

PRECONDITIONS OF SEPARATION IN STR WITH INTEGRATED MEMBRANE FOR ENERGY-SAVING BY RECOVERY OF VALUE-ADDED MATERIALS

УСЛОВИЯ НА СЕПАРАЦИЯ В РЕАКТОР С РАЗБЪРКВАНЕ ИНТЕГРИРАН С ПОТОПЕНА МЕМБРАНА ЗА ЕНЕРГОСПЕСТЯВАНЕ ПРИ УЛАВЯНЕ НА КОМПОНЕНТИ С ДОБАВЕНА СТОЙНОСТ

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Abstract: Energy-saving by recovery of value-added materials from complex dispersions by using semi-permeable membranes has been proved world-wide. The effect is related to fundamental knowledge of fluid flow and mass transfer in complex fluids close to membrane interfaces. Innovative biotechnologies for value-added products such as exopolysaccharides or antioxidants benefit by such explorations in preserving the biological activity of the target components. The paper presents a solution of theoretical model of a stirred tank reactor (STR) Biostat equipped with membrane immersed in a non-Newtonian model solution of exopolysaccharide, e.g. glucomannan and biomass. CFD methodology is employed to reveal original data on shear deformation rates and shear stress at the membrane interface, as well as to predict the average mass transfer coefficient related to the boundary layer at the membrane surface based on the flow information obtained. The results are compared with similar data reported for conventional systems with different impeller and systems with external membranes.

KEYWORDS: ENERGY-SAVING, DESIGN WITH INTEGRATED MEMBRANE, STR, SHEAR STRESS, MASS TRANSFER

1. Introduction

Recent developments in membrane separation technology and increased implementation of various membrane techniques for water purification and recovery of value added products brings attention to the lack of data on the performance of membranes designed as immersed modular systems in stirred tanks [1]. The recent advances of the science of mixing reactors and membranes allowed the superposition of information on fluid flow in STR with data on separation dynamics of immersed membranes, thus generating combined knowledge on the performance of integrated systems. This combined knowledge would allow further exploration of integrated designs for recovery of value-added products possessing complex non-Newtonian physical properties otherwise important for their application in material practice.

Overlooking another aspect, recent advances in process design introduce single-use bioreactors and show them to be amenable for scale-up of data collected from traditional bench-scale fermenters [2]. Related to single-use bioreactors, modeling and characterization of bioreactor environments from mixing and shear perspectives at both small and large scales demonstrated high level of interest [3]. The trend increased the importance of performance data of traditional bioreactors, such as conventional bench-scale Biostats, and suggests further analyses on integrated designs to be performed in such starting vessels. In other words, the performance data of integrated immersed membranes should be related to conventional Biostat STR vessels, in order to ensure further scale-up analysis.

The aim of this study of preliminary research is to reveal two characteristics - shear and mass transfer rates - as important parameters for separations focusing on a design of traditional bench-scale reactor Biostat in original integrated set-up with in-line tubular membrane module immersed in non-Newtonian fermentation fluid for recovery of components of highly viscous biofluids, for example, separation of emulsion stabilizer exopolysaccharide and biomass containing prebiotics, both important for practice. The idea of using combined impeller and membrane designs has been considered as prospective in so far as such designs allow application to separations in highly viscous and complex production fluids where both interface and transport problems occur.

2. Experimental design and simulation details

Fig. 1 shows the experimental system, the corresponding computational domain and its discretization pattern.

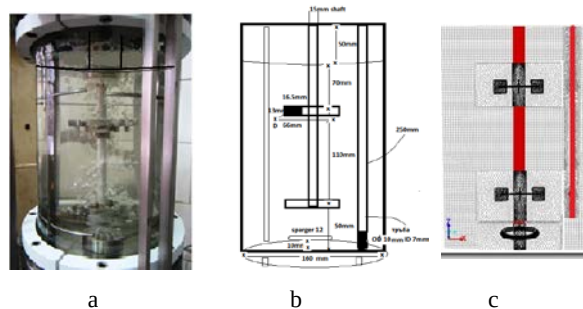


Fig. 1 Experimental reactor and simulation grid.

The vessel (Sartorius Biostat Aplus) was $T=0.16\text{m}$ in diameter equipped with two impellers sized 0.066m . The tubular membrane module was ID 7mm and OD 10mm with 250mm length positioned as shown in the figure.

The design has proved successful for production of exopolysaccharides, e.g. glucomannan that was implemented as viscosity promoter and emulsion stabilizer in cosmetic creams [4]. The optimal operating conditions of this production, namely, mixing impeller speed of 400 rpm and relative volumetric gas flow rate of 1vvm ($4.5\text{dm}^3/\text{min}$ related to 4.5 dm^3 fluid volume), were considered as primary for the assessment of a membrane operating in simultaneous separation with the productive bioreaction. The biofluid containing EPS showed non-Newtonian properties and was classified as a power law fluid with consistency coefficient $K=0.02\text{ Pa}\cdot\text{s}^n$ and flow index $n=0.78$. Considering the impeller speed of 400 rpm , these physical parameters revealed average apparent viscosity μ of the material of $6.7\text{mPa}\cdot\text{s}$ causing flow pattern of complex nature in the targeted stirred volume.

The study was carried out by computational fluid dynamics (CFD) analysis and a mathematical model based on the Reynolds-averaged Navier-Stokes (RANS) momentum equation (1) with

added two equations (4 and 5) to account for turbulent kinetic energy (k) and turbulent energy dissipation (ε) as additional parameters for closure. The set of equations conformed to the standard (k - ε) model [5, 6]. The model was extended to account for the non-Newtonian flow property of the studied biofluid by introducing the above power law parameters K and n (eq. (3)). The computed components of the stress tensor were used to determine the shear rate $\dot{\gamma}$ using eq. (6) and to transform it to shear stress τ using eq. (7):

$$(1) \frac{\partial V_j}{\partial t} + V_j \frac{\partial V_i}{\partial x_j} = -\frac{\partial}{\partial x_j} \left(\frac{p}{\rho} + \frac{2}{3} k \right) + \frac{\partial}{\partial x_j} \left(\frac{\mu}{\rho} \left(\frac{\partial V_j}{\partial x_i} + \frac{\partial V_i}{\partial x_j} \right) \right)$$

$$(2) \mu = \mu_a + \mu_t; \mu_t = \rho C_\mu \frac{k}{\varepsilon}$$

$$(3) \mu_a = K \left(\frac{\partial V_j}{\partial x_i} + \frac{\partial V_i}{\partial x_j} \right)^n$$

$$(4) \frac{\partial k}{\partial t} + V_i \frac{\partial k}{\partial x_i} = \frac{1}{\rho} \frac{\partial}{\partial x_i} \left(\mu_a + \frac{\mu_t}{\sigma_k} \frac{\partial k}{\partial x_i} \right) + \Pi - \varepsilon$$

$$(5) \frac{\partial \varepsilon}{\partial t} + V_i \frac{\partial \varepsilon}{\partial x_i} = \frac{1}{\rho} \frac{\partial}{\partial x_i} \left(\mu_a + \frac{\mu_t}{\sigma_\varepsilon} \frac{\partial \varepsilon}{\partial x_i} \right) + C_1 \frac{\varepsilon}{k} \Pi - C_2 \frac{\varepsilon^2}{k}$$

$$\Pi = \frac{\mu_t}{\rho} \left(\frac{\partial V_i}{\partial x_j} + \frac{\partial V_j}{\partial x_i} \right) \frac{\partial V_i}{\partial x_j}$$

$$(6) \dot{\gamma} = \frac{\partial V_j}{\partial x_i} + \frac{\partial V_i}{\partial x_j}$$

$$(7) \tau = K \dot{\gamma}^n$$

In eq. (1)-(7), V is fluid velocity, x indicates the space coordinate, p is pressure, ρ is fluid density, k stands for turbulent kinetic energy, and ε is the rate of kinetic energy dissipation.

The kinetic energy dissipation rate ε was used to outline the zones of active mass transfer close to the membrane interface where an average mass transfer coefficient k_L could be obtained via eq. (8) reported for transitional flow across vertical cylinder [7]:

$$(8) Sh = 0.43 + 0.193 Re^{0.618} Sc^{0.31}$$

where $Sh = k_L T / D$; $Re = Nd^2 \rho / \mu_a$; $Sc = \mu / \rho D$ are Sherwood, Reynolds and Schmidt numbers on the side of the biofluid, T is the hydraulic diameter of the vessel, D is the diffusion coefficient, here assumed to be for diffusion of sucrose molecular weight 342, $D = 0.45 \cdot 10^{-9} \text{ m}^2/\text{s}$; N stands for impeller revolutions at 6.7 s^{-1} , impeller diameter d is 0.066 m , and ρ density of aqueous phase 1018 kg/m^3 .

Referring to the simulation details, the computational domain was represented by structural conformal mesh composed of tetrahedral cells close to the impeller and with refinements in the near-wall regions, the cells numbering ca. million (e.g. $0.9 \cdot 10^6$ (Fig. 1c).

Simulations were carried out by application software ANSYS FLUENT (release 13.0, Ansys, Inc., 2010). The boundary conditions included symmetry for the free fluid surface, pressure outlet for the gas phase with backflow ratio 1 and volume fraction 1 for the outlet, as well for the air inlet where initial velocity of 8 m/s in vertical direction was applied to account for inlet gas flow rate of $4.5 \text{ m}^3/\text{min}$. Stationary wall boundary condition with zero velocity gradients for the vessel walls and moving wall boundary conditions with rotational velocity of 400 rpm to the moving parts. The presence of gas in the two-phase flow case has been modeled by the Euler-Euler multiphase model accounting for the flow properties of the separate phases, as well to the contact between them. The

convergence criterion was set for velocities and turbulence values equally at 1×10^{-5} . Convergence was judged upon by both residuals and target quantities, i.e. linear velocities and strain rate. A reasonable convergence was achieved and realistic logical values were obtained.

Model validity was studied by comparison of parameters, e.g. moment and power input, and separately by comparing experimental shear rates with shear rates predicted by the model in selected points of the bioreactor volume, more specifically at 20 mm off the impeller tip in the upper impeller plane. Data on validation are reported elsewhere [6].

3. Results and discussion

Fig. 2 illustrates the flow field for the stirred tank and the velocity contours generated by the impeller in the reactor cross section including the tube of the membrane in gas presence. The solution of this complex system shows the areas of major interest are the impeller levels $z=0.05 \text{ m}$, and $z=0.16 \text{ m}$, the membrane surface front, side and rear to the impeller and the stagnant zones, with relatively low backflow and transfer rates within the stirred fluid.

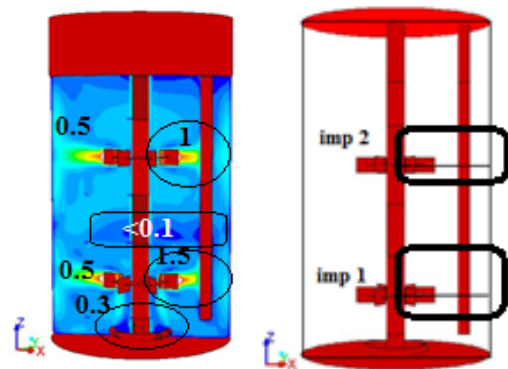


Fig. 2 Velocity (m/s) zones of interest for enhanced trans-membrane wall mass transfer

The variation of shear rate and kinetic energy dissipation rate along the lines across the membrane in the two impeller planes are shown at gas absence in Fig. 3. Referring to Cartesian coordinates with $z=0$ at the vessel bottom, the radial lines of the plots were selected in the $x=y$ plane at off-bottom distance $z=0.05 \text{ m}$ (lower impeller plane) and $z=0.160 \text{ m}$ (at the upper impeller plane) corresponding to the impellers' positions. It is seen that the maximum shear rate $\dot{\gamma}$ and kinetic energy dissipation ε determined in gas absence are seen to be 8 ks^{-1} and $1200 \text{ m}^2/\text{s}^3$, respectively. The corresponding values of shear stress are 17.7 Pa at the maximum and 1.2 at the minimum. It is noteworthy that these values exceed the range of shear stress ($\tau < 10$) reported for membranes with narrow channel with spacers [8].

Contributing to the reported goal, shear distribution along the membrane interface was also of interest. It is illustrated directly by the immersed solid body diagrams in Fig. 4, where also the effect of gas presence is seen clearly. Determining the surface-average values in both cases, i.e. absence versus presence of gas, the effect of the gas shows only slight rise of shear in gas presence in terms of the optimal rate of gas flow registered (e.g. 1 vvm and $4.5 \text{ cub.m. per min.}$). The area-averaged shear rate in both cases (i.e. "no gas" vs. "gassed") differs by only 10% , such as 900 vs. 1050 s^{-1} , yet the distribution in gas presence is largely different, being more uniform

in gas presence and increasing the zones of moderate shear in areas where shear is low in gas absence (marked with red).

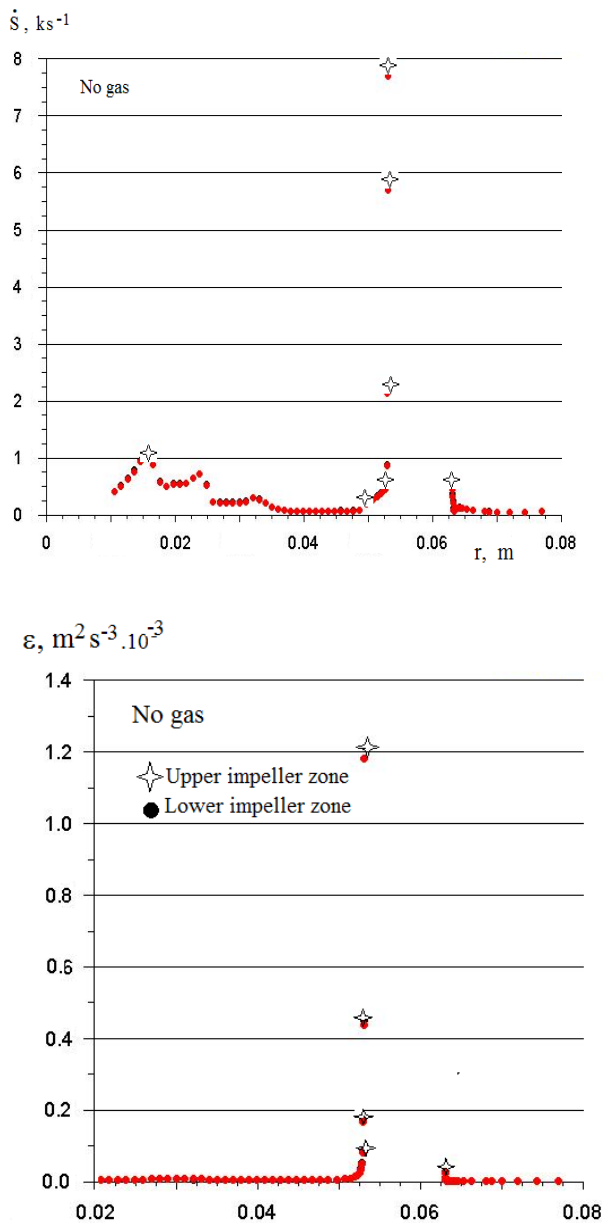


Fig. 3 XY plots of shear and turbulence parameters vs radial coordinate.

The effect can be assessed more clearly by the XY plots along the Z-coordinate adhering to membrane external front shown in Fig. 5, where additional peaks can be observed to correspond to the colored sections in Fig. 4. [The coordinates of the membrane front vertical line has been determined to be x (0.03722, 0.03722), y (0.03722, 0.03722), z (0.035, 0.22)]. The fact proves the positive effect of the gas in achieving more uniform distribution of velocity, shear and viscosity close to the membrane surface accompanied possibly by enhanced mass transfer in the boundary layer. Further analysis of this performance parameter at other gas flow rates seems obligatory to confirm the effect of gas presence on the performance of immersed membranes.

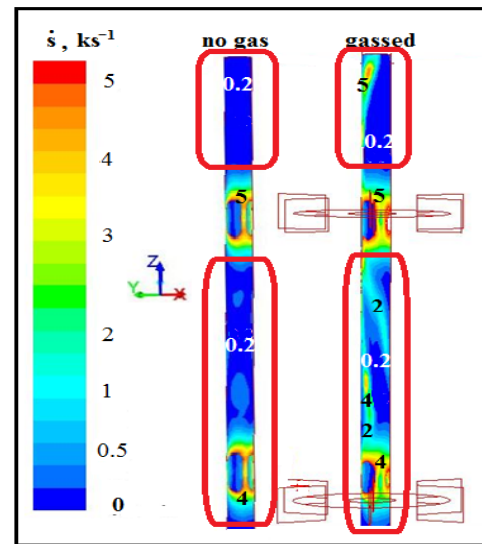


Fig. 4 Membrane contour plots showing the effect of gassing on the distribution of shear rate (in ks^{-1}).

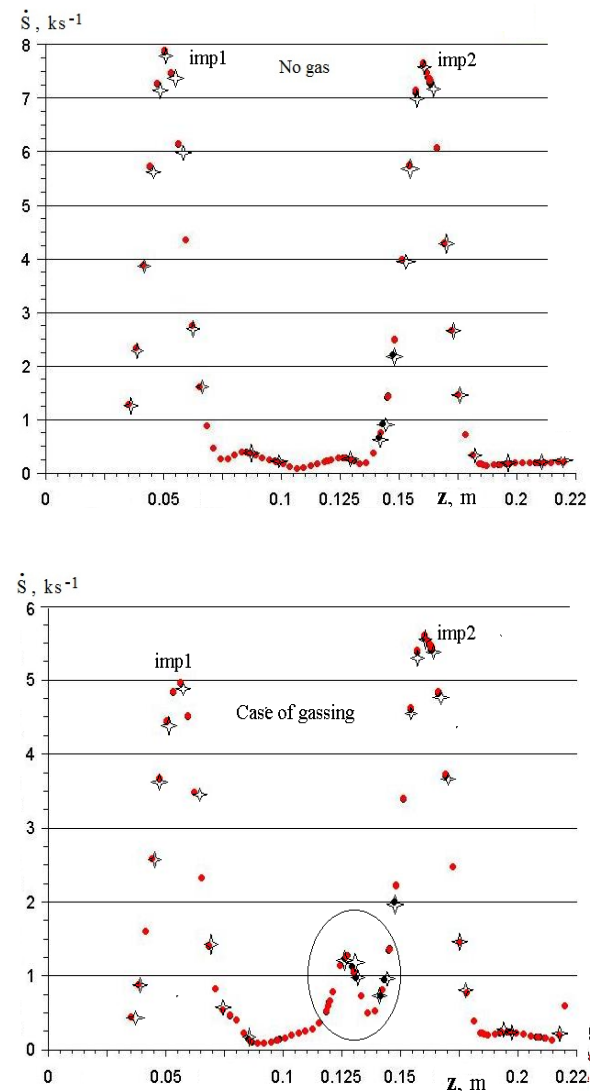


Fig.5 The effect of gassing on the distribution of shear rate (in ks^{-1}).

The values of shear stress and mass transfer rate coefficients obtained in this study are compared with reference data in **Table 1**. The reference data reveal comparable parameters reported for mixing equipment with membranes immersed in fluids with different hydrodynamics, e.g. arc-blade impellers, composite bodies [8], and also membranes operating on different principle as external off-tank designs [9-11]. It is seen that the Biostat with immerse membrane shows characteristics comparable with the reported designs. The mass transfer coefficients vary mainly depending on the size of the diffusing molecule, for the sake of comparison being assumed sucrose (340 Dalton) in aqueous solutions of 6 and 2 mPas in case 1 (this study) and case 3 [8] (with diffusion coefficients $\sim 5 \cdot 10^{-10} \text{ m}^2/\text{s}$), respectively, and dextran (167 kDa) in case 6 [12] (diffusion coefficient of $5 \cdot 10^{-11} \text{ m}^2/\text{s}$).

Table 1: Summary of experimental results on shear stress and mass transfer compared with achievements for various reported membrane systems in diluted aqueous solutions.

Separation system	Reference cConditions	Membrane integrated as	τ , Pa	k_L , $\text{m/s} \cdot 10^4$
STR with flat blades	This study Re=3800, 1m/s $\mu_a=6 \text{ mPa}\cdot\text{s}$, low D	Immersed tubular module	2 (up to 20)	~ 0.1 (Sh ~ 650 , Sc $\sim 12 \cdot 10^3$)
STR with arc blades	This study Re=8200 2.6m/s	Immersed tubular module	2-4	-
Stirred cell	Koutsou [8] Re=8000-10000, 0.3m/s (up to 0.9m/s)	Immersed flat bottom	1-2 (up to 10)	~ 0.5 (Sh $\sim 10^3$, Sc $\sim 5 \cdot 10^3$)
Cross-flow Unit	Dzhonova et al. [9] Re=8500 0.6 m/s	External flat-sheet	5.3 (< 20)	-
Hollow Fiber Unit	Bérubé et al. [10] Re=12000, 0.2m/s (up to 0.4m/s)	External	2.9 (up to 6)	-
UF Unit	Ghosh et al [11] $\sim 0.2\text{m/s}$	External Tubular	-	10^{-3} (Sh $\sim 10^2$)

3. Conclusion

In terms of the theoretical model and CFD simulations employed, the system of STR and immersed membrane explored is comparable with reference membranes, both external and immersed in STR with different circulation pattern in the sense that it allows comparable shear and mass transfer rates close to the membrane interface. The **design of Biostat with immersed membrane** is prospective for further detailed analysis including also other parameters, such as internal mass transfer, as well as wider operating conditions and physical properties of value-added materials.

4. Acknowledgement

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5. Literature

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