Journal of Thermal Analysis and Calorimetry, Vol. 94 (2008) 2, 461–467

THERMAL PROPERTIES AND RELEASE OF *LIPPIA SIDOIDES* ESSENTIAL OIL FROM GUM ARABIC/MALTODEXTRIN MICROPARTICLES

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Microencapsulation of *Lippia sidoides* essential oil was carried out by spray drying. Blends of maltodextrin and gum arabic were used as carrier. Spray dried microparticles were characterized using conventional (thermogravimetry, evolved gas analysis) and combined (thermogravimetry–mass spectrometry analysis) thermal analysis techniques in order to evaluate the abilities of carriers with different compositions in retaining and in releasing the core *vs*. dynamic heating. Thermal analysis was useful to evaluate the physico-chemical interactions between the core and carriers and to determine the protective effect of the carriers on the evaporation of essential oil.

Keywords: *essential oil, gum arabic, Lippia sidoides, maltodextrin, microparticle, spray drying, thermal analysis*

Introduction

Lippia sidoides is a Brazilian aromatic medicinal plant from which an essential oil with high thymol concentration can be extracted. The essential oil has a strong action against fungus and bacteria indicating its activity for medicinal purposes. In general, the essential oils are consisted of volatile substances, which can be one of the reason of their physico-chemical instabilities [1].

Microencapsulation of essential oil by spray drying was reported as an effective way of protecting volatile substances and consequently, providing flavor product which are chemically and physically more stable [2, 3]. In general, matrix type microparticles are produced by spray drying where the core (essential oil) exists in a form of microparticles or microdroplets distributed within a dry matrix [4].

Several studies dealt about how volatile compounds are retained by spray drying and were generally accepted that the process variables [5, 6] and the nature of both volatile substances and the carriers [7, 8] are determining factors.

The influence of carrier types and storage conditions on the stability of matrices and/or release of volatile compounds has also been extensively reported in the literature, e.g. [9–12]. However, the focuses of these studies were mainly related to microparticles core load and release kinetics.

Thermal analysis can be an alternative analytical tool to follow the changes in the physico-chemical properties as well as to the retention and/or release properties of the spray dried matrices. They often provide information how the release of the active core takes place. In this work conventional (TG, EGD) and combined thermal analyses (TG-MS) were used to monitor the release of *Lippia sidoides* essential oil components from different spray dried maltodextrin and gum arabic encapsulating matrices as a function of temperature. The obtained results confirmed the interactions between the carriers and essential oil and showed also the improved retention properties.

Experimental

Materials

Lippia sidoides essential oil was purchased from Pronat (Fortaleza-CE-Brazil). Thymol (99.99%) was used as chemical marker and was supplied from VETEC (Brazil). Maltodextrin DE (Dextrose Equivalent) 10 and gum arabic were kindly donated by Corn Products Brazil and Colloides Naturales Brazil, respectively. The organic chemicals used in the analysis were of analytical grade.

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1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

Preparation of the feed

Blends with different compositions of gum arabic and maltodextrin were used as carrier. The amount of gum arabic in the carrier mixture was: 20, 40, 60 and 100 mass/mass%. The carrier compositions were prepared by blending and rehydrating the solid powders in warm distilled water at 50°C for 2 h, followed by cooling to room temperature. The total solid content of the carrier solutions were set to 50% (*m*/*m* wet basis). Then, the core (essential oil) was added to the carrier solutions at proportion of 1:4 (*m*/*m*). An emulsion was prepared by homogenizing the above mixture by using an Ultra turrax IKA T18 basic homogenizer at 24.000 rpm for 3 min.

Methods

Spray drying

A Lab-Plant SD-05 spray dryer with concurrent regime and two-fluid nozzle atomizer was used to dry the emulsions. The atomizer had 1.0 mm of inside diameter. Compressed air with a rotameter-controlled flow rate was used. Emulsion was metered into the dryer by means of a peristaltic pump. The drying chamber was made of thick transparent glass and with a diameter of 215 and a height of 500 mm. The dried product was collected in a Lapple cyclone with 0.085 mm of diameter (cut diameter of 3.9 μm). The controlled parameters were: infeed emulsion temperature (50°C); atomizer pressure (5.0 kgf cm^{-2}); atomizer air flow rate (17.5 L min^{-1}); flow rate of drying air (60 m^3 h^{-1}) and inlet air temperature (160°C). The selection of the above operating conditions based on several preliminary tests.

Total essential oil retention in the microparticles

Total retention of encapsulated oil was determined by hydrodistillation using a Clevenger apparatus [13]. Powder samples (10 g) were steam-distilled with 200 mL of deionized water for 3 h. The volume of distilled oil multiplied by the density of the *Lippia sidoides* essential oil (0.934 mg mL^{-1} at 20°C) gave the mass of oil retained in the powder. The amount of oil retained in the powder was related to the amount of oil added originally before emulsification.

GC-MS analysis of total retained oil and entrapped thymol in the microparticles

Qualitative analysis of the embedded oil and of the entrapped thymol in the microparticles were carried out on a Shimadzu® GCMS-QP 2010 gas chromatograph coupled to mass spectrometer equipped with autosampler mod. AOC-20I Shimadzu and DB-5 capillary column (30×0.25 mm; 0.25 μ film thickness). The temperature was programmed at 3°C min^{-1} from 60 to 180°C. Other operating conditions were as follows: injector temperature: 240°C; carrier gas (H_2) flow rate: 1.41 mL min^{-1}; detector temperature (300°C); split ratio 1:100. The components of the oil were identified by the comparison of their mass spectra and Kovats indices (KI) to a series of alkanes (C_{10}–C_{22}) published in [15] and presented in the MS computer library (WILEY275.L). Quantification of encapsulated thymol was done by the external normalization method using a calibration curve (R_2=0.9999) plotted from solutions of thymol standard with concentration varying from 0.125 to 2.5 mg mL^{-1}.

Thermal analysis

Simultaneous thermogravimetry and differential thermal analysis (TG-DTA) have been carried out using TA 2960 STA (simultaneous TG-DTA) equipment (TA Instruments Co., Newcastle, Delaware, USA). Experimental conditions were: 5°C min^{-1} heating rate from room temperature up to 350°C and helium purging at a flow rate of 15 L h^{-1}. Sample amounts of about 7 mg were used in the measurements.

Evolved gas detection (EGD) experiments have been done using DuPont 916 (Carle 3000) equipment with a built-in hydrogen-air flame ionisation detector. The experiments were carried out in nitrogen atmosphere at a flow rate of 1.8 L h^{-1} and heating rate of 8°C min^{-1} in the 30–350°C temperature range. Approximately 2 mg of samples were weighed in each measurement.

Combined themogravimetry–mass spectrometry analyses (TG-MS) were carried out in a Balzers Thermostar GSD 300T quadrupole mass spectrometer (Lichtenstein) operating between 1–300 specific mass/charge interval applying a silica capillary transfer tube heated at 200°C and connected to the gas outlet of the TA 2960 STA module.

Results and discussion

The MC-A, MC-B, MC-C and MC-D microparticles produced from infeed emulsions contain maltodextrin and gum arabic. The amount of gum arabic used in the compositions was 20, 40, 60 and 100% (m/m), respectively. The selection of the proper carrier is one of the most important factors in the aspect of encapsulation of volatile substances. The influence of the carrier type can be indirect in the sense carriers can affect the viscosity of infeed emulsion [5, 6].

The effect of the carrier type on volatile retention can also be direct. Carriers, which have effective emulsifying and/or good film forming characteristics

typically yield better volatile retention than carriers do in the lack of these properties [2–4]. This is the reason why in several cases blends of commercially available carriers are used to attain an effective microencapsulating efficiency.

Although maltodextrin shows low viscosity even at high concentration, it has poor emulsifying and consequently retention ability. On the other hand, gum arabic is an excellent carrier for volatile encapsulation providing good retention upon drying [11, 15, 16].

The use of gum arabic and maltodextrin mixtures for microencapsulation of essential oils is a good compromise between the cost and effectiveness for entrapping of many volatile substances [17].

According to Fig. 1, the retention of essential oil increased from 45 to 63% when the concentration of gum arabic increased from 20 (MC-A) to 100 mass/mass% (MC-D). This was attributed to the better film forming and emulsifying properties of gum arabic. Similar results were reported in [18] when spray dried microparticles had been produced by using blends of those carriers and the essential oil retention was less than 80%. Besides the carriers' ratio the essential oil retention might be influenced by other parameters too, e.g. inlet temperature, viscosity and total solid content of the infeed emulsion. However, the study of the effects of these parameters is out of the scope of this work.

Besides the total oil, the amount of entrapped thymol was also determined by GC-MS. According to Fig. 2 it can be seen that the thymol and essential oil content varies depending on the carriers' composition. With increasing amount of gum arabic the entrapped thymol increased too.

The influence of both molecular mass and vapor pressure of volatile compounds on their retention during spray drying is reported in [2–3]. For flavor molecules with increasing molecular size, diffusion rate decreases and then, they do not reach the droplet surface during drying. Vapor pressure (or volatility) plays a secondary role in determining volatiles' retention, due to its influence in controlling volatile losses until the drying droplet becomes semipermeable. The final result is that the small, very volatile molecules will be lost in a larger extent than the larger ones [2].

The major volatile compounds of *Lippia sidoides* essential oil are thymol (71.8%), ortho-cymene (9.8%), caryophellene oxide (5.4%), β-myrcene (4.1%), γ-terpinene (2.4%), methyl-thymol (1.0%), α-terpinene (1.0%) and terpin-4-ol (0.8%). Composition of the original and recovered oil was compared. All major flavor compounds in the original *Lippia sidoides* essential oil were encapsulated in the matrices except γ-terpinene which was not detected in the total recovered oil from MC-A sample.

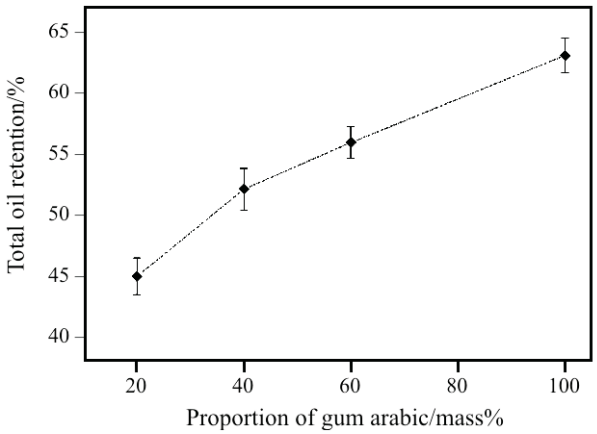

Fig. 1 Retention of total oil *vs*. amount of gum arabic

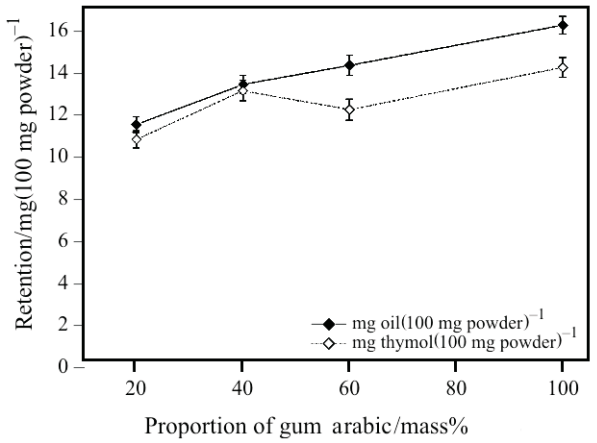

Fig. 2 Thymol and oil content of microcapsules as a function of the carriers' composition

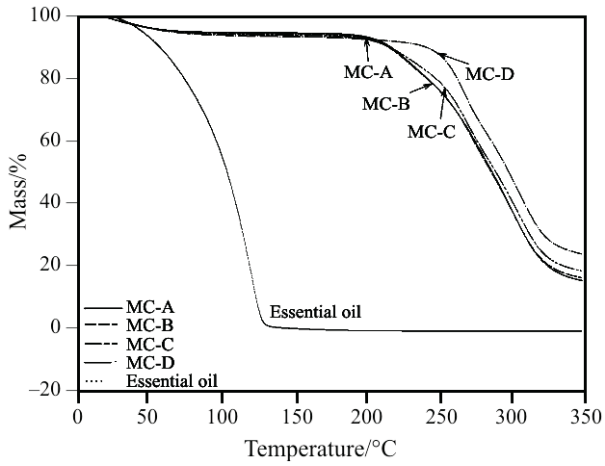

Fig. 3 TG curves of essential oil and microcapsules

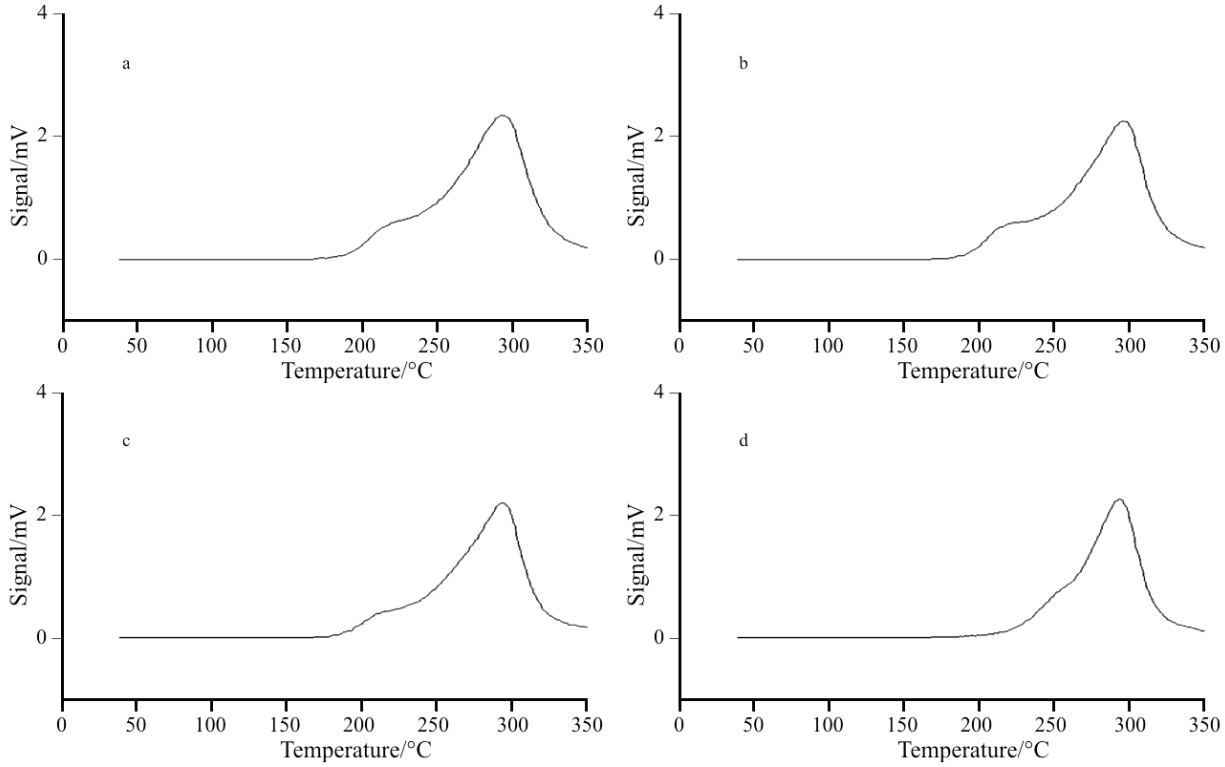

Fig. 4 EGD curves of different proportions of gum arabic: a – 20; b – 40; c – 60 and d – 100 mass%

In the TG curve of the essential oil (Fig. 3) the only mass loss step between 50–120°C indicates the evaporation of the sample. Between room temperature and 105°C the TG curves of the microparticles (Fig. 3) are quite similar. About 5% of detected mass losses are due to the release of water and perhaps to the evaporation of low amount of adsorbed volatiles. For MC-A and MC-B samples about 0.5% further mass loss was observed between 105–178°C, while above 178°C a gradual mass loss leading to cca 15% of final residue was noticed. For MC-C and MC-D samples a slow and continuous mass loss started from 105°C up to their starting decomposition resulted around 0.8 and 1.6% change in mass, respectively. When the temperature increased further on a consecutive multi-step mass loss started at 185°C (for MC-C) and at 212°C (for MC-D), indicating their thermal decomposition. From the TG curves it can be concluded that microencapsulation stabilized the essential oil. Consequently, the evaporation properties of the entrapped oil have changed compared to the original (free) oil itself. Increasing the amount of gum arabic in the carrier mixture the thermal stability of the microparticles increased. The thermal decomposition shifted from 178 to 212°C, when the proportion of gum arabic increased from 20 (MC-A) to 100 mass/mass% (MC-D).

EGD curves of the carriers with different composition are shown in Fig. 4. All effects refer to the thermal degradation of the carriers' mixtures. Concluding from the similar shapes of Figs 4a–c the increasing amount of gum arabic did not affect remarkably the thermal decomposition of the mixtures. Two representative decomposition peaks were observed around 225 and 290°C. In Fig. 4d the peak at lower temperature shifted from 225 to around 250°C and was not so pronounced (rather a shoulder was observed) while the second peak at 290°C was not altered.

EGD curves of the microparticles are presented in Fig. 5. For all the samples the slight deviation from the baseline below 100°C indicates the release of small amount of surface adsorbed essential oil (leaving together with the moisture content of the samples). MC-A and MC-B exhibited similar EGD curves displaying three overlapping peaks with maxima around at 210, 250 and 290°C, respectively. The first peaks indicate the release of the entrapped essential oil from the microcapsules. The peaks around 250°C appear at higher temperatures compared to the unloaded carriers (Figs 4a and b). According to our opinion these peaks are the results of minimum two overlapping processes: in one hand the release of the rest of the entrapped essential oil and, on the other hand the first step of the thermal decomposition of the carrier mixtures takes place. The EGD profile of MC-C sample is quite similar to MC-A and MC-B samples. The only visible difference is the presence of a

shoulder instead of a peak around 210°C, while the two other peaks appear at the same place as they are in the case of MC-A and MC-B samples. The thermal effect at 210°C almost completely disappeared in MC-D sample, showing just two distinct peaks around 260 and 300°C. Concluding from the similar shapes of Figs 4d and 5d, this phenomenon is in correlation with the absence of the maltodextrin.

According to the EGD curves of MC-A and MC-B the evolution of organic substances started at 170–175°C and at slightly higher temperatures (around 180–185°C) for MC-C sample. Detection of evolved gases started at a little higher temperature (210–215°C) for MC-D which is in correlation with the better emulsifying and retardation properties of gum arabic when it is alone itself. The TG and EGD curves are correlated well indicating the beginning of the thermal degradation of the microparticles started 170–175°C for MC-A and MC-B (when relatively high amount of maltodextrin was present in the samples) and shifted towards higher temperatures as the amount of gum arabic was increased.

Selective ion monitoring using TG-MS coupling was attempted as it was described in [19, 20]. Three fragments as the most representative ones for the molecular fragmentation of the essential oil were selected for monitoring its release from the matrices: *m*/*z*=91, 135 and 150. The last two ones are corresponding to base and molecular peaks in the mass spectrum of thymol, respectively (WILEY275.L library). The *m*/*z*=91 is for the tropilium fragmentation when a methylene group is connected to the aromatic ring.

Multiple ion detection curves (MID curves) of all microparticles (Fig. 6) showed a small evaporation of volatile substances below 105°C (good agreement with the results of EGD experiments) and their continuous release as the temperature was further increased. For MC-A, MC-B and MC-C the escape of volatiles started around 205°C. It can be assumed that over 205°C the degradation of the carriers started and became predominant. Peaks around 230–335 and then 275–280°C were detected. For MC-D the release of volatiles started around 235°C indicating that microparticles prepared with only gum arabic are little more stable when maltodextrin in the carrier mixtures was also used. In the MID curves of MC-D only one intensive peak was recognized around 270°C which corresponds to the liberation of the essential oil. Consequently, the blends of maltodextrin and gum arabic seem to influence not only the thermal stability of the microparticles but also the release profile of the essential oil from the matrices. When gum arabic was used alone as carrier, the release of the oil started at higher temperature and took place mainly in one step, while multi-step process was representative to the oil release when mixtures of maltodextrin and gum arabic were used.

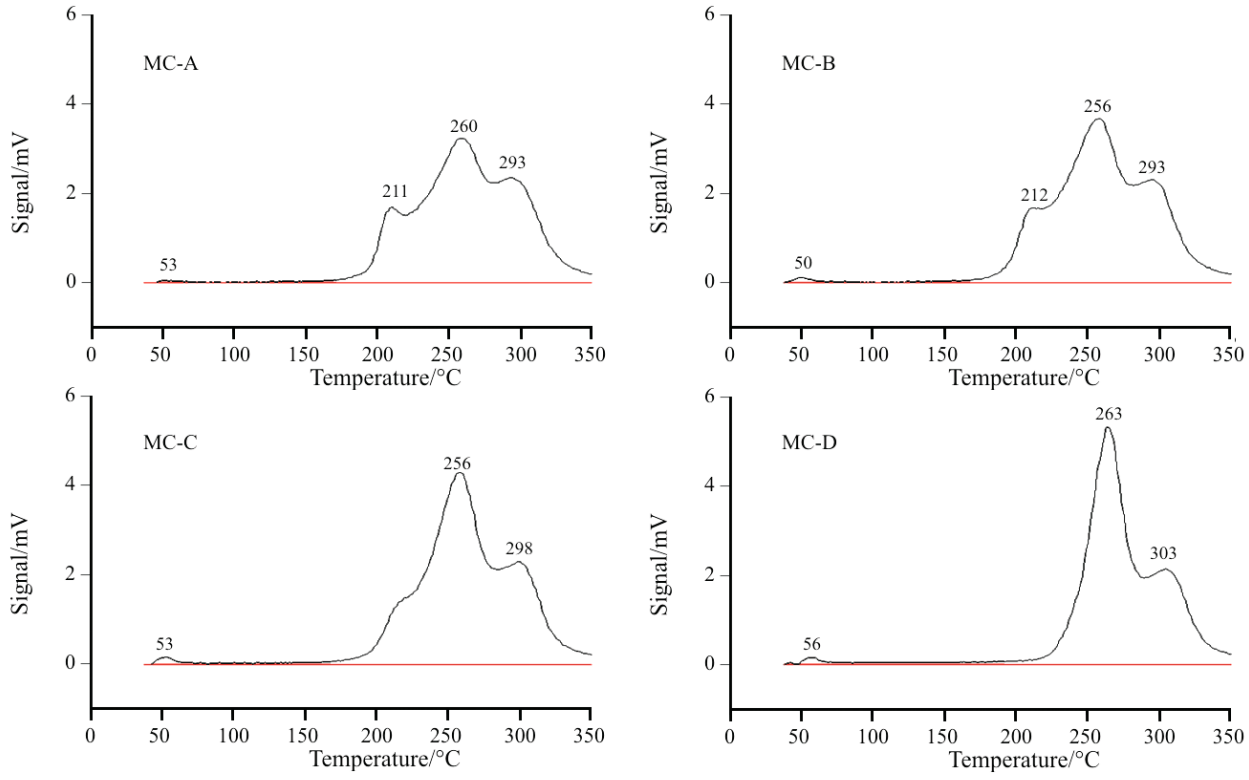

Fig. 5 EGD curves of microcapsules

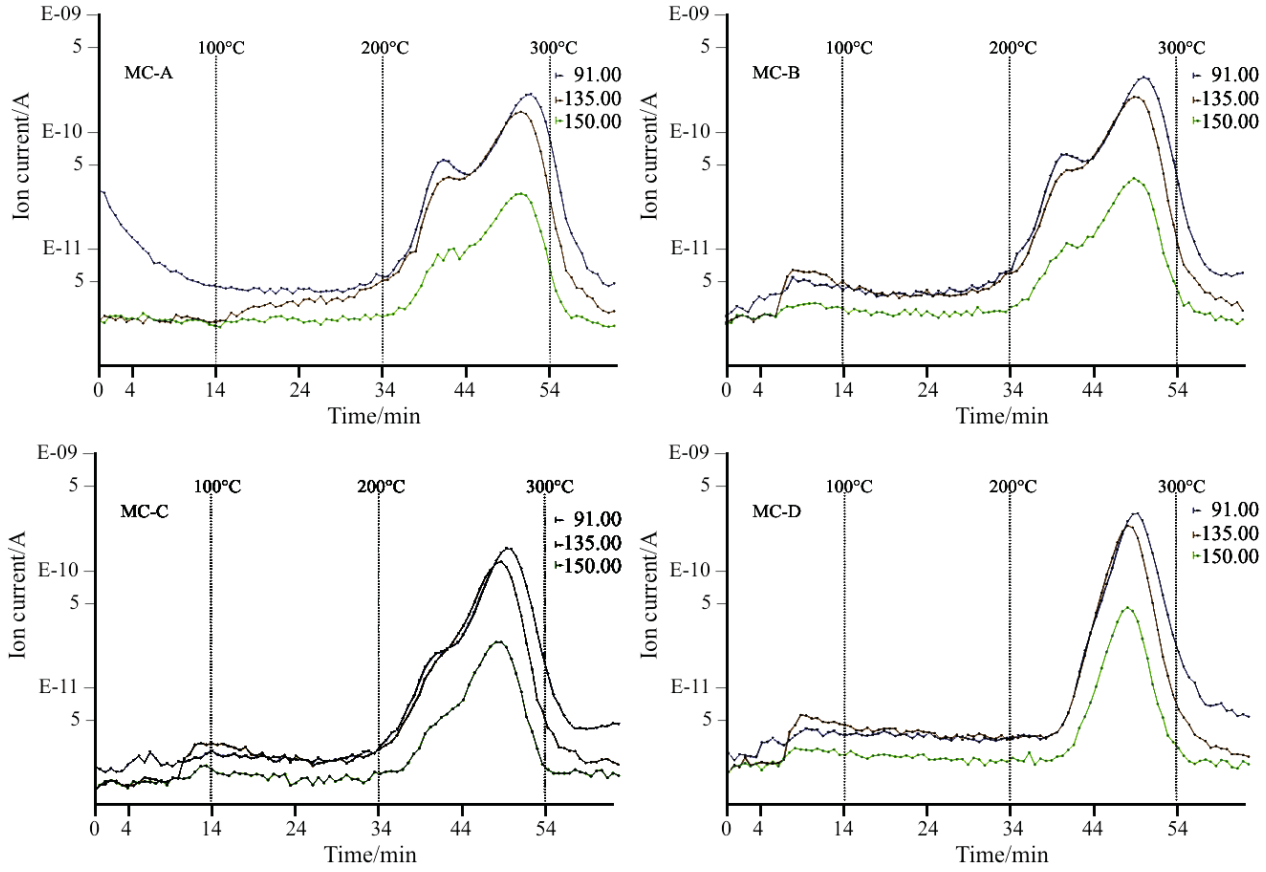

Fig. 6 MID curves

Conclusions

Spray drying is one of the most widely used method to produce solid encapsulated forms of essential oil. In general, it provides good protection to the core and consequently, increases the shelf life of the product. The physico-chemical factors associated to the retention and release of organic compounds from the spray dried matrices are important, so far necessary to determine them. By using conventional (TG, EGD) and combined (TG-MS) thermal analysis the thermal behavior of the different carriers and their retardation effect *vs*. dynamic heating were evaluated. The complete evaporation of the essential oil alone could be observed up to 120°C. The TG and EGD experiments evidenced that evaporation of *Lippia sidoides* essential oil was hidered by microencapsulation. Combined thermoanalytical technique (TG-MS) demonstrated as well as the higher thermal stability of the microparticles compared to the original oil. The thermal stability of the microparticles increased parallel with the increase of the amount of gum arabic, since the starting temperature of the decomposition shifted towards the higher temperatures. The different composition of carriers can affect the release of essential oil from the encapsulating matrices, too. Thus the oil was released in a narrower temperature interval when gum arabic was used alone as carrier and an oil release in a wider temperature interval was observed when blends of carriers were used.

Acknowledgements

The authors thank to Colloides Naturales (Brazil), for supplying gum arabic (Instant gum); Corn products (Brazil) for supplying maltodextrin DE 10 (Mor Rex 1910) and to CNPq for the fellowship to the first author.

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DOI: 10.1007/s10973-008-9170-4