Green Process Design and Operation for Ester Synthesis

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Abstract

In this study an innovative pervaporation aided biocatalytic membrane reactor (BCMR) system has been designed and operated for ethyl lactate synthesis from ethanol and lactic acid. Lipozyme Calb L enzyme has been immobilized on the top surface of alginate based membrane. Effects of enzyme loading, feed molar ratio and temperature on lactic acid conversion, total flux and water selectivity have been evaluated. Optimum enzyme loading was determined as 0.5g enzyme/19.625 cm^2 membrane. Acid conversion increased as the temperature increased from 303 K to 323 K. Also effect of feed molar ratio was investigated as function of acid conversion. When alcohol:acid ratio was 3:1 (M3) better conversion results were obtained. However 1:1 (M1) alcohol:acid ratio gave closer results to M3 so it was concluded that the M1 was effective and sufficient ratio for ethyl lactate production. As the feed molar ratio increased in reactor flux decreased drastically. However selectivity positively affected.

Keywords: Green technology, biocatalytic membrane reactor, ester synthesis

1. Introduction

Green process development is a promising progress in chemical engineering science. Environmental regulations and process intensification are forced to researchers to investigate more effective process design with lower energy consumption. Process intensification can be characterized by reduced plant volume, fewer operation equipment, efficient energy consumption and safety operation conditions.

Membrane reactor (MR) is one of the sustainable and green reactive separation systems that play a key role to optimize the process requirements. In terms of the membrane activity, MR can be used as distributor, extractor or active contactor. In extractor MR, membrane is catalytically inert and one of the products is selectively removed from the reaction media. In this MR, membrane is only used to retain catalyst or unconverted reactant. It is especially used for the thermodynamically limited reactions such as esterification. In distributor MR, membrane contributes controlled contact of reactant so it provides safety nature for gas phase reactions. In this system membrane is catalytically inert. In active contactor MR, membrane has catalytic features. Either membrane material includes functional chemical catalytic groups or catalyst is loaded top surface or inside the membrane pore [1-3]. This group of membrane reactor is also classified as catalytic membrane reactor (CMR). In CMR reaction occurs on the catalytic sites of membrane. Owing to the selective property of membrane, one of the products is preferably separated from the others on the separation layer of the membrane. Thereby, in reversible reactions, reaction runs through the product and conversion increases [1]. Due to the one step reaction-separation ability, CMR contributes to reduce plant volume, capital cost of system and

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energy consumption. Because of the catalyst is being in the structure of membrane, catalyst reusable and recycle is possible.

In case the enzyme is used as catalyst, then the system is converted to bio-catalytic membrane reactor (BCMR) [4,5] Enzymes are used to synthesize important chemical in mild operation conditions. The main factors that enzymes provide to reaction systems are; minor byproduct, non-toxic chemical agents, clear end product and lower energy consumption. However, activity of enzyme is crucial factor to maintain the process efficiency [6] Enzymes are protein structures, hence critical operation conditions such as high temperature and pressure cause a defection in the enzyme body. Also excess of reactant or product such as alcohol, water, acid can act as an inhibitor and cause a decline in enzyme activity. In addition that, enzyme catalyst reaction takes a long time due to the unstable reactive nature of enzymes. Moreover, owing to the production method of enzyme from natural resource, they are quite expensive. In homogenous reaction, recycle and reuse them are quite difficult. With respect to all mentioned drawbacks, in order to enhance the process efficiency it is required to use enzyme appropriate technique [7-8].

Biocatalytic membrane reactor is a key method to profit by the all advantages of enzymes. Membrane separation coupled enzyme reactor which is usually called as enzymatic membrane reactors has long been used for wastewater treatment [9]. However, membrane is only used to separate bulk enzyme and act as a distributor. Meanwhile, the only task of inert membrane is act as a barrier between the enzyme and impurities. In biocatalytic membrane reactors; enzymes are immobilized to the structure of membrane materials. There is lots of technique such from covalent bonding to adsorption for the immobilization of enzyme [5,7]. But the main factor to take into consideration of the preservation of enzyme activity. Immobilization technique, support material (polymeric or ceramic), support-enzyme interaction are the important issues for enzyme immobilization. Several years lipase loaded membrane usage in biocatalytic membrane reactor has become a promising method to overcome process intensification problems. Because of the one step separation-reaction possibilities, biocatalytic membrane reactor is considered as energy intensive, cost effective and environmental friendly innovative system [10-13].

In this study pervaporation aided biocatalytic membrane reactor system has been designed and operated for ethyl lactate production. Enzymes have been loaded to the top surface of membrane separately, then the biocatalytic membrane consists of two different layers as separator and active layer.

2. Materials and Method

2.1 Materials

LipozymeCalb L which is obtained from candida antarctica (Calb) has been kindly supplied from Novazyme Turkey. Sodium alginate polymer, gluteraldehyde, lactic acid (80% purity), ethyl alcohol (97 % purity), ethyl lactate (%99 purity) have been purchased from Aldrich chemicals.

2.2 Membrane preparation

Biocatalytic membrane was prepared by solution-casting method. Enzyme was loaded to the top surface of the membrane. Thereby, the membrane was prepared as two layers. Wt.3.5 % of alginate and water was mixed and this polymer solution was stirred for 24 hours by magnetic stirrer. For smooth top surface, solution was kept waiting a night after the homogeneous solution was obtained. Then it was poured into a glass petri dish. For preparation of enzyme solution; desired amount of Calb was solved in 10 g wt. 0.5 % of alginate-water solution. Membranes were dried in vacuum oven at 50 ºC. After membrane had dried for two days at room temperature, enzyme solution was poured onto selective layer. And then it was cross-linked at gluteraldehyde, HCl, acetone and water solution.

2.3 Membrane Characterization

Enzyme distribution in sodium alginate matrix and polymer characterization were analyzed by using a JEOL JSM-6335 F Field Emission Scanning Electron microscope**.** Liquid nitrogen was used to break the membrane samples. The samples were coated with gold before the analysis.

2.4 Reactor Design and Esterification

Biocatalytic membrane reactor was designed for ester synthesis by lipase loaded non-porous membrane. System was supported by a pervaporation unit. As can be seen in figure 1 and figure 2, BCMR was employed inside an oven. System was kept at desired stable temperature. In order to avoid the mass transfer problem, a mechanical stirrer was connected to the membrane reactor. Reactor capacity was 250 ml, effective membrane area was 19.625 cm^2. Pervaporation unit consists, a circulation pump, a vacuum pump and three cold traps.

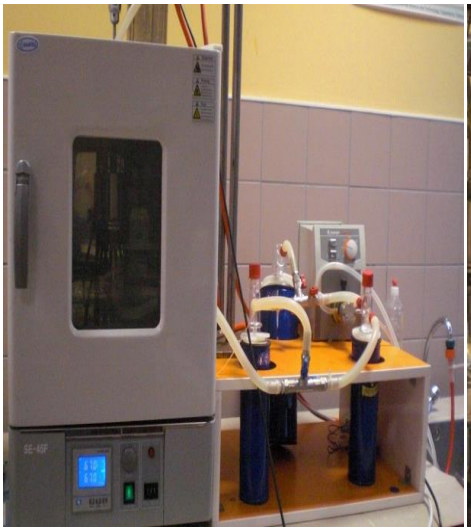

Figure 1. BCMR system

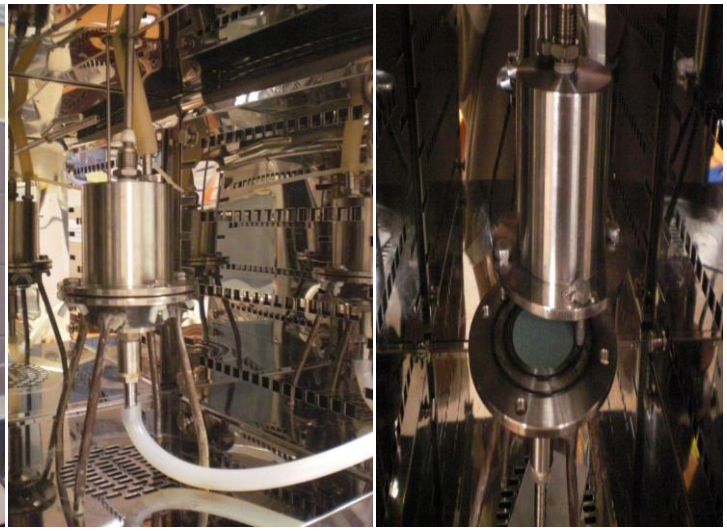

Figure 2. MembraneReactor

Ethyl lactate production is a reversible reaction between ethyl alcohol and lactic acid and water produces simultaneously with ethyl lactate. In order to increase ethyl lactate yield, separation of water from the reaction media is an effective solution. In this innovative reactor, when reaction occurred on the top surface of membrane, water was selectively separated by the non-porous, two layered biocatalytic membrane. Due to the concentration gradient, which was maintained by vacuum pressure, water diffused through the membrane and desorbed downstream side of the membrane. After the diffusion, water left the membrane as vapor phase due to the vacuum pressure which was supplied from downstream side of system then condensed into cold traps which were kept in liquid nitrogen. This stream is called as "permeate"

In this study, effect of enzyme loading, alcohol:acid feed molar ratio and temperature on acid conversion, flux and selectivity were investigated. Enzyme loading was determined as 0.5, 1 and 1.25 (g enzyme/19.625 cm^2 membrane area). After the desired enzyme loading had decided, reactions were carried out at 303, 313 and 323 K. In addition, reaction was carried out with 1:1, 3:1, and 6:1 alcohol:acid feed molar ratio. In order to observe the system efficiency, reactions were also carried out at same operation conditions in batch reactor. Biocatalytic membranes were cut into pieces and they were used as catalyst for batch reactor.

2.5. Calculation

Both in BCMR and batch reactor reaction were carried out about six hours. In BCMR, an hour intervals, samples were taken from reactor and traps and they were analyzed by GC and titrated to determine the solvent concentration and lactic acid weight percentage respectively.

Free lactic acid content and lactic acid conversion was calculated as eq.1 [14], conversion was calculated as shown in eq. 2.

$$F(wt.\%) = \frac{N_{KOH}.V_{KOH}.MW_{LA}}{1000.W_{sample}}.100 \quad \textbf{(1)}$$

$$X = \frac{n_{Ao} - n_A}{n_A} \quad \textbf{(2)}$$

F; free lactic acid concentration, N_{KOH} ; normality of consumed KOH solution, V_{KOH} ; volume of consumed KOH solution, MW_{LA} ; molecular weight of lactic acid, W_{sample}; weight of analyzed sample, n_{A0} and n_A; initial and final mol of lactic acid respectively.

Flux value determines the membrane productivity. Flux (J) ($kg/m^2.h$) is calculated from the measured weight of permeate sample as shown in eq. 3

$$J = \frac{W_p}{t.A} \quad \textbf{(3)}$$

Selectivity (α) obtains the selective character of membrane. Selectivity was calculated from the GC data of permeate concentration as in eq. 4

$$\alpha = \frac{Y_a / X_a}{Y_b / X_b} \quad \textbf{(4)}$$

W_p is the weight of permeate (kg), t is the time (h), A is the effective membrane area (m^2), $Y_a$andY_b are the mass or volume fractions of a and b compounds in the permeate respectively. $X_a$and X_b are the mass or volume fractions of a and b compounds in the feed respectively [15].

3. Results

Lactic acid conversion has been given in the text as X, and it was range from "0" to "1". Enzyme loaded membranes have been entitled according to the enzyme amount. Calb0.5 represents the 0.5 g enzyme/19.625 cm^2 membrane area. Alcohol:acid feed molar ratio has been described as M.

3.1. SEM Results

SEM results of enzyme-alginate surface have been shown in figure 3. Figure 3a indicates the homogeneous distribution of enzymes. Figure 3b shows the orientation of enzyme particles.

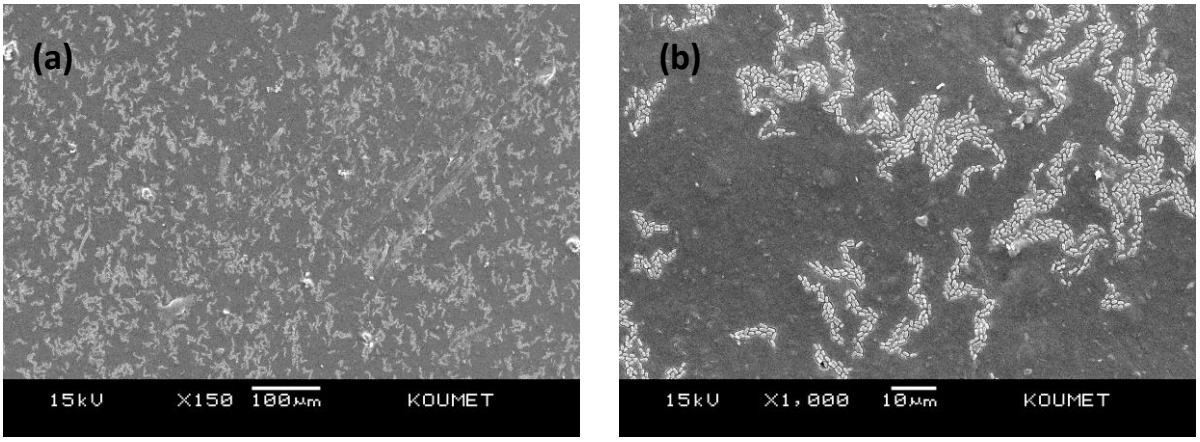

Figure 3. Surface SEM micrographs of Calb0.5 (a) X150 (b) X1000

3.2. Effect of enzyme loading on lactic acid conversion

Enzyme loading limits were determined due to the enzyme-membrane interaction. Before determination of loading, optimization tests were applied. Alginate is a bio-based polymeric material and it is compatible with enzymes. While lower loading than Calb0.5 was unsuccessful to react with substrate, upper loading than Calb1.25 caused a defection on membrane surface. As can be seen in figure 4, highest conversion values were obtained with Calb1. With Calb1.25 a decline in conversion has been seen. Due to the over-loading of enzymes, an agglomeration

might be occurred between the enzyme particles. Resulting the blocking the active sites of enzymes, conversion decreased. Calb0.5 also gave better results than Calb1.25 and results of Calb0.5 was very close to Calb1. Then it can be concluded that the Calb0.5 is sufficient for ethyl lactate production.

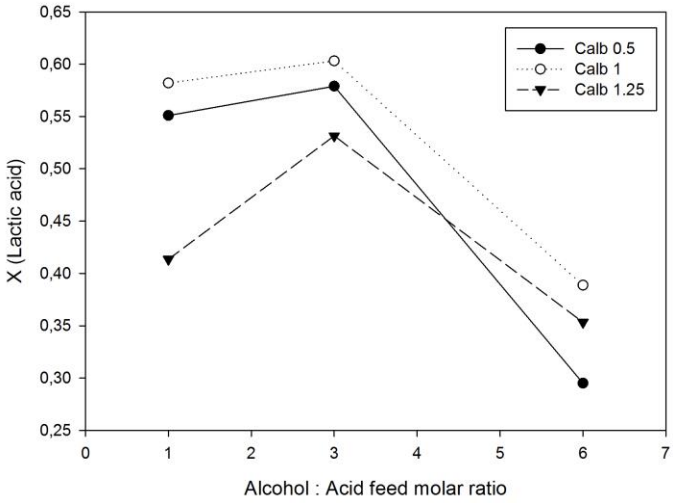

Figure 4. Effect of enzyme loading on acid conversion (T=303 K)

Figure 5 shows the effect of enzyme loading on acid conversion at different reaction temperature. As the temperature increased, conversion increased due to the Arrhenius equilibrium. This figures also indicated that the Calb0.5 and Calb1 gave close results compared to Calb1.25. In case of Calb0.5, conversion difference between the 303 and 323 K was not significant. Figures proved the availability of biocatalytic membrane in mild operation condition such as 303 K.

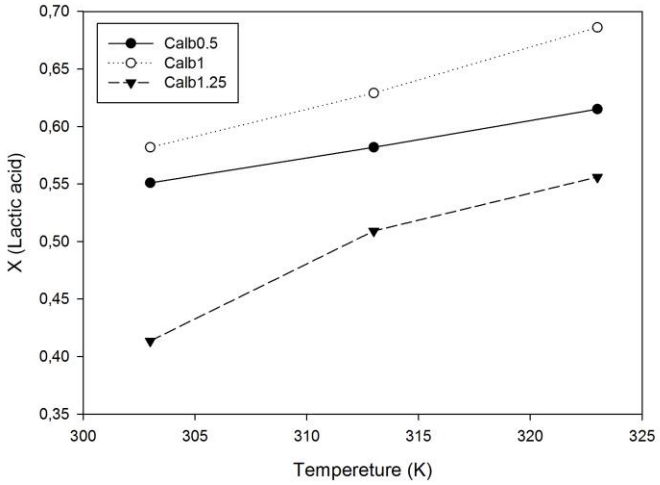

Figure 5: Effect of enzyme loading on acid conversion (M=1)

3.3. Effect feed molar ratio on lactic acid conversion

Figure 6 indicates that the effect of feed molar ratio on acid conversion. Experiments were carried out by Calb0.5. In this figure a comparison trend has been seen between the batch reactor and pervaporation aided BCMR. Conversion results of BCMR are almost two times higher than that of batch reactor.

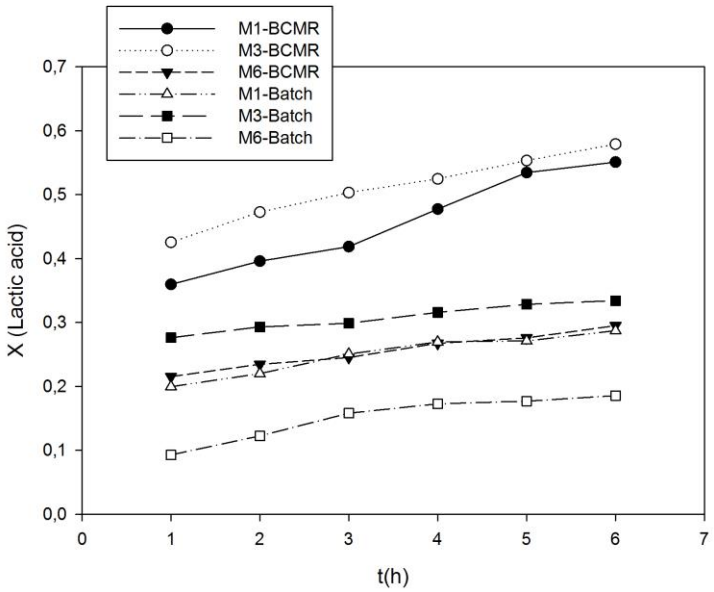

Figure 6. Effect feedmolar ratio on lactic acid conversion

As 0.57 acid conversion was obtained with M1 feed molar ratio in BCMR, in batch system 0.28 conversion was achieved. As seen in figure 6, a significant decline was observed with M6 molar ratio. This can be explained by the inhibition effect of alcohol on enzyme. So it is important to determine optimum feed ratio in order to enhance reaction yield. M1 and M3 molar ratio gave close results.

3.4. Effect feed molar ratio on total flux

Flux results of the reaction which was carried out with Calb0.5 at 303 K have been seen in figure 7. Flux is important factor for defining the membrane productivity. Alter from the other membrane reactor, in pervaporation aided BCMR, non-porous membrane is used so the flux values becomes crucial parameter to determine the system efficiency. It was mentioned before that the alginate is hydrophilic polymer and water existence causes a swelling effect between the intermolecular chain spaces of membrane. Hence, flux values increase as increasing the water content in reaction media. Flux directly contributes to enhance the acid conversion. As the conversion increases in reactor, water is generated, membrane swells and flux increases again. Meanwhile, flux and conversion are dependent each other.

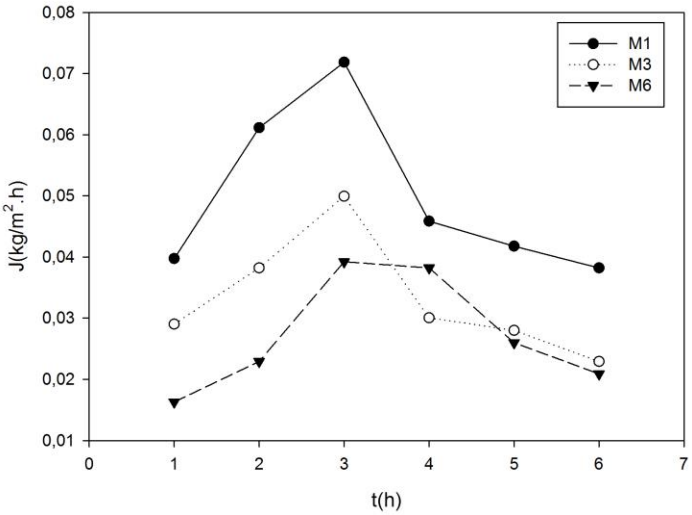

Figure 7. Effect feed molar ratio on total flux

As can be seen in figure 7, higher flux values are obtained with M1. Initial lactic acid also includes approximately wt. 20 % of water. In higher molar ratio (M1), initial water and produced water concentration higher than that of in lower molar ratio (M3 and M6). Although conversion values of M3 higher than M1, the total water content is lower than M1. The same explanation is valid for M6. Therefore, flux values rating can be shown as M1>M3>M6.

3.5. Effect molar feed ratio on water selectivity

Selectivity is another major factor for defining the selective character of membrane. However selectivity and flux usually show a reverse effect. Flexible polymer chains are expanded by membrane swelling.

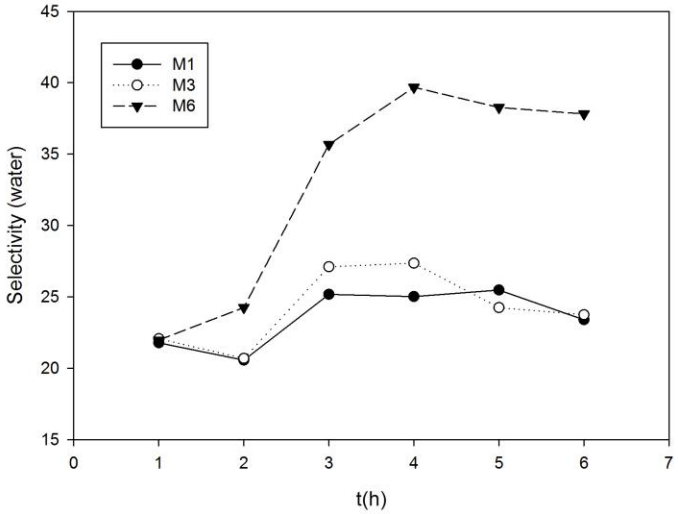

Figure 8. Effect feed molar ratio onwater selectivity

Degree of swelling is a necessary property for membrane material. However excess amount of swelling causes a non-selective permeation of compounds. Alginate is known as quite hydrophilic membrane material, so the water content increases on top surface of membrane, swelling degree increases, but selectivity decreases. It can be clearly seen in figure 8 that the selectivity values of M6 higher than M1 and M3. Because M6 feed molar ratio contains less water percentage due to the excess volume of alcohol. Hence as it mentioned before, it is expected that the swelling degree of membrane lower in M6 mixture than that of M1 and M3.

4. Conclusion

In present work, an innovative reactor system has been designed and operated for ester synthesis. BCMR is an important achievement in order to fulfill "process intensification" requirements. Supported of the system with a pervaporation technique and using non-porous biocatalytic membrane offer some advantages such as selective removal of water simultaneously, enhancing acid conversion and enzyme stability. Also recycle and reusable of enzyme is possible. As observed in whole study, BCMR shows higher conversion values compared to the batch reactor which has been carried out at same conditions. Moreover, flux and selectivity values of membrane are acceptable. As a result of the study applicability of the system has been proved.

Acknowledgements

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References

[1]Jose GSM and Theodore TT, Catalytic Membranes And Membrane Reactors, Wiley-VCH Verlag GmbH, Weinheim, 2002

[2] Ayça Meriç HASANOĞLU, Etil Asetat Uretimine Yönelik Esterlesme Reaksiyonunun degisik Katalizorler Varlıgında Pervaporasyon Membran Reaktorde Incelenmesi, PhD. Thesis, 2008, İstanbul

[3] Baker, RW, Membrane Technology And Applıcatıons, Second Edition, Mcgraw-Hill, 2000.

[4] Peter J, Yamini S, Ludo D, Winnie D, Enzyme immobilization on/in polymeric membranes: status, challenges and perspectives in biocatalytic membrane reactors (BMRs), Green Chem., 2011;13: 1609-1623.

[5] Giorno L, Drioli E, Biocatalytic membrane reactors: applications and perspectives, Trends in Biotechnology, 2000; 18, 8: 339–349

[6] Drioli E, Fontananova E, Membrane Technology And Sustainable Growth, Chemical Engineering Research and Design, 2004, 82(A12): 1557–1562

[7] Gupta S, Bhattacharya A, Murthy CN, Tune to immobilize lipases on polymer membranes: Techniques, factors and prospects. Biocatalysis and Agricultural Biotechnology, 2013;2:171–190.

[8] Hilal N, Nigmatullin R, Alpatova A, Immobilization of cross-linked lipase aggregates within microporous polymeric membranes. Journal of Membrane Science, 2004; 238: 131-141.
[9] Rios GM, Belleville MP, Paolucci D, Sanchez J, Progress in enzymatic membrane reactors – a review, Journal of Membrane Science 242 (2004) 189–196.
[10] Hilal N, Kochkodan V, Nigmatullin R,Goncharuk V, Al-Khatib L, Lipase-immobilized biocatalytic membranes for enzymatic esterification: Comparison of various approaches to membrane preparation, Journal of Membrane Science, 2006; 268: 198–207.
[11] Bayramoglu G, Hazer B, Altıntas B, Arıca, M.Y, Covalent immobilization of lipase onto amine functionalized polypropylene membrane and its application in green apple flavor (ethyl valerate) synthesis, Process Biochemistry, 2011;6: 372–378.
[12] Karla AB, Flavio ML, Fabio Y, Katia FF, Lipase entrapment in PVA/Chitosan biodegradable film for reactor coatings, Materials Science and Engineering, 2013;33:1696–1701.
[13] Zvjezdana F, Gergely N, Durda VR, Katalin BB, Zsofia C, Laszlo G, Pervaporation-aided enzymatic esterifications in non-conventional media, Process Biochemistry, 2012; 47:1715–1722.
[14] Ozge Oguzer, Screenıng and characterızatıon of catalytıc composıte Membranes for ethyllactate productıon, pH thesis, Ankara, 2004.
[15] Nunes SP, Peinemann KV, Membrane Technology in the Chemical Industry ,Wiley, Germany, 2006.