SZENT ISTVÁN UNIVERSITY

FACULTY OF FOOD SCIENCE

EXAMINATION OF FOOD EMULSION PRODUCTION BY MEMBRANE EMULSIFICATION

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1. INTRODUCTION AND OBJECTIVES

We can encounter emulsions in a significant area of the food industry. Examining their manufacturing technology, we can find many different industrial processes, depending on product and economic requirements. Generally, during the production of emulsions, dispersed phase is uniformly dispersed into continues phase, most often with use of some mechanical energy. Widespread emulsion manufacturing equipment in the food industry usually uses conventional methods. Such methods include high-shear mixer and high-pressure homogenizing devices. However, these systems are highly energy-intensive and high shear stresses reach the product, which can adversely affect the thermal and mechanical-sensitive components. This may lead to the loss of functional properties of the components, which is unacceptable in pharmaceutical and food products. In addition, droplet size and distribution are difficult to control, so it is difficult to maintain consistent quality between the various items. To overcome these problems, more and more attention is being paid to new methods such as membrane technology.

Membrane Emulsification (ME) is a novel, simple emulsion production process that is carried out using a microporous membrane. One of its realization options is cross-flow design. In this case, to reach dispersed droplets, the dispersion phase is forced through the membrane pores under pressure, resulting in droplets on the membrane surface. The droplets are sheared off by the flow of

the continuous phase running parallel to the fine pore membrane. They are detached from the surface of the membrane to form emulsified drops. There are many benefits to traditional turbulence-based methods. The most commonly mentioned are: lower energy requirements, simple design, easy expandability, and lower the shearing stress effects of end product. Due to localized shear and geometrically controlled drop formation, we can better control the evolving microstructure. The size of the droplets can be precisely controlled in a wide range, with a narrow droplet size distribution that allows the use of less surfactant. Although the basic principles of membrane emulsification were patented before the 1990s (NAKAJIMA 1998; SHIMIZU 1988, Japan), until the end of the 1990s, we hardly find any sources of literature that would study the development emulsions for food. New areas for the development of membrane processes were opened in the 2000s, and research into membrane emulsion has also gained new strength. From that time onwards, more and more research teams have turned their attention to the research and development of membrane emulsification in pharmaceuticals, cosmetics manufacturing and, last but not least, in the food industry.

During my work, I analyzed the method and possibilities of the membrane emulsification itself. I have done literature research related mainly to the production of emulsions made using this method, specifically for food industry use, and my own research is focused on this area. I designed my experiments along three main lines.

1.1. ME process development using a static mixer in a tubular membrane

The membrane emulsification operation, similarly to several membrane operations, combined with a static mixer, is possible to improve the process. For various membrane operations, the use of a static mixer has proven to be effective in many cases. The essence of the method is to change the flow parameters with the baffles placed inside the membrane, mechanically modifying the diaphragm. In order to detect the possible application of this method, I performed tests using two different pore size membranes. Based on factorial design, I set up models to define the flux values of the dispersion phase as characteristics of the emulsification process, as well as determine the mean droplet diameter and polydispersity index values.

Related tasks include:

- Production of O / W type emulsion by ME process with different pore size membranes (1.4 μm, 500 nm):
- using a static mixer, without the use of a static mixer,
- Investigating the effects of the process by changing operating parameters. The changed parameters are:
- Driving force (DF)
- shear stress (τ) (at the membrane wall).
- Determining the effect of the examined operational parameters on the emulsification process,

- Define optimal manufacturing parameters,
- Analysis of the effect of the static mixer on the properties of the resulting emulsion, analysis of the efficiency of the process,
- Establish a mathematical model that characterizes the process.

1.2. Product development experiments with ME process

In the literature, very few publications can be found, which would expressly design food products based on ME. For this reason, in the framework of product development experiments, I aimed at developing a method of producing ME in food industry emulsions. In any case, a well-known, widespread, non-special, simply nutritional product was the goal. I wanted to use the least amount of ingredient, and I wanted to use easy-to-use raw materials. There are two different types of oil in the water (O / W) as well as a water-in-oil (W / O) food emulsion to test the method and equipment in multiple settings. Another aspect was that the production of the products requires the use of auxiliary operations as little as possible outside the membrane emulsification. This gives the opportunity to compare the products made by conventional way, mixing and membrane dispersion. The two specific products are: a hypoallergenic (milk-free) cream O / W emulsion, the other a W / O salad dressing, made by oil dispersion into vinegar (vinaigrette).

Related tasks include:

- Determination of optimum manufacturing parameters (membrane pore size, driving force, shear stress)
- Product production using the specified parameters,
- The stability of manufactured emulsions,
- Organizing sensory reviews for product testing,
- In the case of cream chewing gum, comparative testing between a commercially available liqueur made with the ME process,
- In the case of salad dressing, compare the ME-method and the traditional hand-made product.

1.3. Microencapsulation based on membrane technique

Microencapsulation experiments are aimed at producing microcapsule based on membrane technology. It is intended to carry out basic research necessary for the production of laboratory conditions. Starting from the analysis of the possible wall materials of the microcapsule, through the preparation of the ME method, by studying the resulting microcapsules.

Related tasks include:

- characterization of maltodextrin, hydroxypropylcellulose, potato starch and maize starch in water (determination of particle size, molecular weight and zeta potential),

- testing of cross-flow membrane emulsifiers for the production of a solid microcapsule precursor,
- Analysis of the production of microcapsules in O / V and V / O systems
- using a surfactant, without the use of a surfactant,
- studying the microcapsule recovery method,
- Investigation of microcapsules created

2. MATERIALS AND METHODS

2.1. The ingredients of the emulsions and their preparation

For making emulsions, I used vegetable oil, most commonly, commercially available sunflower oil and distilled water. To aid emulsification, Tween80 surfactant was used (Sigma-Aldrich Ltd., Budapest). Tween80 is an artificial additive made from sorbitol, oleic acid and ethylene oxide. HLB value 15. In the food industry, it is known as E433 as an emulsifier. The maximum daily intake volume is 25 mg • tkg-1.

Laboratory experiments were performed at room temperature. At the start of each measurement, I dispense the dispersion phase measuring vessel (20 ml) and the continuous phase container (1000 ml) with the basic materials of the experiment. During the production of emulsions, I changed two theoretical parameters: DF-driving force and shear stress at the membrane wall, which is in practice the pressure of the dispersion phase and the recirculation volume flow. The dispersion phase flux was examined during the emulsion preparation, and the time of the dispersion phase of the dispersion phase was measured by a stopwatch from the dispersion phase measuring vessel. The flux can be determined from the measured time and volume data by knowing the surface of the membrane.

2.2. Membrane emulsification apparatus

The emulsions were produced using a laboratory emulsifier designed and constructed at the Department of Food Engineering at Szent István University, Faculty of Food Science. The device is a continuous, cross-flow device, as illustrated in Figure 1, by designating the main units. It is designed for practical applications, can be used effectively.

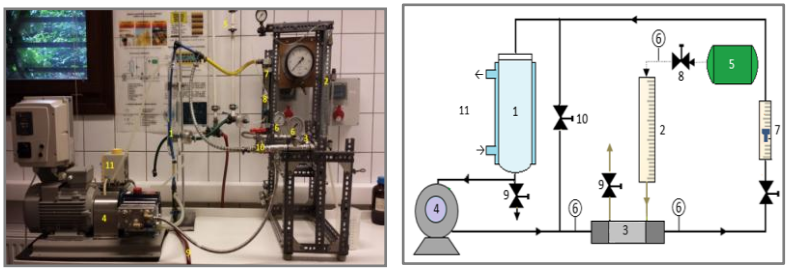

Figure 1: Figure of the membrane emulsification apparatus (1. continuous phase tank, 2. scaled dispersed phase tank, 3. membrane module, 4. compressor, 6. pressure gauge, 7. rotaméter, 8. pressure regulator, 9. valve, 10. valve, 11. thermostat connection)

The principle of operation is as follows: the continuous phase is recirculated by the pump (4) from the 1 liter volume container (1) on the inside of the diaphragm. The recirculation volume of the retentate can be read from the rotameter (7). The input of the membrane (3) On the output side, pressure gauges (6) are indicated by pressure gauges (6), based on the transmembrane differential pressure formula. The pressure of the dispersion phase is provided by compressed air produced by a compressor (5). From the dispersed

dispersed phase tank (2) the material to be dispersed comes to the outer side of the membrane, which can be adjusted with the pressure control valve (8). The resulting product can be removed from the system via drain valves (9). Signal 11 indicates that the continuous medium can be heated by means of a thermostat connected to the tank, but if cold water circulates, it is possible to cool the system to avoid warming. Tank 1 must be filled with the continuous phase necessary for the next experiment to moisten the surface of the membrane. The tubular membrane has a circular cross section, as shown in Figure 2. The diaphragm must be inserted in this position and then properly sealed the gaskets with three screws on both ends.

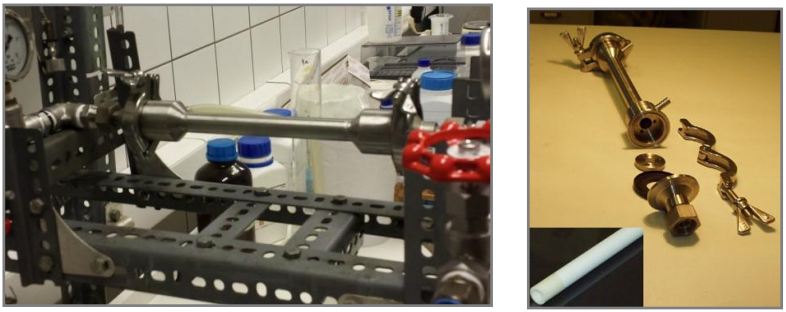

Figure 2: Membrane and its fittings

2.3. Membranes used in the experiments

During the experiments, SCHUMASIV ceramic tubular membranes (PALL Austria Filter GmbH) 500 nm, 800 nm and 1.4 μm in diameter were used. The active layer was aluminium oxide. The

main properties of the membranes used, such as pore size, inner diameter, length and other operating ranges, are shown in Table 1. The membranes are not necessarily used lengthwise by the modules sold by the manufacturer, but have been dimensioned to the equipment used.

Table 1: Parameters of membranes used

Inner diameter	*Outside diameter*	*Membrane legth*	*Active filter surface*	*Operating pH range*	*Operating pressure range*
$7 \cdot 10^{-3}$ m	$1 \cdot 10^{-2}$ m	$2{,}5 \cdot 10^{-1}$m	$5 \cdot 10^{-3}$ m^2	0-14	0-5 bar

2.4. Methods and tested parameters of emulsions

During the analysis of the emulsions, the particle size and distribution examined were examined by Fritsch Analysette 22, Malvern Zetasizer Nano ZS, and Delta Optical Genetic Pro Bino Microscope Instruments.

2.5. Pilot Plan

The parameters analyzed for the initial flux of the dispersion phase (Jd), the average drop diameter (d_d) and the PDI value (using or without the use of a static mixer) were performed using 3^P type full-factor experimental plans. Data processing was performed with Statistica 6.0 software.

2.6. Static mixers used in the experiments

During the experiments the use of two different manufactured individually static mixers were examined. The width of the twin-spiral-shaped reducers is 6.35 mm (the inner diameter of the pipe diaphragm, inside it is 7 mm), the thickness is 1 mm and the thread pitch is 6 mm. 10 mm. The length of the restrictors is equal to the length of the membrane.

Figure 3: Used static mixers

3. RESULTS

During my work, I was dealing with the possibilities of using the process of membrane emulsification in the food industry and its implementation. My research focused on the production of emulsions made using this technique, specifically for food industry use. To accomplish this, my research was conducted along three main lines.

In order to increase the productivity and to reduce the shear loads, I studied the possible applicability of static mixers. I made experiments by changing the flow parameters, with the baffles placed inside the tubular membrane, and compared the results with the conventional method. I have found that there is no significant difference in how the shear stress required for the process is disclosed during the emulsion production. The flux was almost the same in the conventional mode and in the case of a membrane mounted with a static mixer. Furthermore, based on the tests, it can be stated that, with low driving force, less energy is needed to circulate the continuous phase and the emulsion by using a static mixer, but at the maximum drive force the static mixer pipework requires more work. However, it was found that the presence of baffles did not significantly affect the size of the droplets produced.

Based on the literature analysis, I found deficiencies in the production of a food emulsion based on membrane technology. For this reason, experiments were carried out using a membrane emulsification process for the production of two different types of O / V and V / O, food industry emulsion. One is the O / V type emulsion, which can be used as a hypoallergenic (milk-free) creamer in diaphragm technology, unlike traditional mixing liqueur production technology. By emulsifying the membrane, I poured hazelnut drops into an alcohol distilled water mixture and made an emulsion liqueur from the emulsion prepared previously. The product was subjected to repeated sensory testing before its final form was obtained. The liqueur is low in energy, has moderate alcoholic strength and can also be lactose-sensitive because I did not use cream during production. The other product was a V / O salad dressing, a white wine recipe for sunflower-olive oil blend. Sensory evaluation was also carried out with this product, where a hand-made whip and a membrane emulsifying product were compared with the judges. As a result of the study, the evaluators did not find any significant difference between the two products, but the membrane technique produced a higher score for several properties.

My microencapsulation studies were directed to microcapsule production with membrane technology. During the operation, the initial step of microencapsulation was performed using the emulsion preparation membrane. It focuses on basic research for the production of my work in laboratory conditions, starting from the

analysis of the possible microparticles of microcapsules through the preparation of the microcapsule by studying the resulting microcapsules. By experiments, I proved that the membrane emulsification operation in combination with vacuum suppression proved to be suitable for the production of solid-phase microcapsules precursor.

3.1. NOVEL SCIENTIFIC RESULTS – THESIS

1. Measurements have shown that during the production of membrane emulsion, the operational parameters (the driving force, the shear stress, the presence and absence of the individually manufactured static mixer) do not have a significant effect on the size of the resulting droplets. The average drop diameter of the dispersion phase depends mainly on the pore size of the membrane. The average droplet diameter of the membrane with a pore size of 500 nm was 4000 nm and the average droplet diameter of 6,000 nm in the membrane with a pore size of 1400 nm, the operating parameters and the static mixer did not have a significant effect on the average drop diameter.
2. 2. Modules determining the flux value of the initial dispersion phase characteristic of the emulsification process using a membrane were set up by the presence and absence of a uniquely manufactured static mixer (6.35 mm wide, double-spiral reducer, 6 mm thread pitch). Considering the significant

effects, the model equations developed can be described as follows:

$$J_{d,\,NR} = 0{,}008535 + 0{,}002062 \cdot \left(\frac{DF - 2{,}8}{0{,}8}\right) + 0{,}000648 \cdot \left(\frac{Shearstress - 0{,}4}{0{,}4}\right)^2 + \ldots$$

$$\ldots + 0{,}000505 \cdot \left(\frac{DF - 2{,}8}{0{,}8}\right) \cdot \left(\frac{Shearstress - 0{,}4}{0{,}4}\right) \quad [\mathrm{Lm^{-2}s^{-1}}]$$

$$J_{d,\,R} = 0{,}008535 + 0{,}001585 \cdot \left(\frac{DF - 2{,}8}{0{,}8}\right) + 0{,}000935 \cdot \left(\frac{Shearstress - 0{,}4}{0{,}4}\right) + \ldots$$

$$\ldots + 0{,}005109 \cdot \left(\frac{Shearstress - 0{,}4}{0{,}4}\right)^2 + 0{,}005608 \cdot \left(\frac{DF - 2{,}8}{0{,}8}\right) \cdot \left(\frac{Shearstress - 0{,}4}{0{,}4}\right)$$

$[\mathrm{Lm^{-2}s^{-1}}]$

where J_d is the initial flux of the dispersion phase [Lm-2s-1], whose validity is DF (driving force) = 2 - 3.6; Shearstress = (0 to 0.8) • [10^5 Pa], α = 0.05 at the significance level without using a static mixer (NR-No Reducer) and a static mixer (R-Reducer), 500 nm pore size , With a diameter of 7 mm, using a ceramic tube membrane. In this formula, the 2.8 of the DF extracted is the median of the measurement range. The 0.8 in the denominator DF is half the value of the measuring range. Similarly, the cutout value from Shearstress 0.4 to [10^5 Pa] is the median of the measuring range and the value in the denominator is 0.4 to [10^5 Pa] is the center of the measurement range.

3. I have determined that a static mixer is fitted to a ceramic tube membrane (Pall, Schumasiv) with a diameter of 7 mm (500 mm diameter) in a cross-flow mode. Emulsion production can be achieved by lowering the specific energy savings with respect to emulsion production with a static mixer without a tubular membrane. Based on the experiments, the energy savings were 4 and 14% with the driving force, DF = 2 and shear stress = 0.4 and 0.8 • [10^5 Pa]. However, with the maximum driving force, DF = 3.6 and shear stress = 0.4 and 0.8 • [10^5 Pa], the static mixer has a 7 mm and 17% more work.
4. In my attempts to produce microcapsules precursor, I examined the properties of four different wall materials in aqueous solutions of different concentrations. By examining the average drop diameter and polydispersity index (PDI), I found that only two wall materials (maltodextrin and HPC) in low concentrations of non-polydisperse (PDI <0.4) behavior were observed. Using maltodextrin, I proved in my experiments that the membrane emulsification operation in combination with vascular suppression proved to be suitable for the preparation of a solid phase microcapsule precursor.

4. CONCLUSIONS AND SUGGESTIONS

My new scientific results have proved to be true for the instruments and the samples tested, but their significance is increased, although despite the fact that the use of the static mixer has proved to be effective in the case of various membrane operations, the research on the membrane emulsification is small based on the literature sought . Therefore, my investigations do not make it clear that the baffles placed inside the tubular membrane have had a significant effect on the productivity of the process or on the properties of the resulting emulsion. However, the required shear force was provided at a lower flow rate while the shear stresses decreased in the circulated portion. The mechanical impact sensitive components, for example, starch, proteins, flavors, this property of the method can be utilized.

From the point of view of product development, the membrane emulsification deserves a great deal of attention when homogeneity and well-reproducible droplet distribution are important in our final product. By using membrane technology, better homogenization can be achieved, making it easier to digest and produce more bodied flavors. With the development of the experimental membrane emulsifier equipment, the installation of a larger volume dispersion phase tank would expand the range of products to be made. It would provide an opportunity for the production of larger dispersed phase concentrations, e.g. mayonnaise. Furthermore, it may be interesting to examine the difference in the sensory properties of the salad dressing resulting from the reversal of the phases. Non-oil vinegar

dispersion, but after the production of an emulsion oil dispersion in vinegar, sensory evaluation could form the subject of the test.

In the course of further researches, microcapsule extraction methods may be useful in extending the microcapsule extraction methods by other methods, for example. by spray drying. An interesting aspect may be to investigate the effect of microencapsulation on the static mixer during further studies.

LIST OF PUBLICATIONS RELATED TO THE DISSERTATION

Articles in journals with impact factor		
type	***year***	***publication***
journal	*2016*	***K. Albert**, Gy. Vatai, L. Giorno, A. Koris (2016): Energy-saving potential of cross-flow membrane emulsification by ceramic tube membrane, 2014, Membrane Water Treatment, DOI: 10.12989/mwt.2016.7.3.175, IF=0.625 (2015)*
journal	*2015*	***K. Albert**, Cs. Tóth, Gy. Vatai , A. Koris (2015): Microencapsulation analysis based on membrane technology: basic research of spherical, solid precursor microcapsule production. Periodica Polytechnica Chemical Engineering, DOI: 10.3311/PPch.8500, IF=0.296 (2015)*
journal	*2014*	***K. Albert**, A. Koris, S. Ahammed, I. Gáspár, Gy. Vatai (2014): Vinaigrette production by membrane emulsification: Process optimization and product development, Periodica Polytechnica Chemical Engineering, DOI: 10.3311/PPch.7583, IF= 0.296 (2015)*
journal	*2014*	***K. Albert**, A. Koris, I. Gáspár, G. Rácz, Gy. Vatai (2014): Production of microemulsion by membrane emulsification: Comparison of empty ceramic tube membrane and membrane equipped with static turbulence promoters, Acta Alimentaria, DOI: 10.1556/AAlim.43.2014.Suppl.2, IF=0.274 (2015)*

International conference full text		
type	***year***	***publication***
conference presentation	*2016*	***K. Albert**, A. Koris, Gy. Vatai (2016): Application of membrane emulsification process in the food industry, PERMEA 2016 - Membrane Science and Technology Conference of Visegrád Countries, Prague, Czech Republic*
conference presentation	*2016*	***K. Albert**, A. Koris, Gy. Vatai (2016): Food emulsion production by membrane technology, Chemical Engineering Days '16, Veszprém, Hungary*
conference presentation	*2015*	***K. Albert**, A. Koris, Cs. Tóth, Gy. Vatai (2015): Microencapsulation analysis based on membrane technology: basic research of spherical, solid precursor microcapsule production, Chemical Engineering Days '15, Veszprém, Hungary*
conference presentation	*2014*	***K. Albert**, A. Koris, S. Ahammed, I. Gáspár, Gy. Vatai (2014): Vinaigrette production by membrane emulsification: Process optimization and product development, Chemical Engineering Days '14, Veszprém, Hungary (ISBN 978-963-010-3) 2014*
conference presentation	*2013*	*A. Koris, **K. Albert**, S. Ahammed, S. Chakraborty, I. Gáspár, Gy. Vatai (2013): Applied research on fine vinaigrette emulsion production by special membrane technique, Food Science Conference, Budapest, Hungary (ISBN 978-963-503-550-2)*
conference presentation	*2012*	***Albert K.**, Koris A., Vatai Gy. (2012): Mikroemulzió előállítása membrán emulzifikálás módszerével, Műszaki Kémiai Napok '12, Veszprém, Magyarország, (ISBN 978-615-5044-54-0)*

International conference abstract		
type	***year***	***publication***
poster presentation	*2014*	***K. Albert**, A. Koris, S. Ahammed, Gy. Vatai (2014): New engineering approach of salad dressing (vinaigrette) production, 8th International Congress of Food Technologists, Biotechnologists and Nutritionists, Opatija, Croatia*
poster presentation	*2014*	***K. Albert**, A. Koris, D. Simon, Gy. Vatai (2014): New engineering approach of cream liqueur production, 3rd Interdisciplinary Doctoral Conference, Pécs, Hungary, (ISBN 978-963-642-597-5)*
poster presentation	*2013*	***K. Albert**, A. Koris, I. Gáspár, G. Rácz, Gy. Vatai (2013): Production of microemulsion by ceramic tube membrane equipped with static turbulence promoter, Food Science Conference, Budapest, Hungary (ISBN 978-963-503-550-2)*
poster presentation	*2012*	***K. Albert**, A. Koris, Gy. Vatai, E. Piacentini, L. Giorno (2012): Production of microemulsion by ceramic tube membrane equipped with static turbulence promoter, Euromembrane 2012, London, England, Procedia Engineering Volume 44, Pages 1161–1162.*