Characterization of ethyl cellulose (EC) microcapsules for lime oil encapsulation

E Julaeha 1*, R Nugeraha 1, M Nurzaman 2, D Kurnia 1, T Wahyudi 3 and Y Rosandi 4

1Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Padjadjaran, Jatinangor, Sumedang 45363, Indonesia
2Department of Biology, Faculty of Mathematics and Natural Sciences, Universitas Padjadjaran, Jatinangor, Sumedang 45363, Indonesia
3Indonesia Center for Textile, Jl. Jendaral Achmad Yani No. 390 Bandung, 40272, Indonesia
4Department of Geophysics, Faculty of Mathematics and Natural Sciences, Universitas Padjadjaran, Jatinangor, Sumedang 45363, Indonesia

*euis.julaeha@unpad.ac.id

Abstract. We report on the preparation of microcapsules using ethyl cellulose as a shell and lime oil (Citrus aurantifolia oil) as the core. In this work the lime oil was extracted from lime syrup production residue by hydrodistillation method. Microencapsulation is prepared using a simple coacervation method. The size distribution of the microcapsules is observed using the Particle Size Analyzer (PSA). The effectiveness of the encapsulation process was determined by evaluating the images captured by the optical microscope. Whereas, the morphology of the produced microcapsules was identified using the scanning electron microscopy. Our result shows the size distribution ranged from 39 to 104 μm, with oil containment up to 14%. This size distribution is suitable for functional textile products application.

1. Introduction

Microcapsules technology is used to control the containment and release time of oil substances. The technology has a wide spread applications in many sectors, for instance, health, medical, cosmetics, textile, and agriculture. These utilization of the microcapsules is continually developing with broader field of application. Research on the encapsulation process of substances by microcapsules started very recently. The capsules are used to isolate and prevent the mobility of liquids, especially essential and fragrant oil by polymer shell or membrane. By tuning the properties of the membrane, it is possible to control the mechanism to release the encapsulated substances. By encapsulating fragrant liquid in the microcapsule, the release of the fragrant can be made gradual. This mechanism is very suitable to be applied for instance, in the functional textile products [1].

Microcapsules can be prepared from ethyl cellulose (EC) using various methods such as phase separation, coacervation, solvent evaporation [2]. EC is also frequently used as a hydrophobic polymeric coating material for extended drug release applications. In this work the coacervation
method is applied to encapsulate essential lime oil (LO). The essential oil, processed from residue of lime home industry, is used as the core liquid wrapped by capsule shells made from ethyl cellulose.

2. Material and method

2.1. The preparation of lime oil

In this work, we prepared lime oil extracted by hydrodistillation process of lime peel, using the standard distillation equipment (Stahl), by hydrodistillation process of lime peel, using the standard distillation equipment (Stahl). This processing time takes about three hours. In order to remove water content in the oil we add sodium sulfate (NaSO₄) to the yield. In our experiment, 1.281 g of lime peels produce 12.9 mL of lime oil, with yellowish color and a characteristic lime odor. In order to maintain the quality of the lime oil, the obtained oil transferred into an airtight amber-colored vial and stored in a refrigerator at 4°C for further analysis. The quality of the essential oil was determined using the method proposed in [3], which analyses the specific mass, the refraction index, the acid number, and solubility in alcohol.

2.2. Microcapsule preparation procedure

We applied a simple encapsulation procedure of LO proposed by Mirabedini et al. [4]. The amount of LO (0.5 g) is kept constant with the variation of the EC, ranged from 0.6, 0.8, 1.0, and 1.2 g. This process was performed in two stages using the solvent evaporation method. In the first stage (the oil phase), the EC powder was gradually solved in 10% ethyl acetate. The process was performed in 10 minutes and followed by LO addition which take 30 minutes, gradually. Throughout the process the system condition was kept in room temperature and the magnetic stirrer was always activated with the speed of 600 rpm.

In the second stage (the water phase) the oil phase drops to the 1% sodium dodecyl sulfate (SDS) solution, under the same condition for 15 minutes. In this stage the process was performed inside a closed container. The resulted dispersion mixture is removed to the 60°C water bath and the stirrer was running for one hour. The mixture was deposited in the same container and let cooled for one day until the microcapsules was formed. The microcapsules were collected using the millipore filter and dried in a desiccator for one day.

2.3. Microcapsule characterization

The particle size distribution was identified using the Particle Size Analyzer (PSA) apparatus. The morphology of the microcapsules was observed using an optical microscope with magnifications of 40, 100 and 200 times. The on-screen magnification was 128, 320 and 640 times. We also evaluated the morphology using Scanning Electron Microscope (SEM) apparatus. A UV-spectrophotometer was used to analyze the efficiency of the encapsulation process. The spectrophotometer operated at 340 nm wavelength, according to the standard curve. The oil containment in the microcapsules is calculated using linear regression, where the encapsulation efficiency $EE$ (%) is determined by equation (1).

$$EE = \frac{w_o}{w_c} \times 100\%$$

where $w_o$ and $w_c$ is the weight of oil content and microcapsules, respectively.

3. Result and discussion

3.1. Preparation of the lime oil (LO)

Lime oil (LO) was obtained from C. aurantifolia (lime) peels by hydrodistillation. The essential oil is extracted by the water steam pressure from oil cells of the lime peel. The oil is mixed with the water steam, and flows through a condenser device. This mixture was condensed and the separation between oil and water phase occurred. Due to smaller specific mass of oil, the LO will be deposited on top of water [5]. We obtained LO with the yield of 0.89%, and it’s the quality is shown in table 1. Our values fit well with the literature [4].
Table 1. The quality of lime oil produced by hydrodistillation. The reference value is taken from Guenther, 1987 [3].

| Parameter                     | Value     | Ref [3]       |
|-------------------------------|-----------|---------------|
| density                       | 0.854     | 0.862–0.868   |
| refraction index              | 1.4756    | 1.4750–1.4770 |
| acid number (%)               | 0.5148    | 0.5–1.5       |
| solubility in 90% ethanol     | soluble   | soluble       |

3.2. Encapsulation of the lime oil

Essential oils are volatile and chemically unstable in the presence of air, light, moisture and high temperatures. Hence, it is beneficial to microencapsulate volatile ingredients to limit aroma degradation or loss during processing and storage [6]. Microencapsulation has the ability to enhance the oxidative stability, thermostability, shelf-life, and biological activity of oils. In addition, encapsulation can control the release time of the essential oil, hence the volatility and usage time can also be controlled [7]. In the study, we used a simple coacervation method, based on the addition of a poor solvent to a hydrophilic colloidal solution which results in the formation of two phases: one is rich in colloid molecules (coacervate), and the other is almost coacervate free [5].

From this simple method, the yield of the microcapsule is taken from the ratio of the ethyl cellulose (shell) and the essential lime oil (core). In this work, we put 0.5 g of LO to the system with the varied weight of EC from 0.6, 0.8, 1.0, and 1.2 g. The result is shown in Table 2, where the yield of 69% is reached using the membrane shell weight of 1.0 g.

Table 2. The yield of the microcapsule with the variation of the membrane shell. The essential oil weight is 0.5 g.

| Sample no. | Membrane shell | Weight | %yield |
|------------|----------------|--------|--------|
| I          | 0.6037         | 0.4687 | 45%    |
| II         | 0.8014         | 0.4966 | 60%    |
| III        | 1.0067         | 0.9847 | 69%    |
| IV         | 1.2034         | 1.0871 | 69%    |

3.3. Microcapsule morphology

The surface morphology of microcapsules depends on the core material properties and the micro-encapsulation process of the shell. Microcapsule particle size and the thickness of shell are believed to be dependent on the ratio of core to shell material, and it greatly influences the encapsulation efficiency [8]. In the study, four different weight of shell material 0.6, 0.8, 1.0, and 1.2 g were selected while core material fixed at 0.5 g to evaluate the effectiveness on the micro-encapsulation process. The influences of weight of shell to the size of particle size is shown in figure 1, which shows the result of size distribution measurement using PSA apparatus.

The data shows that the average particle size decreases with the increase of EC weight from 0.6 to 1.0 g. However, it increases at the core weight of 1.2 g. At the core/shell ratio of 0.5:1.0 g (1:2) we found the smallest microcapsule particle size. The average particle size distribution is decreased by increasing oil to EC ratio, however, the decrease in most cases was not statistically significant.
The fabricated microcapsule was characterized using optical microscope and scanning electron microscope (SEM) in order to observe the morphology. The result is shown in figure 2 and 3. In figure 2, it is shown the difference between the empty and filled microcapsules in the various magnification. The lime oil appears as bubbles inside the capsule shells. It indicates that on micro-encapsulation, the lime oil (core) has been coated by the ethyl cellulose coating (shell).

![Figure 2. The morphology of empty microcapsules (left column) and microcapsules filled by the essential oil (right column), as seen by the optical microscope. The magnification is shown on the left side of each image, 128, 320, and 640 times magnification.](image)

![Figure 1. The PSA measurement of the particle size, demonstrates the dependence of microcapsule size to the EC shell concentration.](image)
found that the diameter is distributed between 39 to 104 µm. The average size of the fabricated capsules increase by increasing the oil phase. No free oil material is seen in the optical micrographs, indicating that the oil is well contained inside the shell and no air bubbles is present inside the the microcapsule.

We used the digital UV-vis device to determine the content of essential oil inside the capsule shells. From the standard curve of lime oil, we obtained obtain 2.57 g/L oil content with ε value of 14%. We consider that the oil content is low, which might be caused by several factors, such as not optimal ratio between the shell and core (the oil), incomplete encapsulation of the oil, incomplete forming of microcapsules, and the leaking of the shell and the oil during the process.

Figure 3. Scanning electron microscope (SEM) image, shows the morphology of the microcapsules. The measured diameter is indicated by yellow bars. The scale (100µm) is shown by the white bar at right-bottom position.

4. Conclusion
Lime oil microcapsules have been prepared using *C. aurantifolia* oil (lime oil, LO) as core material and *ethyl cellulose* (EC) as shell material by coacervation technique. By analysis of the particle size, the encapsulation efficiency was achieved at the ratio of core material to shell material of 1:2, and stirring speed is 600 rpm, with the yield is 69%. The particle size of microcapsule is around 39 to 104 µm, the encapsulation efficiency, s, of the microcapsule is 14%. The microcapsules are in sphere shape without coacervation. The quality criteria of the produced lime oil agree well with the literature.

Acknowledgment
We are grateful for internal research funding of Universitas Padjadjaran, contract No. 718/UN6.3.1/PL/2017.

References
[1] Wahyudi T, Mulyawan A S, Kasipah C, Prayudie U and Julaeha E 2017 *Arena Tekstil* **32** 1
[2] Badulescu R, Vivod V, Jausovec D and Voncina B 2008 *Carbohydrate Polymers* **71** 85
[3] Guenter E 1987 *Essential Oils* (New York : Robert E. Krieger Publishing Co.)
[4] Mirabedini S M, Dutil I and Farnood R R 2012 *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **394** 74
[5] Asbahani A E, Miladi K, Badri W, Sala M, Addi E H A, Casabianca H, Mousadik A E, Hartmann D, Jilale A and Renaud F N R 2015 *International Journal of Pharmaceutics* **483** 220
[6] Jun-xia X, Hai-yan Y and Jian Y 2011 *Food Chemistry* **125** 1267
[7] Bakry A M, Abbas S, Ali B, Majeed H, Abouelwafa M Y, Mousa A and Liang L 2016 *Comprehensive Reviews in Food Science and Food Safety* **12** 143
[8] Wang J M, Zheng W, Song Q W, Zhu H and Zhou Y 2009 *Journal of Fiber Bioengineering and Informatics* **1** 293