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EFFECT OF THE MICROENCAPSULATION TIME ON THE CHARACTERISTICS OF THE OBTAINED MICROCAPSULES FROM DIFFERENT ESSENTIAL OILS BY *IN SITU* POLYMERIZATION PROCESS

Assist. Prof. Stanislav Bayryamov, PhD
Department of Repairing, Reliability, Mechanisms,
Machines, Logistic and Chemical Technologies,
Agrarian and Industrial Faculty, "Angel Kanchev" Univesity of Ruse
E-mail: sbayryamov@uni-ruse.bg

Abstract: *In the present work, the influence of time during the polymerization step on the microencapsulation of essential oils by in situ polymerization between urea and formaldehyde is considered. The synthesized microcapsules are filled up with rose oil, lavender oil, jasmine oil, eucalyptus oil and orange oil as core materials. The data are obtained by analyzing several important characteristics such as yield (%), microcapsule size (μm), encapsulation efficiency (%) and encapsulated substance content (% sample i. e. encapsulated compound, E% core), which are directly related to the efficiency of the process, the microcapsule shell thickness and quality. The results of the conducted experiments show that the most intensive step of polymerization takes place from the 1st to the 2nd hour, and in the microencapsulation of some oils - up to the 3rd hour. Thus, by controlling the duration of the polymerization step, a successful design of the capsules could be achieved, both in terms of their size and in terms of the yield, type, thickness and quality of the shell that builds them. Furthermore, control of the duration of the polymerization step allows saving time, money and energy, which is of great importance when scaling up the process for large-scale industrial production.*

Keywords: *Microencapsuliation, In situ polymerization, UF polymer capsule shell, Essential oils, Monomethylol urea, Urea, Formaldehyde.*

INTRODUCTION

The inability of an active substance to maintain both its stability and its activity over an extended period of time is one of many significant problems in modern industry. This instability is due to the constant exposure of the substance to adverse environmental conditions, such as temperature fluctuations, direct sunlight, various oxidizers, as well as other chemical agents.

One of the ways to increase the stability and to preserve the action and long-lasting effect of the substance through its controlled release is the application of the microencapsulation process.

The present work examines in detail the change in the duration of the polymerization stage during the microencapsulation process by *in situ* polymerization and how it affects the yield and size of the microcapsules, the thickness and quality of the microcapsule shell, the efficiency of microencapsulation and the content of the microencapsulated substance in the resulting microcapsules. The author draws attention to its impact as one of the main factors on the process and proves its importance, thus the microencapsulation process could be controlled in order to create capsules with desired yields and qualities.

Thus, a successful design of the capsules could be realized, both in terms of their size and in terms of the type, thickness and quality of the shell that builds them.

EXPOSITION

Synthesis of microcapsules by controlling the duration of the polymerization step

Depending on the nature of the encapsulated substance influencing its properties, as well as depending on the target size of the capsules, there is a wide variety of methods, techniques and their associated protocols (Jamekhorshid, A., Sadrameli, S. M., & Farid, M. 2014; Benita, S., 2005).

Based on this diversity, different microcapsules can be obtained, both in terms of the material making up the capsule shell and the type of core substance (Ghosh, S. K., 2006).

In situ polymerization is one of the most commonly applied microencapsulation methods. In the encapsulation by this method, different materials can be used, and the author chose urea and formaldehyde, because of the environmental purity of urea, as well as lower toxicity and environmental acceptability of formaldehyde. There are many data regarding the use of urea-formaldehyde polymer shell in the construction of the microcapsule wall, as well as experimental results regarding the study of the influence of various factors on the efficiency of the process.

For example, Lang, S. and Zhou, Q. synthesized poly(urea-formaldehyde)-coated linseed oil microcapsules by *in situ* polymerization method with the aim of obtaining a self-healing coating on the microcapsules (Lang, S. & Zhou, Q., 2017). They investigated the influence of the molecular weight of the different stabilizers based on polyvinyl alcohol (PVA), the reaction temperature and the stirring speed, on the efficiency of the process and the properties of the obtained microcapsules.

Fan, C. & Zhou, X. (Fan, C. & Zhou, X., 2010) systematically studied the influence of various factors on the efficiency of the process and the quality of the obtained microcapsules, such as the initial pH value, the concentration of the material making up the capsule shell and that of the emulsifier (their ratio) and the stirring speed. Fan, C. and Zhou, X. found that the surface morphology of the microcapsule shell mainly depended on pH and stirring speed, with higher final pH value and higher stirring speed resulting in smoother microcapsule, which affects its stability, i.e. it grows. Furthermore, they found that ammonium chloride (NH_4Cl) is very important for the preparation of urea-formaldehyde microcapsules by *in situ* polymerization, and its addition, even in small amounts, leads to a significant drop in the pH value during the microencapsulation process (the polymerization reaction) and enhances the deposition of urea-formaldehyde nanoparticles on the surface of the microcapsule.

Another group (Park, S.-J., Shin, Y.-S. & Lee, J.-R., 2001) successfully applied the interfacial polymerization method to prepare urea-formaldehyde microcapsules containing lemon oil and found application as a fragrance in the cosmetic, perfumery and textile industries.

Bolimowski, P. A. et al. (Bolimowski, P. A., Kozera, R. & Boczkowska, A., 2018) and Katoueizadeh, E. et al. (Katoueizadeh, E., Zebarjad, S. M. & Janghorban, K., 2019) investigated the influence of different reaction conditions on the preparation of poly(urea-formaldehyde) microcapsules. Katoueizadeh, E. et al. investigate the effect of changing the molar ratio of formaldehyde to urea, reaction time, temperature and pH. On the other hand, Bolimowski, P. A. et al. research the effect of stirring speed on capsules size.

Brown, E. N. et al. (Brown, E. N., Kessler, M. R., Sottos, N. R. & White, S. R., 2003) prepare poly(urea-formaldehyde) microcapsules filled with dicyclopentadiene as healing agent by *in situ* polymerization method in an oil-in-water emulsion, varying the stirring rate and the pH of the reacting emulsion. They observed that increasing of the stirring rate from 200 to 2000 rpm leads to a decrease of the average microcapsule diameter from 1000 to 10 μm and that a linear dependency exists between log(mean diameter) and log(agitation rate). Moreover, by applying electron microscopy they observed that microcapsules consist an inner membrane with a thickness of 160–220 nm, whereas agglomerated urea-formaldehyde nanoparticles are located on the outer surface which has a rough and porous structure reflecting their shape. They reveal that by changing the pH of the reacting emulsion and the area of the emulsion-water interface, the surface morphology of the resulting microcapsules is affected. They observed (by CHN analysis) obtaining spherical microcapsules in high yields (80–90%), in the form of a free-flowing powder and with a filling of 83–92 weight %.

Microencapsulation by *in situ* polymerization consists of several steps: 1) pre-polymer synthesis, 2) emulsification step and 3) microencapsulation (polymerization) step. Studying (The study of) the influence of the main parameters in the conditions during each of these steps, such as stirring speed, duration (time) and temperature, is of great importance to optimize the process conditions to achieve higher yields and to obtain more quality capsules.

In the present work, the influence of the microencapsulation time during the polymerization step, on the efficiency of the process, the yield and the quality of the obtained microcapsules is

considered. Characteristics such as yield (%), encapsulation efficiency (%) and % sample ($E\%_{core}$) are determined by weight methods (Shahabudin, N., Yahya, R. & Gan, S. N., 2016; Rodrigues, S. N., et al. 2009; Alvim, I. D. & Grosso, C. R. F, 2010; Bayryamov, S. G., et al. unpublished results). The capsule size (μm) and size distribution (*N*) were determined by the laser diffraction method (Bayryamov, S. G., et al. unpublished results).

Protocols for the synthesis of microcapsules

Pre-polymer Synthesis

Preparation of the pre-polymer solution was carried out according to the method of Rochmadi, A. P. et al. (Rochmadi, A. P., Prasetya, A. & Hasokowati, W., 2010), Xiong, W. et al. (Xiong, W., Zhu, G., Tang, J., Dong, B., Han, N., Xing, F. & Schlangen, E., 2013), Yang, C.-C. & Pan, I.-H. (Yang, C.-C. & Pan, I.-H.: U.S. Pat. No. 5,576,008, 1996), Matson, G. W. (Matson, G. W.: U.S. Pat. No. 3,516,846, 1970), as well as some of our modifications (Bayryamov, S. G. & Nikolova, M. P., 2019).

Microcapsule synthesis

Experimental procedure for carrying out the emulsification step

The preparation of the microcapsules was carried out according to the combination of the method of Rochmadi, A. P. et al. (Rochmadi, A. P., Prasetya, A. & Hasokowati, W., 2010), Xiong, W. et al. (Xiong, W., Zhu, G., Tang, J., Dong, B., Han, N., Xing, F. & Schlangen, E., 2013), Yang, C.-C. & Pan, I.-H. (Yang, C.-C. & Pan, I.-H.: U.S. Pat. No. 5,576,008, 1996), Matson, G. W. (Matson, G. W.: U.S. Pat. No. 3,516,846, 1970), Vassiliades, A. E. (Vassiliades , A. E.: U.S. Pat. No. 3,993,831), as well as with our modifications (Bayryamov, S. G. & Nikolova, M. P., 2019), at a stirring speed of 1500 rpm, an initial temperature of 70^{o}C (first stage of the emulsification step), and then 45^{o}C (second stage of emulsification step) as well as emulsifier concentration: 3% SDS (Bayryamov, S. G. & Nikolova, M. P., 2019).

In an Erlenmeyer flask, 3% sodium dodecyl sulfate (SDS) was added to 100 mL of the pre-polymer solution at a stirring speed of 1500 rpm. The resulting pre-polymer and surfactant solution is transferred to a 500 mL round-bottom flask equipped with a thermometer, a reflux condenser, and a mechanical or electromagnetic stirrer. Then, 5 mL of essential oil were added to the pre-polymer and surfactant (SDS) solution, at the same stirring speed of 1500 rpm. and a temperature of 70^{o}C. After some time (3,5 hours), the temperature of the reaction mixture was lowered to 45^{o}C (second stage of the emulsification step) and stirring was continued for another 2,5 hours at the same stirring rate.

Experimental procedure for carrying out the microencapsulation (polymerization)step

To the emulsion, at a stirring speed of 750 rpm, a solution of citric acid was added to pH 3, while the parameters of the conditions under which the reaction mixture was stirred remained within the same limits. The reaction mixture is stirred for about 1÷6 hours, changing the duration (1h, 2h, 3h, 4h, 5h and 6h) of the polymerization stage at a temperature of 45^{o}C, after which the obtained microcapsules are filtered, washed with distilled water and dry at room temperature or in a dryer at a temperature of 55÷60°C for 6 hours.

To harden the capsules, after the expiration of the time, the solution is cooled to room temperature (or previously obtained capsules are placed in water), with constant stirring, 2 mL of a 37% alcoholic solution of formalin is added, and the stirring continues for another 15 minutes until their solidification. Then, the obtained microcapsules were filtered, washed with distilled water and dried under the conditions mentioned above.

Analysis of the obtained results

According to literature data (Rochmadi, Prasetya, A., & Hasokowati, W. 2010), shell density is influenced by the time of the microencapsulation step, i.e. the duration of the polymerization step. However, this was observed up to the third hour, after which the efficiency of the shell increased very little from 47.62% at the 3rd hour to 53.82% at the 6th hour (Rochmadi, A. P., Prasetya, A., & Hasokowati, W. 2010).

This provoked us to conduct experiments regarding the influence of this factor on the microencapsulation process and the quality of the obtained microcapsules.

The experiments were carried out at different durations of the polymerization step: 1, 2, 3, 4, 5, and 6 hours, stirring speed during the polymerization step: 750 rpm, temperature: 45°C and surfactant concentration (SDS) - 3 %.

The results of the conducted experiments show that the most intensive step of polymerization occurs from the 2nd to the 3rd hour, as can be seen from the data below (Table 1-5, Fig. 1-5). For example, the percent capsule yield increased most intensively until the 3rd hour for all oils, after which it remained constant. This shows that after the 3rd hour, the polymerization time has no effect on the microcapsule yield, i.e. the polymerization reaction of the monomethylolurea pre-polymer molecules is practically complete by the 3rd hour.

The same dependence is observed in the encapsulation efficiency, i.e. an increase in the yield of the encapsulated substance (%) observed from the 1st to the 3rd hour, with some oils occurring most intensively between the 2nd and 3rd hours (Table 1-5, Fig. 1- 5).

Regarding the content of the encapsulated substance ($E\%_{core}$), giving information about the quality (density) of the microcapsule shell, as seen from the data presented in Table 1-5, a sharp decrease in values is observed between the 1st and 2 -th hour, indicating that the rate of polymerization is the highest in this time period. The lower the values of this indicator, the greater the shell density. After the 3rd hour $E\%_{core}$ remains a relatively constant quantity.

Since $E\%_{core}$ is inversely proportional to the wall efficiency of the microcapsules obtained, as well as to the microencapsulation factor, the sharp decrease in the values of $E\%_{core}$, which is observed between the 1st and 2nd hours, is inversely related to the increase in the values of wall efficiency and microencapsulation factor in this time range. This gives reliable information about the quality and density of the capsule shell, which are highest between the 2nd and 3rd hour, after which they remain constant.

The duration of the polymerization step has no effect on the size of the capsules, as can be seen from the data presented below. This is due to the fact that the size of the microcapsules is determined by the size of the microdroplets formed during the first stage and at the beginning of the second stage of the emulsification step. So, the factors influencing during this step, do not determine the size of the obtained microcapsules (Table 1-5).

Table 1 Influence of the duration of the polymerization step (time) on the characteristics of the obtained rose oil microcapsules

Time (h)	**Yield (%)**	**Encapsulation efficiency (yield of the encapsulated compound, %)**	**% sample (encapsulated compound), *E% core***	**Microcapsules size (Average diameter value, μm)**
1	22.7	32.3	53.4	30-15
2	40.2	43.8	41.2	30-20
3	**63.9**	**87.1**	**38.3**	**30-15**
4	64.1	86.6	37.5	25-15
5	63.2	73.2	39.2	30-25
6	64.2	78.9	36.6	30-15

Other conditions - stirring speed: 750 rpm; temperature: 45°C; surfactant concentration (SDS): 3%.

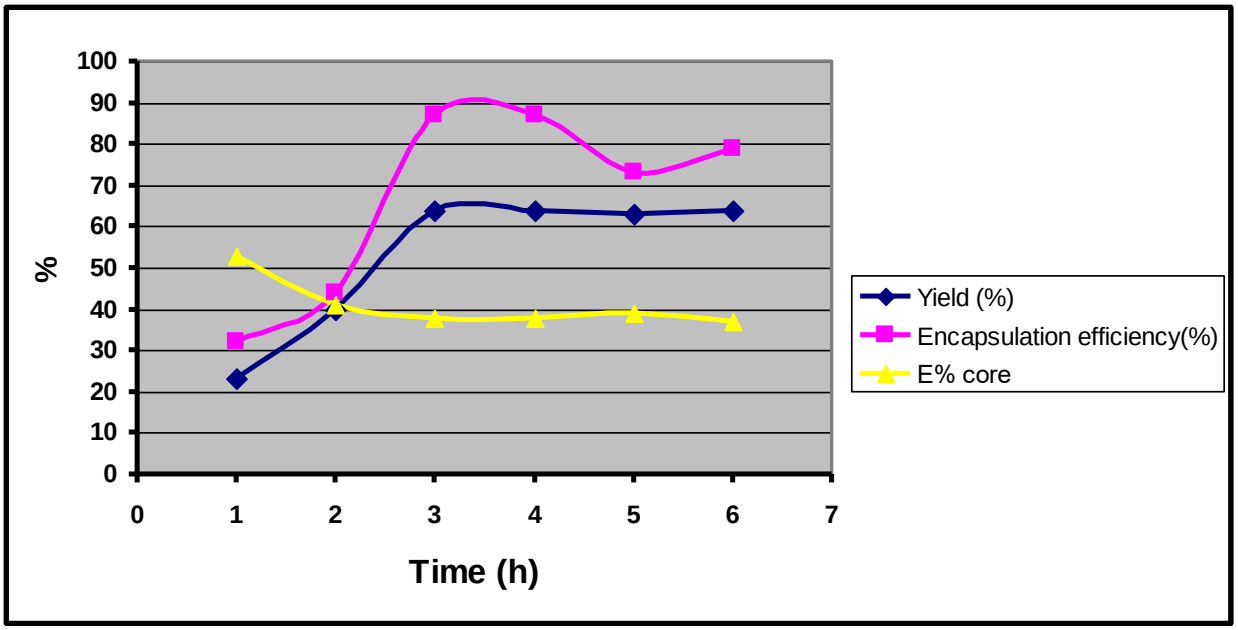

Fig. 1 Effect of time during the polymerization step on the characteristics of the obtained rose oil microcapsules

Table 2 Influence of the duration of the polymerization step (time) on the characteristics of the obtained lavender oil microcapsules

Time (h)	**Yield (%)**	**Encapsulation efficiency (yield of the encapsulated compound, %)**	**% sample (encapsulated compound), *E% core***	**Microcapsules size (Average diameter value, µm)**
1	27.2	43.3	71.1	30-20
2	30.2	67.2	62.3	20-15
3	**54.8**	**76.6**	**56.7**	**25-15**
4	55.6	69.5	58.8	30-15
5	54.7	72.9	57.8	25-20
6	53.1	74.3	55.5	30-25

Other conditions - stirring speed: 750 rpm; temperature: 45°C; surfactant concentration (SDS): 3%.

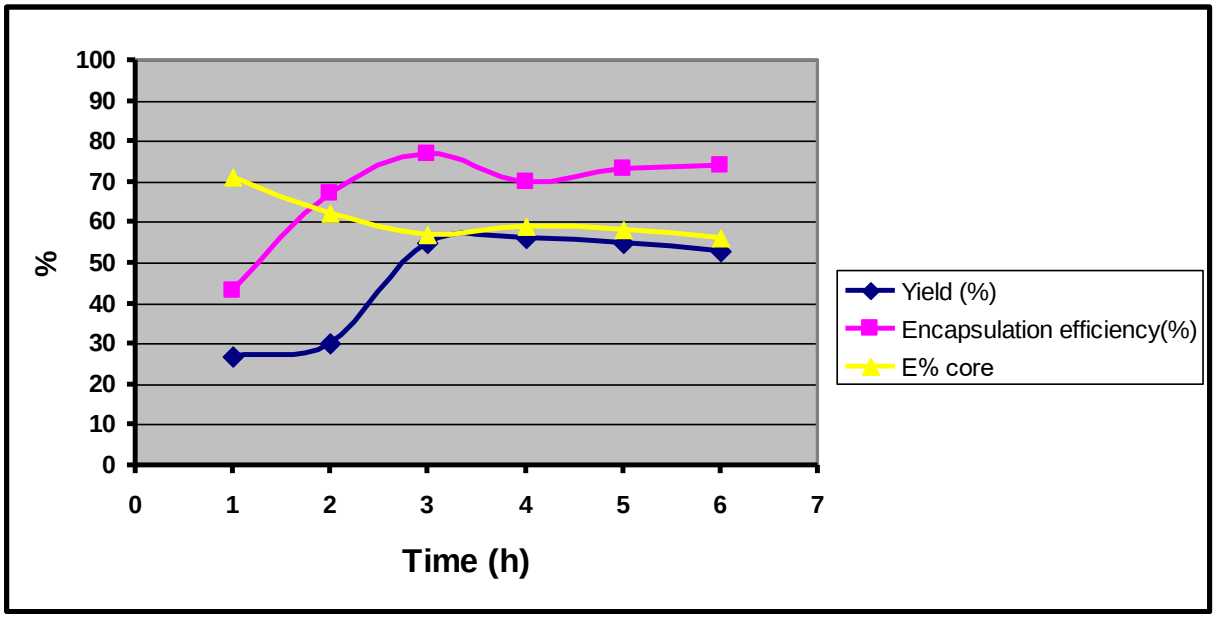

Fig. 2 Effect of time during the polymerization step on the characteristics of the obtained lavender oil microcapsules

Table 3 Influence of the duration of the polymerization step (time) on the characteristics of the obtained jasmine oil microcapsules

Time (h)	Yield (%)	Encapsulation efficiency (yield of the encapsulated compound, %)	% sample (encapsulated compound), *E% core*	Microcapsules size (Average diameter value, µm)
1	10.9	35.2	64.8	45-40
2	23.1	43.7	48.3	40-30
3	**47.7**	**44.1**	**37.8**	**45-30**
4	42.5	42.6	38.3	45-35
5	46.6	43.2	36.9	50-35
6	43.1	46.5	39.0	45-25

Other conditions - stirring speed: 750 rpm; temperature: 45°C; surfactant concentration (SDS): 3%.

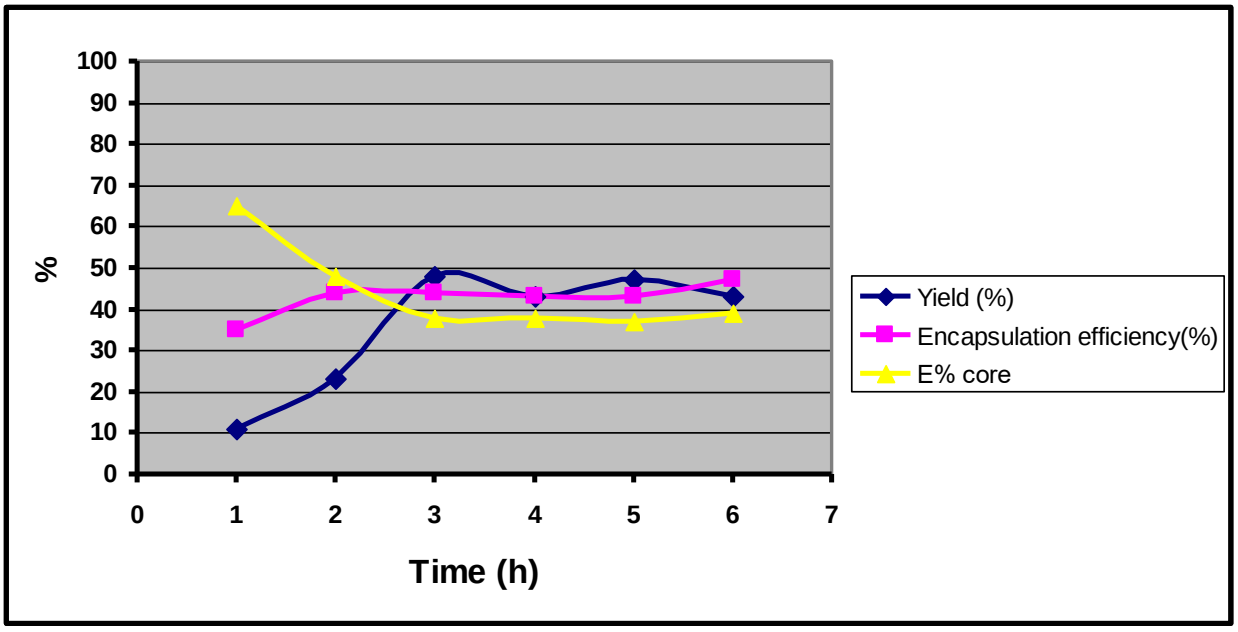

Fig. 3 Effect of time during the polymerization step on the characteristics of the obtained jasmine oil microcapsules

Table 4 Influence of the duration of the polymerization step (time) on the characteristics of the obtained eucalyptus oil microcapsules

Time (h)	Yield (%)	Encapsulation efficiency (yield of the encapsulated compound, %)	% sample (encapsulated compound), *E% core*	Microcapsules size (Average diameter value, µm)
1	18.5	38.8	57.2	60-20
2	37.6	56.1	46.9	55-35
3	**51.9**	**66.6**	**43.1**	**55-30**
4	48.4	67.4	43.3	50-40
5	45.1	63.2	47.7	50-40
6	46.3	68.6	42.8	55-30

Other conditions - stirring speed: 750 rpm; temperature: 45°C; surfactant concentration (SDS): 3%.

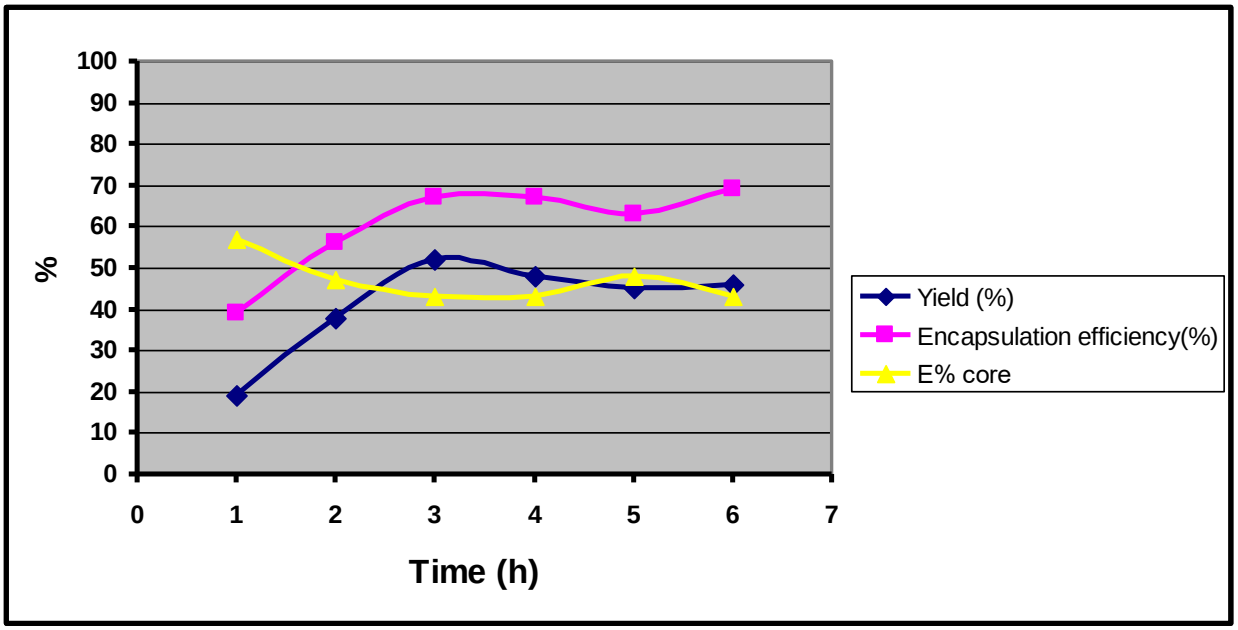

Fig. 4 Effect of time during the polymerization step on the characteristics of the obtained eucalyptus oil microcapsules

Table 5 Influence of the duration of the polymerization step (time) on the characteristics of the obtained orange oil microcapsules

Time (h)	**Yield (%)**	**Encapsulation efficiency (yield of the encapsulated compound, %)**	**% sample (encapsulated compound), *E% core***	**Microcapsules size (Average diameter value, µm)**
1	14.3	35.3	73.5	30-20
2	29.9	45.3	52.9	25-20
3	**35.8**	**57.2**	**40.0**	**25-15**
4	34.4	55.8	42.6	20-15
5	34.7	53.2	38.7	25-15
6	33.6	56.6	41.2	25-20

Other conditions - stirring speed: 750 rpm; temperature: 45°C; surfactant concentration (SDS): 3%.

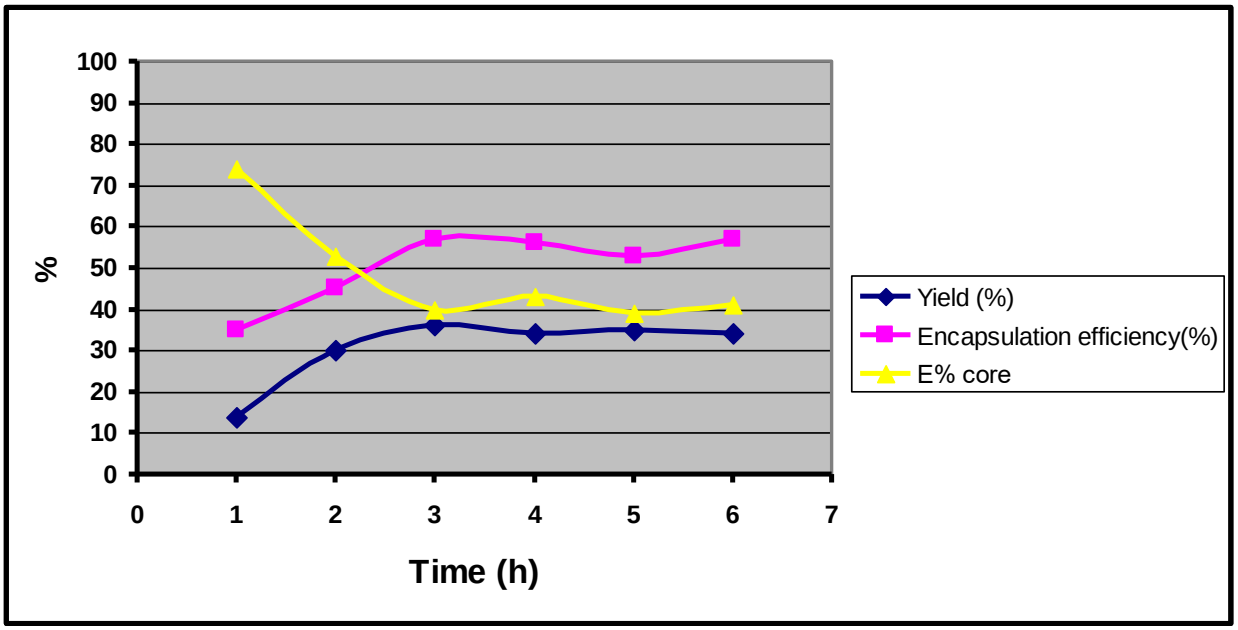

Fig. 5 Effect of time during the polymerization step on the characteristics of the obtained orange oil microcapsules

CONCLUSION

Increasing the duration of the microencapsulation step up to the 3rd hour has a positive effect on the microencapsulation process, leading to an increase in yield (%) and encapsulation efficiency (%), while the content of the encapsulated substance ($E\%_{core}$) decreases. The size of the microcapsules (μm) remained unchanged as seen in the results presented above. A further increase in time during the microencapsulation stage (polymerization step) did not affect the process, with the values of all quantities remaining relatively constant or with a slight increase in yield (%) and encapsulation efficiency (%) in any of them. Therefore, the author chooses the optimal time for the polymerization stage, which is 3 hours.

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