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Energy-saving potential of cross-flow membrane emulsification by ceramic tube membrane with inserted cross-section reducers

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Abstract. In this work, oil-in-water emulsions (O/W) were prepared successfully by membrane emulsification with 0.5 μm pore size membrane. Sunflower oil was emulsified in aqueous Tween80 solution with a simple cross-flow apparatus equipped with ceramic tube membrane. In order to increase the shear-stress near the membrane wall, a helical-shaped reducer was installed within the lumen side of the tube membrane. This method allows the reduction of continuous phase flow and the increase of dispersed phase flux, for cost effective production. Results were compared with the conventional cross-flow membrane emulsification method. Monodisperse O/W emulsions were obtained using tubular membrane with droplet size in the range 3.3-4.6 μm corresponded to the membrane pore diameter of 0.5 μm. The final aim of this study is to obtain O/W emulsions by simple membrane emulsification method without reducer and compare the results obtained by membrane equipped with helix shaped reducer. To indicate the results statistical methods, 3^p type full factorial experimental designs were evaluated, using software called STATISTICA. For prediction of the flux, droplet size and PDI a mathematical model was set up which can describe well the dependent variables in the studied range, namely the run of the flux and the mean droplet diameter and the effects of operating parameters. The results suggested that polynomial model is adequate for representation of selected responses.

Keywords: membrane emulsification; shear-stress; static turbulence promoter; modelling; oil-in-water emulsion

1. Introduction

Membrane emulsification (ME) is a relatively new technique for the highly controlled production of particulates. In this process, the dispersed phase (oil) is pressed through the pores of a microporous membrane directly into the continuous phase (water) flowing tangentially to the membrane surface. Emulsified droplets are formed and detached at the end of the pores with a drop-by-drop mechanism. The droplet detachment is governed by the balance between the drag force on the droplet from the flowing continuous phase, the interfacial tension forces, the buoyancy of the droplet, and the pressure difference between the phases (De Luca and Drioli 2006, De Luca *et al.* 2008). In order to ensure a regular droplet detachment from the pore outlets, shear

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stress is generated at the membrane/continuous phase interface by recirculating the continuous phase using a pump or by agitation in a stirring vessel (Vladisavljevic and Williams 2005).

The advantages of membrane emulsification over conventional emulsification processes are that it enables to obtain very fine emulsions of controlled droplet sizes and narrow droplet size distributions. Successful emulsification can be carried out with much less consumption of emulsifier and energy, and because of the lowered shear-stress effect, membrane emulsification allows the use of shear-sensitive ingredients, such as starch and proteins (Vladisavljevic *et al* 2000).

The manufacturing process of these emulsions must meet a number of constraints such as water fraction, mean droplet size, delivered flow rate and process energy consumption. The size of the droplets and the droplet size distribution strongly depended on the membrane pre-treatment procedure, the transmembrane pressure, the dispersed phase content and the emulsifier concentration. Increasing the pressure increases droplet sizes, and can be related to the different mechanisms of droplet detachment from the membrane. An increase in the linear cross flow velocity was shown to cause a decrease in the diameter of the produced droplets. The different membranes each have different characteristics (Hancocks *et al* 2013).

Among the techniques available for continuous production of emulsions, those based on the formation of droplets through micro pores or membranes allow obtaining droplet sizes characterized by relatively small size distribution and by a mean size of the order 0.1–10 μm (Silvestre De Los Reyes and Charcosset 2010). Between possible techniques, one of the newest focuses on the implementation of crossing michrochannels. The results show the feasibility of obtaining mean size of droplets comprised in the range 1–10 μm in water in oil emulsions obtained using simple T-shape micromixers with several operating conditions. Channel geometry and flow pattern have a significant influence on the possibility of forming emulsions (Montillet *et al*. 2013).

An alternative method of keeping low shear away from the membrane surface is to replace the commonly used stationary membrane by a moving membrane, in which case droplet detachment from the membrane surface is facilitated by rotating (Manga *et al*. 2012, Vladisavljevic and Williams 2006) or vibrating (Zhu and Barrow 2005,) the membrane within an otherwise static continuous phase.

One of the innovative methods for generating shear at the surface of a membrane for the purpose of ME is by pulsing the flow over the membrane surface formed from a tube. This method has a particular advantage of being capable of being interfaced with a reactor downstream of the droplet generation stage, for example, in the case of the formation of polymer particles, coacervates, and so forth where the oscillatory nature of the flow can be used to provide good mixing and conditions approaching plug flow within the reactor (Holdich *et al*. 2010, 2013).

In literature it is reported that helical baffles are likely to perform better compared to rod inserts, implying that the helical vortices improve the mixing between the boundary layer on the surface of the membrane and the bulk fluid to a greater degree than by simply generating turbulent flow using cylindrical rod inserted (Ahmad *et al* 2005).

According to these researches Koris *et al*. (2011) established that, with a simple mechanical method, by insertion of static turbulence promoters, it was possible to increase shear stress at the membrane surface, while maintaining a low shear in the recirculation loop. They could obtain very good emulsion quality in terms of droplet size distribution and stability, even operating at high dispersed phase flux values (Koris *et al*. 2011).

The present paper deals with a simple, static method, which is cost-effective and is able to 7increase the productivity of cross-flow membrane emulsification with satisfying quality. For each preparation, the flux of the dispersed phase through the membrane, the droplet size distribution and PDI (polydispersity index) were measured.

2. Materials and methods

2.1 Materials

In laboratory experiments from conventional, commercially grade sunflower oil (dispersed phase) and from distilled water solution (continuous phase) emulsions were prepared. The 1.5 m/m % continuous phase was formed from Tween 80 (Sigma-Aldrich Chemie GmbH) organic surfactant and distilled water. Concentrations are given as weight percentages (%).

2.2 Membranes

The ceramic tube membrane (Pall Schumacher Corporation) with nominal pore size of 0.5 μm was used in the experiments (active ZrO_2 layer). The membrane length was 0.25 m, the inner diameter 7×10^{-3} m and outer diameter 9×10^{-3} m. Therefore, the active membrane surface was 5×10^{-3} m^2.

2.3 Apparatus

A cross flow membrane emulsification system was used to produce all emulsions. Before the installation the membrane was conditioned, it was wetted with the continuous phase under vacuum (-5×10^4 Pa) in ultrasonic bath to remove the air bubbles from the inside of the pores. The experimental set-up used for the experiments is shown in Fig. 1. The apparatus is very simple; it was designed from practical application viewpoint. It included two manometers, one placed at the

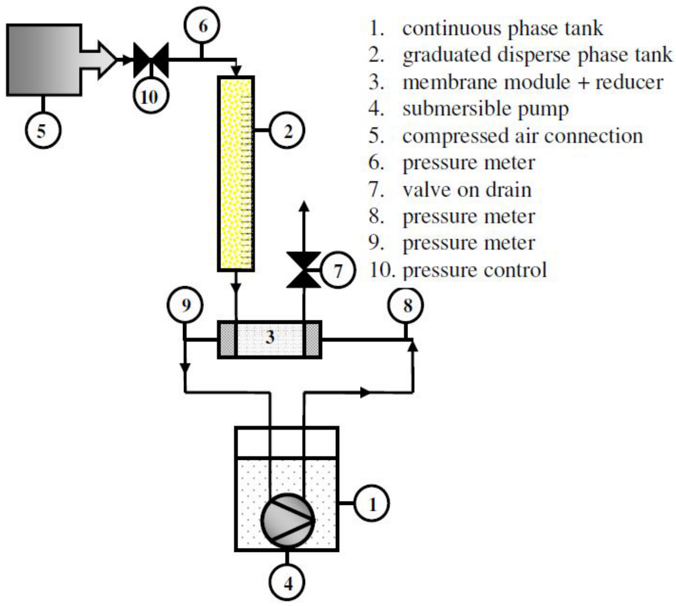


Fig. 1 Scheme of the cross-flow membrane emulsification apparatus

inlet of the membrane and the other placed at the outlet of the membrane, were used to measure the pressure drop through the membrane. The continuous phase was recirculated along the lumen side of the membrane by a submersible pump. The oil pressure was guaranteed by compressed air with an air pump and it was injected from the outer surface of the membrane. The bottom of the disperse phase tank was connected to the membrane and the top was connected with the compressor to ensure the pressure of oil. There was another manometer, between the compressor and dispersed phase tank, which was indicating the pressure of the disperse phase tank.

2.4 Membrane emulsification

In the emulsification experiments two parameters were changed: the pressure of disperse phase (expressed in DF-driving force) and the recirculation flow (shear stress at the wall of the membrane).The disperse phase flux was determined by volume, upon the oil consumption from the graduated feed tube by using formulas. The experiments were carried out at room temperature. The axial cross-flow velocity in the tube membranes was varied by 0.35 m/s and 0.7 m/s when the re-circulated flow-rate (RFR) was set to 50 L/h and 100 L/h respectively on the pump. The shear-stress was observed as 0.4 Pa and 0.8 Pa accordingly. The emulsion was also prepared without any cross-flow in which case the re-circulated flow rate and shear stress were 0. The applied transmembrane pressure (TMP) was varied between 1 and 1.8×10^5 Pa.

The system and the membrane were cleaned between the experiments with ULTRASIL-11 (~1% m/m) solution when it was necessary. After a series of experiments, before storage, cleaning procedures followed, according to the recommendation of the manufacturer (Nakashima *et al* 1991).

In order to increase the shear-stress near the membrane wall (influence the characteristics of the flow regime of the continuous phase), a kind of self-fabricated helical-shaped-ribbon reducer was installed inside the tube membrane. It was a double helix-shaped-ribbon reducer (Fig. 2) with the width of 6.35 mm, as well, 1 mm thickness and the pitch was 6 mm. The promoter has a length equal to the membrane. In these conditions, the shear-stress of a cross-flow membrane emulsification was greatly increased at the membrane level, while maintaining a low value along the circuit.

2.5 Droplet size measurements

The droplet size and the droplet size distribution in the made emulsion samples were measured

Fig. 2 Photo of the helix reducer

by Malvern Zetasizer Nano equipment. The particle size measured in a DLS (Dynamic Light Scattering) instrument is the diameter of the sphere that diffuses at the same speed as the particle being measured. The emulsion samples were measured by a so called SOP measurement. Standard Operating Procedure (SOP) is like a template that pre-defines all the measurement settings. This ensures that measurements made on the same type of sample are made in a consistent way. SOPs are ideal if the same type of sample is regularly measured, using pre-set parameters (that have previously been defined) we can avoid the risk of making errors in the settings.

The pre-set parameters of the SOP created are the followings: the selected measurement type is size measurement, the cell used is DTS0012-Disposable sizing cuvette, the material is sunflower seed oil (Absorption = 0.001, RI (Refractive Index) = 1.46), dispersant is water (RI = 1.33), the temperature of the measurement is 25°C, the equilibrium time is 120 seconds, the angle of detection is 173° Backscatter (NIBS default),the duration of the measurement is automatic, and 2 times make multiple measurements of the same sample.

2.6 Calculations and experimental design

The purpose of the experimentations was to establish a model for the conditions of the operation. To indicate the results statistical methods, 3^p type full factorial experimental designs were evaluated, using software called STATISTICA. In this experiment, the effect of driving force (DF), shear stress (τ) (regulated by flow rate) and pore size were investigated as independent variables. On the contrary, the fluxes, diameter of droplets and PDI were used as dependent

Table 1 Design variables and their ranges

Independent factors	Code	Min. value (-1)	Centre point (0)	Max. value (+1)
Driving force	x_1	2	2.8	3.6
Shear-stress, Pa	x_2	0	0.4	0.8

Table 2 The values of independent factors and responses

Independent factors		Responses without reducer			Responses with reducer		
Driving force	Shear-stress, Pa	Flux, L/m^2/s	Droplet size, nm	PDI	Flux, L/m^2/s	Droplet size, nm	PDI
2	0	6.07×10^{-3}	4343	0.279	4.71×10^{-3}	1010	0.154
2.8	0	8.51×10^{-3}	4361	0.178	7.69×10^{-3}	4572	0.34
3.6	0	9.31×10^{-3}	3839	0.142	1.003×10^{-2}	3297	0.356
2	0.4	7.57×10^{-3}	3714	0.288	8×10^{-3}	4019	0.232
2.8	0.4	9.31×10^{-3}	4718	0.17	9.31×10^{-3}	4466	0.192
3.6	0.4	1.14×10^{-2}	4628	0.321	1.08×10^{-2}	3719	0.248
2	0.8	7.28×10^{-3}	3309	1	5.56×10^{-3}	3440	0.538
2.8	0.8	8.35×10^{-3}	3565	0.831	8.89×10^{-3}	3477	0.161
3.6	0.8	1.08×10^{-2}	3954	0.231	1.02×10^{-2}	3306	0.192
2.8	0.4	9.76×10^{-3}	4871	0.177	1.02×10^{-2}	4032	0.252
2.8	0.4	9.31×10^{-3}	4118	0.201	9.76×10^{-3}	4545	0.292

variables. The effects of independent variables on dependent variables were observed. The centre point (τ = 0.4 Pa and DF = 2.8) was repeated 2 times.

The design variables and their ranges can be found in Table 1 and the factorial experimental design and responses in Table 2.

The cross-flow membrane emulsification method involves using a transmembrane pressure to force the dispersed phase to permeate through the membrane into the continuous phase. The transmembrane pressure, TMP, is defined as the difference between the pressure of the dispersed phase, P_d, and the mean pressure of the continuous phase, Eq. (1)

$$TMP = P_d - \frac{P_{c.in} + P_{c.out}}{2} \tag{1}$$

where $P_{c,in}$ and $P_{c,out}$ are the pressure of the flowing continuous phase at the inlet and at the outlet of the membrane device, respectively. The applied transmembrane pressure required to make the discontinuous phase (e.g., water) flow can be estimated from the capillary pressure, assuming that the pores are ideal cylinders, Eq. (2)

$$P_c = \frac{4\gamma_{ow}\cos\varphi}{d_p} \tag{2}$$

where P_c is the capillary pressure, γ_{ow} the O/W interfacial tension, φ the contact angle of the oil droplet against the membrane surface well wetted with the continuous phase and d_p the mean pore diameter. The actual transmembrane pressure required to make the discontinuous phase flow may be greater than predicted by Eq. (1), due to tortuosity in the pores, irregular pore openings at the membrane surface and the significant effects of surface wettability (Williams *et al*. 1998).

The driving force (DF) is expressed as the ratio of transmembrane pressure (TMP) and critical pressure (CP) according to Eq. (3).

$$DF = \frac{TMP}{CP} \tag{3}$$

P_c are the pressures at the dispersed phase side and at the continuous phase side, respectively. The dispersed phase flux (J_d) increases as the mean pore diameter and/or the transmembrane pressure (TMP) increases. The flux, J_d, is given as a function of TMP by Darcy's law (Schröder and Schubert 1999)

$$J_d = \frac{TMP}{\mu_d R_m} \tag{4}$$

where μ_d is the viscosity of the dispersed phase (Pa·s) and R_m is the intrinsic membrane resistance (m^{-1}). It may be experimentally determined by measuring pure water flux at different TMP values since the resistance depends only on membrane characteristics, such as pore size, porosity and tortuosity (Matos *et al*. 2013).

The critical pressure is equivalent to the minimum pressure required to obtain dispersed phase permeation that is the capillary pressure, P_c. In the present work CP was determined experimentally, following the instructions of the producer (Nakashima *et al*. 1991).

The shear stress (τ) near lumen side membrane surface is calculated from Eq. (5).

$$\tau = \frac{\lambda \cdot \rho \cdot v^2}{2} \text{ [Pa]} \tag{5}$$

where λ is the friction factor (in laminar flow $\lambda = 16/R_e$), ρ is the density of the continuous phase (kg/m^3), and v is axial cross-flow velocity (m/s).

The polydispersity index (PDI) is a measure of the distribution of molecular mass in a given polymer sample. If one were to assume a single size population following a Gaussian distribution, then the polydispersity index would be related to the standard deviation (σ) of the hypothetical Gaussian distribution in the fashion shown below, Eq. (6) (Arzensek 2010)

$$PDI = \frac{\sigma^2}{z_D^2} \tag{6}$$

where Z_D is Z average size, the intensity weighted mean hydrodynamic size (cumulants mean) of the ensemble collection of particles.

2.7 Configuration with helix reducer

The shear stress (τ) near the lumen side of the membrane surface is calculated from Eq. (7)

$$\tau = k \cdot \frac{\lambda \cdot \rho \cdot v^2}{2} \text{ [Pa]} \tag{7}$$

The constant k is a geometry dependent correction coefficient for the system with non-cylindrical insert. In case of empty, cylindrical tube and tube with the smooth reducer the value of k is equal 1. To evaluate the factor k for helix turbulence promoter, the Eq. (8) can be used

$$k = \frac{R \cdot \pi + a + b}{[R \cdot \pi + z(a+b)]} \tag{8}$$

where a and b are the geometric parameters of the helix turbulence promoter (a = 0.00635 m, b = 0.001 m), and R is the inner radius of the tube (R = 0.0035 m). The absolute length ratio of the promoter z is calculated by Eq. (9)

$$z = \frac{H}{c} \tag{9}$$

where H and c are the geometrical parameter of helix turbulence. The equivalent diameter of cross-section in the "helix" system is calculated by Eq. (10)

$$D_e = 4\frac{R^2\pi - a \cdot b}{2R\pi + 2(a+b)} \tag{10}$$

2.8 Calculation of pumping energy

The efficiency of the reducer as a turbulence promoter was also determined by evaluating the reduction of specific energy consumption (ER). One of the most important parameter from an economical point of view is the specific energy consumption, E, defined as the power dissipated per unit volume of permeate. The hydraulic dissipated power can be expressed as the product of the feed flow rate and pressure drop along the module, Eq. (11)

$$P = Q \cdot \Delta P \tag{11}$$

where P (W) is the hydraulic dissipated power, Q (m^3/s) is the feed flow rate, and ΔP (Pa) is the pressure drop observed along the membrane (Jokic *et al*. 2010).

3. Results and discussion

3.1 Determination of critical pressure and dispersed phase flux measurements

The critical pressure (CP) of sunflower oil for 0.5 μm membrane was successfully measured, it was found to be 30 kPa. With the help of this data, driving forces could be calculated for each experiment by Eq. (3). In the experiments, the results of which are introduced in this part, the final concentration of oil in the emulsions was 2 w/w%.

The dispersed phase flux values measured at different driving forces are indicated in Fig. 3. These experiments were carried out to demonstrate how the shear-stress generated by static mixing affects the flux of the dispersed phase compared to conventional (No Reducer) mode. The necessary driving force to achieve a given flux can be determined From Fig. 3, in case of different shear-stresses and 0.5 μm membrane. Since the approximation of the curve as a straight is good, R^2 is bigger than 0.92 in case off every shear-stresses, also with and without an inserted cross-section reducer, the scale up of the process looks comfortable.

There is a nearly linear relation between flux and driving force, the slopes are almost the same. It was observed that flux was increased with driving force while shear stress has less effect on flux. The biggest values of flux was obtained when the shear-stress was medium (τ = 0.4). At low

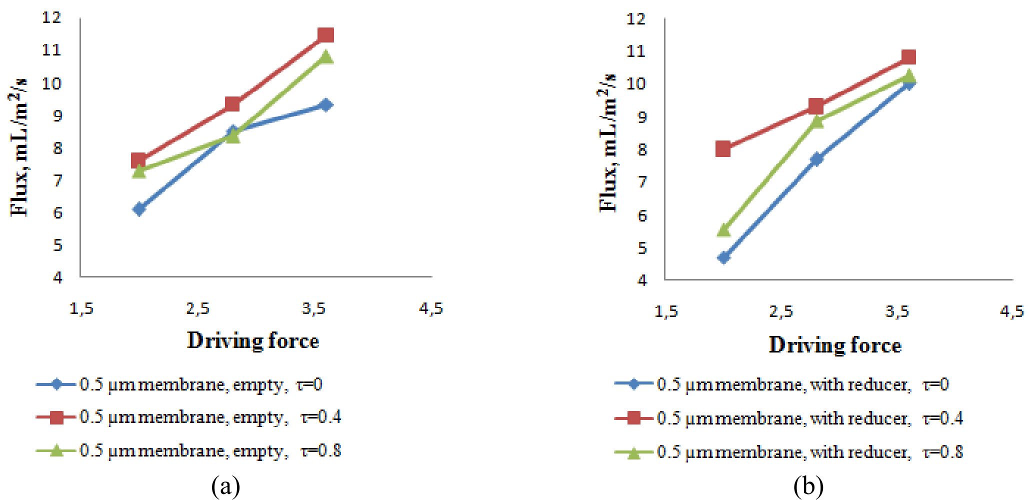


Fig. 3 Dispersed phase flux values on different driving forces and shear-stresses (a) without reducer; and (b) with reducer

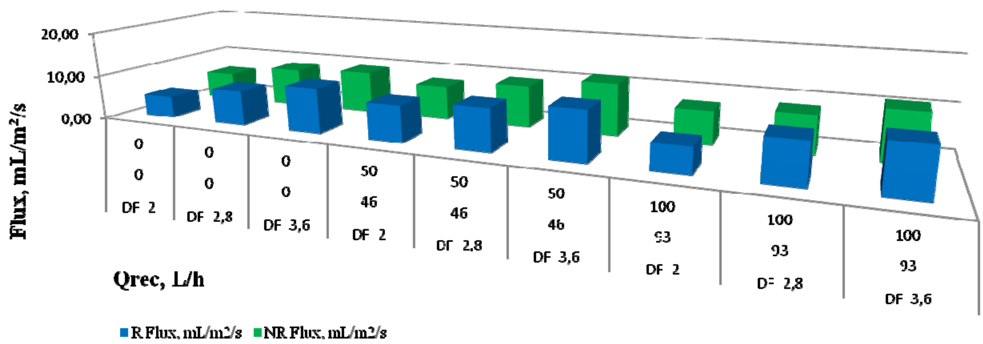
pressure (DF = 2), on τ = 0 Pa and τ = 0.8 Pa, there is a significant difference between the fluxes. In these cases the flux was found a little smaller in presence of reducer compared to the flux obtained without reducer. This phenomenon could be caused because of the reducer which was installed inside the membrane possibly “blocks” the path of oil.

3.2 Relative comparison of NR (No Reducer) and WR (With Reducer) mode for membrane emulsification

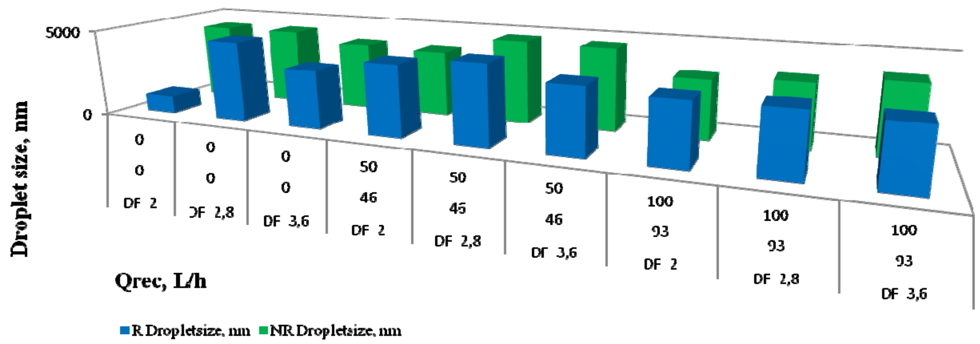
The flow-rate were set 0, 50 and 100 L/h for preparing of emulsion at the absence of reducer while using reducer it were set 0, 46 and 93 L/h in order to keep the same shear stresses (0, 0.4, 0.8), respectively. On the contrary, the driving force was same for both cases. In all Figs. 4(a), (b) and (c), the blue column represents the result obtained by using reducer (*R*). On the other hand, the green column represents the result of similar operating parameters (DF and τ) in the absence of reducer (NR).

The flux was found about the same on every DF in presence of reducer compared to the flux obtained without using reducer (Fig. 4(a)). It seems that there is no significant different in emulsion preparation, whatever the way to impart the shear stress necessary during the process.

The mean diameter of droplets is represented by the Fig. 4(b). In most of the cases (in 6 from 9) the droplet diameter was found bigger for NR than R. At the biggest driving force the droplet size was smaller using reducer in every case. At minimum, medium and maximum shear-stresses can

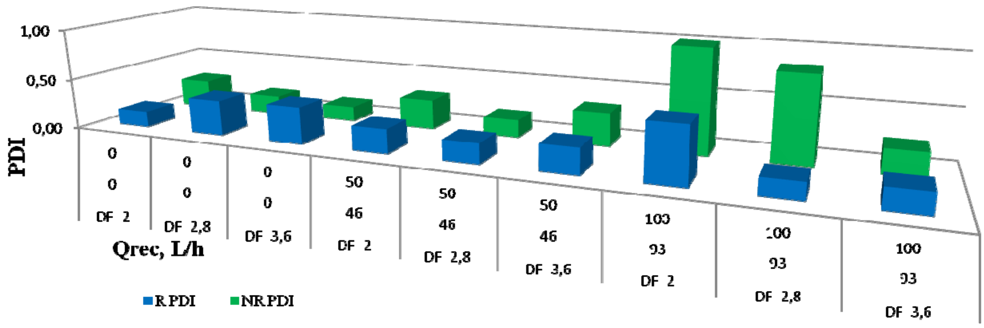


(a)



(b)

Fig. 4 (a) Difference of flux; (b) droplet size; and (c) PDI with or without reducer for 0.5 μm membrane



(c)

Fig. 4 Continued

be observed the same mechanism; from 3 cases in 2 times the droplet size diameter was lower using reducer. It can be concluded that the droplet diameter was a little lower using the reducer.

The PDI of emulsions prepared by using without or with reducer is shown in Fig. 4(c). In most of the cases, the value of PDI was found better when the reducer was used, except when shear stress was at minimum. The best result of PDI was found when the shear stress was medium in the presence of reducer. From the diagram it was observed that on bigger shear stresses with using of reducer we get better quality of emulsions. There was a specific behaviour observed when the emulsions were prepared with or without using the reducer.

In an earlier work of the authors (Koris *et al.* 2011) glass membranes were investigated in parallel use with 2 kind of different static mixer prototype. In present work a ceramic MF membrane was applied with an optimized static mixer. Furthermore, the experiments were carried out on lower DF values to gain more detailed information – compared to previous work - on how the setup is working low DF and shear stress parameters. The little difference between emulsion properties obtained with and without reducer observed in this work is probably due to the low disperse phase percentage and to the low flow rate to reach the desired shear stress. In this case, it was evidenced that the presence of static promoter, for high shear stress range, improved significantly the quality of the emulsion.

3.3 Establishing of model

To establish models for prediction of the flux, droplet size and PDI, 3^p type full factorial experimental design was used. In this method, the unknown to be optimized function is replaced

Effect Estimates; Var.:Flux, mL/m²/s; R-sqr=,9592; Adj:,91839 (3**(2-0) full factorial design, 1 block , 9 runs (3**(2-0) full factorial design, 2 3-level factors, 1 Blocks, 11 Runs; MS Residual=,1977793
DV: Flux, mL/m²/s

Factor	Effect	Std.Err.	t(5)	p	-95,% Cnf.Limt	+95,% Cnf.Limt	Coeff.	Std.Err. Coeff.	-95,% Cnf.Limt	+95,% Cnf.Limt
Mean/Interc.	8,751754	0,140222	62,41347	0,000000	8,391302	9,112207	8,751754	0,140222	8,391302	9,112207
(1)Driving forse(L)	3,550000	0,363115	9,77650	0,000190	2,616582	4,483418	1,775000	0,181558	1,308291	2,241709
Driving forse(Q)	0,010263	0,279411	0,03673	0,972121	-0,707987	0,728513	0,005132	0,139706	-0,353993	0,364257
(2)Shear-stress(L)	0,853333	0,363115	2,35003	0,065557	-0,080085	1,786751	0,426667	0,181558	-0,040042	0,893376
Shear-stress(Q)	1,085263	0,279411	3,88410	0,011594	0,367013	1,803513	0,542632	0,139706	0,183507	0,901757
1L by 2L	0,150000	0,444724	0,33729	0,749598	-0,993199	1,293199	0,075000	0,222362	-0,496600	0,646600

Fig. 5 Effect on principal parameters on oil flux without reducer

ANOVA; Var.:Flux, mL/m²/s; R-sqr=,9592; Adj:,91839 (3**(2-0) full factorial design, 1 block , 9 runs (3**(2-0) full factorial design
2 3-level factors, 1 Blocks, 11 Runs; MS Residual=,1977793
DV: Flux, mL/m²/s

Factor	SS	df	MS	F	p
(1)Driving forse(L)	18,90375	1	18,90375	95,58002	0,000190
Driving forse(Q)	0,00027	1	0,00027	0,00135	0,972121
(2)Shear-stress(L)	1,09227	1	1,09227	5,52265	0,065557
Shear-stress(Q)	2,98375	1	2,98375	15,08626	0,011594
1L by 2L	0,02250	1	0,02250	0,11376	0,749598
Error	0,98890	5	0,19778		
Total SS	24,23607	10			

Fig. 6 ANOVA chart for flux without reducer

with another relatively simple function. The benefit of this method is that with relatively low number of measurements we can reach the objective function, meaning that these factors are not only quantitative, but qualitative as well. With the help of the function describing the process we may find the optimal operating range of typical values of the independent variables.

The modelling result of flux is presented in Fig. 5 where the summary of effect estimate can be found. The value of *R* square was found good which means the model fitting was successful. It was found to be 0.959 which indicates that only 4.1% of the variations could not be explained by the model. The first part of the table contain the effects, its standard deviation, the *t*-test statistics, and the first type I error committed *p* is the probability. Estimated coefficients can be found in the second part of the table. Eq. (12) is the mathematical model for flux with real parameters is introduced

$$J(DS)_{NR} = 4045.19 + 175.83 \cdot \left(\frac{DF - 2.8}{0.8}\right) + 121.4 \cdot \left(\frac{DF - 2.8}{0.8}\right)^2 - 285.83 \cdot \left(\frac{Shearstress - 0.4}{0.4}\right) + 225.04 \cdot \left(\frac{Shearstress - 0.4}{0.4}\right)^2 \tag{12}$$

Mathematical models can be established to describe the flux, mean droplet diameter and PDI, in case of using reducer and without reducer with using the estimated coefficients in Table 3.

From the Fig. 6, it can be observed that the value of *p* for linear effect of driving force and quadratic effect of shear stress found less than 0.05. It can be concluded that all parameters have a significant effect on oil flux. A similar behavior was already observed without reducer. In case of droplet size and PDI the same routine were applied.

3.4 Effect estimation on flux, droplet size and PDI

The experiments were carried out with 0.5 μm membrane without reducer and equipped with helical-shaped-ribbon reducer. For both cases a model was fitted to observe the dependent variables (Flux, Droplet size, PDI), that include main effects for factors, their interactions, linear and quadratic components. The results of the statistical analysis according to the experimental plan are presented in Table 3. The coefficients are related to actual variables. The dependent variables (Flux, Droplet size, PDI) and the different effects are summarized. Relatively high values of R^2 obtained for all responses indicate good fit of experimental data. All polynomial models tested for the selected responses were significant at 95% confidence level (*p*-value; 0.05, Table 3). The significance of each coefficient was determined by p-values. The smaller the magnitude of the p-value the more significant is the corresponding coefficient.

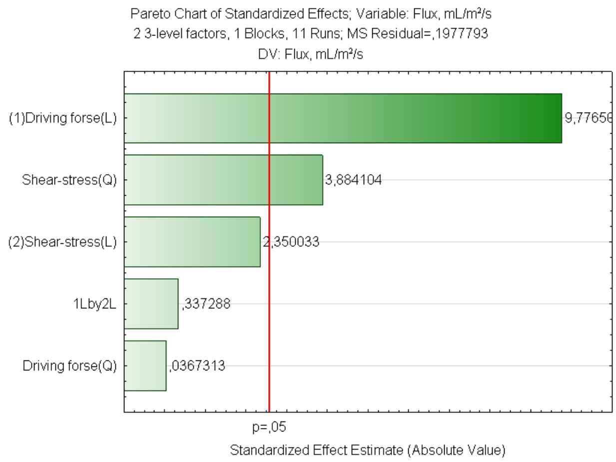


Fig. 7 Pareto chart of standardized effect on flux (0.5 μm, without reducer)

The different effects on various parameters can be observed for example with Pareto charts. The purpose of a Pareto diagram is to separate the significant aspects of a problem from the trivial ones.

3.4.1 Effect estimation on flux for 0.5 µm membrane without reducer

The Pareto chart of effects on flux (Fig. 7) shows the effects of each factor on a visually easily understandable figure. The red vertical line separates the range of the level 95% significance of probability (p) value. Based on this can be concluded that the greatest extent of the main effects is the linear member of the driving force (Driving Force (L)) which affects the magnitude of the flux. Then the second biggest effect on the flux above the effect is the quadratic member of shear-stress. The other effects were not significant ($p > 0.05$), however they are necessary for good-fitting model.

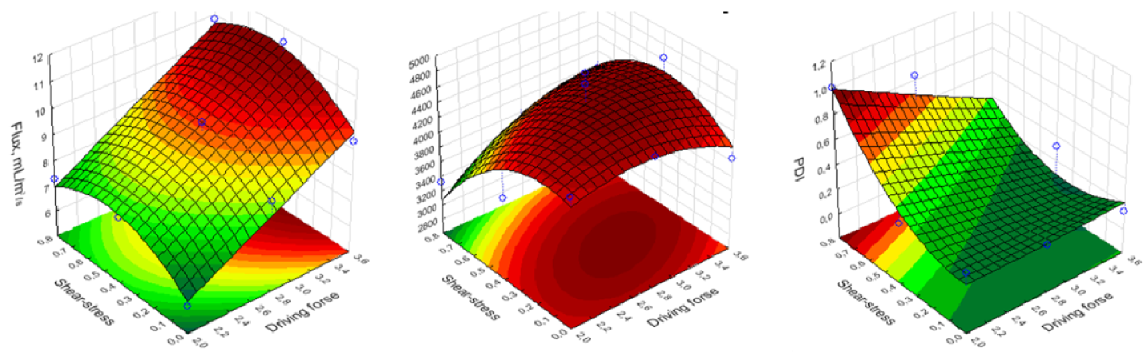
As for significance of the polynomial coefficients, its p-values suggest, that among main effects, the linear member of driving force has significant effect on the flux in both cases, using and without reducer neither does the L (linear) member of shear-stress. Another important effect on the flux is the quadratic member of shear-stress also in both cases. The results show that in case of 0.5 μm membrane the presence of the reducer doesn't effects the droplet size (p-value less than 0.05) It is important since the diameter of the emulsion droplets is mainly controlled by the shear-stress near the membrane surface according to the literature. The results also show that the PDI is mainly controlled by the shear-stress. On the other side, the linear member of driving force, the interactions and the linear member of shear stress have also significant effect on PDI in case of 0.5 μm membrane equipped with reducer. According to the statistical analysis, the linear member of shear-stress has significant effect on PDI in one case: using membrane equipped with reducer. Without reducer only the main effect of shear-stress has significant effect on PDI, inside the investigated rage.

3.5 Graphical optimisation

The effects of driving force and shear-stress above the membrane surface can be seen in the following graphs in case of empty tube (Figs. 8(a)-(c)) and in case of using reducer (Figs. 9(a)-(c)).

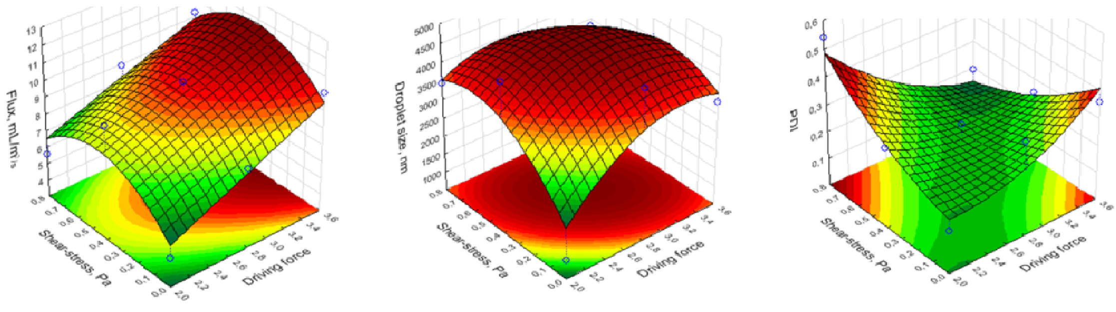
Table 3 Regression equation coefficients for responses (L-linear, Q-quadratic)

Flux, $mL/m^2/s$	Intercept β_0	Driving force (L)	Shear-stress, Pa (L)	Driving force (Q)	Shear-stress, Pa (Q)	Interaction of the two factors
0.5 μm membrane, empty tube	8.75	1.77	0.42	0.005	0.54	0.075
p-value	0.0000	0.0002	0.0656	0.9721	0.0116	0.7496
0.5 μm membrane, with reducer	8.5326	1.8467	0.3800	0.01394	1.0139	-0.1550
p-value	0.0000	0.0125	0.4682	0.9716	0.0417	0.8043
Droplet size, nm	Intercept β_0	Driving force (L)	Shear-stress, Pa (L)	Driving force (Q)	Shear-stress, Pa (Q)	Interaction of the two factors
0.5 μm membrane, empty tube	4045.19	175.83	-285.83	121.03	225.03	287.25
p-value	0.0000	0.2849	0.1093	0.3332	0.1030	0.1712
0.5 μm membrane, with reducer	3470.66	221.16	224	376.75	430.50	-605.25
p-value	0.0001	0.5637	0.5589	0.2296	0.1788	0.2259
PDI	Intercept β_0	Driving force (L)	Shear-stress, Pa (L)	Driving force (Q)	Shear-stress, Pa (Q)	Interaction of the two factors
0.5 μm membrane, empty tube	0.3736	-0.1455	0.2438	-0.0048	-0.1048	-0.158
p-value	0.0007	0.0768	0.0136	0.9281	0.0920	0.1058
0.5 μm membrane, with reducer	0.2770	-0.0313	0.0068	-0.0294	-0.0196	-0.137
p-value	0.0001	0.3709	0.8388	0.2846	0.4597	0.0171



(a) (b) (c)

Fig. 8 Fitted 3D surfaces the effects of driving force and shear-stress on (a) flux; (b) droplet size; and (c) PDI in case of empty tube, 0.5 μm membrane



(a) (b) (c)

Fig. 9 Fitted 3D surfaces the effects of driving force and shear-stress on (a) flux; (b) droplet size; and (c) PDI in case of using reducer, 0.5 μm membrane

Flux:

From the Figs. 8(a) and 9(a) of fitted surface, it was observed that the flux was steady increased with an increasing driving force, as transmembrane pressure is the driving force in emulsification process. The reason for this kind of behaviour may be found in increase in cross-flow velocity when flow rate is increased and in this way the accumulation of oil droplets at the membrane surface is less prominent, so the dispersed phase flux increased.

On the other hand, shear stress has least intensive effect on flux compared to driving force. A bit the interaction of these two factors is also visible, the surface is slightly twisted. In case of using reducer, on the Fig. 9(a) the same method can be observed: the driving force increases the flux, while the shear-stress after the medium point ($\tau = 0.4$) causes the opposite, the flux decreases.

Droplets:

The response surface model for the effects on droplet size is shown in Fig. 8(b) in case of without reducer and in Fig. 9(b) in case of using reducer. The figure clearly shows that in case of using reducer the increase of driving force and shear-stress increases the average values of droplet size diameter. The interaction of the two factors cannot be neglected; it is also a significant effect on the size distribution of the droplets, which is visible from that the surface is twisted.

PDI:

On the Figs. 4(c) and 9(c) the combination of the effects of driving force and shear-stress on PDI are observed. From the Fig. 8(c), when we do not use reducer, it can be observed that driving force did not have any effect on PDI while shear stress was more important for getting fine emulsion. Instead of this in case of using reducer, from the Fig. 9(c) it was observed that PDI was increased gently with shear stress just as with driving force. Even though PDI is increased with increase of shear-stress in both systems, with or without turbulence promoter; this rise is much smaller when promoter was used. This increase is more distinct at higher shear-stress values, while at lower values increase is smaller.

From the aspect of productivity shear stress = 0.4 Pa on DF = 3.6 (with R) is suggested for operation since these conditions ensure high flux (12 mL/m^2/s) with good quality emulsion (droplet size ≈ 3.5-4 μm, PDI = 0.2-0.3). If smaller droplet size (1 μm) is required, then the setup of shear stress = 0 Pa and DF = 2 adjustable but productivity is predicted to be lowered to 5-6 mL/m^2/s.

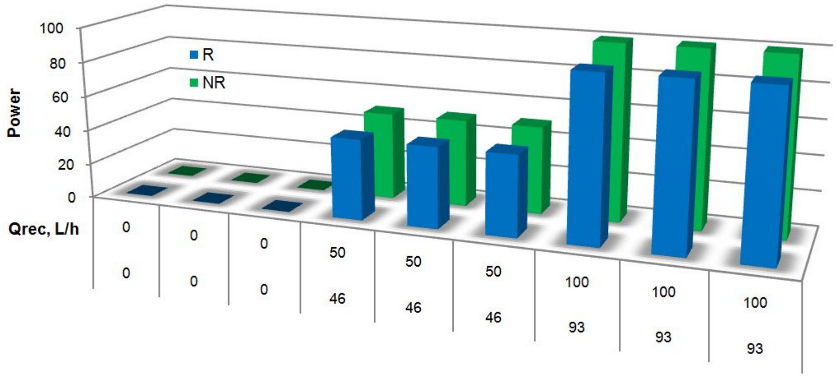


Fig. 10 Relative pumping energy consumption to recycle the continuous phase

3.6 Result of pumping power requirement calculations

One of the most important parameter from an economical point of view is the specific energy consumption i.e., reduction of specific energy consumption. The characteristics of the flow regime of the continuous phase were influenced with a kind of self-fabricated helical-shaped-ribbon reducer. The reducer increases the shear-stress near the membrane wall, so using reducer we could set the flow rate on a smaller value in order that keep the same shear stresses.

Result of pumping power requirement calculations allows concluding that, in most of the cases (except when no recirculation were applied (Q_{rec} = 0 L/h)) around 8% less energy required for recirculation of the continuous phase and emulsion with reducer are comparable to the case when no reducer was used. In Fig. 10 the green bars represent the energy required for preparing emulsion without using the reducer and the blue bars representing the energy required while the reducer was used.

4. Conclusions

Fine quality emulsions were obtained with low PDI values when monodisperse O/W emulsions were prepared using commercial available microfiltration tubular ceramic membranes. The main advantage of these membranes is their low cost compared to others commonly used in membrane emulsification, as SPG membranes.

The response surface methodology proved to be adequate modeling tool for mathematical representation of the process. For prediction of the flux, droplet size and PDI a mathematical model was set up which can describe well the dependent variables in the studied range, namely the run of the flux and the mean droplet diameter and the effects of operating parameters.

The application of helical-shaped reducer has positive effects on emulsification process, when the turbulence promoter is inserted fluid flow pattern are changed. In most of the cases around 8% less energy required for recirculation of the continuous phase and emulsion with reducer are comparable to the case when no reducer was used. Mainly on bigger shear-stress, using reducer the emulsion quality is better than the emulsions made by the conventional emulsification method at high flow rate in point of view of PDI. The droplet size results were about the same in both systems, with or without turbulence promoter, but it can be also concluded that the droplet diameter was a little lower using the reducer.

Optimal conditions for emulsification of O/W emulsions were determined by applying desirability function approach. For maximizing emulsion quality and reduction of specific energy consumption optimal values of design variables were as follows: presence of reducer, driving force 3.6, the axial cross-flow velocity in the tube membrane 0.7 m/s, TMP – 1.8×105 Pa (1.8 bar), the re-circulated flow-rate (RFR) was 100L/h and the shear-stress 0.42 Pa.

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