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

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: *This article represents the preparation of essential oil microcapsules by in situ polymerization of urea and formaldehyde. The research was done with the aim of optimizing the process conditions to obtain better quality microcapsules. In this regard, the influence of temperature during the polymerization stage was investigated, which proved the optimal temperature of the process in the preparation of microcapsules from different essential oils. As it can be seen from the data, the best results were obtained in the temperature interval between 40 °C and 50 °C. This is due, on the one hand, to the fact that the increase in temperature during the polymerization step accelerates the desorption process of the pre-polymer (monomethylolurea) molecules from the surface of the microdroplets obtained during the emulsification stage. Since the polymerization or polycondenzation is an exothermic reaction, increasing the temperature during the polymerization step leads to a decrease in the rate of the polymerization or polycondensation reaction, and hence to a decrease in the intensity of the encapsulation process, which affects the quality and the density of the capsule shell, and hence the yield and quality of the obtained capsules. From this, it can be concluded that the increase in temperature during the polymerization step changes the ratio between the rates of polymerization (polycondensation) and desorption of the pre-polymer from the surface of the microdroplets, accelerating the desorption process and reducing the rate of polymerization (polycondensation). In other words, lower temperature decreases desorption and increases the rate of polymerization or polycondenzation. From the results, it can be seen that regarding the size of the capsules, the temperature during the polymerization step does not affect this size.*

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

INTRODUCTION

Microencapsulation is the process of encapsulating liquids with a thin, strong and semi-permeable polymer shell. This process has two goals – on the one hand, to preserve the active substance for a long period of time by stabilizing it, and on the other hand, to maintain a long-lasting effect of the core substance by means of its controlled release. The present work examines in detail the change in temperature through the polymerization step 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.

EXPOSITION

Both during the emulsification step and during the polymerization step, the influence of temperature, stirring rate of the reaction mixture and time is enormous and has a key role on the efficiency of the process, the yield and the quality of the obtained microcapsules.

One of the most thorough studies on the influence of different reaction conditions on the formation of urea-formaldehyde microcapsules by the *in situ* polymerization method was done by Katoueizadeh, E. et al. (Katoueizadeh, E. Zebarjad, S. M. & Janghorban, K., 2019). By varying the molar ratio of formaldehyde to urea, as well as varying the reaction time, temperature and pH when encapsulating linseed oil, they concluded that for the successful formation of urea-formaldehyde

microcapsules, the reaction of the solution during synthesis must be acidic (pH<7) and the formaldehyde/urea molar ratio value should be above 0.94. Furthermore, they observed a mutual dependence between the influence of temperature and the pH value of the prepared solution.

Other authors (Fan, C. and Zhou, X., 2010) investigated the effect of conditions on the surface morphology of the microcapsule shell during *in situ* polymerization using poly(urea-formaldehyde) as the material for building the capsule shell, and the encapsulated substance were glass beads.

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.

Based on the literature analysis, it was concluded that there is insufficient research and data regarding the influence of the temperature during the polymerization stage (microencapsulation stage) on the efficiency of the process, the yield and the quality of the obtained microcapsules. This led us to study this influence, which will give greater clarity to the solution of the question, and hence controlling the process with the aim of increasing its efficiency.

Preparation of microcapsules

Pre-polymer synthesis

The 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 with our modifications (Bayryamov, S. G. & Nikolova, M. P., 2019). The pre-polymer resin was obtained in an alkaline medium as a solution of mono methylol urea at a specified concentration. 10% NaOH solution, 1N NaOH and 10% citric acid solution ($C_6H_8O_7$) were used to adjust the pH throughout the process.

Microcapsule preparation

The preparation of the microcapsules was 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), Vassiliades, A. E. (Vassiliades, A. E.: U.S. Pat. No. 3,993,831), as well as with some of our modifications (Bayryamov, S. G. & Nikolova, M. P., 2019). In the first stage of the emulsification step, the process was carried out at stirring speed of 1500 rpm, temperature 70^{o}C and stirring time 3,5 h. During the second stage of the emulsification step the reaction conditions were as follows: stirring speed 1500 rpm, temperature 45^{o}C and stirring time 2,5 h. During the polymerization step, the reaction conditions were similar to those of the second stage of the emulsification step, i.e. temperature 45^{o}C and stirring time 3 h except for the stirring speed which was 750 rpm. In addition, the process was carried out using an emulsifier. Surfactant concentration was constant during the whole process (3%).

Product analysis

FTIR spectroscopic analysis

The infrared spectra of the microcapsules, with the characteristic absorption bands of the urea-formaldehyde polymer forming the wall of the microcapsules, are at 2900 cm^{-1} and 2800 cm^{-1}, 1600 cm^{-1} and 1500 cm^{-1}, corresponding to CH, NH and CN vibrations, respectively as well as the NH of the amine are at 3250 cm^{-1} and 3300 cm^{-1} respectively. The OH vibrations of the hydroxyl groups of the rose oil essential alcohols are at 1060 cm^{-1}, 1350 cm^{-1}, 1380 cm^{-1}, 1400 cm^{-1}, 3500 cm^{-1}, 3600 cm^{-1}, 3620 cm^{-1} and 3650 cm^{-1}. The vibrations for the C = O groups of the essential oil aldehydes of the rose oil are at 1380 cm^{-1}, 1720 cm^{-1}, 1730 cm^{-1}, 1735 cm^{-1}, 2750 cm^{-1} and 2780 cm^{-1}; and from the ethereal (essential) ketones: 1615 cm^{-1}, 1715 cm^{-1} and 1720 cm^{-1}. The

characteristic bands for C = C bonds are at 970 cm^{-1} and 1650 cm^{-1}; and for C = C-H: 3080 cm^{-1} and 3090 cm^{-1}.

Weight analysis

In turn, the yield of the microcapsules (%) was calculated on the basis of the ratio of the total weight of the dried product over the total weight of the raw materials required to form the microcapsules.

$$\text{Microcapsule yield (\%)} = m_1 / (m_2 + m_3) \times 100\ \%, \quad (1)$$

Where:

m_1 is the total weight of the microcapsules,

m_2 is the starting weight of the encapsulated substance,

m_3 is the weight of the starting material used to encapsulate the substance

There are several methods for determining the yield of components of the reaction mixture in the preparation of microcapsules. According to literature data, the yield of the encapsulated substance in the microcapsules was determined by solvent extraction (Shahabudin, N., Yahya, R. & Gan, S. N., 2016). The microcapsules are torn by grinding in a porcelain mortar, using a mixture of acetone and ethanol (or hexane instead of the extraction mixture) to extract the encapsulated substance. The resulting dry residue, which is the wall of the microcapsule, insoluble in the extraction solvents, was filtered, washed several times with a mixture of acetone and ethanol (or hexane instead of the extraction mixture) and dried at 70°C for 24 hours in a vacuum oven. The percentage of the microencapsulated substance (the core of the microcapsule) was calculated using the following equation:

$$E\%_{\text{core.}} = (m_{\text{sp.}} - m_{\text{sh.}}) / m_{\text{sp.}} \times 100\ \%, \quad (2)$$

where: $\boldsymbol{m_{sp}}$**.** is the total weight of the sample and $\boldsymbol{m_{sh}}$ is the weight of the insoluble shell

Here we introduce a new, fast and simple method to analyze the encapsulation efficiency by yield measurement of the encapsulated substance (Bayryamov, S. G. et al. unpublished results). It is based on a weight analysis (Rodrigues, S. N., et al. 2009; Alvim, I. D. & Grosso, C. R. F, 2010) by measuring the mass of the starting material to be encapsulated and the mass of the non-encapsulated substance after the encapsulation process. The difference between the masses of the starting material and the non-encapsulated substance gives the mass of the encapsulated compound. The ratio between the weight of the encapsulated substance and the weight of the starting material intended for encapsulation, multiplied by 100, gives a % yield of the encapsulated substance:

$$\text{Encapsulation efficiency (yield of the encapsulated compound)} = (m_a - m_b)/ m_{a.} \times 100\ \%, \quad (3)$$

Where:

m_a is the total weight of the substance to be encapsulated,

m_b is the weight of the non-encapsulated substance.

ANALYSIS OF THE OBTAINED RESULTS

Effect of temperature during the polymerization stage on the characteristics of the obtained microcapsules.

The temperature in the polymerization step, as well as during the emulsification step, plays a key role on the efficiency of the microencapsulation process and the characteristics of the resulting microcapsules. Its increase leads to a decrease in yields, a decrease in encapsulation efficiency, as well as an increase in the content of the encapsulated substance ($E\%_{core}$) (Table 1-5, Fig. 1-5).

In turn, $E\%_{core}$ is closely related to the wall efficiency of the obtained microcapsules, as well as to the microencapsulation factor, which are inversely proportional to $E\%_{core}$**.** The increase in temperature during the polymerization step leads to a decrease in the wall efficiency of the obtained microcapsules, as well as to the factor of microencapsulation. This is due, on the one hand, to the process of desorption of the prepolymer molecules from the surface of the microdroplets obtained during the emulsification step, which takes place under the influence of temperature in the second stage of the emulsification step. An increase in temperature leads to an increase in the desorption of monomethylolurea molecules.

On the other hand, since polymerization and polycondensation are exothermic reactions, increasing the temperature during the polymerization step leads to a decrease in the rate of the polymerization and polycondensation reaction, and hence to a decrease in the intensity of the encapsulation process, which affects the quality and the density of the capsule shell, and hence the yield and quality of the obtained capsules.

From the data obtained by varying the temperature during the polymerization step, when conducting the microencapsulation process, it appears that lower temperatures are preferable for the reasons mentioned above. In other words, lower temperature decreases desorption and increases the rate of polymerization and polycondensation.

Regarding the size of the capsules, the temperature during the polymerization step does not affect this value, since the size of the microcapsules is determined by the size of the microdroplets obtained in the first stage of the emulsification step (Table 1-5).

For this reason, the most suitable temperatures during the polymerization step should vary between 40°C and 50°C or the average temperature of 45°C should be applied.

Table 1 Influence of the temperature during the polymerization step on the characteristics of the obtained rose oil microcapsules

Temperature (°C)	**Yield (%)**	**Encapsulation efficiency (yield of the encapsulated compound, %)**	**% sample (encapsulated compound), *E% core***	**Microcapsules size (Average diameter value, µm)**
40	**63.2**	**77.4**	**37.6**	**25-15**
50	**58.4**	**60.5**	**41.5**	**30-20**
60	46.4	42.3	67.8	25-20
70	35.6	28.4	79.2	30-15

Other conditions - stirring speed: 750 rpm; time: 3 h; surfactant concentration (SDS): 3%

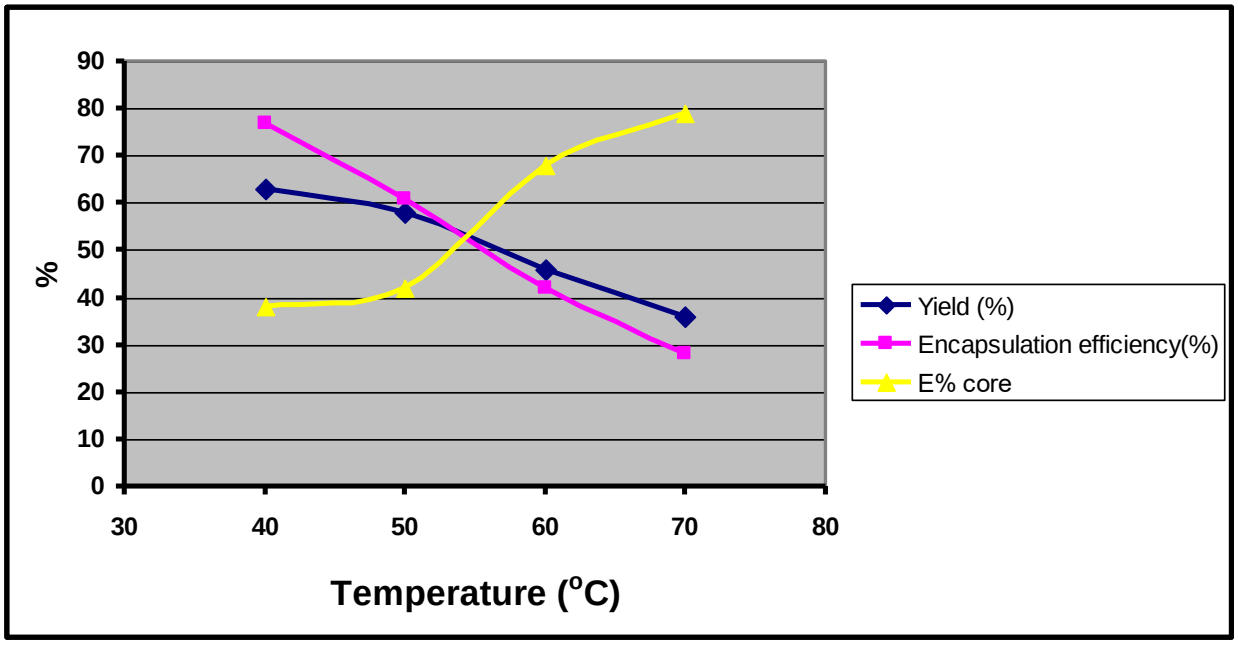

Fig. 1 Effect of temperature during the polymerization step on the characteristics of the obtained rose oil microcapsules

Table 2 Influence of the temperature during the polymerization step on the characteristics of the obtained lavender oil microcapsules

Temperature (ºC)	**Yield (%)**	**Encapsulation efficiency (yield of the encapsulated compound, %)**	**% sample (encapsulated compound), *E% core***	**Microcapsules size (Average diameter value, µm)**
40	**56.1**	**74.8**	**57.2**	**20-10**
50	**52.7**	**72.7**	**59.4**	**25-15**
60	40.2	52.2	78.3	25-10
70	34.6	37.8	82.3	20-15

Other conditions - stirring speed: 750 rpm; time: 3 h; surfactant concentration (SDS): 3%.

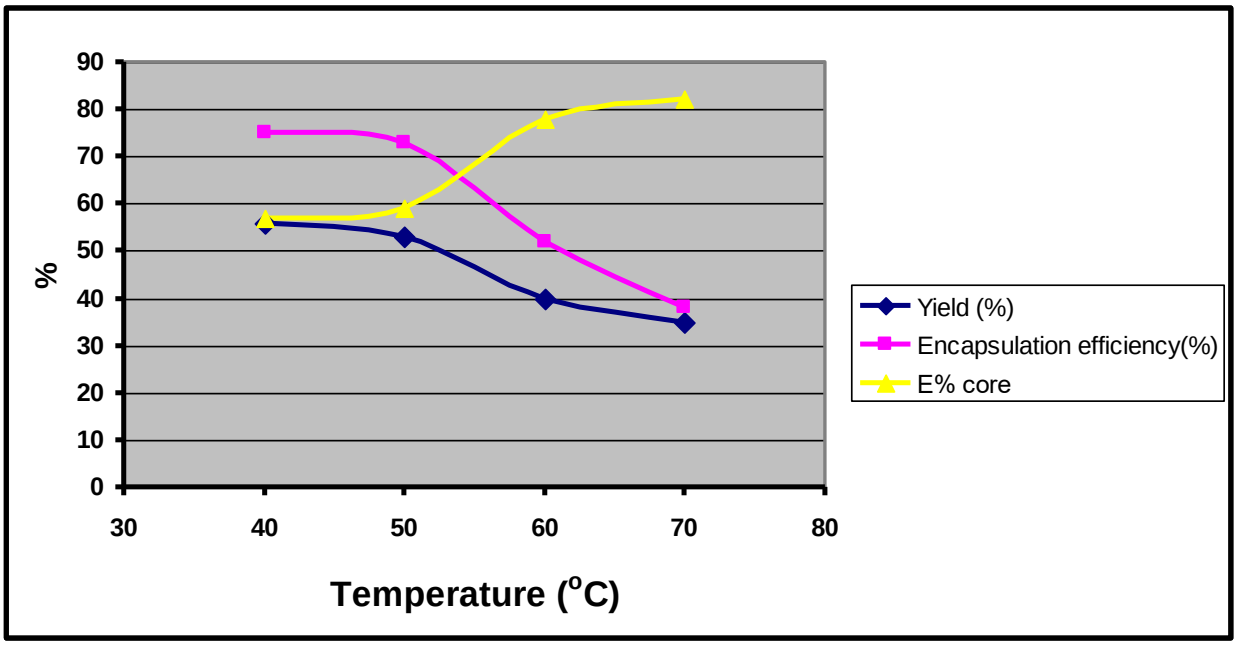

Fig. 2 Effect of temperature during the polymerization step on the characteristics of the obtained lavender oil microcapsules

Table 3 Influence of the temperature during the polymerization step on the characteristics of the obtained jasmine oil microcapsules

Temperature (ºC)	**Yield (%)**	**Encapsulation efficiency (yield of the encapsulated compound, %)**	**% sample (encapsulated compound), *E% core***	**Microcapsules size (Average diameter value, µm)**
40	**45.2**	**44.1**	**37.4**	**45-30**
50	**41.9**	**41.7**	**38.6**	**40-30**
60	24.8	34.7	49.9	45-40
70	14.2	19.6	62.5	45-35

Other conditions - stirring speed: 750 rpm; time: 3 h; surfactant concentration (SDS): 3%.

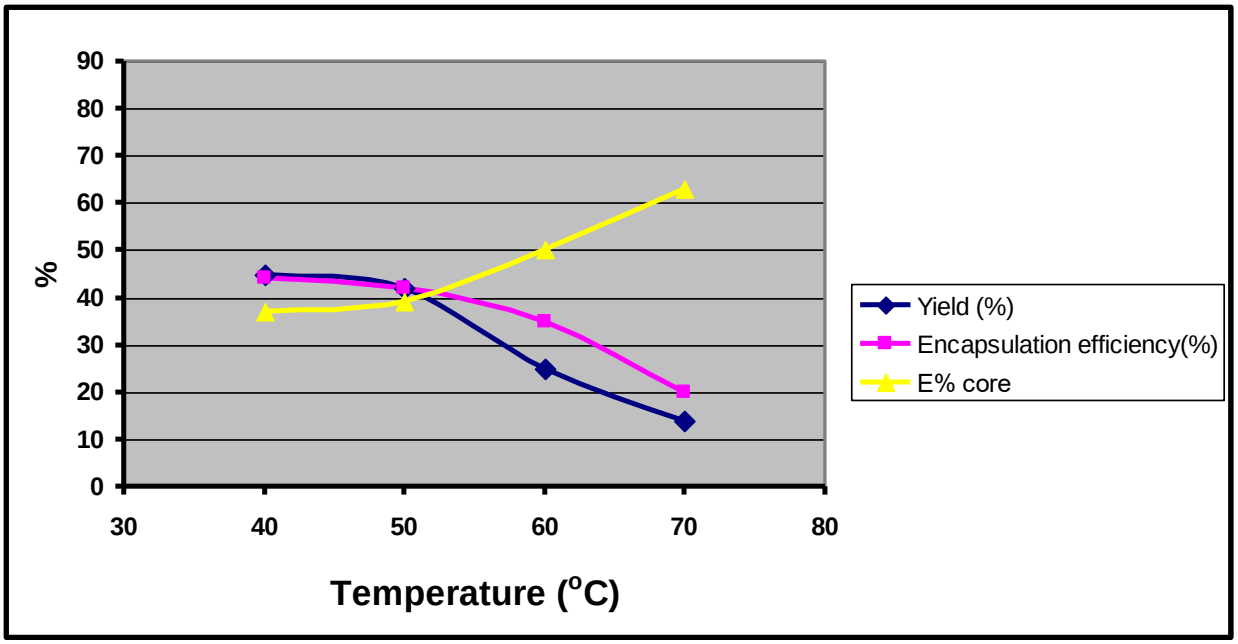

Fig. 3 Effect of temperature during the polymerization step on the characteristics of the obtained jasmine oil microcapsules

Table 4 Influence of the temperature during the polymerization step on the characteristics of the obtained eucalyptus oil microcapsules

Temperature (°C)	**Yield (%)**	**Encapsulation efficiency (yield of the encapsulated compound, %)**	**% sample (encapsulated compound), *E% core***	**Microcapsules size (Average diameter value, µm)**
40	**52.4**	**67.5**	**43.1**	**55-30**
50	**48.2**	**64.9**	**43.5**	**55-30**
60	35.8	45.8	52.2	50-40
70	21.4	29.7	66.3	50-30

Other conditions - stirring speed: 750 rpm; time: 3 h; surfactant concentration (SDS): 3%.

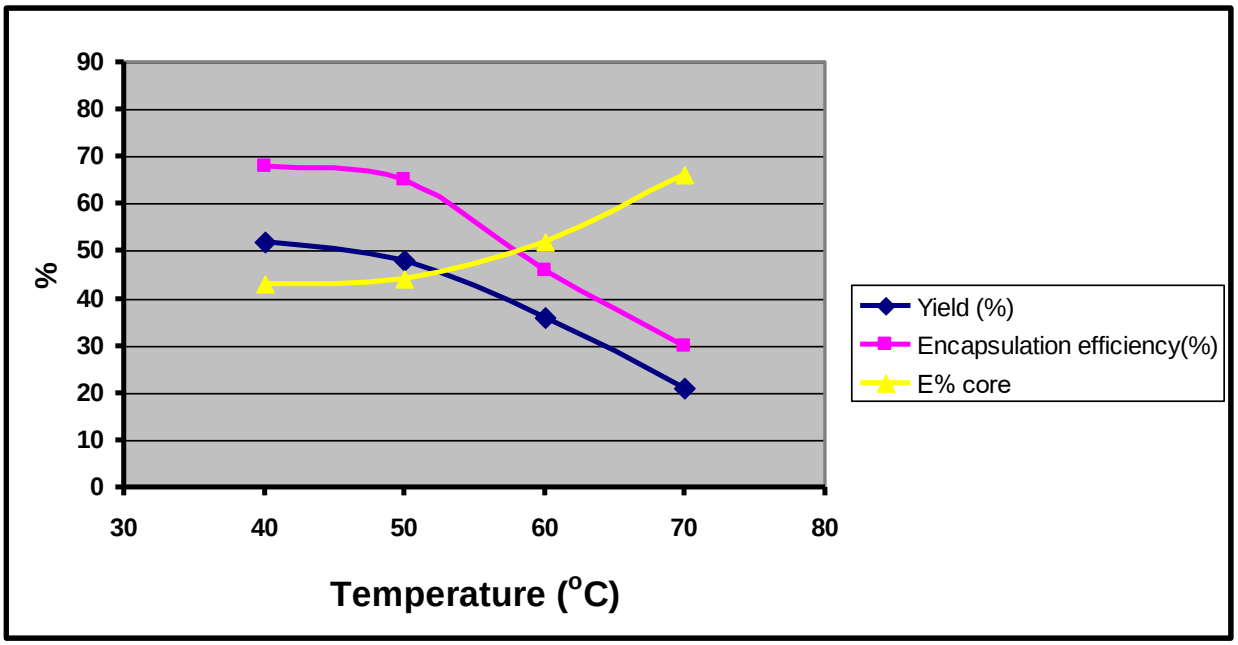

Fig. 4 Effect of temperature during the polymerization step on the characteristics of the obtained eucalyptus oil microcapsules

Table 5 Influence of the temperature during the polymerization step on the characteristics of the obtained orange oil microcapsules

Temperature (ºC)	**Yield (%)**	**Encapsulation efficiency (yield of the encapsulated compound, %)**	**% sample (encapsulated compound), *E% core***	**Microcapsules size (Average diameter value, µm)**
40	**34.5**	**57.0**	**41.0**	**30-20**
50	**33.4**	**54.8**	**41.4**	**30-15**
60	23.7	38.4	55.8	25-20
70	11.2	23.5	71.7	25-15

Other conditions - stirring speed: 750 rpm; time: 3 h; surfactant concentration (SDS): 3%.

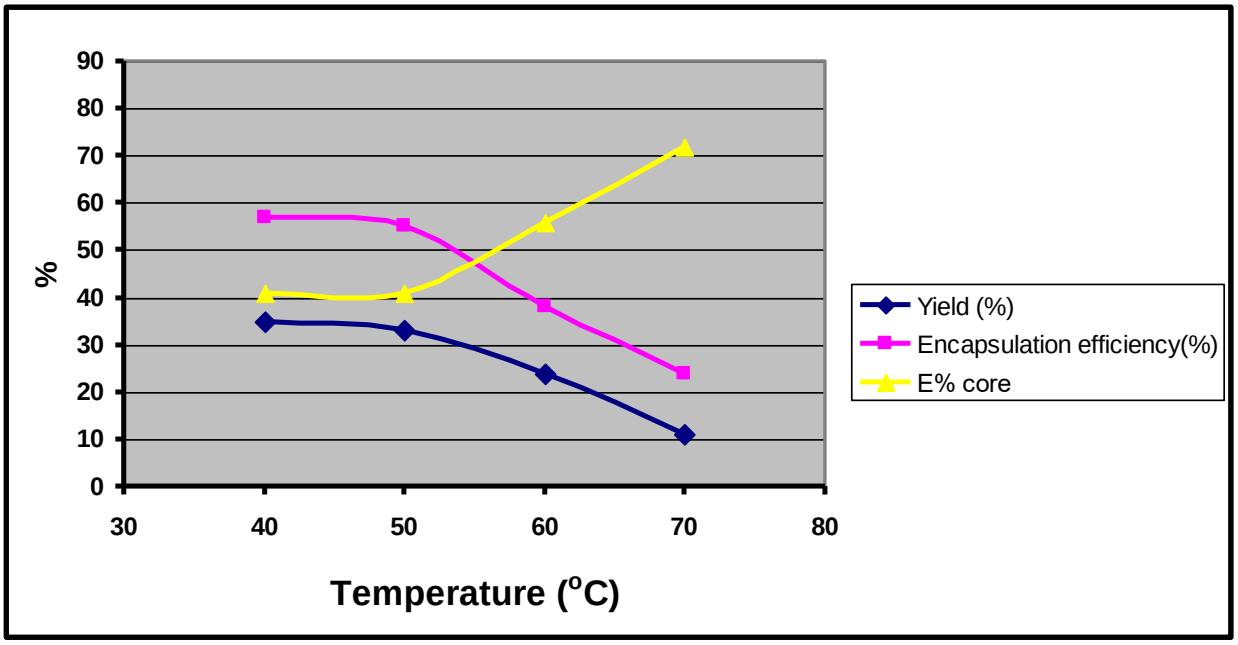

Fig. 5 Effect of temperature during the polymerization step on the characteristics of the obtained orange oil microcapsules

CONCLUSION

Temperature is one of the most important factors influencing the encapsulation of natural products. During the polymerization step, the increase in temperature to certain values (from 40°C to 50°C) leads to a raise in the efficiency of the process, the yield and the quality of the obtained microcapsules. This is mainly due to the favorable temperature, sufficient to maintain the size of the microdroplets obtained during the emulsification step, while preventing their agglomeration. Moreover, this temperature range is favorable for the adsorption of the pre-polymer particles on the surface of the microdroplets, which favorably affects the quality of the capsule wall, and hence the yield and quality of the obtained microcapsules. Increasing the temperature above 50°C (60°C and 70°C) leads to desorption of the prepolymer particles from the surface of the microdroplets, and from there to deterioration of the quality of the capsule shell, which leads to a decrease in yields and the quality of the obtained microcapsules.

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