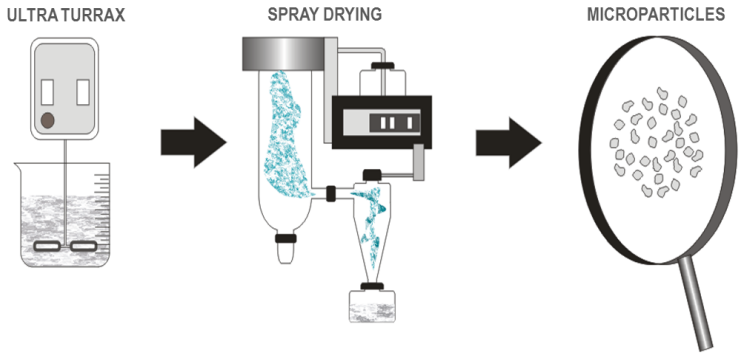


Fig. 2. Scheme of spray drying

Oxidative stability: it was measured by induction time (IT) in Rancimat® 743 equipment according to EN 14112 method but at 80 ºC and air flow 20 $L*h^{-1}$.

Sorption isotherms: were conducted by the static gravimetric method at 25 °C with triplicates samples of 1 g in different glass desiccator for 7 days, with supersaturated salt solution and pure water at different water activity (a_w) rising from 0.091 to 1.0. The adsorbed water variation was measured by mass variation of the samples during the period.

Image analysis: The microphotographs were taken in SEM equipment model JSM-6460LV, JEOL. About 0.1 g of each sample were sprayed in adhesive carbon tabs, mounted on SEM tubs and coated with gold in a sputter coater. The coated samples were then analyzed using the SEM operating at an accelerating voltage of 20 kV with 500x and/or 7000x magnification.

Data analysis: All the data evaluation was performed in Statistica 10.0 Software.

The mixture design may be seen in Figure 3. The vertices represent the pure components, here being maltodextrin, gum arabic and Capsul® (modified starch). The side of the triangle represents binary blending. All the inner part represents ternary blending, with the centroid

point of the triangle being the point where all components appear in the same proportion. In the mixture design, the sum of the fraction of components is always 1.

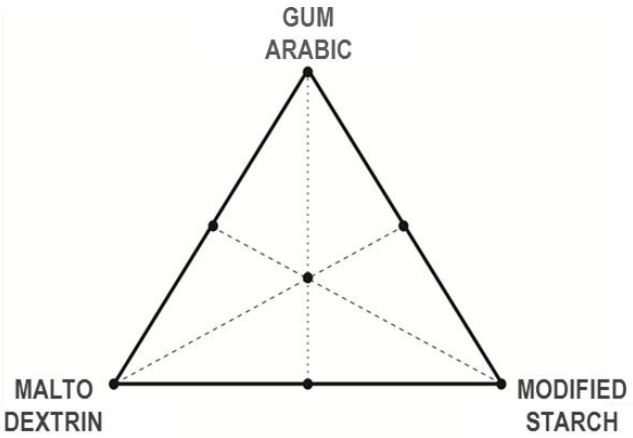


Fig. 3. Triangle of mixture design.

Results

Table 2 shows all the data of the drying process, along with the mass balance and yield. Ranging the parameters inlet air temperature, inlet air flow rate and emulsion feed flow rate it is possible to control the outlet temperature and product humidity, and also the particle diameter. The input air temperature shouldn't be too high if the core is thermo sensitive. On the other hand, if the outlet temperature is too low, the final humidity will be too high, which is not desirable since it will affect the stability of the product. The final humidity of microencapsulated product (pomegranate and soybean oils) was 3.1% and the outlet air temperature was 76 °C. This is the effective temperature achieved by the surface of the particles during the drying, due to thermodynamics equilibrium. The mass balance was calculated for test 6 (which had better results for oxidative stability, as shown in Figure 4b) and shows that the drying process yield was 41%. The calculated quantity of heat necessary to evaporate the water in test 6 was 47 kcal.

Table 2. Input, output and mass balance data from spray drying process

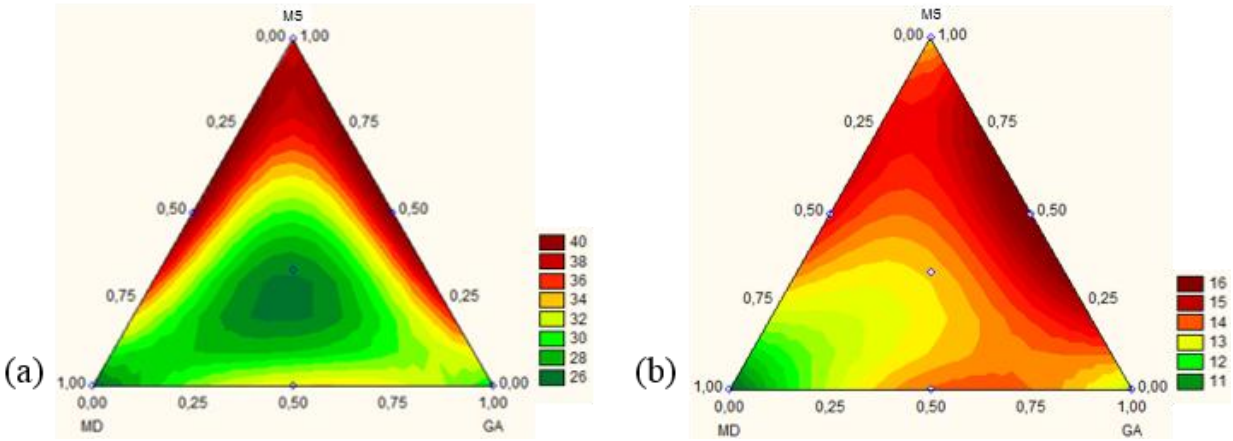
Input current	
Inlet air temperature	150 °C
Room temperature	28 °C
Relative air humidity	37%
Inlet air flow rate	414 $L*h^{-1}$
Emulsion feed flow rate	0.4 $L*h^{-1}$
Output current	
Product humidity	3.1%
Outlet air temperature	76 °C
Mass balance and yield*	
Emulsion feed mass	190 g
Feed dry mass	71 g
Product dry mass	29 g
Evaporated water	115 g
Yield	41%
$Q_{air\ heater}$	47 kcal

*In better conditions

Figures 3a and 3b show the statistical analysis for the dependent variables Process Yield and Oxidative Stability, respectively. For Process Yield, binaries blendings containing modified starch (tests 5 and 6) had better result, with drying yield of 41%. At the centroid point (where the three components are in same proportion) and at the MD (Maltodextrin) vertex there's the lower result. Since maltodextrin has almost none film formation capacity, it was expected that its test expressed a lower process yield.

As for the centroid point, the powder presented high wall retention and some auto-repulsive statics, which hampered the gathering of material, reducing yield. Some interaction among the components at this formulation was disadvantageous for the drying yield. There are negative superficial charges in gum arabic[8], and Capsul® appears to have negative superficial charges since its pH is about 3, as informed in the Technical Service Bulletin[9], but there were no specific information about superficial charges of maltodextrin and Capsul® in the literature.

The induction time (IT) expresses a time interval until the sample reaches a high oxidation level, according to the method in use. For mixing oils 20% the IT was 11.4 h and for the microencapsulated samples the highest IT was found at 16.2 h in MS:GA formulation (test 6), 42% higher. Lutterodt et al (2011)[3] found values of IT among 19.7 and 23.4 h for grape seed oil at 80 ºC and 7 $L*h^{-1}$. At a lower air flow the sample takes more time to oxidize. The response surface for Oxidative Stability and yield are shown in Figure 4.



MS- modified starch; MD- maltodextrin; GA- Gum arabic

Fig 4. Response surface for variables: (a) process yield (%) and (b) induction time (h).

The sorption isotherms were ploted in a graph Ueq × a_w (equilibrium moisture × water activity) and adjusted by GAB and BET models. It was observed that BET model did not provide a good fit. On the other hand GAB model (Figure 5) was able to represent the data with R^2 = 0.9541, C = 9.0765 and K = 0.1010. At the lowers a_w the microcapsules absorb water at a constant rate, until it reaches the maximum moisture at the monolayer about the point 0.6 of water activity, corresponding to a equilibrium moisture of 0.1. From that point, there is an exponential rise in water absorption, corresponding to the humidity were the samples starts to dilute. This curve shows a typical behavior of sugars rich materials, in this case due to the high proportion of encapsulating material.

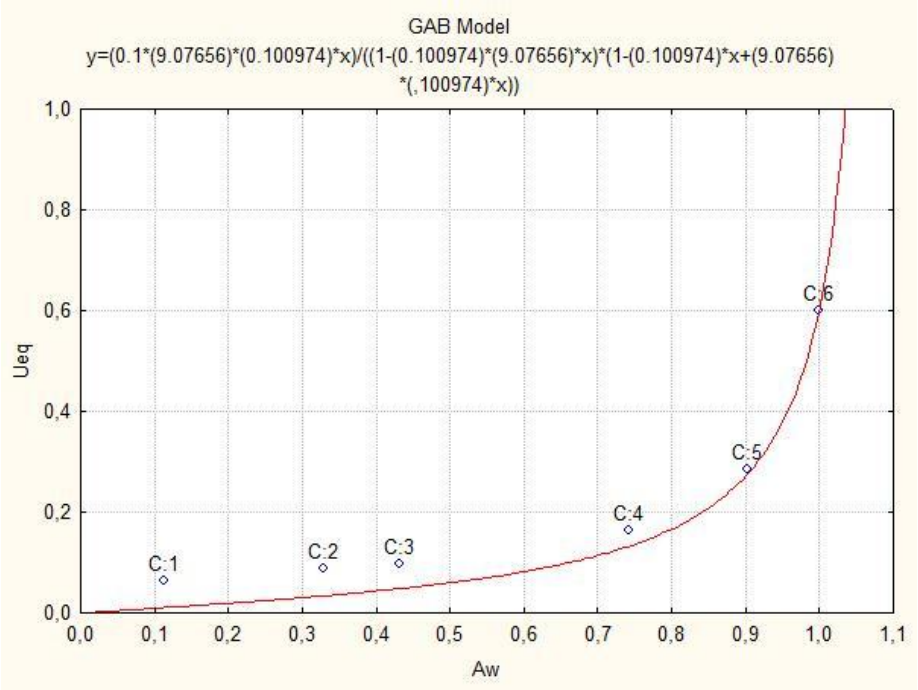


Fig. 5. Fitted sorption isotherms data by GAB model.

In the SEM images at a 500x magnification, shown in Figure 6, it can be observed the influence of wall material in the aggregation of microcapsules. At sample 1, with MD, the aggregation is high due to its low film formation capacity. The sample 3, with MS shows lower aggregation. The aggregation of the particles is important because it has direct influence in fluidity and solubility of microcapsules at the moment of application. Sample 6, the one with better oxidative stability, exhibits low aggregation.

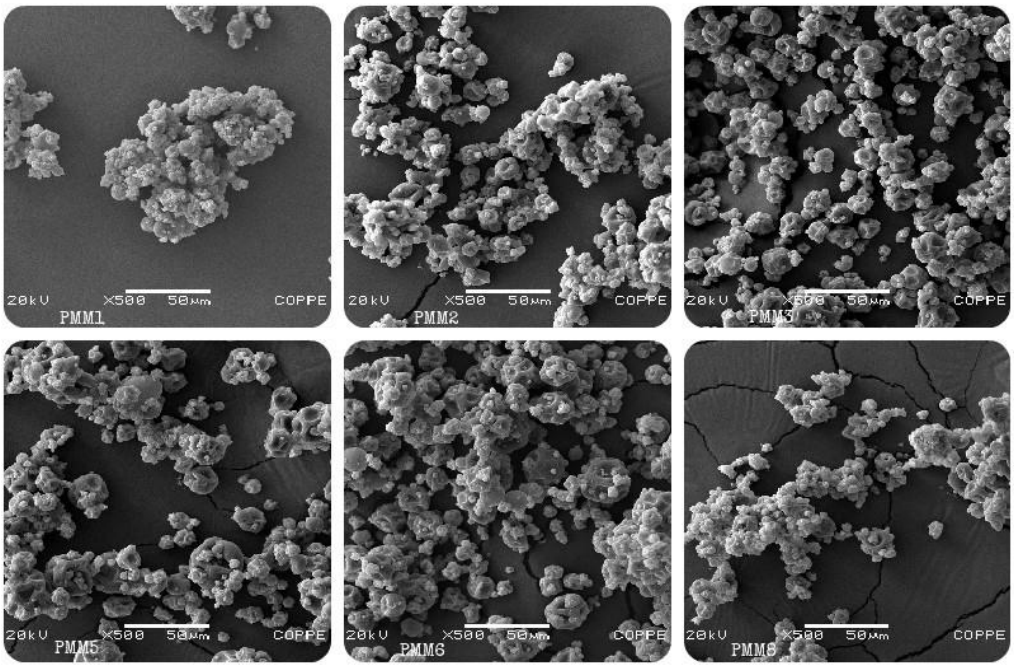


Fig. 6. SEM micrographs of pomegranate oil 20% microcapsules at 500x magnification
PMM= microencapsulated powder of mixed oil

At a 7000x magnification, shown in Figure 6, it is possible to observe rounded capsules with several cavities, measuring about 1-30 µm. Probably, these cavities are formed during the fast drying at spray chamber, where the water evaporates instantly, due to the high contact surface of particles with the hot air. In sample 1 (MD) it appears some cracks, showing that this wall system was too fragile due to the maltodextrin low film formation capacity. Sample 6 exhibits an upright surface.

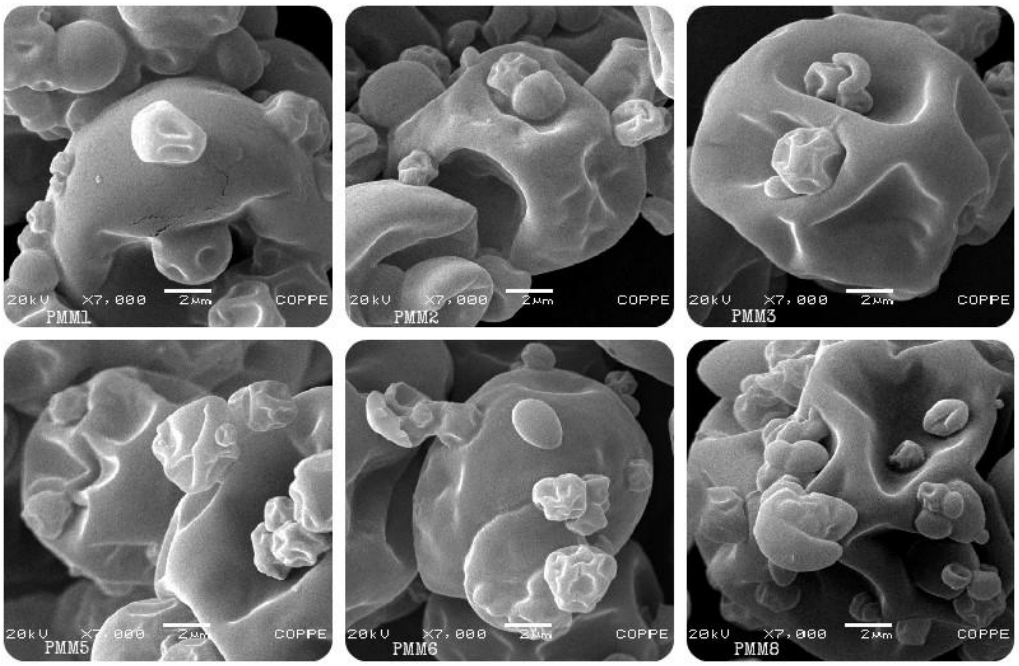


Fig. 6. SEM micrographs of pomegranate oil 20% microcapsules at 7000x magnification
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Conclusion

It can be concluded that the microencapsulation indeed protected the pomegranate oil, increasing the oxidative stability of final powder. The formulation with equal proportions of MS and GA as wall material provided the best results both for drying process yield and oxidative stability, creating stable microcapsules. At this condition, the yield was 41% and the oxidative stability was 42 % bigger for the microencapsulated powder in comparison with the liquid mixed oil.

SEM images show full surface of microcapsules produced at the best conditions.

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