EFFECT OF TIME IN THE EMULSIFICATION STEP ON THE YIELD AND QUALITY OF UREA-FORMALDEHYDE ROSE OIL MICROCAPSULES OBTAINED BY INTERFACIAL *IN SITU* POLYMERIZATION METHOD

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ABSTRACT

There are several parameters in the operating conditions that play a key role in the microencapsulation process by in situ polymerization. These parameters are stirring speed of the reaction mixture, temperature, time, type and concentration of emulsifier, molar ratios between components, pH, ionic strength, etc. All the mentioned characteristics determine the quality of the obtained microcapsules, which would direct us to the selection of optimal conditions for obtaining the target product. Since the emulsification step is one of the most important in the process, the present work examines the influence of the time (duration) of this step on the efficiency of microencapsulation process of rose oil and specifically on the yield, encapsulation efficiency, E% core, the size of the microcapsules obtained, the efficiency of the resin and the encapsulation factor. In this way, more complete clarity could be given on the influence of this parameter in the conditions, thus contributing to the optimization of the process in the large-scale preparation of microcapsules, particularly with rose oil.

Keywords: emulsification step, process of in situ polymerization, essential oil, urea, formaldehyde, pre - polymer.

INTRODUCTION

Due to the huge variety regarding the type of microcapsules, as well as their application, there is a wide variety of methods, techniques and accompanying protocols for microencapsulation [1 - 3]. Moreover, due to the huge variety of methods and products that need to be encapsulated, it is necessary to correctly choose the most suitable one, which satisfies the necessary requirements [4 - 6].

One of the widely used microencapsulation methods is the process of preparation of microspheres by *in situ* polymerization. Specifically, the preparation of microcapsules by chemical *in situ* polymerization method proceeds in several steps (Fig. 1). During the pre - polymer synthesis step, which takes place in an alkaline media, because of a nucleophilic attack of the NH_2 group of urea to the C = O group of formaldehyde, an addition reaction takes place with the formation of a dimeric product - mono methylol urea. Monomethylurea is the important building block used to create the microcapsule shell during the polymerization step. In the emulsification step, the microdroplets of an encapsulated substance are formed, the size of which depends on the conditions of the process. Furthermore, during this step, the pre - polymer molecules are adsorbed on the surface of the formed microdroplets. During the polymerization step, when the pH is lowered to an acidic reaction, the adsorbed pre - polymer molecules polycondensate, resulting in the formation of the capsule shell of the obtained microcapsules.

The size of the substance microdroplets obtained in the second step determined the size of the microcapsules. As a variety of authors pointed out the second step as the most important, because then microdroplets

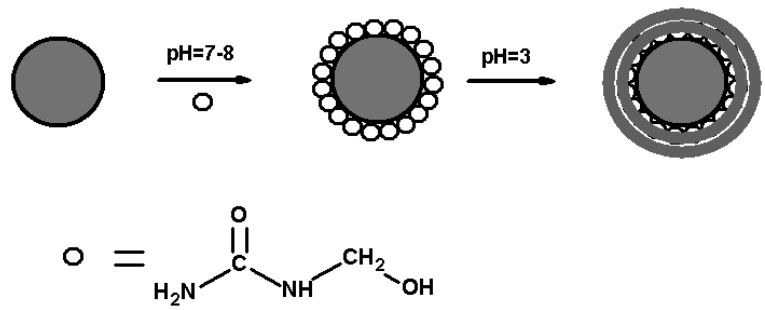

Fig. 1. Schematic representation of the steps and reaction conditions in the *in situ* polymerization method.

are formed, on whose surface the pre - polymer is adsorbed, therefore, studies are directed to this step of the process. Due to their specificity, it was necessary to carefully refine the conditions in the emulsification step, which is why author divided this study into two sub-steps: Stage A. Microdroplet formation; Stage B. Pre - polymeric molecular adsorption on the surface of the resulting microdroplets [7]. Based on the results, he suggested that higher stirring speed and temperature were required in the first part of the emulsification step (stage A: microdroplet formation stage) to produce smaller microdroplets. Conversely, a lower temperature was required for the second part of the emulsification step (stage B of pre - polymer molecular adsorption on the microdroplet surface) to prevent desorption of pre - polymer particles from the surface.

Moreover, in addition to the specified parameters in the conditions, the concentration of the surfactant also affects the efficiency of the microencapsulation process, the yield and quality of the obtained microcapsules. As its concentration increases, the efficiency of the process, yield and quality of the microcapsules rise. Too high concentration, however, has a negative effect, due to agglomeration of the microdroplets obtained during the emulsification step.

Besides the influence of the mentioned parameters in the conditions, time should also play an important role as a factor determining the efficiency of the microencapsulation process and the quality of the obtained microcapsules based on the analysis of characteristics such as yield (%), encapsulation efficiency (EE, %), resin efficiency (RE, %), content of encapsulated substance (E % core), encapsulation factor (EF) and microcapsule size (μm) [8, 9]. Unfortunately, despite the huge number of publications on the influence of duration (time) on the efficiency of the microencapsulation process, there is not much literature concerning the influence of time separately during the emulsification step and the polymerization step (microencapsulation step). In addition, the authors did not divide the emulsification step into two sub - steps (stages A and B) and do not investigate the effect of different conditions, including time, on the efficiency of the process and the quality of the obtained microcapsules (by considering the change in the value of different characteristics) during each sub - step of the emulsification step separately [10].

For example, P.A. Rochmadi et. al. studied the effect of time on the microencapsulation process, i.e. emphasizing the entire duration of the process, although they investigated the influence of homogenization time and microencapsulation time separately [10]. By examining the values of the resin efficiency and oil efficiency, they determine what the effect of homogenization and microencapsulation time is, i.e. the duration of the microencapsulation process by *in situ* polymerization, on the course of the process and the quality of the obtained microcapsules.

They investigated the influence of homogenization time, finding that as homogenization time rose up to 40 min, the total oil and resin efficiencies gradually increased. After 40 min these two characteristics remained constant with the values of oil efficiency around 85 % and the values of resin efficiency around 49 %, thus concluding that homogenization time was sufficient for 30 - 40 min. They observed that a longer homogenization time also resulted in a thicker microcapsule shell i.e. from 3.34 μm at 10 min to

4.09 μm at 50 min, thus concluding that the quality of microcapsule produced at 10 min was not good and the microcapsule was obviously sticky, whereas microcapsule produced at 20 min showed better quality.

According to the literature data, the microencapsulation time also had great influences on the resin efficiency [10]. However, this was observed until the third h, after which resin efficiency increased very little from 47.6 % at the 3rd h to 53.8 % at the 6th. Moreover, studying the microencapsulation step, P.A. Rochmadi et. al. noticed that after 3 h of microencapsulation process, the overall rate of polymerization reaction was very low and the amount of pre - polymer microparticles and microcapsule shells only slightly increased, thus concluding that no more urea - formaldehyde microparticles and microcapsule shells were formed [10]. They concluded that duration of the microencapsulation step of 3 h was sufficient to perform an efficient process and to produce microcapsules of good quality [10].

According to them, due to the long duration of stirring time, a partial separation of microparticles from the surface of the microcapsules was observed, with the separated microparticles passing both on the surface and falling to the bottom, because of which the wall of the microcapsule gradually thinned. As a result, this leads to a decrease in the thickness of the microcapsule shell from 7.61 μm at the 3rd h to 4.25 μm at the 6th h. Despite the low stirring speed, they applied i.e. around 100 rpm they suggested that the stirring shear force was large enough to affect the strength of the microcapsule shell. Furthermore, according to them, as the stirring time increased during the microencapsulation step, the average diameter of the microcapsules decreased from 108 μm at 3 h to about 70 μm at 6 h, possibly due to the destruction of some larger microcapsules to obtain microcapsules with a smaller average diameter.

Our initial study showed that along with stirring speed and temperature, stirring time also had a large effect on the properties of the obtained microcapsules [7]. After stirring for 1.5 h, where the average size of the capsules varied from 120 - 100 μm, by the 6th h (average size: 35 - 20 μm) it was seen that the size of the capsules progressively decreased and was inversely proportional to the time. The stirring time also affected the yield of the capsules: from 10.44 % in the first 1.5 h to 63.12 % in the 6th h. Regarding the other two indicators (encapsulation efficiency and content of the encapsulated substance, E% core), the influence of the stirring time until the 3rd h was most noticeable, as after that, this influence decreased.

Thus, the obtained preliminary results directed us to a more precise study of the influence of time during the two sub - steps (stages A and B) of the emulsification step to optimize this factor.

The time (1 h, 2 h, 3 h, 4 h, 5 h and 6 h) changed both during the first sub - step and during the second sub - step of the emulsification step. When time was varied, the emulsifier concentration was constant (3%). In the first sub - step, when the time was varied, the stirring speed was 1500 rpm and the temperature was 70°C. In the second sub - step, after receiving the milk - like emulsion, when the time was varied, the temperature was lowered to 45°C, but the stirring speed was the same as in the first sub - step. Thus, based on literature data from previous authors as well as his own preliminary studies, the author has precisely selected the time range for carrying out the reaction through the two stages (stage A and stage B) of the emulsification step.

EXPERIMENTAL

Methods and materials

The technical urea was recrystallized from ethyl alcohol. Formalin as a 37 % formaldehyde solution, and the rose oil was purchased from licensed Bulgarian producers. The pre - polymer was obtained in an alkaline media as a solution of mono methylol urea at a specified concentration. Freshly prepared 10 % sodium hydroxide solution, 1N solution of sodium hydroxide, and 10 % citric acid solution were used to adjust the pH throughout the process. Sodium hydroxide and citric acid were purchased. Sodium dodecyl sulfate (SDS) and glutaraldehyde were obtained from Sigma Aldrich.

For the control of the reaction mixture (pH) a professional benchtop pH - meter: BANTE Instruments, Model 920 - UK with a combinative pH electrode with BNC coupling was used. The pH - meter included temperature compensation in the temperature range of 0°C to 100°C. Operating conditions: from 0°C to 50°C with relative humidity up to 95 %. Division of pH = 0.001 pH units, range: from pH = - 2.000 to pH = 20.000, accuracy (at 20°C) pH ± 0.002.

For agitation of the reaction mixture and for

control of the stirring speed from 0 - 1000 rpm, an electromagnetic stirrer with heating was used with an included temperature probe to control the actual temperature, brand DIAB, Model MS7 - H550 - S with a temperature range of + 30 - 550°C, stirring speed 0 - 1000 rpm, Power 1030 W. For agitation above 1000 rpm a homogenizer for solid and liquid media Velp Scientifica, Model OV5 with a stirring speed of 1000 - 22000 rpm was used.

Weight analyses including microcapsule yield (%), encapsulation efficiency (EE, %), % sample (% encapsulated compound, core content, E% core), resin efficiency (RE, %) and encapsulation factor (EF) were performed by weighting various components on an analytical and precise balance with internal calibration - "KERN" model ABJ 120 - 4NM, range 120 g, accuracy 0.0001 g, plate diameter: d = 91 mm; as well as using an analytical and precise balance with internal calibration - "KERN" model ABJ 220 - 4NM, range 220 g, accuracy 0.0001 g, plate diameter: d = 91 mm.

The shape, morphology and approximate size of the microcapsules were analysed with a light microscope CARL ZEISS JENA, model 30 - G0020a, with magnifications of 12.5 x, 25 x, 40 x and 100 x, as well as a reflective optical metallographic microscope Nikon, included in the equipment of CSEM Scratch tester (Switzerland) and digitized with a 14 - megapixel camera. The size of the microcapsules as well as their size distribution were determined using a laser diffraction apparatus brand MICROTRACK MRB model SYNC, with a working range of 0.01 μm - 4 mm.

FT-IR analyses of rose oil microcapsules were carried out on PerkinElmer Spectrum™ 3 FT - IR apparatus (21 CFR Part 11 Compatible) operating at the wavelength range between 7800 cm^{-1} - 225 cm^{-1}. The spectra of the prepared microcapsules were obtained after their freeze drying using KBr pellets or NaCl crystals.

Preparation of microcapsules

Pre - polymer synthesis step. General procedure

To a 500 mL three - necked round bottom flask fitted with a thermometer, reflux condenser and electromagnetic stirrer, 60 g of urea (Mm = 60.06 g mol^{-1}; 1 mol) were added. After that, 120 mL of 37 % formalin solution (44.4 g formaldehyde, Mm = 30.03 g mol-1; 1.48 mol) were added with vigorous stirring, as the pH of the mixture was controlled via adjusting to pH 8 - 8.3 by slowly adding drop wise of 10 % sodium hydroxide solution. The reaction mixture was heated in a water bath for 1 h, all the while ensuring that the temperature of the medium did not exceed 70°C. The heating at this temperature was continued, then the water bath was removed, and the flask was refluxed at room temperature. After cooling, the reaction mixture was diluted with distilled water to 250 mL of pre - polymer solution. As the pH of the reaction mixture decreased during the reaction, therefore it was necessary to maintain the alkalinity in the range of 8 - 8.3 by drop wise addition of dilute sodium hydroxide solution. This decrease in the pH of the reaction mixture is not desirable due to the creation of conditions for the formation of insoluble undesirable side by - products. This lowering of the pH of the reaction mixture was not desirable due to the creation of conditions for the formation of insoluble unwanted by - products. For this purpose, various alkaline salts, such as ammonium carbonate, sodium acetate and its mixture with citric acid were used. Moreover, various bases and their salts such as urotropin, melamine, TRIS. HCl or TRIS - base, triethanolamine, ammonium chloride and others can be used instead of sodium hydroxide solution.

Emulsification step, general procedure

200 mL of pre - polymer solution was placed in a three-necked round - bottom flask with a volume of 1000 mL. After that, sodium dodecyl sulfate (3 % SDS) was added to the solution. A homogenizer was attached to the flask and the reaction mixture was stirred at 1500 rpm. A thermometer and reflux condenser were attached to the round-bottom flask. 10 mL of a 2 % solution of rose oil in medical paraffin was added to the solution and the stirring speed was maintained within 1500 rpm. The duration of the emulsification step from its beginning to obtaining a milky white emulsion (stage A) and then to the end of the step (stage B) was varied from 1 to 6 h for each sub - step (stage A and B), and the influence of time during each sub - step was studied (see below). It was necessary in the stage A of the emulsification step to maintain the temperature in the range of 70 ± 2°C. After obtaining a milky white emulsion in the stage A, in the next stage (stage B) - the temperature range was to be 45 ± 2°C.

Microencapsulation (polymerization) step

The homogenizer was stopped, removed from the reaction mixture and replaced by the electromagnetic stirrer, reducing the stirring speed to 750 rpm. After 20 min, citric acid solution was added to the emulsion (to pH 3), at the same temperature. The reaction mixture was stirred for 3 h under the same conditions. At the end, 4 mL of formaldehyde solution was added with continuing stirring. After 30 min, the product (microcapsules) was filtered and washed with H_2O, H_2O : C_2H_5OH (1 : 1) and finally with C_2H_5OH. After washing, it was dried for 6 h at room temperature or for 2 h in an oven at a temperature of 55 - 60°C.

Product analysis

Weight analysis

The microcapsule yield (%), the percentage of the microencapsulated substance (the core content of the microcapsule) and the encapsulation efficiency were calculated using the equations from our other article [11].

The resin efficiency (%) was calculated using the following equation:

$$RE\% = \frac{m_{Rprod}}{m_{Rsol}}.100 \quad (1)$$

where: RE - resin efficiency; m_{Rprod} - weight of resin in product (microcapsule shell); $m_{Rsol.}$ - initial weight of resin (i. e. pre - polymer - mono methylol urea) in solution.

The encapsulation factor was calculated using equation (2):

$$EF = \frac{m_{mcs}}{m_{mps}} \quad (2)$$

where: m_{mcs} - total weight of microcapsules on the surface of the sample reaction mixture, m_{mps} - total weight of microparticles at the bottom of the sample reaction mixture.

Particle size analysis

The average diameter, size distribution and standard deviation were determined from at least 150 measurements. The average diameter was calculated as arithmetic mean value of the particle size range automatically measured by the laser diffraction apparatus.

Standard deviation was calculated using the following equation:

$$s = \sqrt{\frac{\sum_{i-1}^{n}(x_i - \bar{x})^2}{(n-1)}} \quad (3)$$

where: x_i is the i measurement of the determining element, x - mean value from n measurements; n - number of measurements

FT-IR spectroscopic analysis

The spectra of the prepared microcapsules were obtained after freeze drying of the whole microcapsules (without their breaking by grinding in a porcelain mortar or with ultrasound) and the capsule shell was analysed by the FT-IR spectrometry. The infrared spectra of the microcapsules, with the characteristic absorption bands of the urea - formaldehyde polymer forming the wall of the microcapsules, are at 3450 cm^{-1} and 3350 cm^{-1} 2800 cm^{-1} and 2650 cm^{-1}, 1650 cm^{-1} and 1450 cm^{-1}, 1150 cm^{-1} and 1050 cm^{-1}, corresponding to C - H, N - H, C - N and C = O vibrations, respectively as well as the N - H of the amine are at 3300 cm^{-1} and 3250 cm^{-1} respectively [12 - 15].

RESULTS AND DISCUSSION

Effect of time in the first sub - step (stage A) (duration of the first sub - step) of the emulsification step on the characteristics of the obtained microcapsules

An important factor affecting the encapsulation process and the quality of the obtained microcapsules is the time (duration) of the emulsification step. The duration of both the first sub - step (stage A) and the second sub - step (stage B) of the emulsification step mainly affects the parameters (capsule yield (%), encapsulation efficiency (%), encapsulated substance content (E% core) and capsule size) up to a certain point, then increasing the duration of the emulsification step (time) has no significant effect on the characteristics of the microcapsules. For example, the duration of the first sub - step (stage A) of the emulsification step affects the efficiency of the process and the quality of the obtained capsules until between the 3rd and 4th h (Table 1). Optimal yields of the capsules are achieved between these hours: from 64.6 % to 67.7 %. The same dependence is observed for the other characteristics of

Table 1. Influence of time during the first sub - step (stage A) (duration of the first sub - step) of the emulsification step on the characteristics of the obtained rose oil microcapsules.

№	Time, h	Yield, %	EE, %	$E\%_{core}$	RE, %	EF	Size, μm
1	1	30.4	43.3	37.3	57.5	0.47	70-50
2	2	53.3	67.9	36.8	59.2	1.28	40-25
3	**3**	**64.6**	**84.4**	**38.5**	**60.0**	**2.01**	**30-15**
4	**4**	**67.7**	**83.3**	**37.8**	**62.9**	**2.09**	**25-15**
5	5	65.6	81.2	35.9	61.7	**2.06**	30-20
6	6	63.2	84.7	35.7	60.1	1.92	30-15

Other conditions: stirring speed - 1500 rpm; temperature - 70°C; surfactant concentration (SDS) - 3 %.

the obtained microcapsules (Table 1).

The encapsulation efficiency also follows the analogous trends of the best parameters, i.e. of the highest values in terms of the yield of the encapsulated substance. By the 3rd h, the encapsulation efficiency value rises sharply, e.g. it becomes 84.4 % (Table 1, Fig. 2). Between the 3rd h and 4th h, there is even a slight decrease in the values of this characteristic.

Unlike the parameters listed above, the duration of the first sub - step (stage A) of the emulsification step does not affect the content of the encapsulated substance (E% core), and hence the quality of the capsule shell, and this characteristic assumes relatively constant values (Table 1, Fig. 2). This is explained by the fact that during the first sub - step (stage A) of the emulsification step the microdroplets are formed and the factors such as stirring speed, time and temperature mostly affect the size and yield of the obtained microdroplets (Table 1, Fig. 3). For this reason, the resin efficiency (%), representing the ratio between the weight of the resin in product (insoluble shell of microcapsule wall, m_{Rprod}) and the initial total weight of the resin in solution ($m_{Rsol.}$) multiplied by 100, remains constant with time i.e. is not affected by the duration of the first sub - step (stage A) of the emulsification step (Table 1, Fig. 2).

As for the encapsulation factor (m_{mcs}/m_{mps}), its values increase until the 4th h, after which they either decrease slightly or remain relatively constant, which means that the duration of the first sub - step (stage A) of the emulsification step has a positive effect on this magnitude up to a certain point, after which it stops affecting (Table 1).

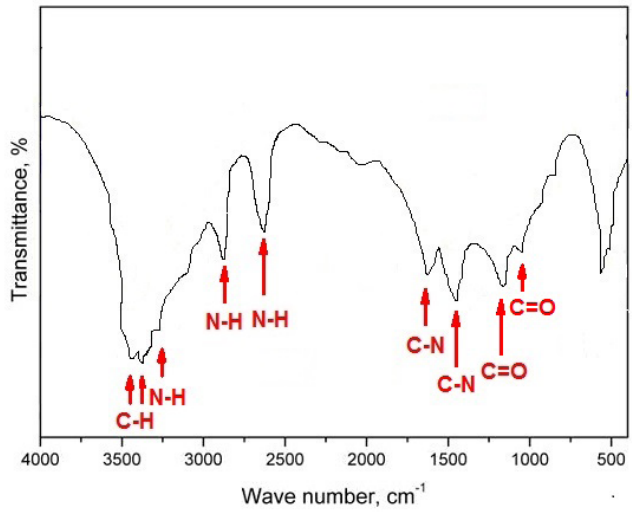

Fig. 2. FT - IR spectrum of poly(urea - formaldehyde) shell of the microcapsules filled with rose oil.

Effect of time in the second sub - step (stage B) (second sub - step duration) of the emulsification step on the characteristics of the obtained microcapsules

The duration of the second sub - step (stage B) of the emulsification step affects the process of obtaining the microcapsules mostly between the 1st and 2nd h, as can be seen from the results presented in Table 2. It is characteristic that, for example capsule yields rise sharply from the first to the second h, slightly from the 2nd to the 3rd h, then decrease slightly, increase or remain relatively constant.

The encapsulation efficiency follows the similar trend as the microcapsule yield, i.e. it rises sharply from the first to the second h (EE = 84.4 %), after which it remains relatively constant (Table 2, Fig. 4).

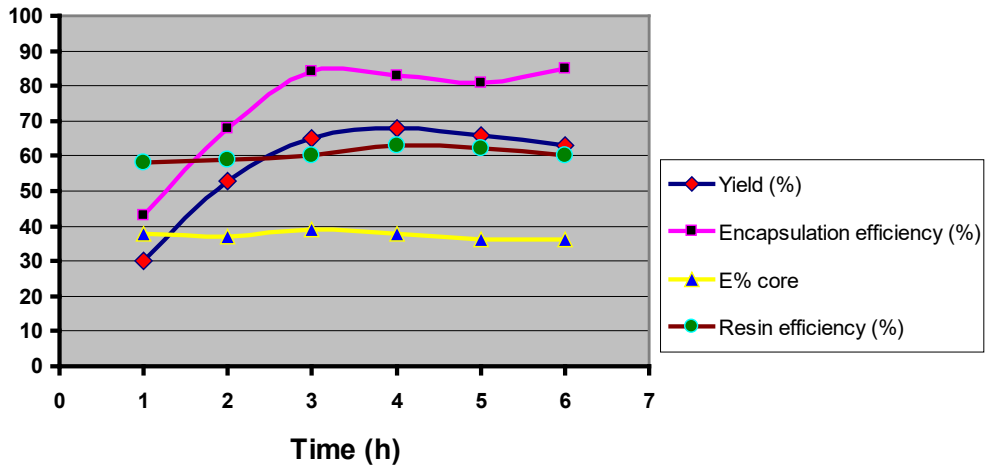

Fig. 3. Effect of time during the first sub - step (stage A) (duration of the first sub - step) of the emulsification step on the characteristics of the obtained rose oil microcapsules.

Table 2. Influence of stirring time during the second sub - step (stage B) (second sub - step duration) of the emulsification step on the characteristics of the obtained rose oil microcapsules.

№	Time, h	Yield,%	EE, %	E% core	RE, %	EF	Size, μm
1	1	40.4	43.2	51.1	36.9	0.74	40 - 30
2	2	64.6	84.4	38.5	60.3	1.87	30 - 15
3	3	67.7	83.3	37.8	64.2	2.09	20 - 15
4	4	64.7	80.3	37.8	61.8	2.03	25 - 15
5	5	65.1	82.8	37.5	62.5	2.01	20 - 15
6	6	63.2	83.6	38.1	60.1	1.92	25 - 15

Other conditions: stirring speed - 1500 rpm; temperature - 45°C; surfactant concentration (SDS) - 3 %.

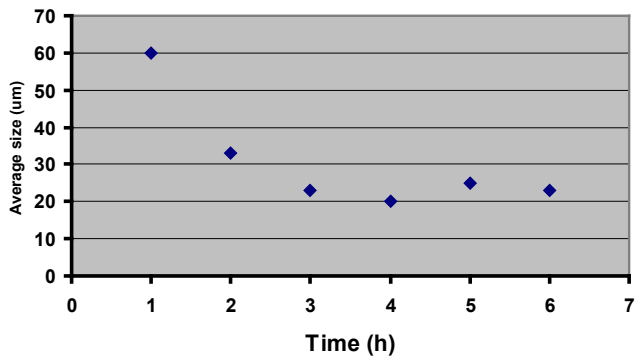

Fig. 4. Effect of time during the first sub - step (stage A) (duration of the first sub - step) of the emulsification step on the size of the obtained rose oil microcapsules, represented by the mean value of the diameter, in μm.

In the microencapsulation of rose oil, during the second sub - step (stage B) of the emulsification step, the content of the encapsulated substance (E% core) sharply decreases from the 1st to the 2nd h, which speaks of the quality of the obtained microcapsules in terms of their capsule wall. Between 2nd and 3rd h E% core decreases slightly, and after the 3rd h the value remains relatively constant. From this follows the conclusion that between the 1st and 2nd h the density of the capsule shell increases, after which it assumes constant values. This is best seen by the values of the other two characteristics: the resin efficiency and the encapsulation factor increase, as represented by the data in Table 2, Fig.4. According to us, these data

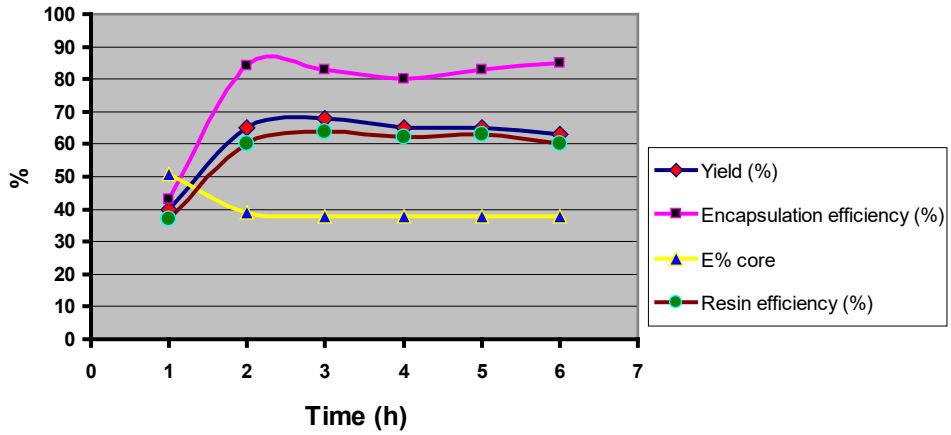

Fig. 5. Effect of time during the second sub - step (stage B) (second sub - step duration) of the emulsification step on the characteristics of the obtained rose oil microcapsules.

indicate that the density of the shell slightly increased after the 2nd h.

The sharp decrease in the content of the encapsulated substance (E% core) from the 1st to the 2nd h during the second sub - step (stage B) of the emulsification step, as well as the increase in the resin efficiency and the encapsulation factor indicate that during this sub - step (stage B) the adsorption of the pre - polymers particles takes place on the surface of the microdroplets formed during the first sub - step (stage A) of the emulsification step. From the efficiency of the adsorption process, determined based on the amount of mono methylol urea molecules adsorbed, the quality of the capsule shell is determined, based on the density and efficiency of the wall (resin efficiency).

As mentioned above, the sorption process is an equilibrium process characterized by the corresponding equilibrium (sorption constant, Ks). Over time, along with the adsorbed molecules, the number of desorbed ones increases until equilibrium is reached, which explains the relatively constant values of the content of the encapsulated substance (E% core) after the 3rd h during the second sub - step of the emulsification step, as well as the constant values of resin efficiency and encapsulation factor. With the microencapsulation of the rose oil, even a slight increase in the values of E% core, correspondingly a decrease in the values of the resin efficiency and the encapsulation factor was observed, which explains to some extent the fact related to an increase in the number of mono methylol urea molecules desorbed from the surface of the microdroplets (Table 2).

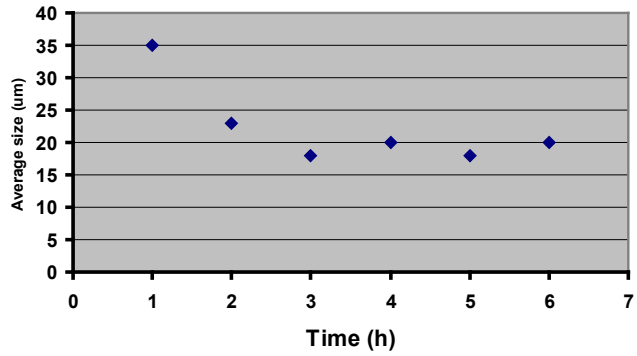

Fig. 6. Influence of time during the second sub - step (stage B) (duration of the second sub - step) of the emulsification step on the size of the obtained rose oil microcapsules, represented by the mean value of the diameter, in µm.

As for the average size of the capsules, it intensively decreases from the 1st to the 3rd h, after which it remains constant (Table 2, Fig. 5). This is since at the beginning of the stage B of the emulsification step (up to the 3rd h) the temperature and stirring speed still affect the formation of microdroplets and the average diameter of the resulting microdroplets, since their high value causes prevention of agglomeration and coalescence of the obtained microdroplets.

In conclusion, it could be said that the influence of time during the two sub - steps (stages A and B) of the

emulsification step is ambiguous, being characterized by an optimum. For the first sub-step of the step, this optimum is between the 3rd and 4th h, particularly on the 3rd, and for the second sub - step - between the 2nd and 3rd h, concretely on the 2nd.

CONCLUSIONS

The influence of the duration of the two sub - steps (stages A and B) of the emulsification step was studied. It was found that increasing the duration up to 3 h in the first sub - step (stage A) of the emulsification step had a positive effect on the microencapsulation process, leading to an increase in the yield (%), encapsulation efficiency (EE, %) and the encapsulation factor (EF), and a decrease in the size of microcapsules (μm), while the encapsulated substance content (E% core) and resin efficiency (RE, %) remained unchanged. A further increase in time during the first stage of the emulsification step did not affect the process, with the values of all characteristics remaining relatively constant or with a slight increase in yield (%) and encapsulation factor (EF).

Therefore, the author chooses an optimal running time of the first stage of the emulsification step between the 3rd and 4th h, more precisely 3.5 h.

It was found that the duration up to 2 h in the second sub - step (stage B) of the emulsification step also had a positive effect on the process, after which its influence sharply decreased. Unlike the first sub - step (stage A) of the emulsification step, in the second sub - step (stage B) of the step, the duration of the process up to the second h had a positive effect on the other two characteristics as well, such as the encapsulated substance content (E% core) and the resin efficiency (RE, %). Between the 2nd and 3rd h, the values of characteristics changed slightly, and some remained constant. For this reason, the author chooses an optimal running time of the second sub - step (stage B) of the emulsification step between the 2nd and the 3rd h, more precisely 2.5 h.

An interesting trend was observed in the prolonged stirring time during the second sub - step (stage B) of the emulsification step, where the highest values of E% core were characterized by the stirring time of 1 h. Between the first and second h, the content of the encapsulated substance dropped sharply. There is a slight decrease between the second and third h. After the third h it remained constant, and after the fifth h it even rose slightly. The same tendency was observed for resin efficiency (RE, %) and encapsulation factor (EF), which changed their values in reverse order i.e. decreased. This is probably due to P.A. Roshmadi and W. Hakosovati's assumption that over time some of the pre - polymer particles detach from the surface of the microdroplets due to the high stirring speed and fall to the bottom of the reaction mixture. This, in turn, leads to thinning of the microcapsule shell and deterioration of its qualities.

As can be seen from the data presented, following the changes in the values of the different characteristics, it is found that time, as well as stirring speed and temperature play a key role during the emulsification step, on the efficiency of the microencapsulation process and the quality of the obtained capsules. The microdroplets obtained during this step determine the sizes and qualities of the future microcapsules, defining the leading role of this step.

Therefore, this step is of particular importance that depends on time, stirring speed and temperature. A study of the effect of stirring speed and temperature in the emulsification step, as well as the influence of time on the encapsulation step (polymerization step) is forthcoming, which will be discussed in another article.

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